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*Supplement of*

## **Multiphase composition changes and reactive oxygen species formation during limonene oxidation in the new Cambridge Atmospheric Simulation Chamber (CASC)**

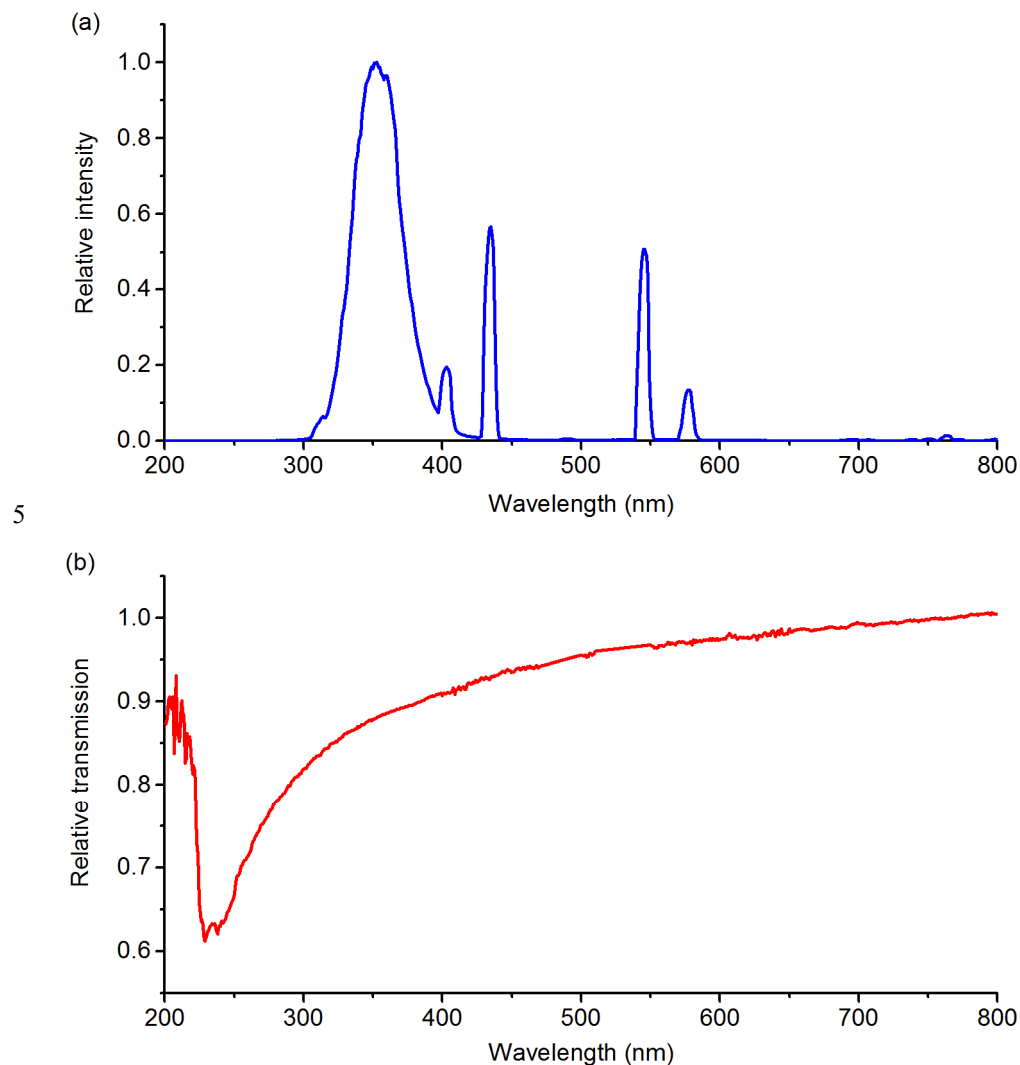
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### Spectra of chamber light sources

The spectrum of the tanning lamps used for photochemistry and transmission characteristics of the FEP used for the chamber walls is presented in Figure S1.



