Point-to-point answers to the comments of Referee #1

We sincerely thank Referee #1 for their time and effort in reviewing our manuscript and for providing thoughtful comments and suggestions. We believe that addressing these points has led to significant improvements in the quality and clarity of the manuscript.

General comments

RC1: 1)

1.1

When reading the ABSTRACT, I assumed the authors had systematically evaluated the aforementioned parameters and quantified their impacts on the reaction. However, it appears only a range of light wavelengths was evaluated (e.g. Figure 5). Salinity, one of the key parameters investigated in the paper, as underlined in the ABSTRACT, was discussed in only two lines of words in the main text (Page 12 Line 1-2) and the authors stated “it is not the focus of this paper to discuss the details of the salinity….”, and only two pHs were present in this work because of the interfere of carbonation on pH rather than intentionally designed. I suggest the authors revise the abstract to better reflect the study’s core findings and objectives.

1.2

The literature cited in the INTRODUCTION is quite outdated, as all references are from before 2020, many recent related studies concerning the chemistry at SML have not been introduced in the INTRODUCTION.

AC1:

1.1

We appreciate the referee’s insightful comment and agree that the Abstract did not clearly reflect the core findings and objectives of the study. Accordingly, we have revised the Abstract to more accurately represent the scope of our investigation, emphasizing the primary focus on interfacial photochemistry and specifying the extent to which parameters such as light wavelength, pH, and salinity were addressed.

1.2.

Regarding the citations in the Introduction, our original references were selected to provide background specific to the studied system and the reference work by Tinel et al. (2016), which served as the motivation for this study. Given the referee’s valid point, we have now updated the Introduction to include recent and relevant studies related to chemistry at the sea surface microlayer (SML). We welcome further suggestions from the referee for any additional literature that would enhance the context of our work.

New citations can be found in (P3: L 10,17,19,21,29, 33,34), (P4: L1,4,7,19, 21), and (P5: L6)

RC1: 2)

In the CHEMICAL COMPOSITION section, the data comparison with Tinel et al. (2016) is missing, the comparison should be highlighted as this study built upon this previous work. Additionally, error bars only present in Figure 10, they are absent in Figures 7-9 and 13, which is critical for accurately representing variability and ensuring clarity in the results.

AC2:

While the comparison with Tinel et al. (2016) was already included in various sections of the original manuscript, we have now made it more prominent in the revised version and added a clearer and more structured comparison in Tables S4–S6, which list the photoproducts identified in both studies and indicate which were detected by either or both. The relevant text of the revised manuscript where this comparison is now explicitly highlighted include:

P10, L18-25

P16, L16-18

P20, L16-19

P22, L5-8

P24, L7-9

P25, L5-10

Tables S4 - S6

Regarding the figures, we have added error bars to Figures 7, 8, 9, and 10 (now Figures 8, 9, 10, and 11 in the revised manuscript, respectively) to better represent data variability. For Figure 13 (now also Figure 13 in the revised manuscript), which is a pie chart, adding error bars as suggested by the referee would reduce clarity. Instead, we now report the associated error values in Table S7 of the revised SI.

RC1: 3)

I recommend that the authors integrate the "Results" and "Discussion" sections into one cohesive section. Solely describing the experimental results made it difficult for me to understand the intended purpose of the designed experiments. For example, paragraphs describing Figure 4&5 began by starting "To quantify the influence of the solar radiation…..", and then evaluated three different lights on the SFG signal of a solution with pH=4.5, it abruptly shifted to investigation on another solutions with pH=5.6 without drawing any insights from the data presented in Figure 4.. Separating these sections can reduce readability and make it challenging for readers to grasp the key points quickly derived from the experimental data, at the same time it can help in simplifying the paper because many contents are overlapped in these two sections.

AC3:

We appreciate the reviewer's valuable suggestion. In response, we have combined the "Results" and "Discussion" sections into a single, cohesive section (section ***3 Results and Discussion****). This restructuring has significantly improved the clarity, flow, and readability of the manuscript by aligning interpretations more directly with the experimental findings and reducing redundancy.*

We would also like to clarify a potential misunderstanding: the manuscript does not include any data for solutions at pH = 4.5. To minimize the complexity associated with pH effects, particularly those observed at pH = 8 in Figure 2, we continued our experiments from Figure 3 onward using solutions with slightly lower pH values, specifically within the range of pH = 5.4 to 5.6 (reported in the revised manuscript as pH = 5.5 ± 0.1).

