

**Surface-Bulk Photochemical Coupling of Nonanoic Acid and 4-Benzoylbenzoic
Acid: The Dual Role of the Photosensitizer and Environmental Influences**

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1 Abstract

2 Organic compounds concentrated at air–water interfaces, such as the sea–surface microlayer (SML),
3 or aerosol and cloud droplets, are key contributors to complex photochemical reactions. Nonanoic
4 acid (NA) is surface active and 4-benzoylbenzoic acid (4-BBA) is a photosensitizer. This study
5 combines investigations at the air water interface by sum-frequency generation (SFG) spectroscopy
6 and in the liquid and gas phases by mass spectrometry (MS) to study the photochemical interactions
7 of both substances at the air–water interface. We identify a novel interfacial aromatic signal via SFG,
8 revealing surface-localized photoproducts previously undetected ($C_9H_{10}O_5$). The study demonstrates
9 that 4-BBA not only acts as photosensitizer but also undergoes photodegradation. Our experiments
10 show the critical influence of the UV portion of the solar spectrum on photoproduct formation, as
11 significant amounts of benzene (C_6H_6) and benzaldehyde (C_7H_6O) were detected as degradation
12 products of 4-BBA in the gas phase particularly for the lowest wavelengths (280–310 nm). In the
13 liquid phase, we identified the following photoreaction products: $C_8H_{12}O_4$, $C_8H_{12}O_5$, $C_9H_{10}O_5$,
14 $C_9H_{14}O_3$, $C_9H_{16}O_3$, $C_9H_{16}O_4$, and $C_{10}H_{14}O_4$. Among these, $C_8H_{12}O_4$, $C_9H_{10}O_5$, and $C_9H_{16}O_3$ were
15 most enhanced (by a factor of ~ 11) in the presence of 4-BBA, with $C_9H_{10}O_5$ strongly dependent on
16 the presence of oxygen. The formation of $C_9H_{10}O_5$ increased at shorter wavelengths due to
17 photodegradation of 4-BBA, while $C_8H_{12}O_4$ and $C_9H_{16}O_3$ were dominant at longer wavelengths,
18 consistent with photooxidation of NA. While pH and salinity were not varied systematically in this
19 study, we found that decreasing the pH from 8 to 5.4 affected the water restructuring at the interface
20 and increased the rate of photoproducts formation. Increasing salinity from zero to ~ 38 ppt enhanced
21 the photoreaction rates by a factor of two. These findings highlight the importance of environmental
22 factors in modeling interfacial photochemistry and demonstrate how SFG reveals surface–bulk
23 coupling relevant to ~~aerosol~~-product formation in diverse aquatic systems.

24

25 **Keywords:** Sum-frequency generation (SFG) spectroscopy; Mass spectrometry; Air–water interface;
26 Sea surface microlayer; Aerosol formation; Volatile organic compounds.

1. Introduction

The Earth's climate system is impacted by atmospheric chemistry and air–water interactions, which affect the energy budget through scattering of sunlight and absorption of thermal radiation (Meerkötter and Vázquez-Navarro, 2012). Atmospheric aerosols have both natural and anthropogenic sources which vary depending on the location, time of year, and meteorological conditions (Boucher, 2015). These sources include dust, sea spray, volcanic ash, wildfires, biological particles, industrial and agricultural processes, transportation, and waste disposal (Ouafo-Leumbe et al., 2018). It has been estimated that the secondary reaction products of volatile organic compounds (VOCs) can contribute significantly to secondary atmospheric aerosols (SOA), influencing cloud properties and radiative balance, with the vast majority originating from biogenic sources (Wang et al., 2023). Moreover, up to 91.9 TgC per year of organic vapors could be emitted from the oceans into the marine atmosphere and have a potential contribution to organic aerosol mass of more than 60 % over the remote ocean (Brüggemann et al., 2018).

Organic compounds are highly concentrated at the sea-surface microlayer (SML) or as surfactant coatings on cloud droplets (Carpenter and Nightingale, 2015). The SML contains dissolved organic carbon (DOC) and chromophoric and fluorescent dissolved organic matter (CDOM and FDOM, respectively), which are transferred to the atmosphere via sea spray aerosol (SSA) (Yang et al., 2022). While sea salt dominates the cloud condensation nuclei (CCN) activity of SSA, organic matter contributes primarily to aerosol mass (Hendrickson et al., 2021). Biological and physicochemical processes in the SML, such as the enrichment of long- and medium-chain fatty acids (LCFAs and MCFAs), further enhance SSA surface activity and influence atmospheric processes (Dommer et al., 2024). Atmospheric nutrient deposition can also influence short-term enrichments of organic matter in the SML, particularly when associated with biomass burning emissions (Milinković et al., 2022).

The air–water interface is ubiquitous in the environment and frequently exposed to the atmosphere and/or solar light, making photochemical interactions highly probable (Liss and Duce, 2005), particularly in the presence of light-absorbing CDOM at surfaces. 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). Organic coatings on water surfaces can increase the concentration of natural photosensitizers and facilitate the generation of reactive species and VOCs through photochemical and oxidative processes (Tinel et al., 2016; Wang et al., 2023). Ozone oxidation in the SML, for example, generates VOCs such as acetone and aldehydes (Wang et al., 2023). Photobleaching of CDOM leads to the formation of low-molecular-weight DOM and CO₂, with reaction rates dependent on solar radiation intensity and DOM composition (Yang et

al., 2022). This process is influenced by the intensity and duration of solar radiation, as well as the composition of DOM, which varies seasonally and spatially.

Solar radiation and wind intensity shape SML chemistry by modifying organic content and regulating air-sea CO₂ exchange (Stolle et al., 2020). Natural bodies of water exhibit a range of pH and salinity values typically between pH 6 and 9 (Dickson, 1993; Jiang et al., 2019) and salinity between 0.5 ppt (parts per thousand) (~~Dommer et al., 2024~~) and 35 ppt ([Dommer et al., 2024](#); Millero et al., 2008), although hydrogeochemical factors can cause deviations (Cui et al., 2022). The presence of mineral ions such as calcium, magnesium, sodium, chloride, and sulfate further influence the salinity and pH, thereby modulating the surface activity of the organic compounds (Covington and Whitfield, 1988; Marion et al., 2011). These geochemical parameters play vital roles in processes such as rock weathering, mineral precipitation, gas solubility, corrosion, biological shell formation, and water hardness (Morgan, 1995). Prior reports on the existence and significance of organic layers at air–water interfaces, such as the SML (Bernard et al., 2016; Ciuraru et al., 2015; Mmereki and Donaldson, 2002; Tinel et al., 2016) and sea spray (Sellegri et al., 2006; Wilson et al., 2015), emphasized the need to investigate this critical interface, particularly at the molecular level and under atmospheric conditions. 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). Despite numerous studies aimed at investigating the emission and uptake of gases and aerosols in the atmosphere, limited information is available on the molecular composition and structure of surface entities (e.g. adsorbed on cloud droplets or sea surfaces) and their role in influencing interactions. A deeper understanding is ~~urgently~~still needed, as interfacial chemistry strongly governs atmospheric reactivity.

The air–water surface interactions occur in a variety of bodies of water and involve both biogenic and abiotic emissions (Bernard et al., 2016; Brüggemann et al., 2018), with organic materials from the SML being emitted into the atmosphere through bubble bursting and forming sea-spray aerosols (Gantt and Meskhidze, 2013; Sellegri et al., 2006). These organic materials can be oxidized in the air and contribute to the creation of SOAs, which can then act as ice nuclei in mixed-phase clouds and high-altitude ice clouds (Liss and Duce, 2005). 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

1 systems, enhances VOC emissions and secondary aerosol formation (Tinel et al., 2016). A subsequent
2 study by Alpert et al. (2017) reported the formation of SOA particles through photochemical reactions
3 and ozonolysis of saturated long-chain fatty acids and alcohol surfactants at the water surface (Alpert
4 et al., 2017). More recently, Freeman-Gallant et al. (2024) showed that the efficiency of NA
5 photooxidation in thin films depends on the type of organic photosensitizer, with 4-BBA identified
6 as the most effective among those tested (Freeman-Gallant et al., 2024).

7 Previous studies primarily employed chemical, elemental and linear spectroscopic methods (such as
8 UV-visible absorption, laser-induced fluorescence, and mass spectrometry). In contrast, molecular-
9 level spectroscopic insights into interfacial chemistry under atmospheric conditions are scarce. In-
10 situ information on molecular alignment, bonding, and the formation or degradation of surface
11 functional groups remains limited, ~~but~~ yet is critical for predicting the evolution of aerosol aerosols
12 and water surfaces-evolutions.

13 In this work, we combine sum-frequency generation (SFG) spectroscopy and mass spectrometry (MS)
14 to probe the interfacial and bulk-phase photoproducts, respectively, of NA at the water surface in the
15 presence of 4-BBA under varying irradiation spectra. We didn't vary pH, and salinity systematically
16 but only report their impact for relatively small ranges. This system was particularly chosen due to
17 the availability of prior bulk-phase study relying on linear techniques (Tinel et al., 2016), which
18 verified that the interaction takes place at the water surface. Since SFG technique is suitable to probe
19 the surface layer, we applied it here to probe the chemical and structural changes in the system. We
20 employed an LED solar simulator with a spectrum closely resembling natural sunlight, improving
21 upon earlier Xenon lamp-based studies. The following section describes our experimental approach,
22 followed by results and discussion beginning with the air–water interface and progressing to the
23 molecular analysis of products in the aqueous and gas phases.

