**Figures associated with the manuscript “Influence of Relative Humidity on the Heterogeneous Oxidation of Secondary Organic Aerosol”**

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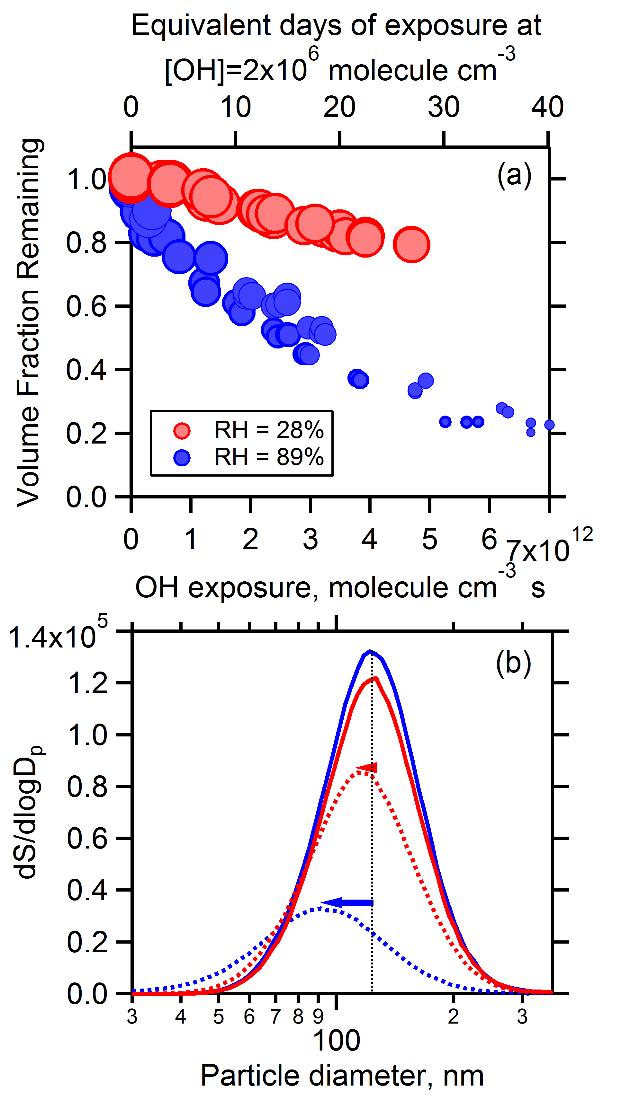
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Original Version (v1): May 8, 2018

Updated (v2): September 24, 2018

* A new figure was added during revision of the manuscript (Fig. S3). This has led to renaming of all subsequent figures, e.g. Fig. S3 🡪 Fig. S4, Fig. S4 🡪 Fig. S5, etc.. All data files have been re-uploaded with the correct associated figure name.

