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The literature cited in the INTRODUCTION is quite outdated, as all references are from before 2020, many recent related studies concerning the chemistry at SML have not been introduced in the INTRODUCTION.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

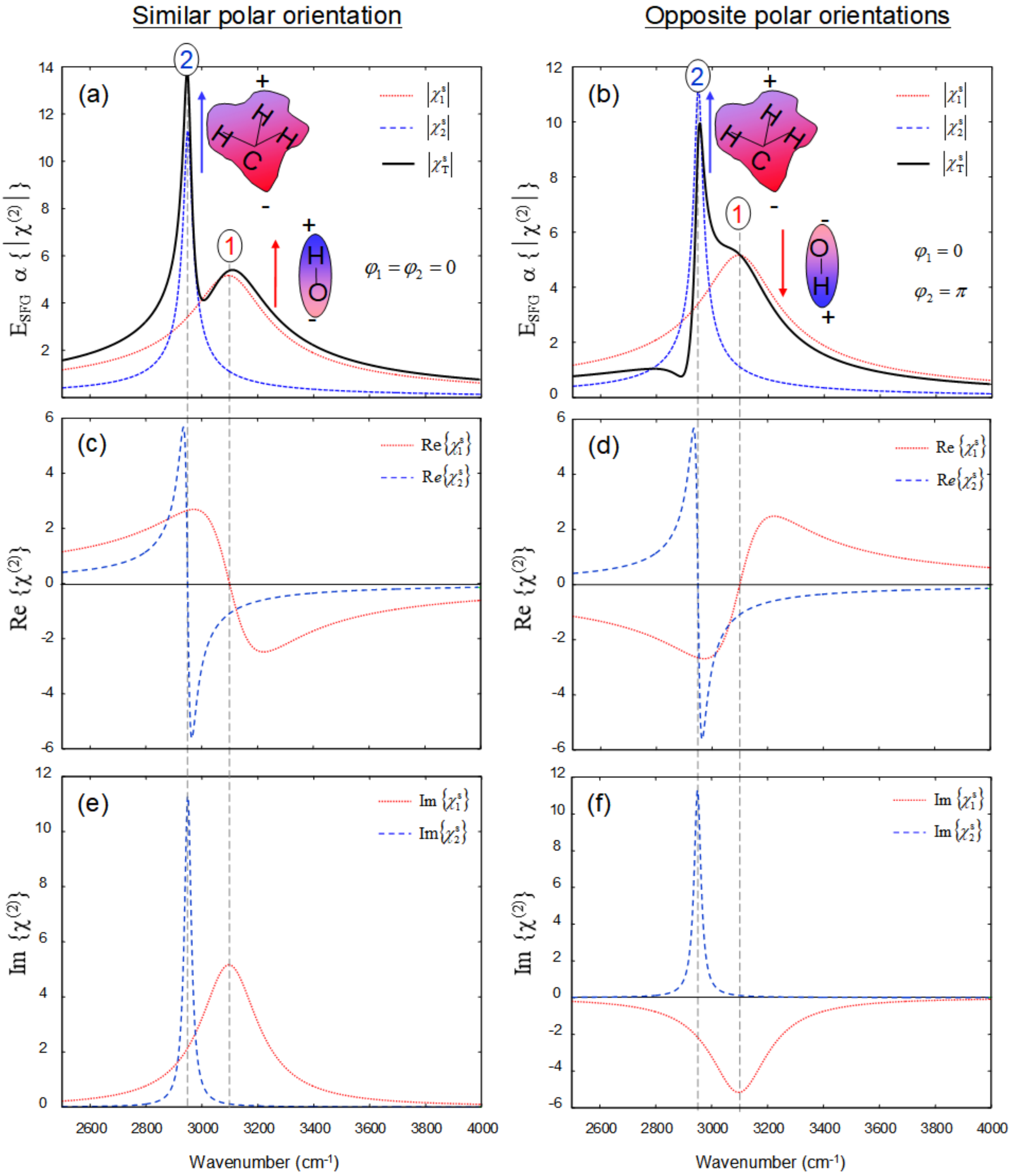
RC1: 10)

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.

