We would like to take this opportunity to thank both reviewers for the critical review and constructive suggestions, which are much appreciated.

The specific comments by referee #2 are addressed one by one in the following. The corresponding changes in the manuscript are highlighted in a marked-up version accordingly. Here, we structure our responses in the following scheme:

Referee's comments/questions in bold font.
Author's response in blue regular font, including *actions in blue italic font and new text in green italic font*.

More substantial general comments:

1) Why weren't gas-phase UV spectra measured? The authors should at least briefly comment on this.

We agree that a direct gas-phase measurement would always be preferable. However, we have not had the instrumental capabilities to measure gas-phase UV-vis. spectra. Due to the low density of gas, much longer pathlengths are needed for gas-phase UV-vis. spectrometry than for solution-phase UV-vis. spectrometry.
The UV-vis. spectrometer that we used (UV-2600, Shimadzu) can be equipped with gas cells of max. 10 cm length (single path). Given the need to remain considerably below the vapor pressure of the studied compounds at around 20 °C (laboratory temperature) to avoid condensation on the windows of the cell, we could not have reached high enough optical densities to obtain accurate determinations of the absorption cross-sections.
A dedicated experimental set-up to determine gas-phase UV-vis. spectra was beyond the scope of this study. However, we show that our method works well enough to approximate gas-phase conditions, providing useful insights in cases where gas-phase UV–vis. absorption data would otherwise be entirely unavailable.

***ACTION**: We added “As direct gas-phase measurements were not feasible with the available instrumentation, […]” to the very first sentence of section 2.1.1 (“Quasi-gas-phase spectroscopy”).*

2) EA is used as a proof of concept for the solution phase measurements, but it may not be representative of the other compounds. What scaling factors would apply more generally? While not required to include in this manuscript, additional validation results across a broader set of compounds would strengthen this point.

We have chosen ethyl acetate specifically because of the ester functional group and its structural similarity to the studied compounds. However, we do agree with the referee that validation across a broader set of compounds would strengthen the methodology.
This is why we refer to other carbonyls and the respective factors needed to derive ‘quasi-gas-phase’ spectra from solution-phase spectra. We do this relatively briefly in the main text (lines 118-120 and 227-229 in the original manuscript), to not make the photolysis section longer than necessary (see referee comment 3).
However, we do elaborate on this more in section S2.1 “EA proof-of-concept-study” in the Supplementary Information, where we use all of the second paragraph to point out that the factor that we have derived for ethyl acetate (0.86) and applied to ethyl butyrate and its derivatives is very similar to the factors identified for a range of other carbonyls studied elsewhere (Mapelli et al., 2023; Nakashima et al., 1982). We do refer to this section of the SI in line 225 in the original manuscript.

***ACTION:** No change.*

3) The photolysis aspect feels somewhat overemphasized relative to the rest of the study. No specific changes are suggested here, but something to consider generally.

We agree with the referee that photolysis is not a relevant loss process for ethyl butyrate and its derivatives under atmospheric conditions, and we understand that this aspect may therefore feel over-emphasized. This is why we had already moved some parts of this section into the Supplementary Information (section S2.1 "EA proof-of-concept-study"), so that the section 3.1 in the main text ("UV absorption cross-sections and rates of photolysis") was reduced to about 4 pages (original manuscript) compared to the larger and more relevant section 3.2 ("Kinetics of OH with EB and its derivatives") spanning about 6 pages (original manuscript).

We believe that even though photolysis does not normally occur in the atmosphere, it is important to present such findings as well in order to make an informed assessment of the overall atmospheric fate of the studied compounds. Also, the detailed discussion of the absorption bands may help predict the behaviour of structurally related compounds. Lastly, the UV-C absorption of ethyl butyrate and its derivatives may still be of relevance for laboratory experiments or specific environments (e.g. irradiated with UV-C germicidal lamps), as pointed out in the text.

ACTION*: No change (but note that we shortened some parts in response to referee comment 7).*

4) The limitations of the SAR approach for derivatives could be discussed in more detail; more generally, SAR tends to perform poorly at temperature extremes.

We agree that the SARs should only be used within the temperature ranges they are designed for. This is why we only looked at the range of 250-375 K for the Jenkin et al. (2018) SAR, and the range of 250-700 K for the Kwok and Atkinson (1995) SAR. For the Kwok and Atkinson (1995) SAR, this selection was made based on the validation of the SAR as described in their article. We did not include the extreme temperature range of up to 1000 or 1200 K, even though the performance of the SAR is demonstrated for these ranges as well. For the Jenkin et al. (2018) SAR, we specifically based our decision on their training set for saturated esters as listed in their supplementary information (SI_2). We do believe that our usage of the SARs in these temperature ranges is appropriate and robust within the general limitations and uncertainties of the respective SARs, but we have added a few statements for better clarification and context.