RC1: 4)

In the DISCUSSION section, While I expected this section to provide deeper insights into the key findings and the key parameters influencing this reaction mechanism and how they compare to Tinel et al. (2016), the authors instead devoted two full pages (23-24) to explaining why the aromatic peak is absent in Figure 1b but appears in Figure 2b. Unfortunately, their speculative claims lack solid evidence or any supporting references.

AC4:

We appreciate the reviewer's observation regarding the extent of the discussion presented on pages 23–24 of the original manuscript. Our intention was to explain the absence of the aromatic SFG signal from 4-BBA in the presence of NA, despite the previously reported surface partitioning of 4-BBA by Tinel et al. (2016). However, we acknowledge that the level of detail may have detracted from the main focus of the discussion and lacked sufficient supporting evidence.

In the revised manuscript, we have substantially refined the discussion to focus more directly on the comparison with the reference study (see AC2). Based on feedback from both referees and revising the MS data, we revised the structure and interpretation of the discussion to provide a clearer and more evidence-based explanation. We now include additional supporting references, quantitative fits, and a more concise interpretation (see for example P10, L18-25, and P23, L5 – P24, L6). The original speculative discussion in pages 23–24 has been removed in the revised version to maintain clarity and relevance.

RC1: 5)

Although it is interesting that the authors found that the shorter UV part of the solar spectrum is responsible for the studied reaction and the product abundances, this is a case study, and in my opinion, I question whether these findings could be generalized to other similar reactions (e.g. imidazole-2-carboxaldehyde or other chromophoric dissolved organic matter that serve as photosensitizers). As a result, the conclusions may have limited utility in refining photochemical models.

AC5:

We appreciate the Referee's thoughtful comment and understand the concern regarding the generalizability of our findings. While the specific compounds mentioned, such as imidazole-2-carboxaldehyde or other chromophoric dissolved organic matter (CDOM), were not included in this study, we can only offer a perspective based on the mechanisms observed in our system.

Our results "likely" extend to similar photosensitized reactions, particularly those involving short-UV-absorbing organic chromophores at the air–water interface. However, direct experimental validation using other compounds, such as those suggested by the Referee, is essential to confirm the broader applicability of our conclusions. Mechanistically, compounds like 4-BBA and the Referee's examples often act as photosensitizers through processes such as photoinduced electron or energy transfer, which can drive secondary interfacial chemistry. The ability of 4-BBA to facilitate the photolysis of nonanoic acid under shortwave UV suggests that similar behavior may be expected from other sensitizers absorbing in the same spectral range. Nonetheless, the generalization of this behavior depends on factors such as surface activity, interfacial partitioning, and radical-generating capacity. If these characteristics are comparable, similar reactivity patterns might be observed.

We also acknowledge that environmental systems are far more complex than the controlled case studied here, as was already mentioned in the Conclusions section (now refined in the revised version, P25, L28-32). CDOM, for example, is highly heterogeneous in both structure and reactivity, and real-world conditions involve mixtures of substrates and sensitizers, fluctuating irradiation, and dynamic interface properties. Therefore, while our study provides valuable mechanistic insight, broader conclusions would require further investigation using additional model systems and environmentally relevant mixtures.

RC1: 6)

In my view, this manuscript is poorly organized and has provided limited value-added insights to the community.

AC6:

We agree with the referee that the original manuscript lacked clarity in both structure and detail. In the revised version, we have significantly improved the organization, presentation, and interpretation of our results.

While the reference study by Tinel et al. (2016) demonstrated the relevance of this system using bulk techniques, the added value of our work lies in the application of SFG spectroscopy. This surface-specific technique allowed us to probe molecular interactions and reaction pathways at the air–water interface that are inaccessible through bulk analysis. As highlighted in the revised manuscript, a key example of this contribution is our detection of interfacial aromatic photoproducts, which indicate the photolysis of 4-BBA, presented only as a photosensitizer in the reference study, under solar irradiation. This allowed to understand the production of aromatic compounds.