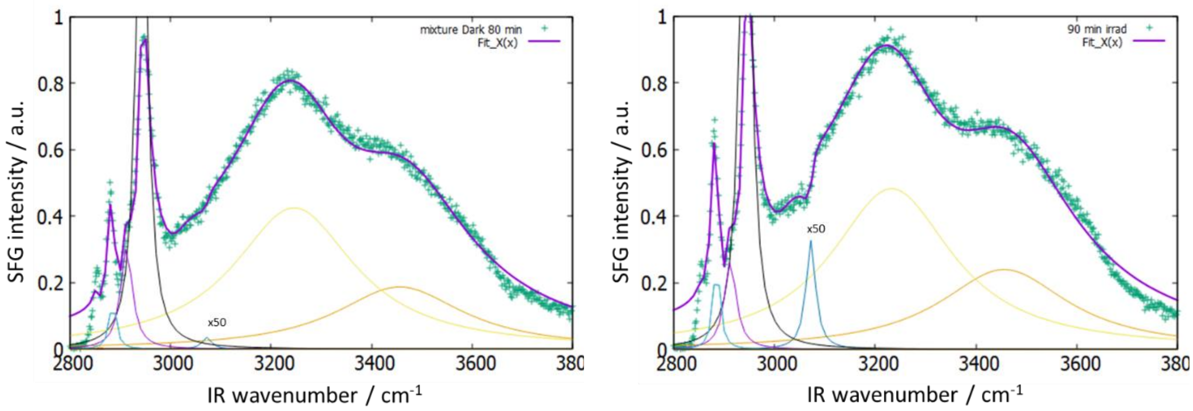
AC10:

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.

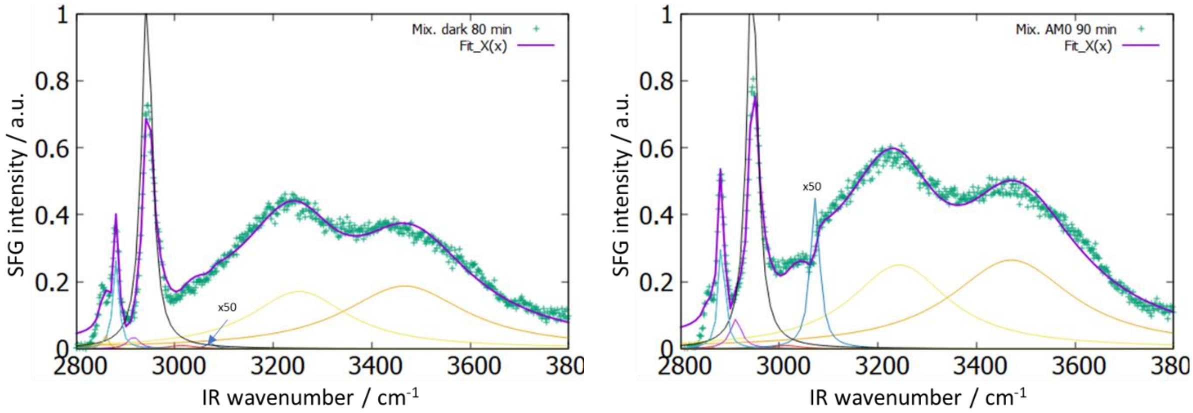
To illustrate this, we have included a simulated SFG spectrum (see below) showing the response from two resonance modes: one broad band ($\Gamma_1 = 250$, $A_1 = 4$, $\omega_1 = 3100\ \mathrm{cm}^{-1}$) and one narrower band ($\Gamma_2 = 30$, $A_2 = 1$, $\omega_2 = 2950\ \mathrm{cm}^{-1}$). We show two 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.*

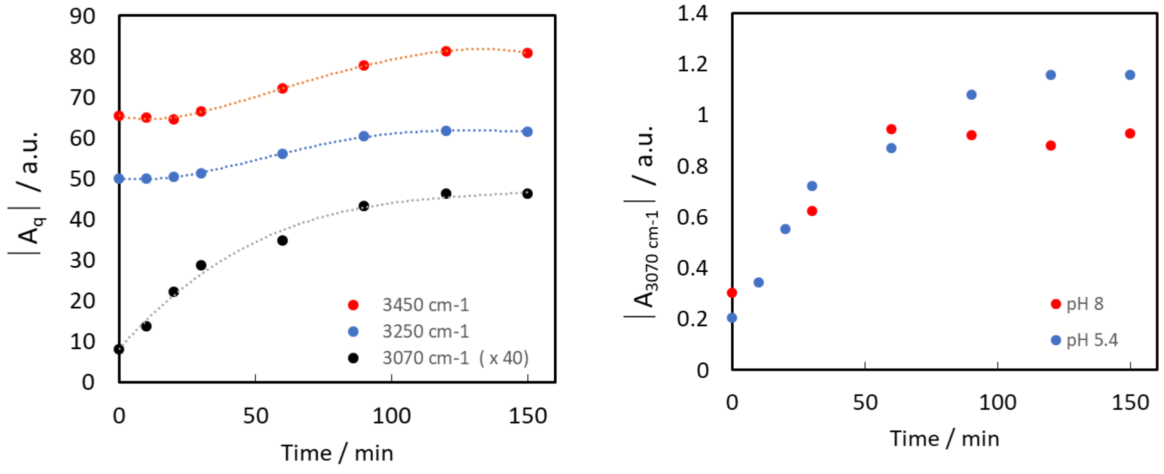


(a) pH 8 – Dark **(b) pH 8 – AM0**



(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.*

Point-to-point answers to the comments of Referee #2

We thank Referee #2 for the time and effort dedicated to reviewing our manuscript, as well as for the constructive comments and valuable reference suggestions. We are particularly grateful for the insightful remark in Comment **RC2: 21**, which prompted a substantial revision of the findings presented in this work. We believe that addressing the referee's suggestions has significantly improved the clarity and quality of the manuscript.

