
Comment on “Probing the Origins of Photodegradation in Organic-Inorganic Metal Halide Perovskites with Time-Resolved Mass Spectrometry”, *Sustainable Energy & Fuels*, 2018. Updated response (March 14, 2019)[†]

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An article in *Sustainable Energy & Fuels* authored by Song *et al.*¹ reported time-resolved mass spectrometry (MS) of evolved gas species during photo-induced degradation of methylammonium lead iodide perovskite (MAPbI₃). The composition of volatile species observed in this work for MAPbI₃ is significantly different than that in an early work by Juarez-Perez *et al.*² Even though both studies used identical MS equipment and similar illumination conditions, the divergent results obtained regarding the composition of evolved gases could lead to conflicting approaches to increase the stability of hybrid perovskite solar cells. In this comment, a set of possible explanations are offered to explain the experimental discrepancies and conclusions outlined in the two works. Understanding the origins of degradation in methylammonium (MA)-based hybrid perovskites is important for a detailed understanding of how to prevent such degradation in photovoltaic devices. The key discrepancy between these two studies, hot carrier-induced vs. a thermal-driven process as the origin of degradation, is discussed.

Summary of different output results

Briefly, there are three fundamental differences between these works in relation to degradation of MAPbI₃ and to degradation-mitigating measures to improve stability. In the work by Song *et al.*¹,

1. The release of methyl iodide (CH₃I, 142 m/z) was never observed during light-induced degradation experiments.
2. When applying photon energy illumination to MAPbI₃, there was a wavelength threshold of >395 nm, above which release of gaseous organic species ceased.

[†] The authors of the commented article released a response to these observations on February 1, 2019. This document has been updated including new comments to their response on March 14, 2019, see page 4.

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Therefore, hot carrier-induced deprotonation of MA⁺ cations was concluded to be the cause of photodegradation, inevitably leading to release of volatile species.

3. The proposed remedy was to avoid using MA⁺ in perovskite formulation, due to the high release of volatile organic species. They proposed that degradation can be alleviated to a significant extent by filtering out high-energy wavelengths (UV filtering).

In contrast, Juarez-Perez *et al.*² found that,

1. Gas products of two simultaneous paths of degradation are observed at temperatures as low as 60 °C, namely, the detrimental and irreversible release of CH₃I + NH₃, and the benign reversible release of CH₃NH₂ + HI.
2. There was no observed photon energy threshold for MAPbI₃ degradation. Unlike the PbI₂ sample, MAPbI₃ does not have a wavelength ceiling above which gaseous products cease to be released by photodecomposition. Volatile organic release from MAPbI₃ is a temperature-controlled process. The experimental demonstration of this fact is that CH₃I, NH₃, CH₃NH₂, HI and I₂ m/z molecular peaks are observed during on-off, low-temperature heating pulses even in the dark.
3. Hybrid halide perovskite materials undergo dynamic processes of formation and decomposition at photovoltaic operational temperatures. Therefore, the presence of organic MA⁺ undergoing irreversible degradation (CH₃I + NH₃) in hybrid halide perovskite formulations has to be minimized, if not completely suppressed. Encapsulation of the device is necessary not only to avoid contact with humid ambient air, but also to prevent leakage of unavoidably released volatile products, such as I₂.

An explanation for the lack of detection of CH₃I

Tentatively, we attribute the lack of CH₃I detection by MS methods in the work of Song *et al.*¹ to three fundamental details in their experimental design.

a) Faraday cup or electron multiplier detector?

Song *et al.*¹ did not mention in their Experimental Section what kind of detector they used for the MS experiments. However, we assume (because we used exactly the same MS equipment) that a Faraday cup detector was used to collect the data shown in their Figure S2, in view of the absolute background partial pressure recorded and shown in log scale. Probably, one of the causes (but not the only one) of the failure to detect CH₃I was the use of the Faraday cup detector, which has lower sensitivity than the electron-multiplier type detector optionally incorporated in this MS equipment model. Nonetheless, the Faraday cup is the standard detector used in this MS equipment.

b) Sample weight.