**Figure S1: (a) Spectrum of tanning lamps installed in CASC facility. (b) Relative transmission of FEP film used for chamber walls, demonstrating good transmission at wavelengths above 300 nm.**

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### Photolysis frequency of NO<sub>2</sub>

A common approach to assess light intensity in atmospheric simulation chambers is to quantify the photolysis frequency of NO<sub>2</sub>,  $J_{\text{NO}_2}$ . Irradiation of NO<sub>2</sub> results in a photo-stationary state between NO, NO<sub>2</sub> and O<sub>3</sub>.  $J_{\text{NO}_2}$  can be calculated from these measured steady-state concentrations and the known bimolecular rate constant ( $k_{\text{NO}+\text{O}_3} = 2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , (Atkinson et al., 2004)) according to Equation S1:

$$J_{\text{NO}_2} = \frac{k_{\text{NO}+\text{O}_3}[\text{NO}][\text{O}_3]}{[\text{NO}_2]} \quad (\text{S1})$$

$J_{\text{NO}_2}$  was determined to be  $0.49 \pm 0.09 \text{ min}^{-1}$ . Values of  $J_{\text{NO}_2}$  from various chambers are compiled in Table S1.

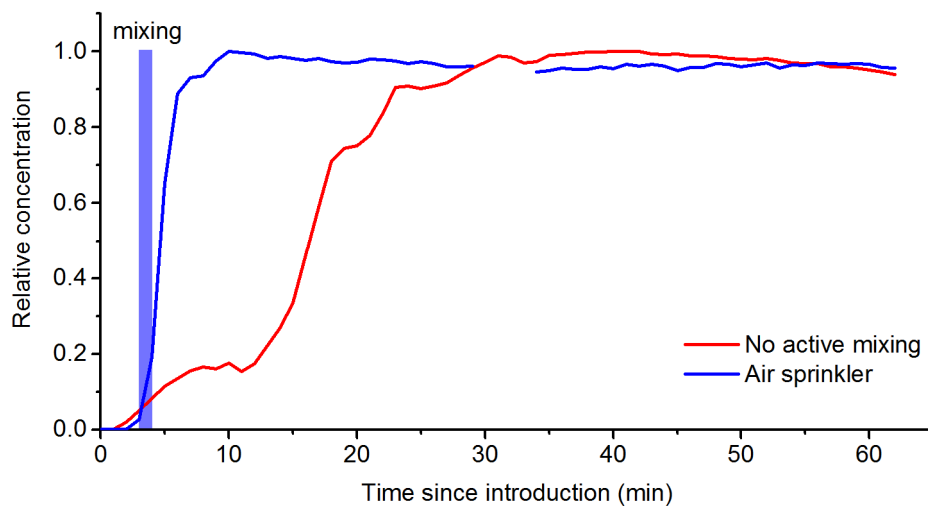
**Table S1: Comparison of NO<sub>2</sub> photolysis rates for different indoor chambers using artificial light sources.**

Chamber	$J_{\text{NO}_2}$ (min <sup>-1</sup> )	Light source	Reference
CASC	0.49	Tanning lamp	This work
Caltech	1.5	Black lamp	Cocker et al. (2001)
PSI	0.12	Xenon arc lamp	Paulsen et al. (2005)
GIG-CAS	0.49	Black lamp	Wang et al. (2014)

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## Chamber mixing

The mixing performance of the “air sprinkler” system was assessed by introducing  $\alpha$ -pinene into chamber via the reactant port and monitoring its concentration over time at the sampling port via PTR-MS.



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**Figure S2: Relative concentration of  $\alpha$ -pinene measured at the sampling chamber port after evaporation into the reactant chamber port. The use of  $3 \times 10$ s “bursts” of the air sprinkler mixes the chamber in a few minutes (blue curve) rather than 30-40 minutes by diffusion alone (red curve). The short gap in the blue data set at 30 minutes corresponds to an interruption to PTR-MS sampling.**

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### Particle wall losses

The lifetime of particles in a simulation chamber is affected by wall losses which are dependent on the size distribution of the aerosol as well as chamber-specific properties such as volume and wall material. Wall losses were determined for the CASC facility by monitoring the evolving size distribution of ammonium sulfate (AS) aerosol over ten experiments between 0 and 70 % RH. Particles were generated from a 0.01 M aqueous AS solution dried prior to introduction. A Kr-85 neutraliser (TSI 3077) was used to ensure an equilibrium aerosol charge distribution in some experiments, but the wall loss rates were not found to be substantially different without the neutraliser. No significant dependence on chamber RH was found for the range tested (0-70 %).