General comments

RC2: 1)

The reader remains frustrated as the study focusses on results at pH 5.4-5.6 since their solution at pH 8 did not sufficiently buffer to work with this pH under stable conditions. Further, the announced study in function of the salinity, is contradicted and resumed by a simple sentence 'The SFG study also showed that the salt concentration of the bulk accelerates the photo reaction. It is not the focus of this paper to discuss the details of the salinity effect on the photochemistry at this surface, we only register the observed phenomenon' (P11,L28 - P12,L2). This is contrary to the statements in the conclusions and the abstract of the paper, and really limits the scope of the paper. It would have been very interesting and novel to explore more in detail the influence of salinity on this reaction, especially since the preliminary results in the SI seem encouraging. Since the experiments discussed finally neither fully explore the effect of pH nor salinity, the paper can no longer claim that it is providing insights for interfaces of diverse natural water systems.

AC1:

We thank the referee for this thoughtful and constructive comment. We acknowledge that the Abstract and Conclusion in the original manuscript did not fully reflect the actual scope and core findings of the study. In response, we have revised both sections to more accurately represent our primary focus on interfacial photochemistry, and to clearly delineate the extent to which the influences of light spectrum, pH, and salinity were addressed.

Salinity:

While a detailed analysis of the salinity effect was beyond the intended scope of this study, we agree that its influence is scientifically relevant and warrants further investigation. Our current data showed a clear trend of salinity accelerating the interfacial photoreaction, which we have now clarified in the revised manuscript. We view this observation as a valuable preliminary result and have included it in order to motivate and support future studies, including our own planned work, contingent on funding availability.

pH:

Regarding pH, we have refined the manuscript to better explain the differences observed between low and high pH conditions. Although high pH conditions were challenging to *maintain due to uncontrolled carbonation, we were able to indirectly assess their effects on interfacial structuring and photoproduct formation. In the revised version, we now include additional analysis based on SFG data fitting, highlighting the behavior of the aromatic band (~3070 cm^{-1}) at both pH 5.4 and pH 8 (P13, L6-12 and Figure 4b in the revised manuscript). This comparison demonstrates a more pronounced increase in the aromatic signal at pH 5.4 following identical light exposure (AM0, 150 minutes), indicating that lower pH conditions are more favorable for the formation of surface-active aromatic species. We attribute this trend to the higher availability of protons at lower pH, which facilitates the formation of the* $C_{14}H_{11}O_3$• *radical from photoexcited 4-BBA (see Eq. 1 in the revised manuscript). This radical plays a key role in subsequent surface reactions, as detailed in the "Tentative reaction pathways" section in the revised manuscript.*

We believe these revisions provide a more accurate representation of the study's scope and clarify how our findings contribute to the broader understanding of interfacial photochemistry.

RC2: 2)

There are further no citations in the discussion section, although quite a few works work using this photosensitizer exist which could help clarify the observations made. This is particularly the case when the authors propose reaction mechanisms that seem quite original and rather unlikely. Citing previous works that have observed or proposed mechanisms would make their propositions more convincing. In several places, the discussion section is repetitive and the reasoning seems to turn in circles, in particular when discussing the SFG spectrum features of the aromatic band and the OH group. The discussion section needs thorough reworking, in light of all remarks in this review (here and following). Once this is done, the abstract and the conclusion section should be reworked as well to better reflect the main points developed in the work..

AC2:

In response to the referee's comment, we have thoroughly revised the manuscript to improve clarity, reduce redundancy, and better substantiate our interpretations. Specifically, we have merged the "Results" and "Discussion" sections into a single integrated section. This restructuring has enhanced the logical flow of the manuscript by aligning the interpretation of findings more directly with the corresponding experimental results.

We have also refined the proposed reaction mechanisms and included relevant citations in the revised ***Section 3.2.3 (Tentative reaction pathways)*** *to support and contextualize our interpretations within the existing literature.*

We acknowledge that the previous discussion of the SFG spectral features, particularly concerning the aromatic band and the OH group, was overly detailed and at times unclear. Our original aim was to reconcile the absence of an aromatic SFG signal from 4-BBA in the presence of NA with earlier findings by Tinel et al. (2016), who reported the surface partitioning of 4-BBA under similar conditions.