Moreover, we uniquely observed the UV-dependent formation of benzaldehyde, in the gas phase, from 4-BBA in the absence of NA, and the formation of stable interfacial products resulting from the interaction of photoproducts from both 4-BBA and NA. One such example is the amphipathic compound $C_9H_{10}O_5$*, which exhibits surface activity and was not reported in the reference work. These findings represent important value-added insights into interfacial photochemistry and contribute to a deeper understanding of atmospheric processes.*

Relevant texts in the revised manuscript include:

P20, L21-24

P22, L14-16

P23

P24, L7-9

Specific comments

RC1: 7)

Page 3. Line 29: I would suggest the authors to define ppt as parts per thousand to avoid confusion with parts per trillion.

AC7:

Done, P4, L6 in the revised manuscript..

RC1: 8)

Page 5. Line 33: SI should be defined here.

AC8:

Done, P6, L16 in the revised manuscript.

RC1: 9)

Section 2.2: This section is actually describing the light source rather than the photochemical reactor.

AC9:

This was a typo, now corrected to "light source". P6, L18

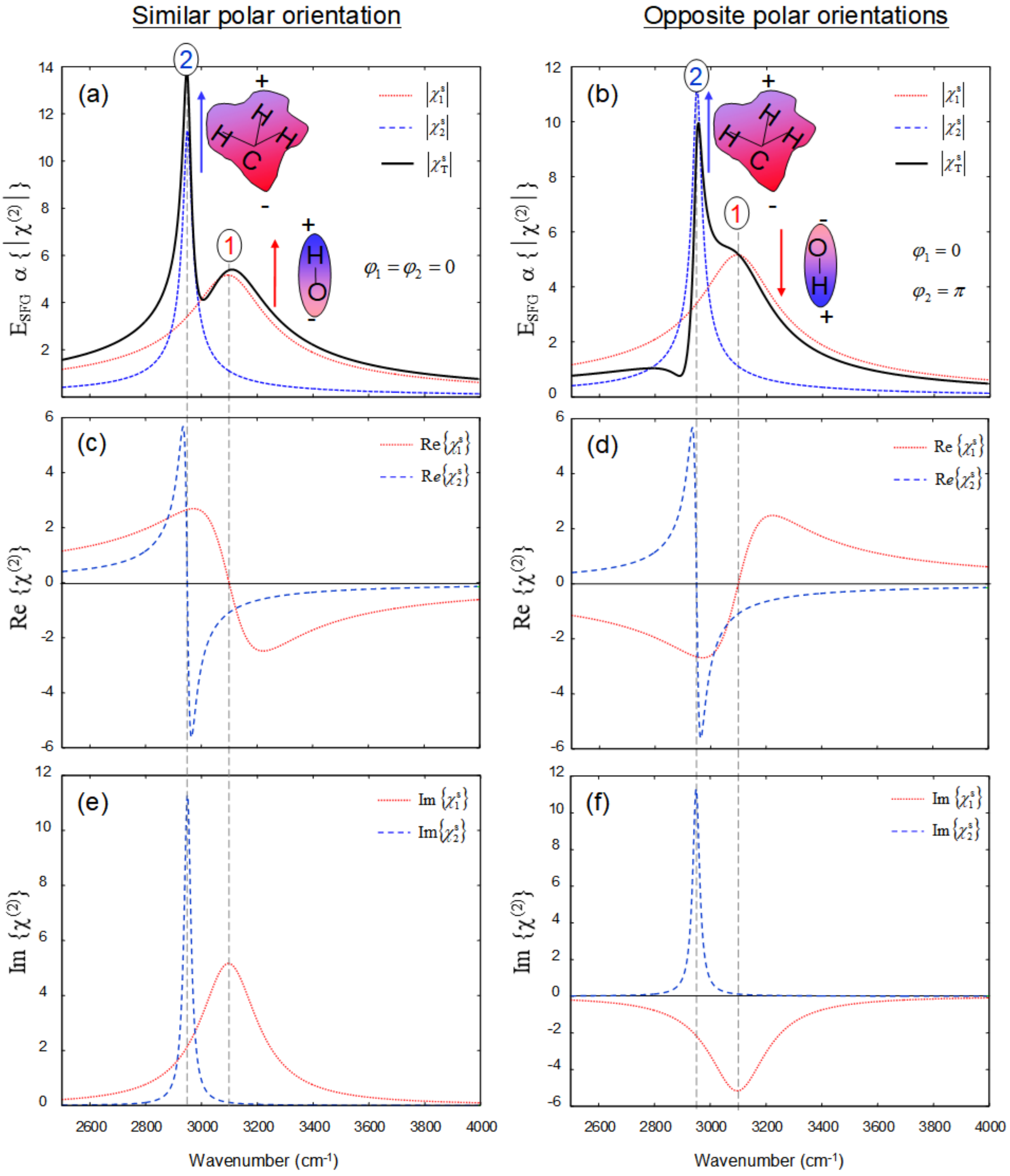
RC1: 10)