Song *et al.*¹ used a perovskite thin-film as their sample in MS experiments. The sample mass would have been approximately 0.26 mg (1 x 0.25 inch² x 400 nm x 4.16 g/cm³). This means that they sampled a mass of perovskite ~700x smaller than that used in Juarez-Perez *et al.*². A sample weight of 180 mg was used in Juarez-Perez *et al.*² to ensure that volatile material was not exhausted during the tens of cyclic pulses of light or heat applied to the sample. In this fashion, activation energies for release of volatile species are conveniently calculated. For detection purposes, we could have used only tens of milligrams, but we probably could not have detected I₂ or CH₃I release with samples below 1 mg, even using the electron multiplier detector. Therefore, another reason for the failure of Song *et al.*¹ to detect CH₃I could be the low quantity of perovskite used in their measurements.

c) Distance between sample and gas collection input stream for the MS.

The distance between sample position and the gas collection point for the mass spectrometer is critical during MS measurements. In our work, we placed the sample as close as possible to the gas collection input (~1 cm) because i) only by this means could the entire spectrum of gaseous products released (CH₃NH₂, HI, CH₃I, NH₃ and I₂) be clearly observed and ii) a more nearly instantaneous response between applied stimuli and MS detection was obtained.² It seems plausible that the long delay required for molecule detection in the work of Song *et al.*¹ reflects the distance

between the sample and the gas collection point of the equipment (Figure S1 in Song *et al.*¹). In fact, the delayed maximum peak of CH₃NH₂ relative to HI could be attributed to different molecular gas diffusivity, unrelated to the perovskite degradation process.

Therefore, the MS detector used, sample mass and distance to collection could hinder to identify the key compound CH₃I for full understanding of the photo-, thermal-decomposition of MAPbI₃ perovskite at working temperatures (< 85 °C).

Hot carrier or thermally driven process? The origin of degradation in hybrid halide perovskite.

In contrast with Song *et al.*¹ where high energy photons are assumed responsible for the photodegradation, Juarez-Perez *et al.*² found that decomposition-release is likely a thermally induced process. Figure 1 shows selected m/z scans extracted from the contour plot in Figure 2 of Juarez-Perez *et al.*², with sample temperatures recorded during heating cycles in the dark. It is an experimental demonstration that the release of such species is not necessarily a hot carrier-induced decomposition.

The problem is that Song *et al.*¹ did not report simultaneous sample temperature recordings during their illumination tests. Sample temperature is affected during irradiation measurements depending on the optical filters applied. It could be inferred that low sample temperature could potentially explain the threshold observed when filtering out high photon energy below <395 nm. Hot carrier-induced degradation is not discarded as the origin of degradation during illuminated experiments. However, it is obviously problematic to ascribe the release of these gases to hot carrier-induced degradation when such gases are observed heating the sample under dark conditions.

Other remarks

CH₃I and NH₃ are not exclusively high-temperature decomposition products of MAPbI₃

Song *et al.*¹ mentioned that "Interestingly, the photodegradation products of MAPbI₃ differ from thermal degradation in which CH₃I and NH₃ were detected at above 300 °C by MS measurements", citing our early work in regard to TG-DTA/MS-coupled tandem experiments.³ Song *et al.*¹ concluded that CH₃I could be only observed during high-temperature degradation. However, CH₃I was already observed at relatively low temperature in such work (see Supporting Information in Juarez-Perez *et al.*³). In fact, one problem that we encountered there was that the Faraday cup