In the revised version, we have streamlined this discussion, focusing specifically on comparisons with the reference study. We now provide a clearer and more concise interpretation, supported by data fitting, figures, and appropriate citations

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

The abstract and conclusion have also been updated to reflect the key points and improved structure of the revised discussion.

Specific comments:

RC2: 3)

L10: 'volatile organic compounds (VOCs) can make up a significant fraction of atmospheric aerosols, particularly in urban and industrial areas.' As is, this statement is incorrect to my knowledge. I think the authors mean that the secondary reaction products of VOCs can contribute significantly to aerosols. Please adjust.

AC3:

We thank the reviewer for this valuable observation. The sentence has been revised for accuracy and now reads:
"It has been estimated that the secondary reaction products of volatile organic compounds (VOCs) can contribute significantly to secondary atmospheric aerosols (SOA)…"

P3, L7-9 in the revised manuscript

RC2: 4)

L19-20: the CDOM references are very old and it has since been shown that CDOM is not always enriched at the surface, see for Van Pinxteren et al.[1], Stolle et al.[2] or Tilstone et al.[3] for more recent work on this. Please modify the sentence to reflect this.

AC4:

We thank the reviewer for highlighting this important point. The sentence has been revised to reflect the more current understanding of CDOM distribution. The revised sentence:

"It was previously believed that CDOM is more concentrated at surfaces than in the bulk (Carlson, 1983; Carlson and Mayer, 1980), however, more recent studies have shown that CDOM is not always enriched at the surface (van Pinxteren et al., 2020; Stolle et al., 2020; Tilstone et al., 2010)."

P3, L26-29 in the revised manuscript

RC2: 5)

P4, L3-4: please add some more recent and environmentally relevant references for the existence of SML and its contribution to seaspray (e.g. review by Tinel, L. et al. Impacts of ocean biogeochemistry on atmospheric chemistry. Elementa: Science of the Anthropocene 11, 00032 (2023) and Sellegri, K. *et al.* Influence of open ocean biogeochemistry on aerosol and clouds: Recent findings and perspectives. *Elementa: Science of the Anthropocene* **12**, 00058 (2024)).

AC5:

We thank the referee for the helpful suggestion. The following sentence has been added to the revised manuscript along with the recommended citations:

"Recent studies have highlighted the critical role of ocean biogeochemistry in shaping atmospheric composition and influencing aerosol–cloud interactions. In particular, the sea surface microlayer has been recognized as a key interface for biologically driven gas emissions, with important implications for their representation in large-scale atmospheric models (Tinel et al., 2023). Moreover, oceanic biogeochemical processes have been shown to affect aerosol formation and cloud properties, thereby contributing to climate-relevant feedback mechanisms (Sellegri et al., 2024)."

P4, L16-21 in the revised manuscript

RC2: 6)

P4, L18-20: the list of publications is not well reflecting the work 'in recent years' – please update the references, in particular the paper by Freeman-Gallant, et al. (Photooxidation of Nonanoic Acid by Molecular and Complex Environmental Photosensitizers. *J. Phys. Chem. A* **128**, 9792–9803 (2024)) is of interest for the current manuscript and should be included in the introduction.

AC6:

Thank you for the suggestion. The outdated citations have been removed in the revised manuscript. We have incorporated the recent study by Freeman-Gallant et al. (2024), which presents new findings on the NA–4BBA system and offers relevant insights following the earlier reference work. The updated text now reads:

“Tinel et al. (2016) demonstrated that the photosensitized degradation of fatty acids at the air–water interface, specifically nonanoic acid (NA) in the presence of 4-benzoylbenzoic acid (4-BBA) and imidazole-2-carboxaldehyde as model systems, enhances VOC emissions and secondary aerosol formation (Tinel et al., 2016). A subsequent study by Alpert et al. (2017) reported the formation of SOA particles through photochemical reactions and ozonolysis of saturated long-chain fatty acids and alcohol surfactants at the water surface (Alpert et al., 2017). More recently, Freeman-Gallant et al. (2024) showed that the efficiency of NA photooxidation in thin films depends on the type of organic photosensitizer, with 4-BBA identified as the most effective among those tested (Freeman-Gallant, et al., 2024).”

P4, L32 – P5, L6 in the revised manuscript

RC2: 7)

P5, L13-15: this sentence relates results obtained and does not seem at its right place here; I suggest to remove.

AC7:

We agree with the referee and removed the mentioned sentence.

RC2: 8)

P5, L18: what do the authors consider a ‘normal pH’ ? Please specify.