Page 9 Line 10: I don't see the appearance of the new band at 3070 in Figure 2b, it is too weak to be seen, perhaps a zoom-in inset would improve clarity. This problem also applies to Figure 4&5, where I question how did the authors distinguish the signals around 3000 as C-H from aromatic compounds rather than background noise? To me, there signals appear nearly identical to the background. I reviewed the two cited studies (Gautam et al., 2000; Hardt et al., 2024) but didn't see a standard SFG spectra peak that assigned as aromatic compounds.

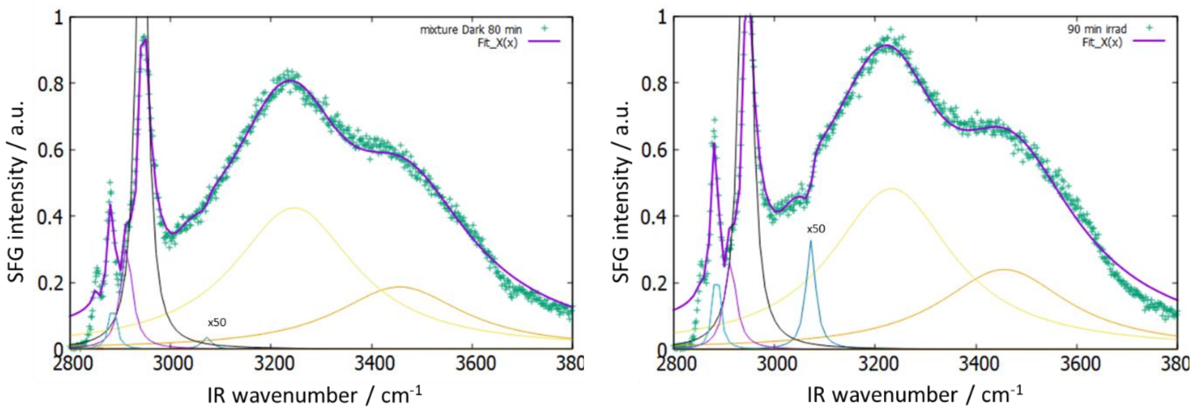
AC10:

We have to clarify here that the convolution of bands in SFG spectroscopy is more complex than in linear IR spectroscopy. In SFG, the resulting spectral shape is not solely determined by the intensity, central frequency, and linewidth of individual bands, but also by their relative phase, which depends on molecular orientation. This is particularly important when resonances are close in frequency, as interference effects can either enhance or suppress individual features.