2. Experimental procedures

2.1 Materials

4-benzoylbenzoic acid (4-BBA, 95 %,) and nonanoic acid (NA, 97 %) were purchased from Sigma Aldrich and Alfa Aesar, respectively. NA was used as received without further purification. We did not observe any evidence that impurities in NA influenced the photochemical reactions under the irradiation conditions used in this study. In contrast, 4-BBA was purified due to the presence of surface-active impurities. All solutions were prepared using ultrapure water (18.2 MΩ.cm; total oxidizable carbon <5 ppb) that was obtained from a Milli-Q Reference A+ (Merck) purification system. Unless stated otherwise, all mixtures examined here are aqueous solutions of 2 mM NA and 0.2 mM 4-BBA and with a total volume of four milliliters. The solution of 4-BBA was prepared using ultrasonication for three hours and then steering over night at pH 7. The solution of NA was prepared using ultrasonication for one hour. The pH was adjusted using 0.1 M NaOH from Fischer Chemical and controlled with SevenExcellence pH/Cond meter S470 from METTLER TOLEDO. Lab experiments were conducted under either synthetic air (ALPHAGASTM, 20.5 ± 0.5 % O₂ in N₂) or Nitrogen gas (99.9999 %) from Air Liquid. The exact conditions for each experiment can be found in the supporting information (SI).

2.2 Light source

To study photochemistry under atmospheric conditions, an irradiation source that closely mimics solar light is essential. It should be tunable to simulate different latitudes, altitudes, and seasonal variations, requiring a wavelength range starting at ~275 nm, adjustable intensity, and homogeneous illumination. For this purpose, a compact custom-built LED-based solar simulator, the “Atmospheric Surface-Science Solar Simulator”, was developed. The device is optimized to irradiate a 30 mm diameter sample area from a 50 mm distance, ensuring controlled photochemical reactions. The spectral characteristics of the simulator, including its spectral overlap with solar radiation and intensity adjustments, were determined using a calibrated spectrophotometer and a custom-built variable current source. In this work, two different irradiation spectra were employed to simulate solar radiation: AM1, representing ground-level sunlight after atmospheric filtering, and AM0, representing sunlight before absorption by the atmosphere, including wavelengths below 300 nm. Additionally, individual wavelengths (280, 310, 345, 365, 385, 405, 430, 470, 490, and 520 nm) as well as the UV portion of the AM0 spectrum were employed. Additional technical details, including LED spatial distribution, irradiation spectra of AM0 and AM1, and homogeneity calibration, are provided in the SI. The irradiation cell was placed on a large metal table that served as an effective

heat sink, inside a well temperature-controlled room. A Quartz window allowed light to pass through for irradiation. The LED light source emitted at wavelengths below 550 nm and produced no thermal radiation. Cooling air from the light source electronics was vented away from the measurement cell.

2.3 SFG spectroscopy

Surface sum-frequency generation (SFG) spectroscopy is based on second-order nonlinear optical effect that in dipole approximation only occurs where the inversion symmetry is broken which is always the case at interfaces between two phases (Miranda and Shen, 1999; Zhang et al., 1994). SFG is generated by a temporal and spatial overlap of two different frequency light pulses (usually visible and a tunable IR) at an interface between two isotropic media. It provides information about the interface by probing the individual species from their IR vibrational absorption (Shen, 1989). SFG has proven effective in probing aqueous solutions containing soluble ionic and molecular species, and in determining the role of these substances in changing the water structure at the interface (Schultz et al., 2002; Shultz et al., 2000). Surfactants partition to the interface and can displace or bind water into hydrated complexes. Various SFG investigations on air–water interfaces have centred on examining organic surfactants adsorbed at the water surface (Backus et al., 2012; Doughty et al., 2016; Ghosh et al., 2009; Henry et al., 2003; Rao et al., 2011; Truong et al., 2019; Varga et al., 2005). However, it is mandatory to focus on studies that include atmospherically relevant substances under atmospheric conditions.

The description of the SFG spectrometer used in this study can be found elsewhere (García Rey et al., 2019). The irradiation and ray geometry used in the present work are shown in Fig. S3. Details of the SFG experiments and data analysis can be found in the SI (Sect. S3). The individual bands fitted to the different species are shown in Fig. S7. Table S2 lists the experimental conditions of all SFG experiments conducted in this work. At first glance, due to the distinguished feature of SFG as a sub-monolayer surface-sensitive technique, we realized that the delivered 4-BBA contained surface-active contaminants. The purple spectrum in Fig. S6 shows vibrational bands in the CH region detected at the surface of a 0.2 mM aqueous solution of 4-BBA. These bands are attributed to surface active organic contaminants in the solution. 4-BBA is not surface active (Mora Garcia et al., 2021) and there are no free CH bonds that could produce the CH-vibrations. To purify the 4-BBA, it was recrystallized twice from Ethanol. The green curve in Fig. S6 shows the SFG spectrum of 4-BBA aquatic solution after the recrystallization. It is worth mentioning that we tested samples from different providers, including the provider mentioned in the reference work (Tinel et al., 2016), and found that 4-BBA was never delivered pure enough to not show surface-active contaminants. The

1 contamination in the 4-BBA should be considered when comparing our results with those in the
2 reference work.

3 4 **2.4 Mass spectrometry**

5 The analysis of liquid-phase products was carried out using the Filter Inlet for Gas and Aerosols
6 (FIGAERO, Aerodyne Inc.) in combination with a high-resolution time-of-flight chemical ionization
7 mass spectrometer (HR-ToF-CIMS, Aerodyne Inc.), employing I⁻ as the ionization reagent. A 2.5 µL
8 liquid sample was applied to a PTFE filter via a syringe and subsequently subjected to thermal
9 desorption in FIGAERO-CIMS. To ensure that the sampled liquid solution was representative of the
10 entire system, the solution was thoroughly stirred prior to sampling to homogenize any surface-
11 enriched compounds with the bulk. The syringe tip was then inserted into the center of the bulk phase
12 to draw the sample. Ultra-high-purity nitrogen served as the carrier gas, facilitating desorption as the
13 temperature was gradually increased from 296 K to a peak of 473 K over 35 minutes. The total liquid-
14 phase signal for each compound was determined by integrating its thermal desorption profile
15 (thermogram). Data processing was performed using Tofware v3.1.2, with mass-to-charge ratios
16 adjusted by subtracting the reagent ion I⁻. To enable comparisons, all ion signals were normalized to
17 10⁶ cps I⁻. Proton-transfer-reaction time-of-flight mass spectrometer (PTR-ToF-MS 4000, Ionicon
18 Analytic GmbH) was utilized to measure the concentrations of gas-phase compounds. The data was
19 analyzed by PTR viewer 3.3.12. The gas phase was sampled by a syringe and transferred to the PTR-
20 MS. Table S3 lists the experimental conditions of all MS experiments conducted in this work. Since
21 the photoreactor cannot be considered completely air-tight the measured concentrations cannot be
22 converted into absolute yields of the gas phase reaction products. Results of the mass spectrometry
23 given in the results section were subtracted by the background signals measured in the reference
24 experiment MS_BG1.

25 The choice of analytical instrumentation significantly impacts the range and type of compounds
26 detected in complex samples. In the reference work by Tinel et al. (2016), after PFBHA
27 derivatization, the use of reversed-phase ultra-performance liquid chromatography coupled to high-
28 resolution mass spectrometry (UPLC/(±)HESI-HRMS) allowed for the separation and detection of a
29 broad range of compounds from the aqueous phase. The FIGAERO-CIMS employed in this study is
30 particularly well-suited for the detection of semi- to low-volatile organic compounds, especially for
31 organic compounds with three or more oxygen atoms (Riva et al., 2019). Thus, the two techniques
32 offer complementary insights, with UPLC-HRMS capturing a wider polarity range of dissolved
33 species and FIGAERO-CIMS covering products with higher O/C ratios.

34

1 **3 Results and Discussion**

2 **3.1 SFG at the air-liquid interface**

3 Figure 1 shows the SFG spectra at air-water interface for NA, (a), and 4-BBA, (b), in dark conditions
4 and after exposure to AM0 light. AM0 was chosen because it includes the maximum portion of sun
5 UV that can lead to photo-induced chemistry in the atmosphere. Solution's pH was first adjusted to
6 pH 8, which is the approximate pH value of the ocean (Jiang et al., 2019). Appropriate data fitting of
7 the SFG spectrum of NA in dark, black curve Fig. 1a, shows vibrational broad OH bands from
8 hydrogen-bonded interfacial water centered at $\sim 3450\text{ cm}^{-1}$ and $\sim 3250\text{ cm}^{-1}$, and narrow CH bands
9 (CH_3 Fermi peak at 2946 cm^{-1} , CH_2 Fermi peak at 2917 cm^{-1} , CH_3 symmetric-stretch 2885 cm^{-1} , and
10 CH_2 symmetric-stretch at 2858 cm^{-1}) (Lu et al., 2005; MacPhail et al., 1984; Snyder et al., 1982). The
11 CH_2 Fermi resonance appears as a shoulder next to the CH_3 Fermi peak and could be identified by
12 the SFG data fitting as shown in the SI. The so-called dangling OH band ($\sim 3700\text{ cm}^{-1}$), which
13 characterizes neat air-water interfaces and arises from water molecules with one non-hydrogen-
14 bonded OH group pointing into the vapor phase (Sovago et al., 2008), was not detected in Fig. 1a.
15 This indicates full coverage of the water surface by NA. The dark SFG spectrum of 4-BBA, blue
16 curve Fig. 1b, shows an SFG spectrum very similar to that of the neat air-water interface, black curve
17 Fig. 1b. There are no noticeable signs of 4-BBA at the interface, as expected, since 4-BBA is not
18 surface-active.

19 As shown in the SFG spectra in Fig. 1a, AM0 irradiation of the NA solution without 4-BBA produced
20 no detectable changes in the SFG signal, indicating negligible photoreactivity in the absence of 4-
21 BBA. In contrast, Fig. 1b shows that while the OH stretching modes of hydrogen-bonded interfacial
22 water (~ 3250 and $\sim 3450\text{ cm}^{-1}$) remain within the signal-to-noise range upon AM0 irradiation of 4-
23 BBA alone, a decrease in the dangling OH band ($\sim 3700\text{ cm}^{-1}$) is observed after 30 minutes of exposure
24 (green curve) compared to the dark signal (blue curve). Interestingly, after one hour of irradiation,
25 the dangling OH signal (red curve) returns to its initial intensity, matching the dark signal. Although
26 subtle, these variations in the SFG signal suggest perturbations in interfacial water structure, possibly
27 due to the formation of photoproducts.