AC8:

The phrase "normal pH" was a typographical oversight. During the refinement of the introduction to better align with the study’s core focus, we removed the entire sentence in question.

RC2: 9)

P5, L23: Did the authors take any precaution as to the purification of nonanoic acid? This is important to precise, since Saito, S. *al.* (Impurity contribution to ultraviolet absorption of saturated fatty acids. *Science Advances* **9**, eadj6438 (2023)) reported that impurities can play a role in the photochemistry observed.

AC9:

NA was used as received, without additional purification. We did not observe any evidence that impurities in our NA sample influenced the photochemical reactions under the irradiation conditions used in this study. This information has been added in the revised manuscript (P6, L4-7).

RC2: 10)

P6; 2.2: how was the temperature kept stable upon irradiation?.

AC10:

The irradiation cell was mounted on a large metal table that acted as an efficient heat sink, within a temperature-controlled laboratory environment. Quartz windows were used to allow light transmission during irradiation. The LED light source, emitting only at wavelengths below 550 nm, generated negligible thermal radiation. Additionally, cooling air from the light source electronics was directed away from the measurement cell to avoid thermal influence. This information has been added in the revised manuscript (P6, L33 – P7, L3).

RC2: 11)

P7, section 2.4: the transfer of the sample with a syringe of a surface-active solution can induce biases due to more or less sampling of the surface layer and adsorption to the syringe (or filter). Can the authors detail what part of the solution was sampled with the syringe and if they assessed the reproducibility of this sampling + measurement method?.

AC11:

In the MS experiments, distinguishing surface-derived signals from bulk-phase contributions is inherently challenging. To ensure that the sampled liquid solution was representative of the entire system, the solution was thoroughly stirred prior to sampling to homogenize any surface-enriched compounds with the bulk. The syringe tip was then inserted into the center of the bulk phase to draw the sample. In contrast, the SFG technique is intrinsically surface-specific due to its selection rules, which exclude contributions from the isotropic bulk. This distinction underscores the complementary nature of the two methods. In the revised manuscript, we have clarified how SFG data help identify surface-active compounds among those detected by MS.

Sampling from the liquid phase has been revised in P8, L9 -12 in the revised manuscript.

RC2: 12)

P10, L1-9: Have the authors tried to increase the strength of the buffer solution to try and stabilize the pH at 8?.

AC12:

Yes, we attempted to stabilize the solution at pH 8 using a buffer. While the pH remained stable, the SFG experiments showed no detectable changes upon irradiation. Additionally, we had concerns that the use of a pH 8 buffer in the photochemical system involving NA and 4-BBA could quench reactive intermediates or alter the surface activity of both reactants and products. This may suppress or modify interfacial photochemical pathways that are central to the observed reactivity.

RC2: 13)

P11, L26-P12, L2: this does not seem an appropriate conclusion to this section. Please state clearly what the main observations are from the study under different wavelengths. The influence of the salinity should be discussed separately or be omitted altogether.

AC13:

13.1

We would like to clarify that the statement on P11, L26–L28 ("The individual irradiation wavelengths have both different wavelengths and intensities, which was done on purpose to mimic the corresponding solar irradiance for each wavelength.") was not intended as a conclusion but rather as an explanation for the choice of irradiation settings. This point is further elaborated in the Discussion section (P18, L17–25) of the original manuscript. In the revised version, where the "Results" and "Discussion" sections have been merged, this part has been restructured to more clearly present the observations related to the effects of different irradiation wavelengths (P14, L9 – P15, L5).

13.2

Regarding the salinity effect mentioned in the sentence, "The SFG study also showed that the salt concentration of the bulk accelerates the photoreaction (see Sect. S5 and Fig. S14),…" we acknowledge the reviewer's concern. As noted in our response AC1, this is a preliminary observation and not the central focus of the current study. Nevertheless, we felt it was important to document the finding and share it with the community to encourage further investigation. We have reworded the statement in the revised manuscript to clarify that we are reporting the phenomenon without drawing detailed conclusions (P15, L10-14). We are also open to the reviewer's suggestion for a more appropriate placement of this statement within the manuscript.

RC2: 14)

P13, section 3.2.1: the authors discuss aqueous products under irradiation of NA solution and NA+BBA solutions, however in the previous section the changes in spectra with only NA at pH 5.8 are not discussed. Did they see changes there and expected products to be formed from pure NA solutions? Do they see evidence of impurities as well, as discussed by Saito, S. et al. (Impurity contribution to ultraviolet absorption of saturated fatty acids. Science Advances 9, eadj6438 (2023))?.