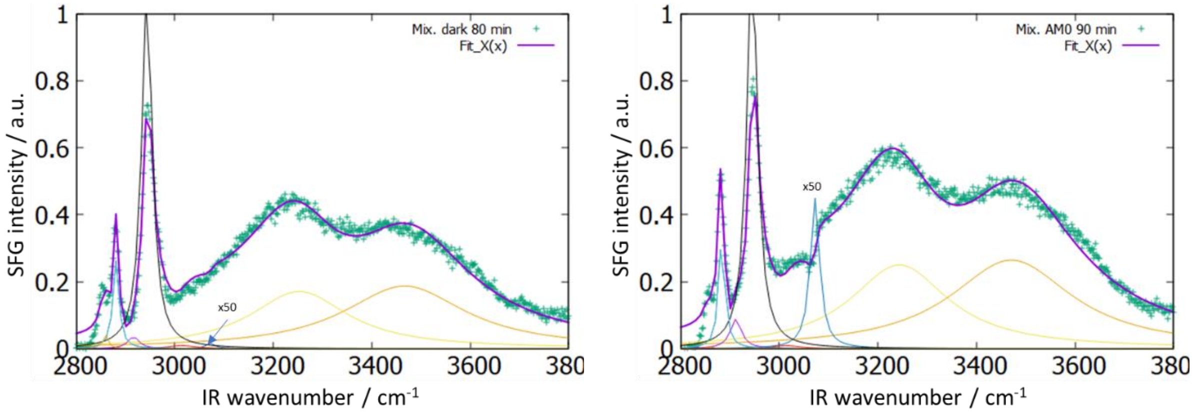
To illustrate this, we have included a simulated SFG spectrum (see below) showing the response from two resonance modes: one broad band (Γ_1 = 250, A_1 = 4, ω_1 = 3100 cm^{-1}) and one narrower band (Γ_2 = 30, A_2 = 1, ω_2 = 2950 cm^{-1}). We show two cases: (a) both resonances in phase ($\varphi_1 = \varphi_2 = 0$), and (b) the resonances out of phase ($\varphi_1 = 0$, $\varphi_2 = \pi$). Panels (c) and (d) compare the real parts of $\chi^{(2)}(\omega_{IR})$ for cases (a) and (b), and panels (e) and (f) show the corresponding imaginary parts (i.e., the absorptive component). In all simulations, the non-resonant contribution $\chi^{(2)}_{NR}$ was set to zero. This highlights how the overall spectral shape, and even the visibility of individual bands, can be significantly affected by phase relationships.



Due to such effects, the individual contribution of bands, such as the aromatic C–H stretch near 3070 cm^{-1}, may not be visually obvious in raw SFG spectra. Therefore, proper spectral fitting is essential. As detailed in Section S3 of the SI, we used a fitting model incorporating a non-resonant background and a sum of Lorentzian functions to extract key band parameters (center frequency, amplitude, and FWHM). An example of the result of this fitting procedure is shown in Fig. S7 (original SI), applied to the spectrum under dark conditions. To address the reviewer's concern directly, we have now added new Figure (Fig. S11) to the SI. We also added new figure to the manuscript (Figure 4) where we compare the change in water bands with the aromatic band, and the behavior of the aromatic bands at different pHs.

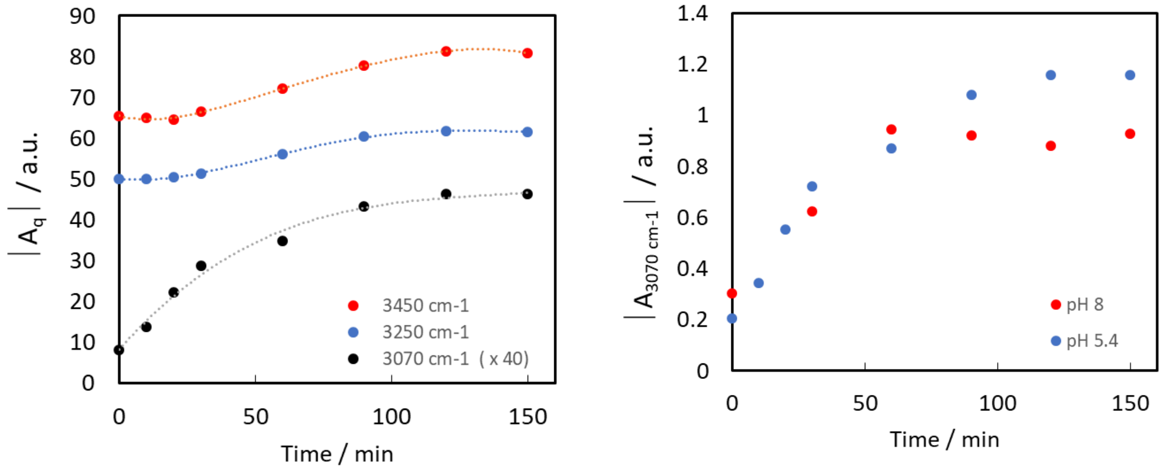


(a) pH 8 – Dark **(b) pH 8 – AM0**



(c) pH 5.4 – Dark **(d) pH 5.4 – AM0**

Figure 11 illustrates the individual bands, including the aromatic C–H band at ~3070 cm⁻¹ for the mixtures at pH 8 and pH 5.4 before and after AM0 irradiation for 90 min.