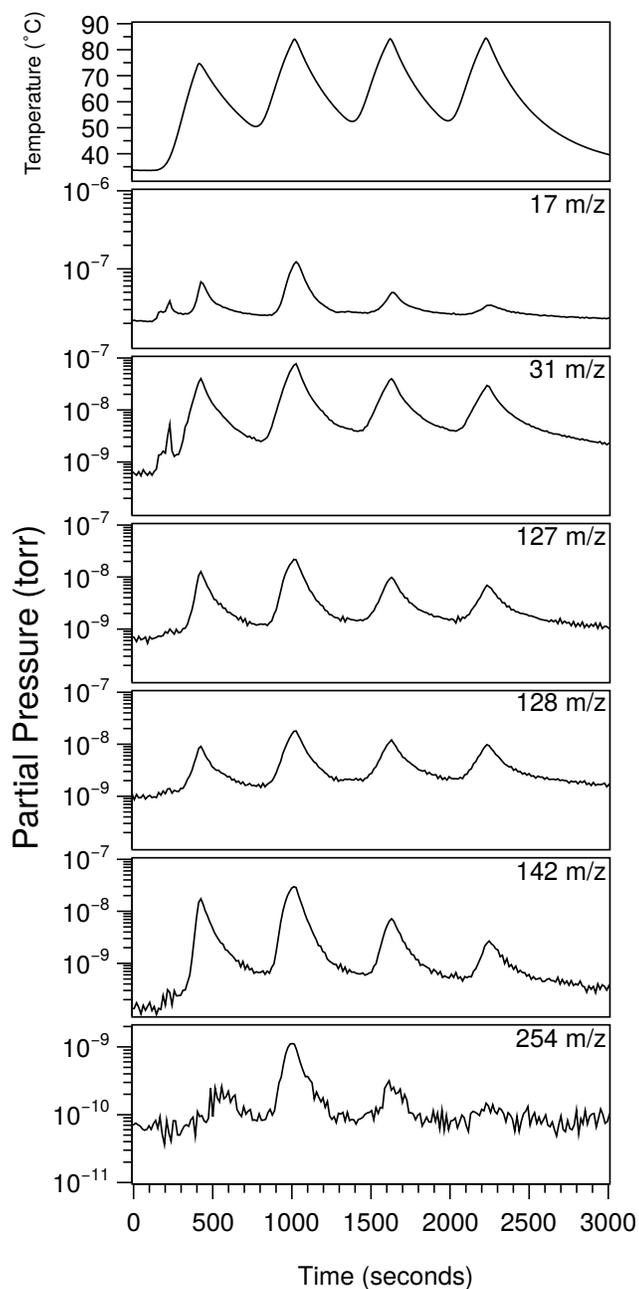


Figure 1 Top panel, sample temperature recorded during heating cycles under dark conditions. Note that temperature maxima are $\sim 85^\circ\text{C}$. Lower panels show the corresponding raw m/z mass traces (non-calibrated) recorded for NH_3 , CH_3NH_2 , I , HI , CH_3I and I_2 species using the electron multiplier detector of one Stanford Research System RGA 300 MS.²

detector was working at its limit of detection. At that time, we resolved the problem by using low-temperature cyclic ramps instead of constant low temperatures. Only then, the CH_3I m/z signal followed the low temperature cycles

inferring CH_3I release. Nonetheless, our subsequent work used the electron multiplier detector for increased sensitivity in MS experiments (Juarez-Perez *et al.*²). Then, we were able to reliably measure all volatiles released at low temperature (Figure 1), and the $\text{CH}_3\text{I}/\text{CH}_3\text{NH}_2$ molecular ratio of released volatiles was quantified (2-12%) at low-temperature ($35 - 85^\circ\text{C}$) in the dark. Therefore, CH_3I is not exclusively high-temperature decomposition product of MAPbI_3 . However, temperature determines the $\text{CH}_3\text{I}/\text{CH}_3\text{NH}_2$ ratio observed.

Why is the degradation reaction releasing $\text{CH}_3\text{I} + \text{NH}_3$ so important to long-term stability required for MA based photovoltaic cells?

The matters discussed above are critical because of the irreversible degradation of MA/I-based perovskite is produced via the $\text{CH}_3\text{I} + \text{NH}_3$ route.^{2,3} Contrarily, the reaction involving $\text{CH}_3\text{NH}_2 + \text{HI}$ release is an evaporation-like decomposition that is totally reversible to form back perovskite.⁴ There would be no degradation problems with $\text{CH}_3\text{NH}_2 + \text{HI}$ release in encapsulated devices. In fact, MAPbI_3 can be synthesized from PbI_2 under sequential or simultaneous exposure to HI and CH_3NH_2 gases.⁵ On the other hand, the $\text{CH}_3\text{I} + \text{NH}_3$ decomposition route is not selectively reversible back to MAI.⁴ The mere existence of the $\text{CH}_3\text{I} + \text{NH}_3$ decomposition path is the cause by which the organic cation MA^+ would be completely depleted in the long term while Le Chatelier's Principle attempts to restore chemical equilibrium.

