

## Response to Reviewer #1

The authors have put in good efforts to improve on the manuscript based on the reviews. I am still hesitant to believe that the effects they observe are purely due to the sCI reactions they propose. However, I can accept that this manuscript will have value for the wider community. My only requirement at this stage is that the authors make it very clear in the manuscript that the reactions they suggest are indeed suggestions, and that other factors might also be of importance.

**Response:** we thank the referee for providing the feedback on our revised manuscript, we have fully considered the comments, responded to these comments below in blue text and made the associated revisions to the manuscript as shown in red text. The response and changes are listed below.

Despite a vast literature on chemical reactions taking place in the particle phase, the authors currently dismiss such reactions by stating that they see an equivalent increase in particle number and in mass, which to them suggests that the change happens in the gas phase. This is a very speculative conclusion, as aerosol dynamics of small clusters and particles are very complex. One could also ask the authors to explain why they do not see any change in the particle phase chemistry as a function of RH.

In order to avoid making a very strong claim that large changes happen in the gas phase chemistry, and no changes happen in the condensed phase chemistry, my strong recommendation to the authors is to highlight both in the abstract, discussions, and conclusions, that they cannot rule out that other reactions may also be taking place, for example in the particle phase, and that the presented findings are their interpretations. Phrases like "This hypothesis is further proved..." in the abstract and conclusions should thus be reformulated, e.g. by using "supported" instead of "proved", in addition to adding some discussion that other potential mechanisms could also be taking place.

**Response:** We agree with the referee that reactions in particle phase may also play a role. Following the Referee's suggestion, we have added and changed some text in the revised manuscript.

Page 1, Line 17-19: Although the complex processes in the particle phase may play a role, we primarily attribute it to the water-influenced reactions after ozone attack on the exocyclic double bond of limonene, which leads to the increment of lower volatile organic compounds under high RH condition.

Page 1, Line 20-21: This hypothesis is further supported by the SOA yield enhancement of  $\beta$ -caryophyllene, a sesquiterpene that also has an exocyclic double bond.

Page 13, Line 259-260: Therefore, the increased ozone consumption by limonene seems primarily attributed to the presence of its exocyclic double bond.

Page 15, Line 285-286: Overall, the promoted dimer and HOM formation may greatly enhance the new particle number concentration under high RH condition (Fig. 6).

Page 17, Line 314-315: Overall, it is likely that the different fate and partitioning of SVOCs largely enhance the amount of SVOCs in the particle phase (Fig. 6).

Page 17, Line 317-319: While our study highlights significant changes in gas-phase chemistry, we cannot exclude the possibility of concurrent reactions occurring in the condensed phase.

Page 18, Line 348-349: This result suggests that the enhancement effect on limonene SOA by high RH is still valid for low precursor concentrations.

Page 19, Line 373-376: Moreover, this hypothesis is supported by a similar behavior of the ozonolysis of  $\beta$ -caryophyllene (sesquiterpene with an exocyclic double bond) in SOA enhancement under high RH condition. However, since aerosol dynamics of small clusters and particles are very complex, we do not rule out a series of reactions that may occur in the particle phase.

Minor comment: The argument that sCI chemistry produces carbonyls and that these explain changes in SOA yields still seems questionable, as gas phase chemistry in general produces carbonyls. Also in the mechanism figures in this paper, carbonyls are the major functionalities in almost all reaction pathways.

Response: We agree with the referee that carbonyls can be formed in other gas-phase reactions, e.g., during the production of OH and oxygen addition process as illustrated in Figure 3. For limonene, the presence of exocyclic double bonds allows these carbonyl compounds to produce compounds with multiple carbonyl groups, further lower its volatility and enhancing the SOA formation. Furthermore, Gong and Chen (2021) indicated that the SOA formation potential of SCIs under high-humidity conditions was nearly double that under dry and low-humidity conditions. Since carbonyl compounds are the major products in the SCI channel (Leungsakul et al., 2005), it is reasonable to infer that the carbonyl compounds generated via SCI under high humidity conditions significantly contribute to SOA formation.

Furthermore, the oligomerization of these carbonyls generates more dimers including hemiacetal (or acetal) formation and aldol condensation, and the intensity of dimer formation originating from multi-carbonyls are enhanced under high RH conditions to low RH conditions (Table S6) (Jang et al., 2003). The corresponding revision in the manuscript is in Page 15, Line 274-275: “As shown in Table S6, the intensity of dimers generating from multi-carbonyls under high RH is higher than that under low RH.”

**Table S6.** The intensity of dimers from multi-carbonyls under high RH and low RH

Molecular formula	Absolute intensity (Low RH)	Relative intensity (Low RH)	Absolute intensity (High RH)	Relative intensity (High RH)
$C_{19}H_{28}O_5$	$3.60 \times 10^2$	$6.87 \times 10^{-5}$	$9.28 \times 10^3$	$2.06 \times 10^{-3}$
$C_{19}H_{28}O_7$	$5.00 \times 10^3$	$9.5 \times 10^{-4}$	$2.73 \times 10^4$	$6.08 \times 10^{-3}$
$C_{19}H_{28}O_6$	$1.78 \times 10^3$	$3.40 \times 10^{-4}$	$1.39 \times 10^4$	$3.10 \times 10^{-3}$
$C_{18}H_{28}O_6$	$3.19 \times 10^3$	$6.08 \times 10^{-4}$	$4.30 \times 10^3$	$9.56 \times 10^{-4}$
$C_{18}H_{24}O_6$			$6.06 \times 10^2$	$1.35 \times 10^{-4}$
$C_{18}H_{26}O_5$			$6.28 \times 10^2$	$1.40 \times 10^{-4}$

**Reference:**

- Gong, Y. and Chen, Z.: Quantification of the role of stabilized Criegee intermediates in the formation of aerosols in limonene ozonolysis, *Atmos. Chem. Phys.*, 21, 813-829, <https://doi.org/10.5194/acp-21-813-2021>, 2021.
- Jang, M. S., Carroll, B., Chandramouli, B., and Kamens, R. M.: Particle growth by acid-catalyzed heterogeneous reactions of organic carbonyls on preexisting aerosols, *Environ. Sci. Technol.*, 37, 3828-3837, 10.1021/es021005u, 2003.
- Leungsakul, S., Jaoui, M., and Kamens, R. M.: Kinetic Mechanism for Predicting Secondary Organic Aerosol Formation from the Reaction of d-Limonene with Ozone, *Environ. Sci. Technol.*, 39, 9583-9594, <https://doi.org/10.1021/es0492687>, 2005.