(a) (b)

Figure 4 shows the time-dependent changes in the fitted SFG peak amplitudes with AM0 irradiation. (a) The aromatic band (~3070 cm⁻¹) and the two water bands (~3250 cm⁻¹ and ~3450 cm⁻¹) for the mixture at pH 5.4 (Dashed lines are included as visual guides). (b) The aromatic band (~3070 cm⁻¹) for the mixtures at pH 5.4 and pH 8.

Regarding the cited references (Gautam et al., 2000; Hardt et al., 2024), while they examined different systems, both studies clearly identify SFG bands assigned to aromatic C–H stretching modes in the 3030–3085 cm^{-1} range:

1. *Gautam et al., 2000*
    - *Page 3854: "The phenyl side groups in PS exhibit five vibrational modes composed of C-H aromatic stretches, which are both Raman and infrared active. These five modes are believed to have resonance frequencies at 3084, 3069, 3057, 3036, and 3024 cm^{-1} …"*
    - *Page 3855: "SFG spectra for both PS/air and PS/sapphire interfaces contain peaks between 3000 - 3100 cm^{-1}, corresponding to aromatic C-H stretching vibrations. A sharp resonance at 3069 cm^{-1} corresponding to the v2 vibrational mode dominates the Ippp and Issp spectra …"*

      These attributions were supported by their references [10] and [11] in the cited paper.

2. *Hardt et al., 2024*
    - *Section: CnAAP/PDADMAC mixtures at the interface:*
      "… Whereas the antisymmetric stretching bands are centred at ∼2930 (d−) and ∼2965 cm^{-1} (r−), bands at ∼3030 cm^{-1} and ∼3060 cm^{-1} are attributed to the C–H stretching modes of the aromatic ring. …"

Together, these citations justify our assignment of the ~3070 cm^{-1} band to aromatic C–H stretching vibrations, in agreement with previous SFG studies.

RC1: 11)

Page 11 Line 3: Please define the "UV part".

AC11:

Done, P13, L19 in the revised manuscript.

RC1: 12)

Page 11 Line 23-24: What are the so-called increase and decrease compared to? Based on my understanding from Figure S11, it should be except for 310nm, there is always an increase and then a decrease in the water bands with irradiation (compared to the dark condition).

AC12:

This sentence was wrong. It has been corrected in the revised manuscript (P14, L26-28 in the revised manuscript).

RC1: 13)

Page 18 Line 5-7: A reference is needed here.

AC13:

Done, P13, L6 in the revised manuscript.

RC1: 14)

Page 18 Line 5-7: Why do not discuss in details here? Dividing the discussion into separate subsections will significantly reduce the readability of this paper.

AC14:

We have refined this paragraph with more details. The new paragraph (P12, L19 – P13, L9):

"… . The OH stretching modes in the 3100 cm^{-1} – 3500 cm^{-1} region, associated with interfacial water, increased after irradiation with AM0. See the fitted spectra in Figure S11. There is a clear proportion between the increase of the water band with the aromatic band, Fig. 4a. We attribute this to the formation of amphipathic aromatic compounds after irradiation, which can alter the hydrogen-bonding structure of water at the interface. Since SFG spectroscopy is inherently sensitive to the net polar orientation of interfacial molecules detecting vibrational modes only when molecular ordering breaks inversion symmetry, an increase in the SFG signal of hydrogen-bonded OH stretches indicates that water molecules at the interface have adopted a more ordered, non-centrosymmetric arrangement. This provides evidence for the presence of amphipathic species at the air–water interface, which promote directional hydrogen bonding via their polar headgroups. As a result, interfacial water molecules become more aligned, breaking the random symmetry of bulk water, orienting OH dipoles, and enhancing the net polar order, manifested as an increased SFG signal in the OH stretching region (Gragson and Richmond, 1998; Kusaka et al., 2018). A direct comparison between the fitted SFG peak amplitudes of the aromatic band (~3070 cm^{-1}), Fig. 4b, for pH 5.4 and pH 8 mixtures shows that the pH 5.4 have higher relative increase in the band strength indicating a better environment for the formation of the corresponding amphipathic aromatic compound."