A word of caution inferring release of I_2 from only the 127 m/z MS trace

Song *et al.*¹ assigned the 127 m/z ratio to molecular iodine release. Certainly, it corresponds to the half I_2 molecule and this fragment is observed when there is I_2 release. However, we encountered a situation in which we observed the 127 m/z ratio, but no 254 m/z . This counterexample corresponds to truly induced photodegradation of PbI_2 using irradiation wavelengths below its band-gap or low-temperature heating under dark conditions. Under dark conditions, only the 127 m/z ion is observed. A more detailed description of this experiment can be found in the Supplementary Information of Juarez-Perez *et al.*² In regard to the degradation of MAPbI_3 , the observation of an ion at 127 m/z can be ascribed to I_2 release (see for example 254 and 127 m/z traces in Figure 1). Notably, Song *et al.*¹ inferred the release of I_2 (254 m/z) by tracking the abundant signal corresponding to the 127 m/z ion. However, the Stanford Research System RGA 300 mass spectrometer equipment is able to detect masses as high as 300 m/z . We suspect that the 254 m/z I_2

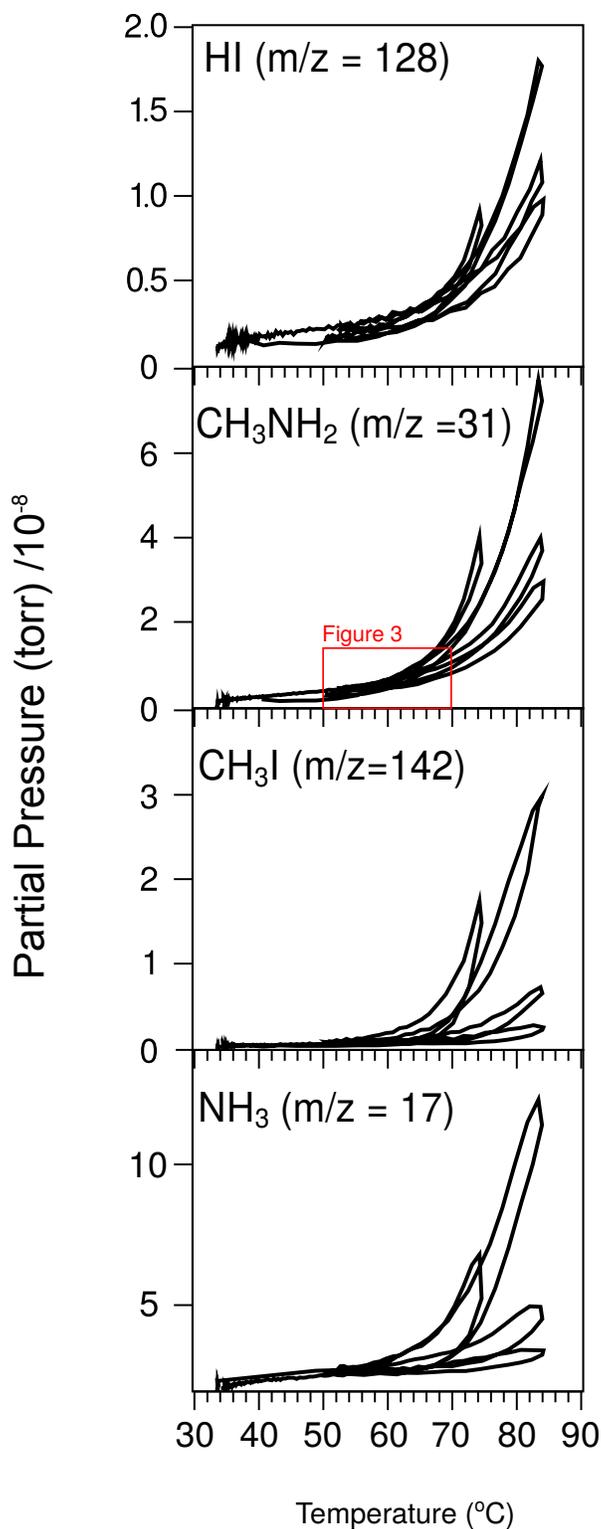


Figure 2 Temperature dependent gas release for Figure 1 including raw non-calibrated m/z mass traces for HI, CH_3NH_2 , CH_3I and NH_3 gas components using the electron multiplier detector of one Stanford Research System RGA 300 MS. Adapted with permission from reference 4. Copyright 2019 American Chemical Society.

peak was not detected because of the low sample mass.