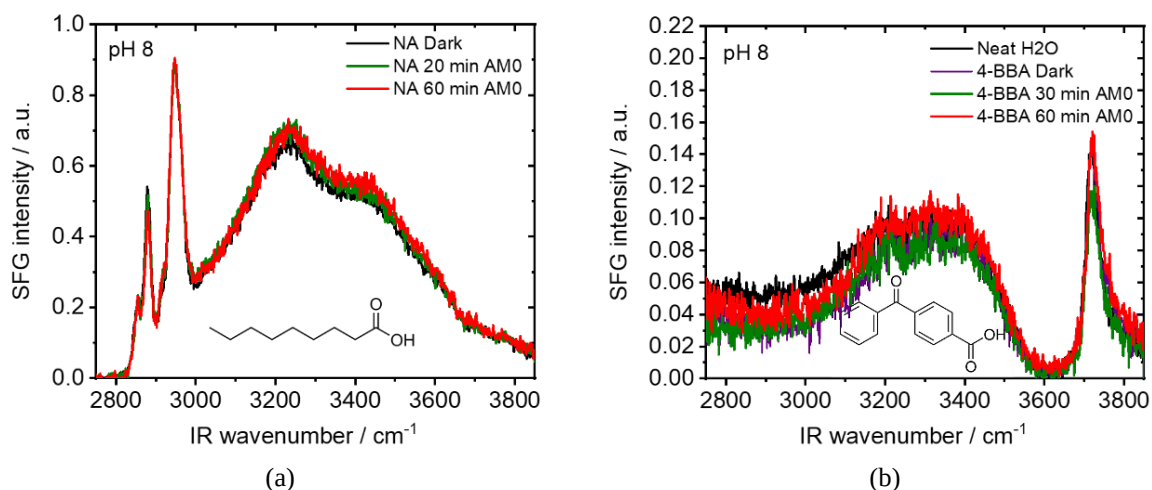


Figure 1: SFG at (a) air–water interface for NA (2mM), and (b) 4-BBA (0.2mM) as a function of time in dark conditions and after exposure to AM0 light. Both solutions were adjusted to pH 8.

Figure 2a shows the SFG spectra from air–water interfaces for mixtures of NA and 4-BBA at a solution pH 8 as a function of time after which the interface was established, while the samples were continuously kept in the dark conditions (no light exposure). There is a visible change in the signal along the whole frequency range. Close inspection of Fig. 2a reveals that the dangling OH band decreased with time to negligible intensity after ~50 min under dark conditions. We have fitted the dangling OH band at different times and present the results in Fig. S8 which clearly showing the decay of dangling OH intensity as a function of time. These changes reflect the adsorption rate and structuring of NA at the air–water interface at pH 8, which are accompanied by a slight increase of the OH bands at $\sim 3450\text{ cm}^{-1}$ and $\sim 3250\text{ cm}^{-1}$ from interfacial water (Fig. 2a and Fig. S9), indicating a relatively slow restructuring of water molecules at the interface. At the same time, the $\text{CH}_3\text{-SS}$ peak intensity, which we assume to be proportional to the number of interfacial NA, slightly increases with time when the sample was kept in the dark (see Fig. S10). The small increase in the CH bands are expected due to ongoing interface adsorption until equilibrium is reached with full surface coverage and is not expected to be caused by photochemistry as all the experiments with the mixture so far were performed under dark conditions. Although it was confirmed that 4-BBA partitions to the surface in the presence of NA (Tinel et al., 2016), no significant spectral signature of 4-BBA is observed at the air–mixture interface. Only a very weak narrow band at $\sim 3070\text{ cm}^{-1}$, which can be ascribed to a $=\text{C-H}$ stretch in an aromatic compound (Gautam et al., 2000; Hardt et al., 2024), could be identified after the data fitting of the dark spectrum of the mixture, Fig. S11a for pH8 and S11c for pH 5.4. We attribute this negligible contribution to the dominant presence of NA forming the top layer, hindering the 4-BBA from directly interfacing with air, limiting its contribution to surface signal, particularly since 4-BBA itself is not inherently surface-active.

Figure 2b shows SFG spectra at air–water interface for the mixture at pH 8 which was first equilibrated for 80 min in dark and, then, exposed for different times to AM0 irradiation. There are two observed phenomena: 1) A significant increase in the aromatic band at 3070 cm^{-1} as identified from the data fitting, Fig. S11b. (Gautam et al., 2000; Hardt et al., 2024) 2) A bidirectional change, decrease and then increase, in the peak intensity of the water bands as identified directly from the spectra. The latter means that two opposing processes occur simultaneously at the interface. The appearance of the new band is expected and can be attributed to the photochemistry taking place at the water surface.

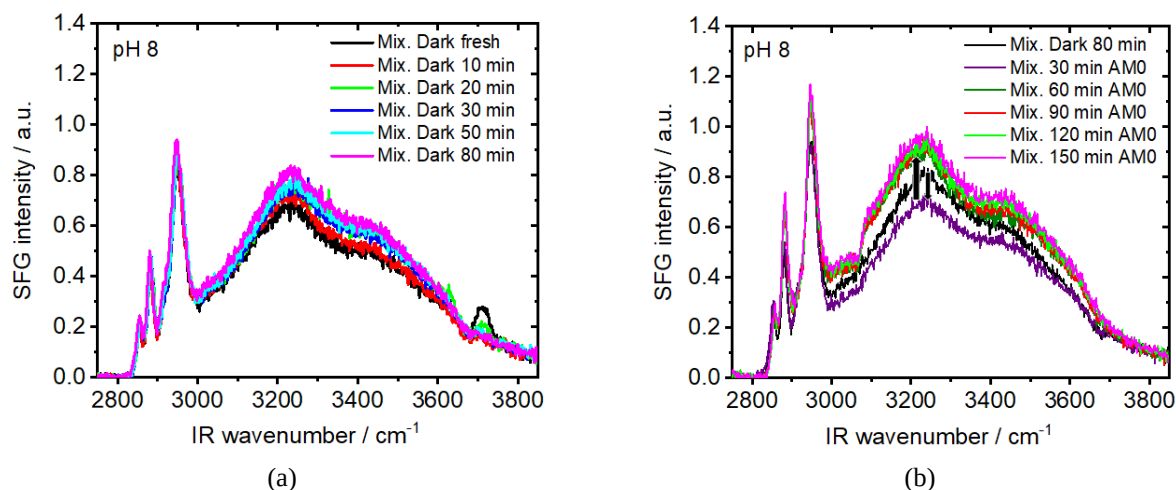


Figure 2: Changes of SFG spectra at air–water interface of a 2 mM NA mixture with 0.2 mM 4-BBA at pH 8 as a function of time under (a) dark conditions as well as for (b) irradiation with AM0.

One possible reason for the bidirectional amplitude changes of the water bands under light conditions, as well as the slight change under dark conditions, is the change of pH of the bulk solution. Indeed, we found that the pH decreases with time for the same mixture under dark and light (UV) conditions until the pH stabilizes around a neutral pH, Fig. S13a. Under dark conditions, the solution's pH decreases exponentially with time, however, under irradiation conditions, the pH also decreases but with a higher rate, blue curve in Fig. S13a. The decrease in pH under dark conditions is due to the carbonation of the solution under room conditions as was observed for a pH 8 solution without the mixture, orange curve Fig. S13a. The enhanced decrease in pH upon UV irradiation is only observed at pH 8 of the mixture solution which indicates a contribution from the reaction products. On one side, the water molecules at the surface are directly affected by the surface charge (Nihonyanagi et al., 2013). On the other side, the change in bulk pH changes the dissociation fraction of NA, Fig. S13b, and accordingly its concentration at the surface which in turn indirectly affects the water structuring and hence the SFG signal. The influence of pH on the detected SFG signal is described in details in the SI (section S4).

To eliminate the complexity of pH effect and to reduce the number of variables, we examined the same system but at a slightly lower pH value ($\text{pH} = 5.5 \pm 0.1$) which is not sensitive to carbonation and other factors that may change the pH value over time (green curve Fig. S13a). Indeed, the behavior of water bands (increase under dark conditions and decrease and then increase under light conditions) was not observed for low pH solution, Fig. 3b. In addition, the dangling OH, which characterizes the neat air–water interface, was not observed at low pH in the first dark measurement, Fig. 3a. This means that the spread of NA on the surface was faster than that in the case of high pH. This is in line with the dependency of the dissociation constant of NA on pH. At intermediate pH, a considerable portion of negatively charged molecules are neutralized to create neutral fatty acid molecules, which have a much greater adsorption constant than their anionic counterparts (Badban et al., 2017). The aromatic CH stretching band at $\sim 3070 \text{ cm}^{-1}$ was visible in the SFG spectrum after 60 min which is about the same time when it appeared for solution with pH 8 (Fig. 2b). However, the data fitting, shows that the aromatic band, for both pH values, started to increase directly after starting irradiations (Fig. 4b).

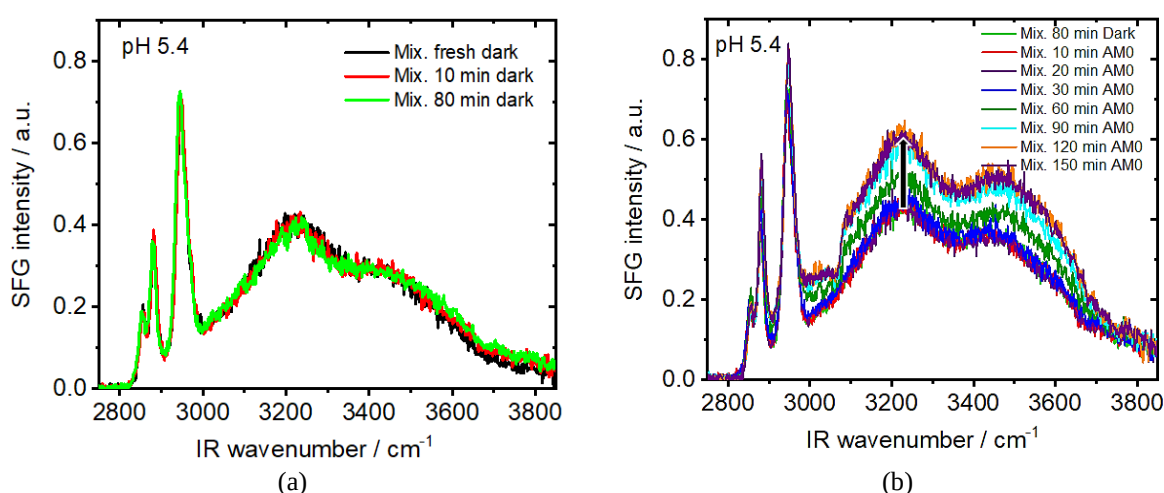


Figure 3. SFG spectra at air–water interface of the mixture, (2 mM NA + 0.2 mM 4-BBA) at pH 5.4, under dark (a) and irradiation with AM0 (b) conditions.