RC1: 15)

Page 18 Line 13-16: What is the “UV part”? I would argue that the UV part above 300nm of the solar spectrum can reach the sea surface.

AC15:

Indeed, the spectrum at sea surface includes UV above 300 nm, as has been illustrated in Fig. S4b. However, its intensity is significantly lower than that of AM0, Fig S4a, which results in a reduced, though not entirely absent, formation of aromatic compounds under AM1 conditions for the same irradiation time. This is reflected in the weaker aromatic band observed under AM1 conditions. We have revised the wording in the manuscript to clarify the meaning:

The original sentence was:

“This means that the main effect producing the aromatic compound comes from the UV part of the solar spectrum and such a photoproduct would be produced in the atmosphere (e.g. in cloud droplets) than at the sea surface. On the other hand, the visible part of the spectrum produces fewer photoproducts.”

The revised sentence is (P13, L 24 – P14, L4):

“Irradiating the mixture with only the UV portion of AM0 ($\lambda <$400 nm) shows a clear aromatic band with minimal changes in the water bands, Fig. 5c. This provides an evidence that the UV contribution plays a primary role in the formation of the surface-active aromatic compounds. Consequently, this photoreaction is likely more pronounced in the atmosphere (e.g. in cloud droplets) than at the sea surface where the UV intensity below 300 nm is very weak (see Fig. S4).”

For clarity, in this study, “UV part” refers to radiation with wavelengths below 400 nm. We selected the UV portion of AM0 in this particular part of the manuscript to highlight the maximum photochemical effect.

Note: in the revised manuscript we use the term “UV portion” instead of “UV part”.

RC1: 16)

Page 18 Line 18-25: How do you see these? I strongly recommend that the authors combine the Discussion with the Results section. This integration will help to elaborate on the key findings more effectively while enhancing the overall flow and coherence of the pape.

AC16:

We have combined the “Results” and “Discussion” sections into a single section “3 Results and Discussion” in the revised manuscript.

RC1: 17)

Page 18 Line 32: A reference is needed here.

AC17:

This paragraph has been modified and moved to the revised SI (SI P11, L22 – P12, L4).

RC1: 18)

Page 23 Line 1-19: References are needed to support the proposed two reaction pathways.

AC18:

Based on the refined interpretations of our results, pages 23–24 have been removed from the revised manuscript.

RC1: 19)

Page 24 Line 1-6: Green curve in Figure 1b is overall lower than others, not only the dangling HO band. How do you say it is because of benzaldehyde?

AC19:

Please note that it the green curve in Fig. 1b is overall lower than the black curve. Black curve is pure water and it is plotted hear to compare the existing features with and without 4-BBA.

The paragraph the Referee refers to is comparing the dark 4-BBA signal (blue curve) to the signal after 30 min AM0 irradiation (green curve). This comparison shows small but noticeable decrease in the dangling OH. The changes in the broad water bands (in the region 3100 cm-1 to 3500 cm-1) is entirely within the signal-to-noise, even if compared to the signal after 60 min of AM0 irradiation (red curve). The formation of benzaldehyde, as detected in the gas phase by the MS results, may temporary interrupt the water network at the interface during formation and evaporation. (see P9, L21-24 in the revised manuscript)

In the revised manuscript we removed the speculations about this subtle effect and focused on the main findings.

Technical corrections

RC1: 20)

Typing errors: Page 5. Line 25-26; Page 7 Line 19; Line 31: vapor-water → air-water (Maintain consistency in terminology);

AC20:

Done (P6, L7-10), (P8, L15-17), and (P9, L3) in the revised manuscript

RC1: 21)

Others: “SI” and “supporting information” were interchangeably throughout this paper. This inconsistency also applies to “Fig. X” and “Figure X”, which should be unified throughout this paper.

AC21:

- *SI has been now defined in the first appearance and then SI used along the rest of the manuscript (P6, L16 in the revised manuscript).*
- *“Figure” and “Fig.” are being interchanging along the manuscript based on the journal instructions. “Figure” is used in the beginning of the sentence and “Fig.” is used elsewhere.*