A new stability quantifier parameter for mixed perovskites.

Despite no full determination of composition of all gases released by MS, one of the most interesting insights reported by Song *et al.*¹ is the quantitative observation of smaller amounts of organic species released from pristine formamidinium-based perovskite and ternary mixed perovskites including Cs^+ cations compared to full MA-based perovskite. This low gas release signature property seems interesting for quantification purposes on relative stability of mixed hybrid perovskite formulations. In principle, the full compositional space of hybrid perovskite (including organic/inorganic A site cations, mixed halides, dopings and recently considering mixed 2D/3D perovskite compositions) is being too broad to explore blindly, so *a priori* stability quantifiers are interesting for accelerating the gathering of optimal compositions in arbitrarily mixed hybrid perovskites (see for example García-Fernández *et al.*⁶).

Update after response (March 14, 2019)

Recently, Song *et al.*⁷ published a response to the above observations adding three new pieces of information relevant to understand completely their previously published article in SE&F:¹

1. They confirmed that a Faraday cup detector was used during all MS measurements.
2. They reported the temperature measured in the sample compartment as 65, 63, 62, 60, 58 and 57 °C depending of the filtering cut-off wavelength used 280, 320, 370, 395, 420 and 455 nm, respectively.
3. They confirmed the release of CH_3I carrying out a programmed temperature decomposition of MAPbI_3 thin-film (1 °C /min) using the same setup and sample size. They observed the release of CH_3NH_2 and HI after 80 min (~ 100 °C) followed by CH_3I after 160 min (~ 180 °C) see Figure 1 in their response.⁷

To provide a fair comparison with this programmed temperature experiment, the Figure 1 above in this commentary was converted to show the thermal pulses in terms of temperature rather than a time based x-axis, see Figure 2. It is important to be aware of three facts comparing this Figure 2 here and Figure 1 reported in Song *et al.*⁷ response:

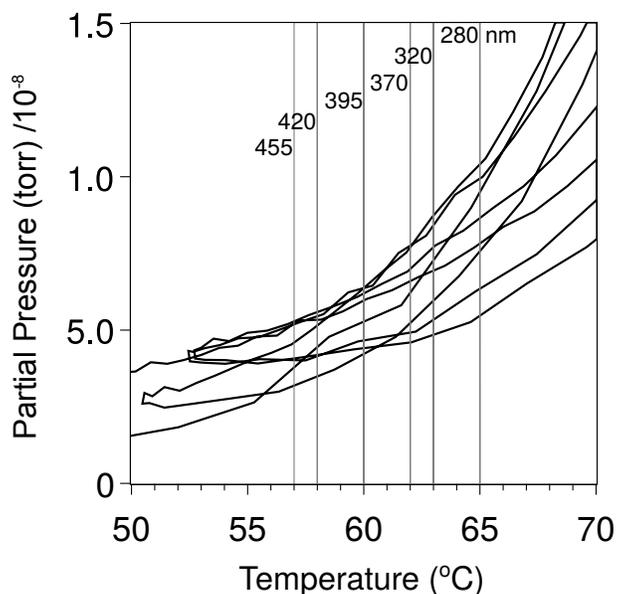


Figure 3 Inset from temperature dependent gas release from CH_3NH_2 panel in Figure 2. The eye-guide vertical lines are the recorded temperature achieved depending of the filter wavelength cut-off used as noted in reference 7.