Deposition to the walls was treated as a first order process (Cocker et al., 2001). The total aerosol number and mass concentrations as a function of time can be described by Equations S2 and S3 respectively:

$$\frac{dN(D_p, t)}{dt} = -\beta_N N(D_p, t) \quad (\text{S2})$$

$$\frac{dM(D_p, t)}{dt} = -\beta_M M(D_p, t) \quad (\text{S3})$$

Where  $\beta_N$  and  $\beta_M$  are the characteristic number and mass weighted first order wall loss coefficients. 10 aerosol experiments were used to calculate  $\beta_N = 0.201 \pm 0.025 \text{ h}^{-1}$  and  $\beta_M = 0.166 \pm 0.020 \text{ h}^{-1}$ , respectively. This corresponds to aerosol lifetimes of 5-6 hours, comparable to other chambers as illustrated in Table S2.

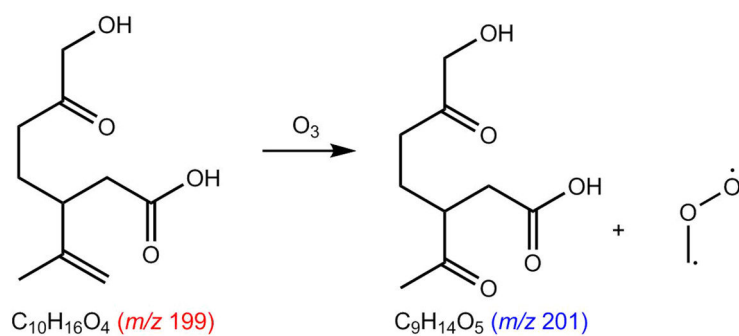
**Table S2: Comparison of number-weighted and mass-weighted particle wall loss rates for different Teflon chambers.**

Chamber	Volume (m <sup>3</sup> )	$\beta_N$ (h <sup>-1</sup> )	$\beta_M$ (h <sup>-1</sup> )	Reference
CASC	5.4	0.201	0.166	This work
Caltech	28	0.09- 0.18	-	(Cocker et al., 2001)
PSI	27	0.209	0.139	(Paulsen et al., 2005)
EUPHORE	200	0.18		(Martin-Reviejo and Wirtz, 2005)
SAPHIR	270	0.27	-	(Rollins et al., 2009)
CMU	12	0.40	-	(Donahue et al., 2012)
GIG-CAS	30	0.17	-	(Wang et al., 2014)

- The procedure for particle wall loss correction is similar to that described by Rollins et al., (2009) who assume that particle concentration changes between consecutive measurements (~2 minutes) can be decomposed into two separate terms: wall deposition and SOA production. By iteratively increasing the measured concentration at each time step to offset the losses calculated from Equation S3, a loss-free concentration is calculated.
- 10 The resulting loss-corrected time series (Figure 3) suggests that for limonene ozonolysis SOA production continues for 2-3 hours via multi-generational reactions in the chamber and reaches a maximum value of 375  $\mu\text{g m}^{-3}$ . This corresponds to an aerosol yield (defined as the mass of SOA formed per mass of reacted VOC) of 32 %. Aerosol yields are dependent on a number of parameters including aerosol mass loading and oxidation conditions, as well as
- 15 chamber-specific factors. Our yields are consistent with previous studies at similar mass loadings, which occupy a broad range from ~30-90 % (Chen and Hopke, 2010; Leungakul et al., 2005; Youssefi and Waring, 2014; Zhang et al., 2006).

### Heterogeneous oxidation mechanism in PG-AM

The proposed mechanism which forms  $C_9H_{14}O_5$  from  $C_{10}H_{16}O_4$  is shown in Figure S3. This reaction is represented in PG-AM with a yield of 0.4 based on *exo*-C=C ozonolysis for  $\beta$ -pinene (Jenkin, 2004). The alternative branch which forms a  $C_9$  Criegee intermediate and formaldehyde, is not included due to the uncertainties surrounding particle-phase Criegee intermediate chemistry.



10 **Figure S3: Proposed reaction of unsaturated  $C_{10}H_{16}O_4$  (treated as 7-OH limononic acid in the model) with ozone to form the carbonyl product  $C_9H_{14}O_5$ . Model results from PG-AM are compared with time series for  $m/z$  199 and 201 respectively (Figure 5(b)).**

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