For higher consistency, we have also changed Fig. S5 (SI) to only show the 250-375 K range (we had originally wanted to show a larger range to emphasize the temperature trends of the different sites, but we agree that this is not meaningful).

ACTION*: We have elaborated the part "The Kwok and Atkinson (1995) SAR approximates the Arrhenius behaviour at higher temperatures albeit with a large shift of around 150 K, but does not capture the non-Arrhenius behaviour. This is likely due to the fact that the SAR is not targeted towards esters, […]". The updated section now reads "The SAR proposed by Kwok and Atkinson (1995) was originally tested and validated for oxygenated compounds over a very extensive temperature range, and is applied here for temperatures between 250 and 700 K. It follows the observed Arrhenius behaviour at higher temperatures albeit with a large shift of around -150 K compared to the experimental data. However, it fails to describe the strong curvature and the*

non-Arrhenius behaviour at lower temperatures. This is likely due to the fact that the SAR was not designed or trained for esters, […].”
We have also added the following statement at the end of the paragraph (describing the Jenkin et al. (2018) SAR): “Specifically, we restricted our calculations to the range between 250 and 375 K, based on the temperature range covered by the training data set for saturated esters of the SAR. There is a slight disagreement at the higher end of this range, where the SAR appears to underestimate the curvature observed in the experimental data. This behaviour is not unexpected, as SAR predictions tend to become less accurate towards the limits of their designated temperature ranges.”
We have updated Fig. S5 in the SI (now only showing the same 250-375 K range).

5) The authors should comment on why calculations were performed to predict spectra but not kinetics/relative energies of reactant/product stable geometries.

For the UV-vis. absorption spectra, we were only able to obtain solution-phase spectra, which are a useful approximation of gas-phase spectra, but require additional validation and are a second choice compared to direct gas-phase spectra (see referee comment 1 and 2). Hence, we calculated the spectra to evaluate whether we would be able to reproduce trends. For further evaluation (e.g. the calculation of photolysis rates), we do however use the experimental data, which we consider to be more reliable and accurate than the computational results.
For the OH radical kinetics, on the other hand, we have reported high-quality PLP-LIF data, and we do not believe that we would be able to obtain more accurate rate coefficients using computational approaches. We agree that we could learn more about reaction mechanisms and products through calculations, however this would require a degree of effort and skill that we cannot provide. Especially for reactions involving pre-reaction complexes, very high-level ab initio calculations would be needed to obtain meaningful results. Still, by reporting our experimental kinetic data, we provide important reference points for groups that are capable of running such calculations. This is why we recommend (at the end of the conclusions) that future studies should focus on these aspects. We have added another statement where we acknowledge that products studies could not be covered in this work.

ACTION: *The sentence “Regarding EB specifically, we evaluated the first steps following the reaction with OH at its most reactive sites using the Generator for Explicit Chemistry and Kinetics of Organics in the Atmosphere, GECKO-A in short (Aumont et al., 2005).” was changed to “While detailed product studies – either experimental or computational – were beyond the scope of this work, we evaluated the first steps following the initial reaction of EB with OH at its most reactive sites using the Generator for Explicit Chemistry and Kinetics of Organics in the Atmosphere, GECKO-A in short (Aumont et al., 2005).”*

6) Is any pressure dependence expected, particularly given the potential role of a pre-reactive complex, especially at lower temperatures?

No, we do not expect any pressure dependence, even at low temperatures when the pre-reaction complex is important. The lowest temperature that we have worked at in this study is room temperature. For ethyl butyrate, several absolute determinations of the room temperature rate coefficient for the reaction with OH are available. In this work, these values were obtained at pressures of 29 and 26 Torr in York, and at pressures of 37 and 38 Torr in Leeds. Meanwhile, the PLP-LIF experiments by Cometto et al. (2009) were performed at around 100 Torr, whereas the flash photolysis resonance fluorescence (FP-RF) experiments by Wallington et al. (1988) were performed between 25 and 50 Torr. The room temperature rate coefficients obtained in all these different experiments agree well within their respective uncertainties (see Table 2 in manuscript), demonstrating that they were all at the high-pressure limit. At 477 K, we have also measured the rate coefficient at 6 Torr and at 38 Torr and found that the results agreed within their respective uncertainties (see Table S4 in the Supplementary Information).