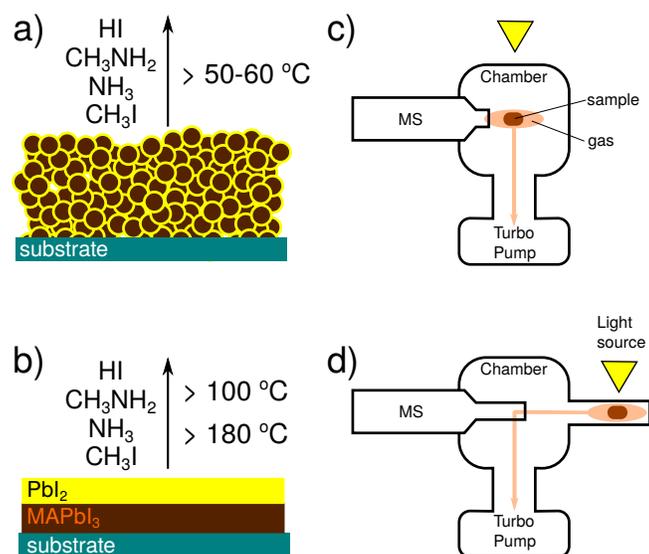


Figure 4 A schematic comparison of the sample morphology studied: a) powdered type sample² and b) thin-film sample.¹ Schematic comparison of chamber-MS configurations used: c) sample placed in the core of one UHV 6-ways cross chamber² and d) external sample chamber (see picture in Figure S1 in reference 1).

1. The temperature threshold for release of volatile species is $\sim 60^\circ\text{C}$ here in our experimental setup using thermal pulses in dark conditions and electron multiplier as MS

detector. Instead, $\sim 100^\circ\text{C}$ (CH_3NH_2) and $\sim 180^\circ\text{C}$ (CH_3I) were the temperature thresholds observed using a Faraday cup detector.⁷

- Released components become exhausted with each consecutive thermal pulse in Figure 2. Noticeably, the amount of CH_3I detected during the fourth pulse becomes almost negligible compared to early pulses.
- The temperature of the sample measured depending of the filtering cut-off wavelength used would have a large influence in the amount of gases detected. We have placed vertical eye-guide lines tagging each one of these temperatures in the CH_3NH_2 panel of Figure 2, see Figure 3. Interestingly, there would be a difference of $\sim 50\%$ in partial pressure detected in our data if we had used a 280 nm (65°C) or a 455 nm (57°C) cut-off filter. Therefore, one could suspect that the apparent demonstration of photodegradation process could have a more straightforward explanation considering that it as a pure thermal driven degradation process. On other words, thermal heating, rather than high energy photons, is the main cause responsible of the release of volatile species of MAPbI_3 .

Ostensibly, the type of MS detector used during degradation tests would have a large influence on the type of inferred degradation mechanism accounted for MAPbI_3 . However, there would be a non-highly speculative situation where both mechanisms could be accommodated. It could be speculated that first, the outermost perovskite losses organic components by thermal degradation meanwhile a PbI_2 cover crust is generated in its place acting as UV filter. Then, inner or core MAPbI_3 could lose organic components but detected at considerably higher temperature and also influenced by the crust of PbI_2 covering core MAPbI_3 . This scenario would be supported by the fact that probably our powdered sample would have a higher surface area ratio than a perovskite thin-film and degradation has been verified as a surface initiated process.⁸ Figure 4(a,b) depicts schematically the morphology of the samples.

In any case, it is hard to assume that filtering off the high energy photons by using UV filters is a valid solution to stop the degradation if it does not lead to sustained temperature drop. Even without considering that there would be a loss of efficiency by filtering off useful photons to achieve a good photovoltaic efficiency.

Additional comments

- In their response, Song *et al.*⁷ suggest that our results would be influenced from a perovskite sample contaminated of MAPbI_3 -DMF intermediate. Our

sample contains adsorbed solvent as detected by MS in ref. 2, but in no case it could be a crystalline structural solvent. It has been reported before that the resulting perovskite material after annealing still contains a significant amount of residual adsorbed solvent.⁹ However, the presence of MAPbI₃-DMF intermediate is evidenced with a distinctive diffraction pattern for 2θ below 10°. ^{10,11} But our MAPbI₃ sample does not show such diffraction pattern, see Figure 5.