AC14:

We partially addressed this point in our response to Comment AC9. NA was used as received, without further purification. Under the irradiation conditions applied in this study, we observed no evidence that photochemical reactions were taking place upon the UV absorption of impurities in the NA sample. When NA was irradiated in the absence of 4-BBA, the product signals remained at background levels, indicating minimal or no photochemical activity.

*We acknowledge that a typographical error in the first sentence of Section 3.2.1 may have contributed to the reviewer's confusion. The original sentence, "**The products of the photochemical reactions of NA were detected under different irradiation and at a fixed pH of ~5.8.**", was missing the phrase "**in the presence of 4-BBA**" This has been corrected in the revised manuscript. The updated sentence now reads: **"The products of the photochemical reactions of NA in the presence of 4-BBA were detected under different irradiation and at a fixed pH of ~5.8."** (P 16, L12-13)*

RC2: 15)

P13, Fig 6: the caption currently reads 'concentrations of each of the photoproducts': since quantifying with CIMS is particularly challenging, especially for compounds for which no standards are available, I suggest to replace this by 'normalized intensities of each…'. Further, it is unclear what the error bar for the sum of products indicates here.

AC15:

The authors agree with the Referee, it should be the "normalized intensities", as already indicated on the y-axis label. We have rephrased the figure caption to indicate the normalized intensities and also clarified in the caption that the error bars represent the analytical uncertainty associated with the measurements.

Note: Figure 6 in the original manuscript has become Figure 7 in the revised manuscript.

RC2: 16)

P13, L24-26: the much larger increase of some products under O2 conditions, is probably also indicative of primary and secondary products formed; hence it looks like $C_8H_{12}O_4$ could be one of the primary products formed and the other products secondary products, that are more limited due to the lack of oxygen available. Did the authors also see new products formed under oxygen low conditions? This would be interesting to help elucidate formation mechanisms.

AC16:

We did not observe the formation of new products under low-oxygen conditions. Only changes in the relative contributions of the main products listed in Table S4 to the total $C_xH_yO_z$ signal were detected. Signals from other compounds remained at background levels and did not indicate the emergence of additional products under these conditions.

RC2: 17)

P17, L13-14: the authors state that the study was done in conditions '…similar to the real environment at sea water and droplets in the atmosphere.' I'm not convinced this is indeed the case, as most experiments were done without no salinity and at pH 5.8 and irradiation at AM0, conditions that are neither representative for aerosol, droplets nor sea surface. I suggest to nuance this statement..

AC17:

This sentence has been removed from the revised manuscript.

RC2: 18)

P18, L22-25 and P25, L13-15: do the authors suggest that differences due to different wavelengths (through geographical location, time etc) are currently not taken into account in models? What kind of models are they thinking of here? The reference is not correctly cited as well.

AC18:

We do not suggest that differences in spectral power distribution, arising from factors such as geographical location or time of day, are currently excluded from models. Rather, our intention is to emphasize the importance of accounting for such variations, as they can significantly influence photochemical processes at the air–water interface. The citation has been corrected in the revised manuscript.

RC2: 19)

P18, L31: the authors suggest that the reason for the rapid decrease of the pH is the decarboxylation of 4-BBA. This is a little surprising to me, as this is not the main pathway for 4-BBA reactions (which is expected to be a reduction of the carbonyl group, e.g. Calvert & Pitts, 1966), and should thus only be a minor CO2 source. It should be noted that NA can also undergo decarboxylation, which is a likely a major pathway, as expected for an aliphatic organic acid (and seen some major products observed are C8). Could the authors make a quantitative estimate of how much CO2 they need to change the pH as observed and what sources they think contribute (solubilisation of gas vs decarboxylation) ? This could help better understand how much 4-BBA or NA is expected to disappear.

AC19:

*We thank the referee for this insightful comment and acknowledge that the original paragraph was unclear. The discussion referred to the behavior of the "**mixture of NA and 4-BBA**" under UV exposure, rather than 4-BBA alone, as can be seen in Figure S12 (in the original manuscript), which was cited in the paragraph. We have now revised the text for clarity and scientific accuracy.*

To maintain the focus of the main manuscript, we have moved the entire section previously titled "4.2. Evolution of pH values", including the corrected paragraph, to the revised Supporting Information, now under section "S4. Changes of pH with time and UV exposure."

See revised SI P11, L22 – P12, L7

Note: Figure S12 in the original SI has become Figure S13 in the revised SI.

RC2: 20)

P19, L12: 'Normally NA is only partially dissociated' Can the authors please precise here what 'normal' they referred to? It would be good to relate this behaviour to the pKa of NA at 5.23, pH at which NA will thus be present at a proportion of 50/50 in ionic and deprotonated form.