The slight changes in the CH bands ($2800 \text{ cm}^{-1} - 3000 \text{ cm}^{-1}$ region) in Fig. 3b indicate variations of the chemical composition in the topmost layer at the air–water interface. The significant increase in the aromatic band ($\sim 3070 \text{ cm}^{-1}$) indicates the formation of surface-active aromatic compound(s). The OH stretching modes in the $3100 \text{ cm}^{-1} - 3500 \text{ cm}^{-1}$ region, associated with interfacial water, increased after irradiation with AM0 (see the fitted spectra in Fig. 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 amplitudes of the aromatic band ($\sim 3070\text{ cm}^{-1}$) for pH 5.4 and pH 8 mixtures, Fig. 4b, shows a greater relative increase at pH 5.4, indicating a more favorable environment for the formation of the corresponding amphipathic aromatic compound. We attribute this tendency to the excess of hydrogen ions at lower pH which can be abstracted by the photoexcited 4-BBA resulting in the formation of $\text{C}_{14}\text{H}_{11}\text{O}_3\cdot$ radical in the solution (Eq. 1). This radical plays an important role in the consequent reactions shown in the Tentative Reaction Pathways section.

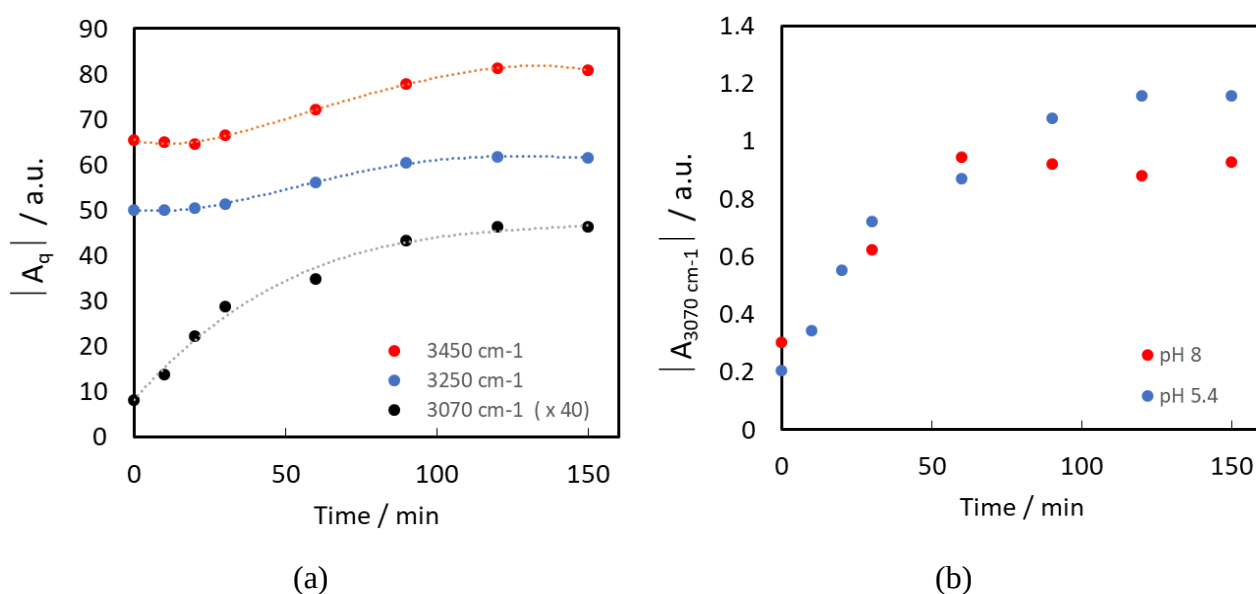
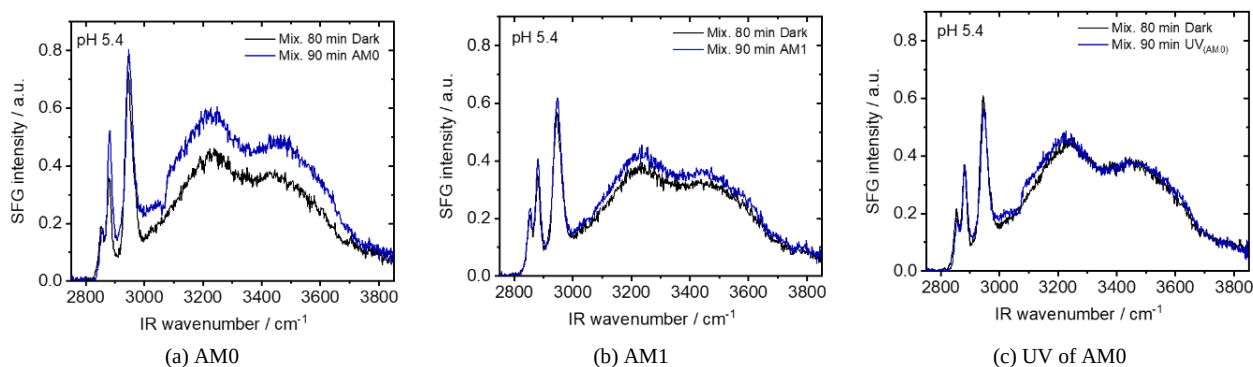


Figure 4: Time-dependent changes in the fitted SFG peak amplitudes with AM0 irradiation. (a) The aromatic band ($\sim 3070\text{ cm}^{-1}$) and the two water bands ($\sim 3250\text{ cm}^{-1}$ and $\sim 3450\text{ cm}^{-1}$) for the mixture at pH 5.4 (Dashed lines are included as visual guides). (b) The aromatic band ($\sim 3070\text{ cm}^{-1}$) for the mixtures at pH 5.4 and pH 8.

The real solar radiation spectrum depends on weather, latitude, altitude and season. These factors qualitatively and quantitatively affect the photochemistry in the hydrosphere. In Fig. 5, we compare the effect of three irradiation conditions; AM0, AM1, and solely the UV portion ($\lambda < 400\text{ nm}$) of AM0 for 90 min on the same mixture. The SFG spectra show strong variations after continuous irradiation with AM0 for 90 min, Fig. 5a. In contrast, the solution exposed to AM1 shows little presence of an aromatic band and a slight increase in water bands after the same irradiation time, Fig. 5b, which is in line with the reduced intensities of all spectral wavelengths, particularly the UV

1 portion. Irradiating the mixture with only the UV portion of AM0 ($\lambda < 400$ nm) shows a clear aromatic
 2 band with minimal changes in the water bands, Fig. 5c. This provides an evidence that the UV
 3 contribution plays a primary role in the formation of the surface-active aromatic compounds.
 4 Consequently, this photoreaction is likely more pronounced in the atmosphere (e.g. in cloud droplets)
 5 than at the sea surface where the UV intensity below 300 nm is very weak (see Fig. S4).
 6



7 **Figure 5: SFG spectra at air–water interface of 2 mM NA aqueous mixtures with 0.2 mM 4-BBA at a pH of 5.4, before and**
 8 **after irradiation with (a) AM0, (b) AM1 and (c) UV portion of AM0.**

9 Solutions at pH 5.6 were irradiated by ten different wavelengths for the same time (18 h) and an SFG
 10 spectrum was collected for the fresh solution, then after 0.5, 3 and 18 h of irradiation time. Each
 11 irradiation wavelength was individually adjusted to match the corresponding intensity in the AM0
 12 solar spectrum, so that in separate irradiation experiments, each wavelength independently reflected
 13 its relative contribution to the AM0 spectral power. The SFG spectra are shown in Fig. 6 and Fig.
 14 S12. Both figures correspond to the same set of measurements, but with different display formats to
 15 illustrate the change in the aromatic band and the changes in water bands respectively. Figure 6 shows
 16 that the aromatic band was considerably visible in the SFG spectrum, without data fitting (see black
 17 arrows), only in the short UV wavelengths, mainly 280, 310, and 345 nm, confirming the
 18 responsibility of the UV portion of the light for the generation of the aromatic compound(s). The
 19 effect of different wavelengths has different weights due to the changes in intensity and wavelength
 20 simultaneously. The shorter wavelength and/or higher intensity have a stronger effect on both the
 21 surface-active and bulk species. For the sample irradiated by 280 nm, the aromatic band was visible
 22 already after three hours although it has the lowest intensity in the irradiation spectrum. Figure S12
 23 shows that the water bands were changing differently with different wavelengths. In most of cases,
 24 the change in the aromatic CH stretching band was stronger at shorter wavelengths. The solution
 25 irradiated with 365 nm shows a change in the water band after three hours similar to that of the
 26 solution irradiated with 280 nm. Except for the 310 nm, there is always an increase or negligible
 27 change in the water bands after three hours of irradiation. Except for 280 nm and 310 nm, the water
 28 bands after at 18 h of irradiation showed a minimum. These variations in the water bands indicate

changes in the hydrogen bonding structure at the interface due to the composition and abundance of the different photoproducts with different irradiations. The results highlight the complex impact of solar spectrum composition on reaction pathways. They also emphasize the importance of incorporating these variations into the photochemical models used in atmospheric science for more accurate predictions of the complex chemical interactions that occur in the atmosphere (Xing et al., 2022).