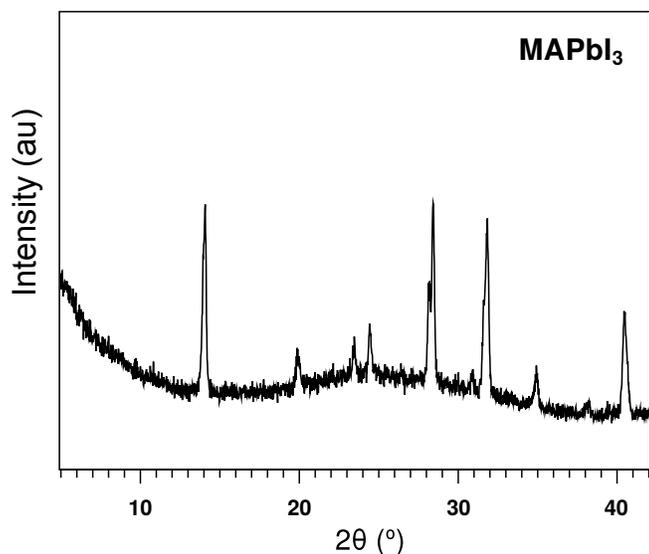


Figure 5 XRD powder diffraction of MAPbI₃ powdered polycrystalline samples. This diffractogram was already reported as Figure S1 in reference 2 but the diffraction pattern showed there was for $2\theta > 10^\circ$.

- In their response, Song *et al.*⁷ claimed to carry out a thermal gravimetric analysis (TGA) in nitrogen at 80 °C for 5 hours and they did not observe any significant change in the sample weight. It is plausible for a 5 hours eye-blink in photovoltaic time terms. However, one would have to carefully consider what time interval could be significant to state that there would be no changes during the life cycle of this material used in photovoltaic applications.
- In their response, Song *et al.*⁷ claimed to place the sample in the “line-of-sight” of the MS detector needing less amount of sample for detection. Certainly, our sample is not located in the pumping flow direction. Instead, we placed the sample as close as possible to the detector (~1 cm) assuring the almost instantaneous detection response demonstrated in matter of few seconds in contrast with hundred of minutes. Figure 4(c,d) summarize the main differences and similarities between both configurations.

- In their response, Song *et al.*⁷ suggest that the ratio of the released CH₃I and NH₃ should be close to 1. Instead, the amount of NH₃ is almost one order of magnitude higher than CH₃I. We agree that this ratio should be close to one but only after proper calibration of compounds in this specific MS setup. In fact, identical problem appears for the CH₃NH₂/HI ratio being the amount of CH₃NH₂ also ~4x higher than HI in our data. The explanation for this fact is that our data in Figure 1 contains only non-calibrated m/z ratio traces as notified in the caption of such figure. In our previous work, we obtained the sensitivity factors for CH₃NH₂ and CH₃I to quantify the relevant CH₃NH₂/CH₃I ratio (see Section 6 in SI of reference 2). But we ruled out calibration for NH₃ because it is a problematic molecular peak. It would need to discount the OH fragment from water and methylamine fragment adding intensity current to the 17 m/z ratio and account losses from protonated NH₃ becoming NH₄⁺ and rising the intensity current in 18 m/z. Instead of perfect quantitative matching between intensity recorded, it is more important to note the resemblances between the shapes of the pulses observed in Figure 2 between the pairs CH₃NH₂/HI and CH₃I/NH₃. These similarities could indicate that the release is connected by the same process or reaction.

- In their response, Song *et al.*⁷ disagreed that the CH₃I + NH₃ route could be detrimental at relatively low temperature because

“many have demonstrated decent stability of encapsulated MAPbI₃ solar cells. For example, a report by the Grätzel group on the outdoor tests of encapsulated MAPbI₃ in the hot desert climate with longterm light soaking at 80 - 85 °C for three months with no evidence for device degradation.”

In my opinion, those outdoor tests were probably one of the best operational stability tests ever reported since 2015. It is no coincidence that such superb operational stability was achieved using a back contact carbon electrode. Furthermore, it is not necessary to exaggerate the conditions under which the tests were carried out. A careful reading of this article reveals that the conditions indicated by Song *et al.*⁷ in their response were never applied simultaneously. But the results are still excellent. In regards of long term stability tests on encapsulated devices, my opinion is that the “reversible-kinetic-abundant-benign” CH₃NH₂ + HI route could be not able to explain solely the frequently observed slow fade out of the devices when using pure MA-based perovskite. Therefore, an “irreversible-thermodynamic-sparse-nonselective-and-detrimental”

route is likely to be running in parallel. It could be the $\text{NH}_3 + \text{CH}_3\text{I}$ route.⁴ Otherwise, a total absence of detrimental routes would mean that the encapsulated MA-perovskite would never deteriorate. However, it is widely known not to be the case.^{12,13}

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