AC20:

In this context, we meant that nonanoic acid (NA) in aqueous solution is partially dissociated across a wide range of pH values (see P12, L13-15 in the revised SI). To clarify, we now include a plot (Fig. S13b) showing the dissociation fraction of NA as a function of pH. As expected, the dissociation fraction increases with pH, which corresponds to a decrease in NA's surface activity, and vice versa.

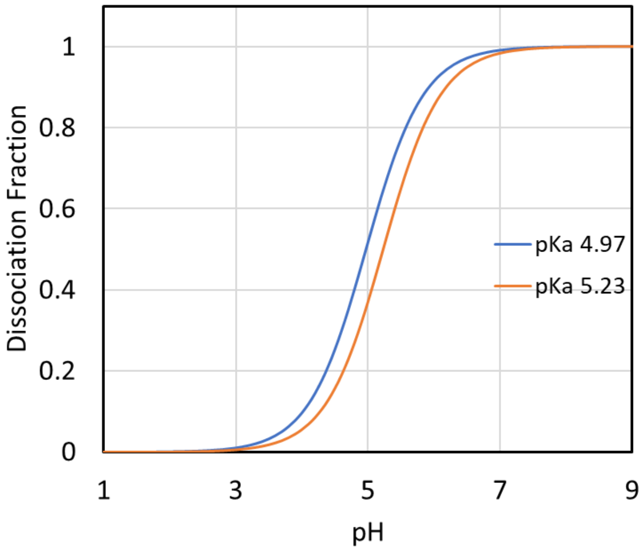


Fig. S13b (here we include the pKa value cited by the referee (5.23) and the pKa value 4.97 from the literature (Luo et al., 2020; Wellen et al., 2017) for NA).

In support of this, the offline experiment shown in Fig. S13a demonstrates this behavior. The gray curve represents a mixture, initially at pH 8.4, irradiated with 280 nm UV light. After two hours, the pH decreased by approximately 20%, indicating a measurable shift in NA dissociation during the experiment. By contrast, the green curve, corresponding to a mixture starting at pH < 6, shows a stable pH throughout. This suggests that, in our SFG and MS experiments under low pH conditions the dissociation fraction of NA remained constant over the course of the experiments.

The new dissociation plot referenced above has been included in the revised (SI).

RC2: 21)

P20, L2-5: The formation of the C9H10O5, suggested to be an aromatic compound, from irradiation of 4-BBA alone is quite surprising. Are the authors sure this is not contamination from a previous experiment (e.g. rinsing several times, repeated results)? If precautions were taken to avoid contamination, further investigation is needed to better understand this unusual reaction mechanism. The reaction mechanism proposed P22, L11 (and also L16) indicates an addition of bicarbonate. The probability of this reaction taking please again depends on the concentration of CO2 expected to be dissolved (see remark above). Bicarbonate would also be majorly under its fully protonated form at pH 5.4, and should thus better be written as H2CO3.

AC21:

We sincerely thank the Referee for this insightful and constructive comment. It prompted a careful revise of our mass spectrometry data, which in turn led to more accurate and supported interpretations. Based on this review, we confirm the following:

1. ***$C_9H_{10}O_5$ was not produced by the irradiation of 4-BBA alone.***
2. ***It was also not the result of contamination****, as appropriate rinsing procedures were followed, and the finding was consistently reproduced across independent experiments.*
3. ***$C_9H_{10}O_5$ was exclusively observed in the irradiation experiments of NA + 4-BBA****, with its relative abundance varying depending on irradiation conditions and the presence or absence of oxygen. (see P20, L21-24 in the revised manuscript)*

In light of these findings, we have revised the proposed reaction pathways accordingly in the manuscript (see section 3.2.3 Tentative reaction pathways).

Furthermore, we now attribute the aromatic band observed in the SFG spectra to $C_9H_{10}O_5$ rather than benzaldehyde. While our original hypothesis suggested benzaldehyde as the source of the interfacial aromatic signal, its detection in the gas phase makes this assignment less likely. In contrast, $C_9H_{10}O_5$ is non-volatile and may possess amphipathic, surface-active aromatic characteristics. This makes it a more plausible candidate for the origin of the interfacial aromatic signal, as now described in the revised manuscript.

RC2: 22)

P22, L8-11, L13-17: it would be very helpful to have a developed reaction mechanism schematic instead of the brut formulas here. There are several steps that seem unrealistic, notably the additions of bicarbonate as mentioned before, and in particular L16 where the addition of bicarbonate on an RO2 radical leads to further unsaturations. This could also help clarify the quite unclear discussion of the mechanism P23, L10-14.