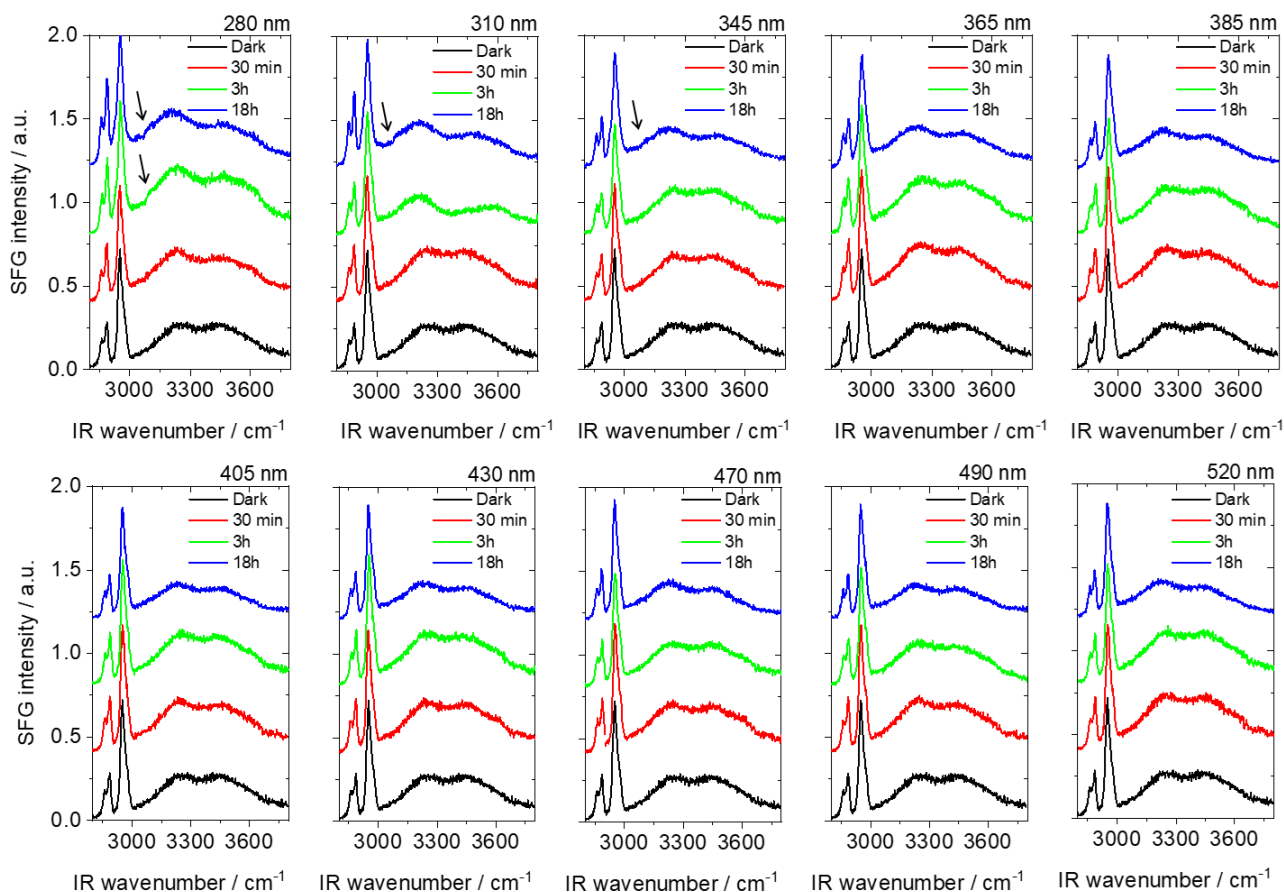


Figure 6: SFG spectra at air–water interfaces of (2 mM NA + 0.2 mM 4-BBA) mixtures at pH 5.6 after different times of irradiation with different wavelengths. Note that the spectra have a constant with offset.

Finally, although it is not intended to investigate the salinity effect on the photochemistry at the surface in this study, we report on its potential influence on the photoreaction of the NA-4BBA system. SFG pilot experiment showed that the salt concentration of the bulk accelerates the photo reaction (see section. S5 and Fig. S15). We only register the observed phenomenon and aim at detailed study in future work.

3.2 Organic compounds in liquid and gas phase

The aromatic compound detected at the air–water interface by SFG spectroscopy is a result of a photoreaction occurring for the studied samples when they are irradiated with UV containing radiation e.g. AM0. The reactions in the visible wavelength range were neither expected nor previously reported. Considering these facts and recalling that the mass spectroscopic results in Tinel et al., (2016), although very thorough, were collected from samples irradiated with a commercial Xenon lamp as a light source, and that the 4-BBA sample was not purified as ours, we decided to repeat the mass spectrometry measurements using our solar simulator and purified 4-BBA samples (see experimental details).

10

3.2.1 Aqueous phase analysis

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. Figure 7 shows the evolution of seven main liquid-phase products detected in experiment MS.1 under irradiation with AM0 and in the presence of 4-BBA as photosensitizer with the following sum formulas: $C_8H_{12}O_4$, $C_8H_{12}O_5$, $C_9H_{10}O_5$, $C_9H_{14}O_3$, $C_9H_{16}O_3$, $C_9H_{16}O_4$, and $C_{10}H_{14}O_4$. Among the photoproducts identified in the liquid phase, only $C_9H_{16}O_3$ and $C_9H_{16}O_4$ were also reported in the reference study (see table S4). Conversely, the reference study reported additional products that were not detected in our analysis (see table S6). This could be attributed to the purity of the sample, the spectral intensity distribution of the light source and/or the different analytical instrumentation as mentioned in the experimental section. The suggested assignments of the detected compounds in the liquid phase are listed in Table S4 of the SI. Some of the products showed faster production rates during the first hour, while the others showed a slower rate. We do not observe any correlation between the production rate and chain length nor the molecular weight. However, the differences are close to the experimental uncertainties. The sum of all $C_xH_yO_z$ signal intensities in the liquid phase shows a linear relation with the time of irradiation, Fig. 7. Figure 8 shows the ratio of signals detected for the main liquid-phase photoproducts of the mixture (NA + 4-BBA) versus the signals detected in the absence of 4-BBA with irradiation of AM0 and in the presence of synthetic air. The results show the largest promotion in the formation of $C_8H_{12}O_4$, $C_9H_{10}O_5$ and $C_9H_{16}O_3$ in the presence of 4-BBA.

30

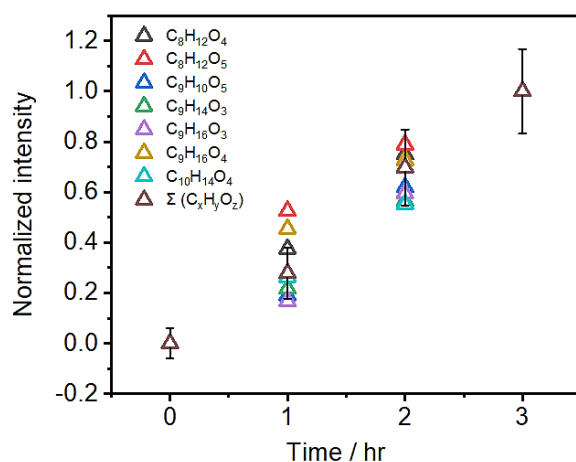


Figure 7: Intensities of individual photoproducts as a function of exposure time to AM0 irradiation (Exp. MS.1), normalized to the total liquid-phase signal intensity $\Sigma(C_xH_yO_z)$. Error bars represent the uncertainty associated with the analytical measurements.

To examine the role of oxygen in the reactions, we repeated the AM0 experiment with pure nitrogen, instead of the synthetic air, and deoxygenated liquid solutions (Exp. MS.3). The solution was deoxygenated by bubbling with nitrogen for 10 min and the measuring cell was purged before closing it hermetically. Figure 9 shows the ratio of signals detected in the presence of synthetic air versus those in the presence of N_2 . The results show that the presence of oxygen causes an increase of $C_8H_{12}O_5$, $C_9H_{14}O_3$, $C_9H_{16}O_3$, and $C_9H_{16}O_4$ by a factor of 10 to 12. The presence of oxygen shows only a limited promotion on the formation of $C_8H_{12}O_4$ (factor of ~ 2), but a significant promotion on the formation of $C_{10}H_{14}O_4$ (factor of ~ 19) and $C_9H_{10}O_5$ (factor of ~ 34). This emphasizes the vital role of dissolved oxygen in the natural bodies of water to develop multiple pathways of interactions.

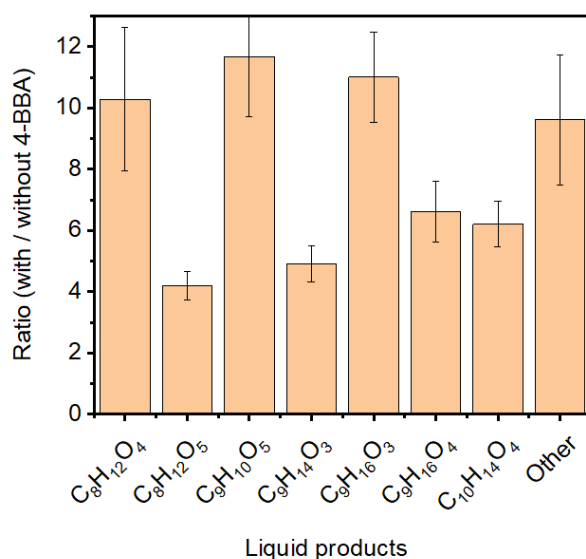


Figure 8: Ratio of the signal detected in the presence of 4-BBA to that without 4-BBA for the main photoproducts detected in the aqueous phase of NA solution irradiated with AM0 for three hours in a synthetic air environment.