The same is true for instance for the reaction of acetone with OH radicals, where the observed curvature and negative temperature dependence at low temperatures has been linked to pre-reaction complexes as well, and where no pressure dependence was found between 20 and 100 Torr (Wollenhaupt et al., 2000).

We acknowledge that collisional stabilization can occur for pre-reaction complexes at extremely low (not tropospherically relevant) temperatures, inducing a pressure dependence (Caravan et al., 2015; Shannon et al., 2010), however this would require much lower temperatures than the ones we worked out and would not be relevant under our conditions.

Hence, we expect the transition from the low-pressure to the high-pressure limit at very low pressures (much lower than the pressures in this study) for the entire temperature range that we investigated. As the pressure in the troposphere ranges from roughly 760 Torr at sea level to around 150-250 Torr near the tropopause, rate coefficients in the low-pressure limit are of no immediate atmospheric interest. A full exploration of the rate coefficients of the reactions between OH and ethyl butyrate or any of its methylated derivatives in all pressure regimes is beyond the scope of this work.

ACTION*: We have inserted the following paragraph after the paragraph where the literature values are discussed:*

"The room-temperature values of k_1 reported in this work were obtained at 26 and 29 Torr (N_2 bath gas) using the York set-up and at 37 and 38 Torr (Ar bath gas) using the Leeds set-up. Their agreement with the PLP-LIF results by Cometto et al. (2009) at 100 Torr (He bath gas) and with the flash photolysis resonance fluorescence (FP-RF) results by Wallington et al. (1988) at 25-50 Torr (Ar bath gas) suggests that all of these measurements were obtained in the high-pressure limit. This is in accordance with other reactions of oxygenated VOCs with OH, such as acetone where strong curvature was observed but no pressure dependence was found between 20 and 100 Torr (Wollenhaupt et al., 2000)."

We have also inserted the Wollenhaupt reference in the list of references:

"Wollenhaupt, M., Carl, S. A., Horowitz, A., and Crowley, J. N.: Rate Coefficients for Reaction of OH with Acetone between 202 and 395 K, J. Phys. Chem. A, 104, 2695–2705, https://doi.org/10.1021/jp993738f, 2000."

We've noticed a few instances where we accidentally wrote "torr" instead of "Torr" – these were changed accordingly.

Line-specific comments:

7) Line 145: The authors should add a few sentences explaining why they chose to measure Hg lamp absorption at 185 nm rather than, e.g., 254 nm which would allow them to directly compare to the solution phase absorption spectra measured with UV-Vis.

Originally, we planned to measure the absorption at 185 nm with the goal of monitoring [EB] during the experiments. This was based on the assumption that the absorption at this wavelength would be relatively high, and because this wavelength has been shown to be useful for monitoring the concentration of oxygenated compounds in previous studies (e.g. Feierabend et al., 2008; Wollenhaupt et al., 2000). However, as previously reported in the original manuscript, the determined absorption cross-section had a substantial uncertainty, even when high concentrations of EB were used (and determinations at low EB concentrations were not possible). Hence, the absorption of EB was never used for quantification in the kinetic experiments and only reported for interest. For the same reason, we did not measure the absorption at 254 nm to compare the gas-phase results against the quasi-gas-phase ones, as we believed that the uncertainty of the gas-phase absorption cross-section would make any comparison meaningless. For future attempts, longer pathlengths or a set-up that enables working with the pure non-diluted vapour of EB would be needed. Reflecting on the referee comment, we understand that our presentation of this datapoint is confusing and a distraction in the already quite long photolysis section (see referee comment 3). Given the large uncertainty, it does not provide much additional insight. Hence, we've decided to remove it.

ACTION: *We have deleted the short description of the acquisition of $\sigma_{185\ nm}$ in section 2.1.1 ("Quasi-gas-phase spectroscopy"). We have moved Eq. (3) and the description of the parameters in that equation a bit further up, and have extended the statement "In the next step, the extinction coefficient was converted to the gas-phase absorption cross-section using Eq. (2):" to now read "In the next step, the extinction coefficient was converted to the gas-phase absorption cross-section using Eq. (2), based on the relationship between Eq. (1) and the Beer Lambert law for gas-phase conditions as shown in Eq. (3):"*
We have deleted the sentence "The absorption observed at λ = 185 nm for EB arguably relates to the Rydberg←n transition, as observed analogously for EA (Śmialek et al., 2016)." in section 3.1 ("UV absorption cross-sections and rates of photolysis").
We have removed the datapoint at 185 nm from Fig. 2 panel (a), and have deleted the following sentence from the caption: "The single marker for EB shows a direct gas-phase measurement (2σ statistical error.".
We have removed the datapoint from the supplementary text file containing the spectral data.