AC22:

As noted in our response to comment AC21, the proposed reaction pathways and corresponding text have been revised in the updated manuscript. A schematic representation of the refined reaction mechanism is now provided in the revised Supporting Information (Fig. S15). Additionally, the unclear discussion in pages 23–24 has been removed to improve clarity and focus, as they lacked sufficient supporting evidence and detracted from the main interpretation of our findings.

RC2: 23)

L23, L1-6: this seems like an unnecessary repetition and can be removed

AC23:

Removed

RC2: 24)

P23, L20-P24, L25: The explanation for the appearance of the aromatic band given here is not very convincing; it seems a little far-fetched to use an observed gas-phase product (benzaldehyde) to explain changes in the SFG spectrum at the surface and link these to the lower OH band. It seems like the aromatic band should form with and without NA. Since it is only observed in the presence of NA, this could be due to having less NA at the surface, as it will be more oxidised and hence more solubilised, which would lead to an increase in the aromatic signal from 4-BBA. The appearance of the aromatic band could also be due to other liquid phase products formed from a self-reaction of 4-BBA alone; however, these products are not discussed in the paper explicitly and would not explain why the aromatic band is not observed with BBA alone. Furthermore, benzaldehyde may interact with OH groups from water in a similar way as 4-BBA, since they both have a carbonyl function. This discussion should be revised thoroughly; quantitative (or estimations) of photolysis yields for primary photoproducts from 4-BBA or estimated loss rates of 4-BBA could be helpful in this discussion.

AC24:

Pages 23 and 24 have been removed from the revised manuscript in the light of our refined interpretations (see AC21 and AC22).

Note: The increase in the aromatic band cannot be due to 4-BBA, particularly after having less NA at the surface. 4-BBA is not surface-active. The appearance of the aromatic band is indeed due to other liquid phase products however formed from the photolysis of NA + 4BBA as described in the revised manuscript. This is now discussed in the revised manuscript with the potential reaction path ways.

RC2: 25)

P24, L26-31: it’s unclear what the authors are trying to convey in this paragraph; is this meant to further explain the dangling OH band feature? Or is this supposed to explain photoreaction products (which should be mainly radical reactions however)? It’s also unclear why the presence of catalysts is invoked here.

AC25:

Pages 23 and 24 have been removed from the revised manuscript in the light of our refined interpretations (see AC21 and AC22).

Language and minor edits:

RC2: 26)

P4, L24: nonanoic acid should not take a capital here, to be consistent with other chemicals.

AC26:

Corrected (P4, L33 in the revised manuscript)

RC2: 27)

SI: S6, Table S3: pH =MilliQ, please replace by the measured pH value of the ultrapure water.

AC27: (Table S3 in the revised manuscript)

Replaced

RC2: 28)

P8, L5 & L23: neglectable: should be negligible

AC28:

Replaces (P10, L8 in the revised manuscript)

RC2: 29)

P9, L25: seens the following discussion, I suggest to remove ‘simply’

AC29:

Removed

RC2: 30)

P10, Fig 3a: the legend indicates AM0 but the caption indicates these are dark experiments. Please correct.

AC30:

Corrected (Fig 3a in the revised manuscript)

RC2: 31)

P11, L1: one and a half hours: please write as 1.5 h

AC31:

We replaced it by “90 min” (P13, L21 in the revised manuscript)

RC2: 32)

P16, L12: ‘…(see Table S5). Only…’ this is the same sentence, please remove the capital.

AC32:

This sentence has been reworded in the revised manuscript. (P22, L2-5 in the revised manuscript)

RC2: 33)

P16, Fig. 11: please indicate for which solutions these results are shown.

AC33:

Indicated (Fig 12 in the revised manuscript)

RC2: 34)

P17, L18: the year of the reference is missing

AC34:

Corrected. (P16, L5-6 in the revised manuscript))

RC2: 35)

P18, L28: for solutions with a higher pH value of 8; the whole sentence is not grammatically correct

AC35:

This sentence has been corrected and reformulated in the revised manuscript.

(P11, L15-17 in the revised manuscript)

RC2: 36)

P22, L5: improved: please replace by increased

AC36:

Replaced (P20, L9 in the revised manuscript)

RC2: 37)

P22, L1: please add '…the solution with 4-BB **and NA'**

AC37:

Added (P20, L17 in the revised manuscript)

RC2: 38)

P24, L16: afterword: should be afterwards

AC38:

Pages 23 and 24 have been removed from the revised manuscript in the light of our refined interpretations (see AC21 and AC22).

RC2: 39)

P24, L29: I think I should be a conjugate **base**, not acid?

AC39:

Pages 23 and 24 have been removed from the revised manuscript in the light of our refined interpretations (see AC21 and AC22).

RC2: 40)

SI, S5, Table S1: last column: please correct the units to mM.

AC40:

Corrected (Table S1 in the revised manuscript)