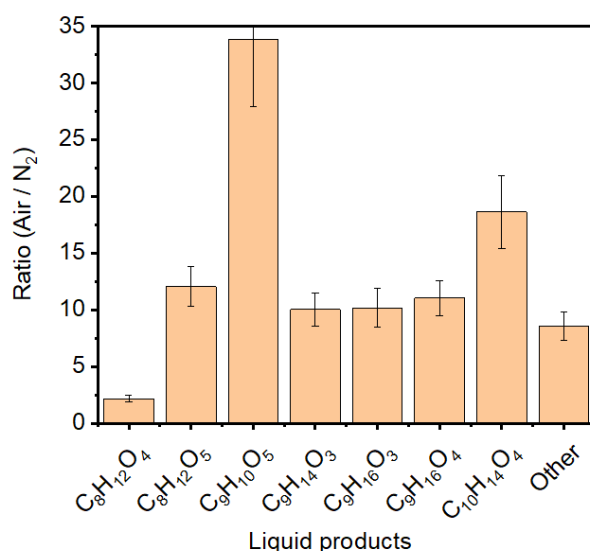


Figure 9: Ratio of the signal detected in synthetic air environment to that in the absence of oxygen in gas and liquid phase for the main photoproducts detected in the aqueous phase of NA with 4-BBA, after irradiation with AM0 for three hours.

The SFG spectra of solutions irradiated with different single wavelengths, Fig. 6, exhibited varying changes in the water bands regardless of the appearance of the aromatic CH stretching band. To quantify the effect of different irradiation wavelengths on the generation of photoproducts, we further examined the solution mixture irradiated with four selected single wavelengths in the UV and Visible part of the spectrum (Exp. MS.4 - 285 nm, MS.5 - 310 nm, MS.6 - 365 nm, and MS.7 - 405 nm) and also with sunlight during a clear sunny day in Karlsruhe, Germany, on the 1st June 2023 from 11 am to 2 pm (Exp. MS.8) and also. The day and time in the sunlight experiment were chosen to guarantee minimal changes in the solar radiation spectrum. Figure 10 shows the total C_xH_yO_z signal detected in the liquid phase for different irradiation conditions as illustrated at the x-axis. As can be inferred from Fig. 10, with stronger UV light at AM0, the formation of major aqueous photoproducts was promoted, with the increase of total C_xH_yO_z signal by a factor of about 2.4 compared to that at AM1. After being irradiated by real solar light for three hours, the total C_xH_yO_z signal observed was ~0.9 of that observed at AM1. Hence, our experiments with AM1 irradiation are indeed comparable to typical atmospheric conditions at earth surface.~~with four selected single wavelengths in the UV and Visible part of the spectrum. Figure 10 shows the total C_xH_yO_z signal detected in the liquid phase for different irradiation conditions as illustrated at the x-axis.~~ Figure 11 shows a comparison between the ratios of the photoproducts for the mixtures irradiated with AM0 (Exp. MS.1) and with AM1 (Exp. MS.2) versus irradiation with real sun light ~~(Exp. MS.8), during a clear sunny day in Karlsruhe, Germany, on the 1st June 2023 from 11 am to 2 pm (Exp. MS.8).~~ The day and time were chosen to guarantee minimal changes in the solar radiation spectrum. As can be inferred from Fig. 10, with stronger UV light at AM0, the formation of major aqueous photoproducts was promoted, with the increase of total

1 $C_xH_yO_z$ signal by a factor of about 2.4 compared to that at AM1. After being irradiated by real solar
2 light for three hours, the total $C_xH_yO_z$ signal observed was ~ 0.9 of that observed at AM1. Hence, our
3 experiments with AM1 irradiation are indeed comparable to typical atmospheric conditions at earth
4 surface. The same main set of photoproducts observed under artificial irradiation in the laboratory
5 were also detected under sunlight. The relative product fractions for irradiation with sunlight are very
6 similar to those of the lab irradiation and mostly lie between those of irradiation by AM0 and AM1.
7 The fractions of the photoproducts that constitute of 2 % or more of the total products under real
8 sunlight (i.e. $C_9H_{16}O_4$, $C_{10}H_{14}O_4$, $C_8H_{12}O_4$, $C_9H_{16}O_3$, and $C_9H_{10}O_5$, in order of ascending fraction) are
9 closer to those of AM1, which is consistent and emphasizes the capability of our homemade light
10 source to simulate ambient solar radiation.

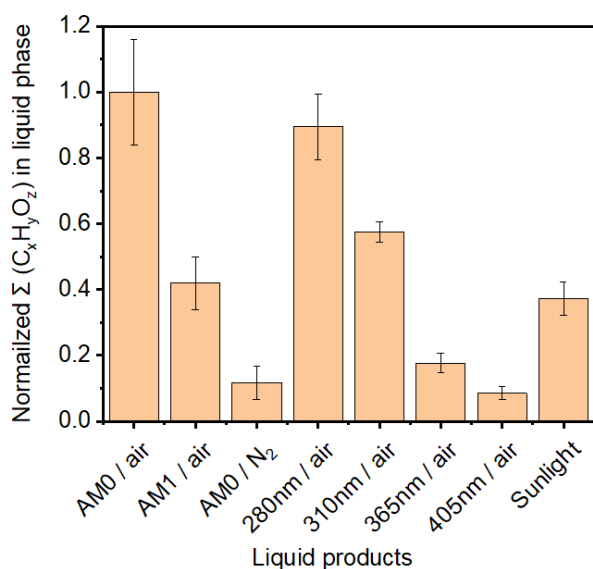


Figure 10: Normalized total $C_xH_yO_z$ signal in aqueous phase at different irradiation conditions for three hours. [Exps. MS.1 to MS.9 (SI)]

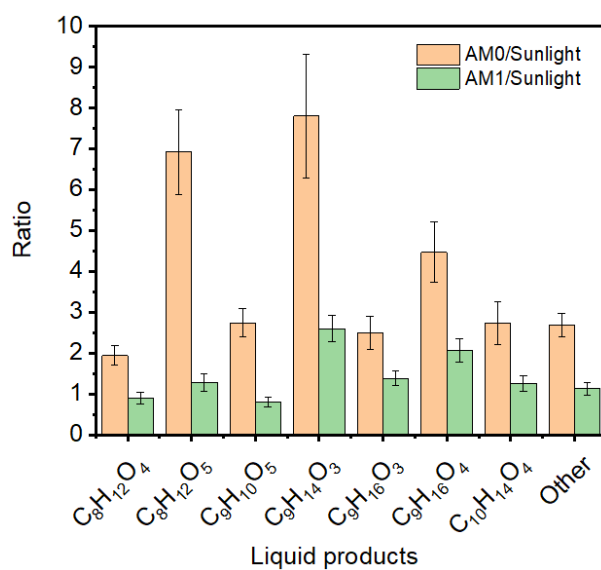


Figure 11: Ratio of the compounds detected with AM0 or AM1 versus the signal with sunlight, for a NA aqueous solution with 4-BBA after irradiation for three hours.

To address the wavelength dependence of the photoproducts further, we plot the fraction of the three most dominating products, namely $C_8H_{12}O_4$, $C_9H_{10}O_5$, and $C_9H_{16}O_3$, versus irradiation wavelength in Fig. 12. The fractions of $C_8H_{12}O_4$ and $C_9H_{16}O_3$ increase with longer wavelength while the fraction of the $C_9H_{10}O_5$ increases with shorter wavelength indicating two different mechanisms as will be described below.

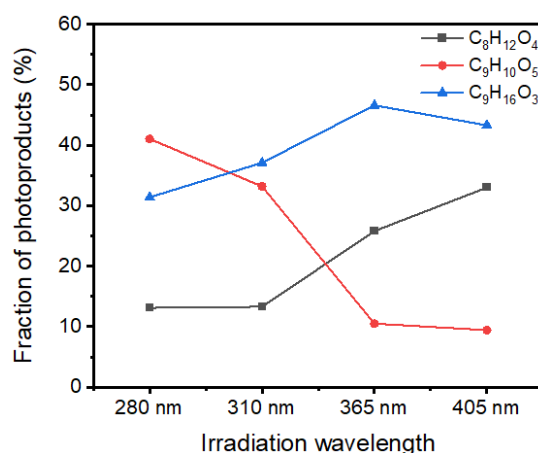


Figure 12: The fraction of photoproducts versus wavelength for the three most dominating products ($C_8H_{12}O_4$, $C_9H_{10}O_5$, and $C_9H_{16}O_3$) in a NA aqueous solution with 4-BBA after irradiation with 280, 310, 365, and 405 nm for three hours.

In all MS experiments, $C_8H_{12}O_4$, $C_9H_{10}O_5$, and $C_9H_{16}O_3$ were the most abundant products detected in the liquid phase. However, the fractions of the liquid-phase compounds varied under different irradiation conditions, Fig. 13a to h. The $C_8H_{12}O_4$ is a major product from the photoreaction of NA with limited dependence on oxygen compared to other products. This is evident from the relative increase of the fraction of $C_8H_{12}O_4$ in total liquid-phase $C_xH_yO_z$ products in during the experiment in with pure nitrogen, Fig. 13c, where it becomes the main product, despite a much lower overall production. The formation of $C_8H_{12}O_4$ was also significantly increased in the presence of 4-BBA, Fig. 8, indicating that $C_8H_{12}O_4$ was a photodegradation product from NA in the presence of 4-BBA. For $C_9H_{16}O_3$, which is suggested to form through RO_2 radical reactions after hydrogen abstraction on (Tinel et al., 2016), its fraction of total liquid-phase $C_xH_yO_z$ was higher with irradiation of AM1 than AM0 Fig. 13b and a, respectively. This stands in agreement with the measurement with irradiation from 280 nm to 405 nm, Fig. 13e to h. With more UV at 280 nm and 310 nm, $C_9H_{16}O_3$ accounted for about ~31 % and ~37 % of total $C_xH_yO_z$, respectively; while with less UV at 365 nm and 405 nm, the fractions of $C_9H_{16}O_3$ increased to ~47 % and ~43 %, respectively. In previous work by Tinel et al. (2016), the solution with NA and 4-BBA showed that the formation of $C_9H_{16}O_3$ increased by a factor of ~2.5 in the presence of air. In our study, with 4-BBA the formation of $C_9H_{16}O_3$ increased by a factor of ~11. The oxygenated C_9 products are promoted when O_2 is abundant, which agrees with Tinel et al. (2016). In contrast to $C_8H_{12}O_4$ and $C_9H_{16}O_3$, the fraction of $C_9H_{10}O_5$ in total liquid-phase $C_xH_yO_z$ decreased from ~41 % at 280 nm to ~9 % at 405 nm and also from ~34 % at AM0 to ~24 % at AM1. We observed a higher fraction of $C_9H_{10}O_5$ in experiments involving NA and 4-BBA under enhanced UV conditions, suggesting that $C_9H_{10}O_5$ is likely an aromatic compound formed through reactions between photoproducts generated from the photolysis of both NA and 4-BBA. This interpretation aligns with the presence of two distinct reaction mechanisms, as inferred from Fig. 12, where 4-BBA functions both as a photosensitizer for NA, producing nonaromatic products such as

- 1 $\text{C}_8\text{H}_{12}\text{O}_4$ and $\text{C}_9\text{H}_{16}\text{O}_3$, and as a photolabile compound that yields aromatic photoproducts which may
- 2 undergo further reactions.