8) Line 182: Please state the laser fluence as well, if it was measured.

We have now added this information.

ACTION: *The previous sentence "To photolyze H_2O_2, the fourth harmonic output from a Nd:YAG laser (Quantel, Q-Smart) was used to provide a 266 nm laser beam with 10 Hz frequency." was appended to now read "[...] and a fluence of <20 mJ cm^{-2}.".*

9) Line 245: Is there any explanation as to why TD-DFT calculated CS values show markedly better (/less poor) agreement with measured spectra for EM compared to the other three molecules?

In our opinion, the dataset is not sufficient to make an informed guess. We believe that we would need to study more groups of compounds (with methyl groups in different positions) to assess whether specific sets of structural features tend to be predicted with higher accuracy than others.

ACTION: *No change.*

10) Line 307: Absorption of a photon with energy far above the BDE threshold does not always result in a molecule being photolyzed (e.g. fluorescence, internal conversion can compete significantly depending on the species' electronic structure). The authors should perhaps instead consider something like "...assuming a quantum yield of 1 gives an upper limit to the photolysis rate."

We agree with the referee. This is why we have already included a statement that the quantum yield of 1 is the upper limit of the photolysis rate in the following line in the original manuscript. However, we do see that the way that we have originally phrased this still implied too strongly that the quantum yield should be 1. We have adjusted the wording.

ACTION: *The previous wording: "Since λ_{max} of the EB π*←n absorption band and the spectral range of the atmospheric window in the UV-C range are far below the threshold wavelength corresponding to the estimated BDE and since the incoming energy is hence significantly higher than the energy needed to break the bond, we consider it appropriate to assume a quantum yield of 1 (Fig. 2c). This results in the photon absorption rate, which is an upper limit to the photolysis rate." was changed to: "Since λ_{max} of the EB π*←n absorption band and the spectral range of the atmospheric window in the UV-C range are far below the threshold wavelength corresponding to the estimated BDE and since the incoming energy is hence significantly higher than the energy needed to break the bond (Fig. 2c), a quantum yield of 1 is principally possible. Using an assumed quantum yield of 1 in Eq. (4) results in the photon absorption rate, which is an upper limit to the photolysis rate.".*

11) Figure 5: The authors may want to consider removing the two/four parameter fits from the plots, especially b and c, as there may not be sufficient data points on the high temperature end to justify the different curve shapes. If the fits are removed from plots b and c, for instance, it's not as (visually) clear which dataset should be fit to a curve or a straight line.

We understand the concern of the referee and agree that more data would be needed to fully describe the temperature trend. However, we did what worked best for the available data, e.g. refraining from using a 4-parameter expression for El where this would have resulted in two terms describing a negative temperature dependence. We think that the visualized fits in the plots help to grasp the overall picture better and quicker. Likewise, we would like to keep quoting our fits in the text so that others can use them within their recommended range. However, we have added a statement which draws attention to the limitations of the fits.

ACTION: *We have inserted the following statement after the descriptions of the parameterisations: "Given the limited scope of the datasets for the methylated esters, we would like to emphasize that the reported temperature dependencies are only valid within their specified ranges and that any extrapolations may be subject to large uncertainty. This is particularly true at the high-temperature end, where more data would be needed to accurately describe the curvature."*

Structural/grammatical issues:

12) Line 58: Change "source" to "sources."

Yes, the referee is correct.

ACTION: *Implemented as suggested.*

13) Line 502: These two sections should perhaps be separated from one another to give a more succinct conclusions section while maintaining the in-depth discussion of the atmospheric implications of the work.

We have a considered a separation but found this difficult in practise as the conclusions and atmospheric implications are tightly interlinked, and a separate conclusion section for our study very brief and would largely function as a summary of the preceding findings. We regard the atmospheric implications as an important aspect of the conclusions, as it puts the findings into a larger context. Indeed, the same structure that we have chosen here can be found in previous similar studies (e.g. Baumann et al., 2025; Mapelli et al., 2022).

ACTION: *no change.*

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