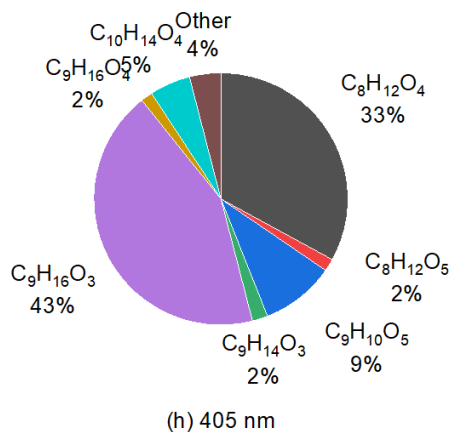
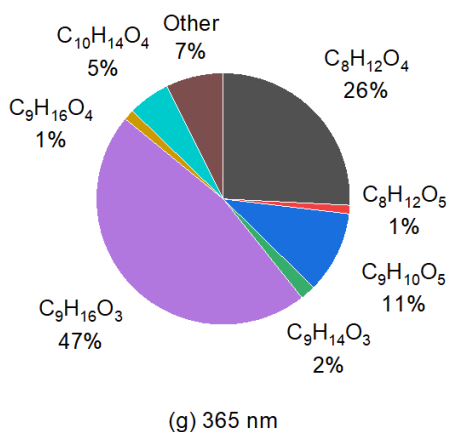
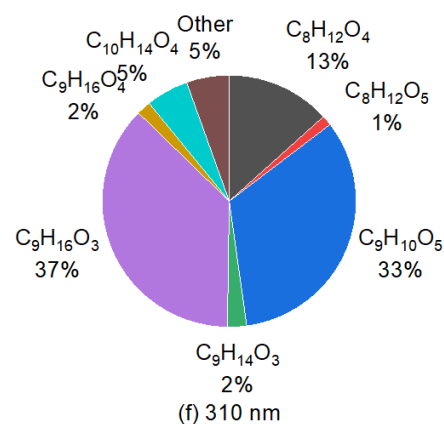
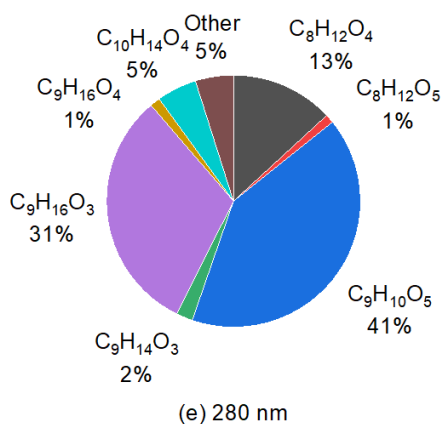
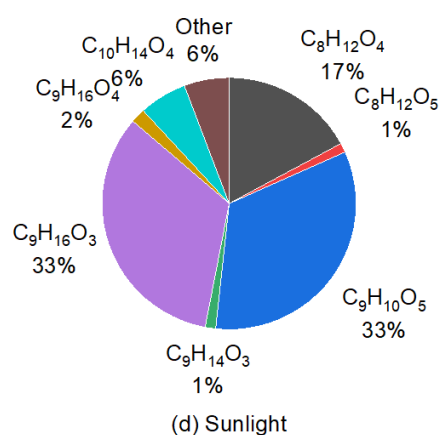
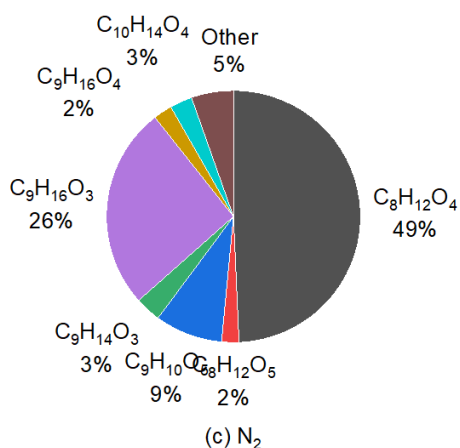
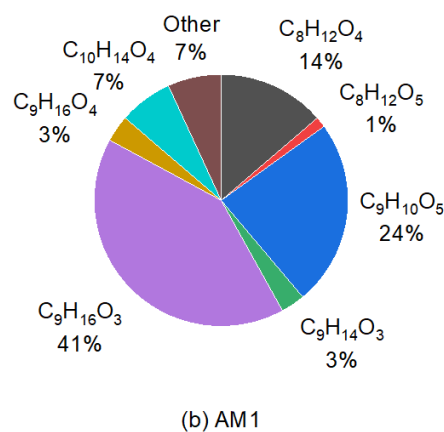
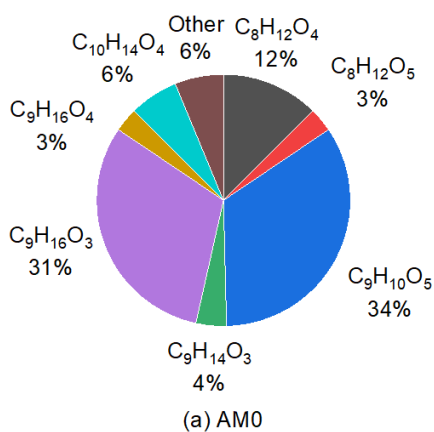


Figure 13: Fractions of products in total liquid-phase $C_xH_yO_z$ under different irradiation conditions. All panels represent experiments conducted in air, except panel (c), which corresponds to an experiment performed in pure nitrogen.

3.2.2 Gas phase analysis

Examining the gas phase is important to detect the volatile photoproducts. A series of compounds, such as C_4H_8 (butene), C_4H_8O (butanal), C_5H_{10} (pentene), $C_5H_{10}O$ (pentanal), C_6H_6 (benzene), C_7H_8 (toluene), C_7H_6O (benzaldehyde), $C_8H_{16}O$ (octanal), as well as some undefined fragments such as C_6H_5 and C_7H_6 were detected in the gas phase (see Table S5). Similar to the liquid phase, only a subset of the photoproducts identified in the gas phase, namely C_4H_8 , C_4H_8O , C_5H_{10} , $C_5H_{10}O$, and $C_8H_{16}O$ were also reported in the reference study, which, in contrast, identified additional products not observed in our analysis (see Table S6).

Only two of the photoproducts detected in the gas phase showed a significant increase compared to the background experiments (BG1-3). Figure 14 shows the normalized signals of the two main gas-phase compounds: benzene (C_6H_6) and benzaldehyde (C_7H_6O) under different irradiation conditions. When NA was irradiated in the absence of 4-BBA, the signal from both products remained at background levels. However, when either the mixture or 4-BBA alone was irradiated with AM0, both compounds exhibited strong signals. This is a further confirmation that, in addition to the previously reported photosensitized degradation of NA in the presence of 4-BBA as a photosensitizer, 4-BBA itself undergoes photolysis under the influence of the UV portion of the light spectrum. For other gas-phase compounds detected in this study, no significant differences were observed between the irradiation experiments and the background experiments.

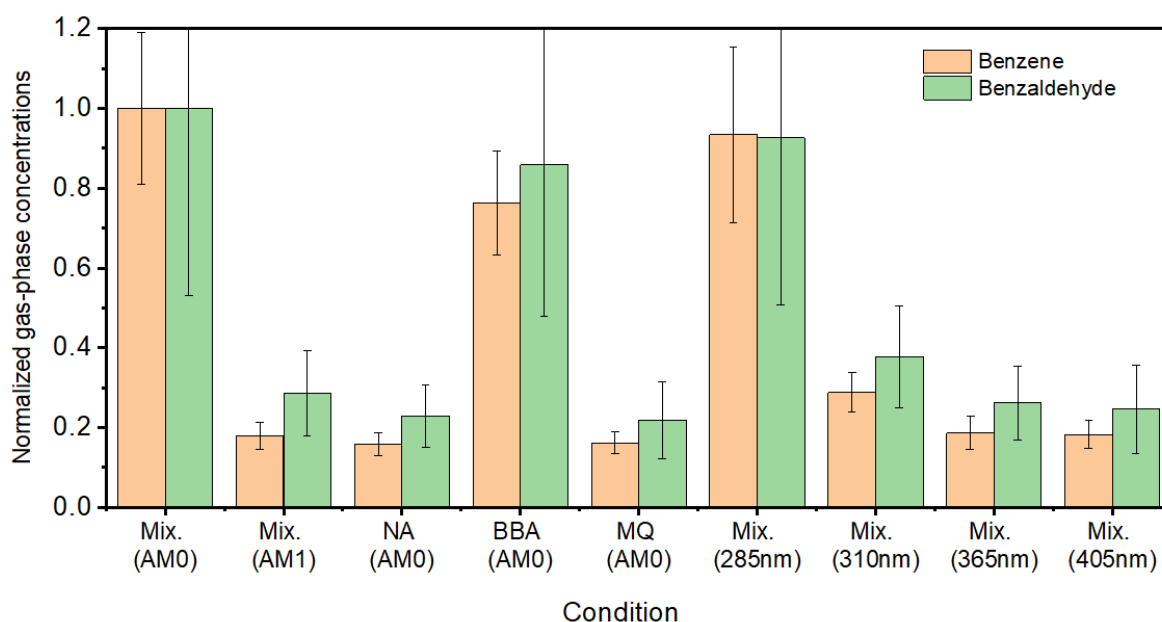
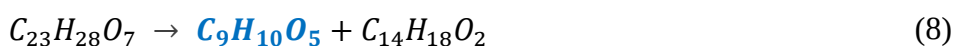
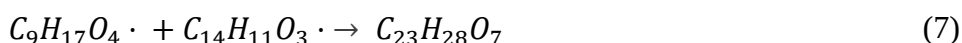
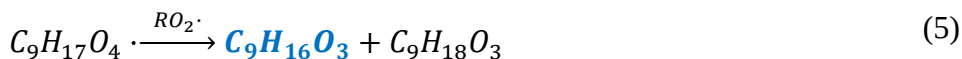
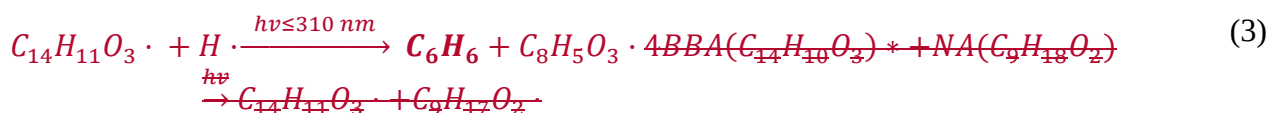
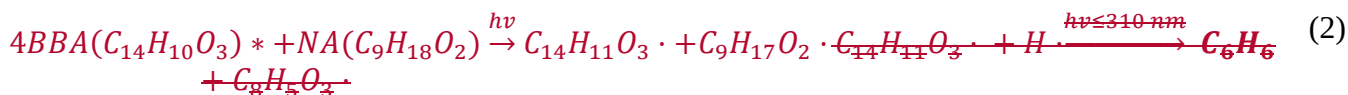


Figure14: MS signals of benzene and benzaldehyde detected in the gas phase for different solutions under different irradiation conditions for three hours. Signals are normalized to that of the mixture under AM0 irradiation condition. MQ: Milli-Q water (pH ~ 6.2).

3.2.3 Tentative reaction pathways

The following scheme shows the suggested photolysis of NA in the presence of 4-BBA:



Bold blue are compounds that have been observed.

The photochemical degradation of NA in the presence of 4-BBA proceeds through a series of radical-mediated reactions. The proposed mechanism begins with the photoexcitation of 4-BBA generating a reactive triplet state 4-BBA* (Eq-1) (Dalton et al., 2025), which abstracts a hydrogen atom from either the solvent or NA, generating $C_{14}H_{11}O_3\cdot$ (Eq-1) (Jiménez and Miranda, 2018) and forming a NA-derived alkyl radical ($C_9H_{17}O_2\cdot$) (Eq-2). ~~This~~ The $C_{14}H_{11}O_3\cdot$ radical undergoes Norrish I-type cleavage to produce benzene (C_6H_6) and a benzoyl fragment ($C_8H_5O_3\cdot$) with UV absorption at $\lambda \leq 310 \text{ nm}$ (Eq-23) (Goswami et al., 1985). $C_8H_5O_3\cdot$ may further react with O_2 to form oxygenated intermediates. In parallel, 4-BBA's triplet state interacts with NA, abstracting a hydrogen atom to form a The NA-derived alkyl radical ($C_9H_{17}O_2\cdot$) (Eq-3), which reacts with oxygen to yield a peroxy radical ($C_9H_{17}O_4\cdot$) (Eq-4) (Atkinson, 2000). Subsequent reactions of this peroxy radical include: (1) reaction with other RO_2 forming $C_9H_{16}O_3$ and $C_9H_{18}O_3$ (Eq-5) (Freeman-Gallant et al., 2024), (2) oxidation with bicarbonate radicals ($HCO_3\cdot$) (Yan et al., 2019) to form $C_{10}H_{14}O_4$ (Eq-6), and (3) cross-coupling with the 4-BBA ketyl radical ($C_{14}H_{11}O_3\cdot$) to produce an unstable adduct ($C_{23}H_{28}O_7$) (Eq-7), having peroxide bond (-O-O-) which is very reactive and unstable under light (You et al., 2020). The unstable $C_{23}H_{28}O_7$ undergoes rapid intramolecular rearrangement and fragmentation. It

1 could fragment into the observed aromatic product $C_9H_{10}O_5$ and a NA-derived byproduct ($C_{14}H_{18}O_2$)
2 (Eq-8). $C_9H_{16}O_3$ may undergo photooxidation under UV light in the presence of hydroxyl radicals,
3 resulting in the formation of one oxidized product ($C_9H_{16}O_4$) and one dehydrogenated product
4 ($C_9H_{14}O_3$), suggesting radical-mediated transformation (Eq-9) (Numadate et al., 2022). Alternatively,
5 the formation of $C_9H_{16}O_4$ and $C_9H_{14}O_3$ could also result from the $RO_2^\bullet + RO_2^\bullet$ self-reaction (reaction
6 5), which requires additional H-abstraction from 4-BBA to generate sufficient NA-derived radicals.-
7 The $C_9H_{10}O_5$ product, observed in higher concentrations particularly after irradiation with AM0, can
8 be formed in an amphipathic, aromatic, surface-active structure via peroxide intermediates that react
9 with water and give OH-radicals (Kroll et al., 2015; Lankone et al., 2020). This product ($C_9H_{10}O_5$)
10 gives rise to the SFG signal at 3070 cm^{-1} and leads to the increase in the water bands in the region
11 3100 cm^{-1} to 3500 cm^{-1} . Our proposed chemical structures with pathways can be seen in the SI, Fig.
12 S16. Compared to the reaction path ways suggested by Tinel et al. 2016 our reactions involve the
13 consequences of the photolysis of 4-BBA under the influence of the UV portion on the irradiation
14 source.

1 **4 Conclusions**

2 This study focuses on the correlation between the photochemical products at the surface and bulk
3 regions. We spotlighted the complex contribution of solar spectral distribution, pH, salinity and
4 surface photoproducts on the reaction. NA was selected as surfactant and 4-BBA as a photosensitizer,
5 and our combined surface-bulk study was compared to the bulk-phases study by Tinel et al., (2016).
6 Our analysis revealed several photoproducts in both the gas and liquid phases that were not reported
7 in the reference study, while conversely, the reference study identified additional products not
8 detected in our work. We attribute these differences to differences in the analytical techniques used,
9 ~~differences in~~ sample purity, sample volume, duration of irradiation, and ~~discrepancies in~~ the spectral
10 characteristics of the light sources applied.

11 The SFG technique enabled us to detect and confirm the partition of the non-surface-active
12 compounds to the organic surface layer where it can induce radical reactions leading to the formation
13 of a variety of compounds. We also identified photoproducts at the water-air interface that cannot be
14 assigned by the bulk analysis. Under the environmental conditions applied in this work, the 4-BBA
15 was found to be acting as a source of photoproducts in addition to its expected role as a photosensitizer
16 for the NA. The photolysis of the 4-BBA is more active when exposed to shorter wavelengths of the
17 UV portion of the light spectrum. The subsequent reactions between the photoproducts can lead to
18 the formation of aromatic compounds including compounds with amphipathic structures that are
19 surface-active and responsible for the restructuring of the water molecules at the interface. Lower pH
20 values were found to be more favorable for the formation of these amphipathic aromatic compounds.

21 The spectral power distribution of the irradiation light significantly affects the photoreactions. The
22 shorter wavelength and/or higher intensity has stronger effect. The change in pH changes the
23 concentration of partially dissociated fatty acids at the surface and influences the photo reaction rate,
24 and possibly pathways. Preliminary results also showed that the salinity accelerates the photoreaction
25 rate. We attribute this effect to the increase in the concentration of the 4-BBA at the air–water
26 interface caused by the bulk dissolved salts. Further investigation of the mechanism under varying
27 pH and salty conditions is necessary to be addressed in future work. Finally, dissolved oxygen
28 develops multiple pathways of the interactions. While our study provides valuable mechanistic
29 insight, broader conclusions would require further investigation using additional model systems and
30 environmentally relevant mixtures. In nature, these processes are even more complex due to the
31 presence of a large variety of fatty acids at the SML which enrich more organic photosensitizers at
32 the surface. Similar photochemistry can apply to all water surfaces, e.g. at ocean, rivers, lakes and
33 even cloud droplets.

1 **Author contribution**

2 All authors have made significant contributions to this research. AA proposed the research idea,
3 conducted the literature review, designed and built the custom solar simulator, and conceived and
4 designed the experiments. AA led the SFG and MS experiments, performed data analysis and
5 interpretation, and wrote and compiled the manuscript. DG conducted the SFG experiments alongside
6 AA, contributed to the SFG data analysis, and provided critical revisions to the manuscript. DG
7 additionally revised and corrected the chemical composition part of the MS study after Referee's
8 reports. YG performed the MS experiments, analyzed and interpreted the MS data in collaboration
9 with AA and drafted the MS-related sections. BB supervised the SFG experiments, discussed the
10 results with AA and DG, and reviewed the SFG-related sections. HS supervised the MS experiments,
11 discussed the results with AA and YG, and revised the MS sections. JL contributed to the chemistry
12 aspects of the experiments, assisted with methodology development and data collection, and
13 participated in manuscript revisions. MF supported the estimation and validation of the solar
14 simulator output and characteristics and assisted in final manuscript preparation.

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1 **Supplementary information**

2 Supplementary information related to this manuscript, including additional figures, tables, and
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6

7

8 **Ethical approval**

9 This article does not involve any studies or experiments conducted on human participants or animals
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