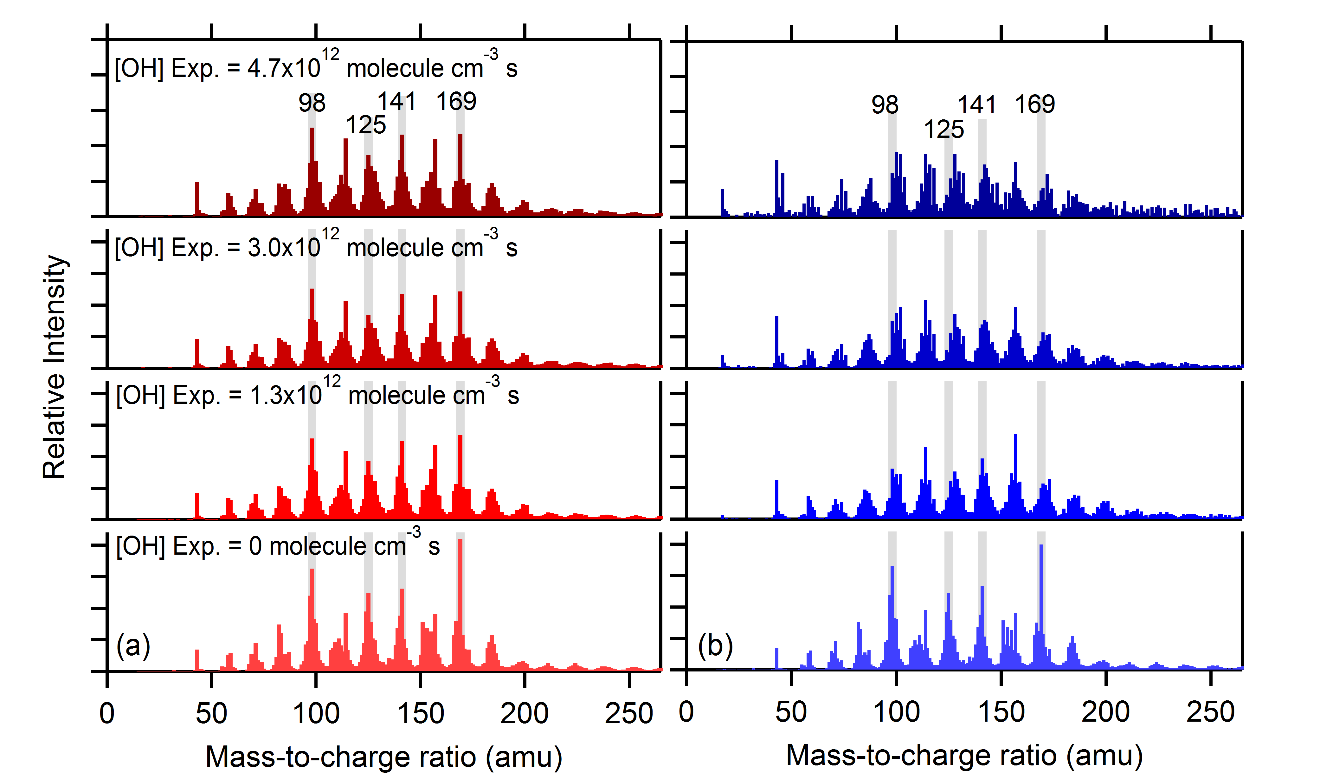
The associated \*.csv files contain all data shown in the figures in the manuscript “Influence of Relative Humidity on the Heterogeneous Oxidation of Secondary Organic Aerosol” by Li et al. that has been submitted to Atmospheric Chemistry and Physics. The figures are shown on the following pages, for reference.



**Figure 3.** Influence of photochemical aging on SOA volume for low RH (red) or high RH (blue) conditions. (a) The volume fraction remaining as a function of OH exposure. Sizes of markers correspond to particle size. (b) Example surface‑weighted size distributions of particle before OH exposure (solid lines) and after oxidation at an OH exposure = 4.7 x 1012 molecule cm‑3 s (dashed lines).

Associated data files: Fig3a.csv, Fig3b.csv

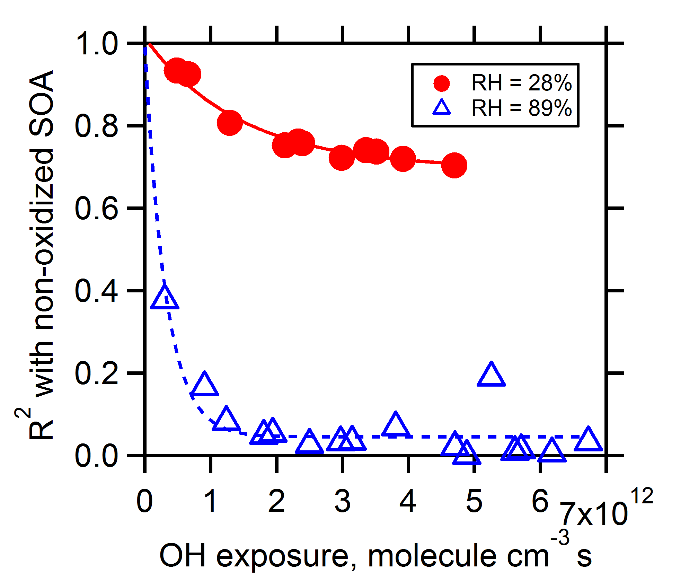
* Fig3a.csv: Normalized volume loss of particles as a function of OH exposure for four independent experiments, two at low RH and two at high RH
* Fig3b.csv: Surface weighted size distributions of non‑oxidized particles and oxidized particles for low and high RH



**Figure 4.** Example mass spectra of SOA as a function of OH exposure for (a) low RH (red, left panels) and (b) high RH (blue, right panels) conditions. OH exposure increases from the bottom to the top panels, with values listed in the panels. Vertical gray bars highlight four ions that exhibited a dramatic decay at high RH, but only small changes at low RH. The mass‑to‑charge ratio of these four ions are indicated in the figure.

Associated data files: Fig4a.csv, Fig4b.csv

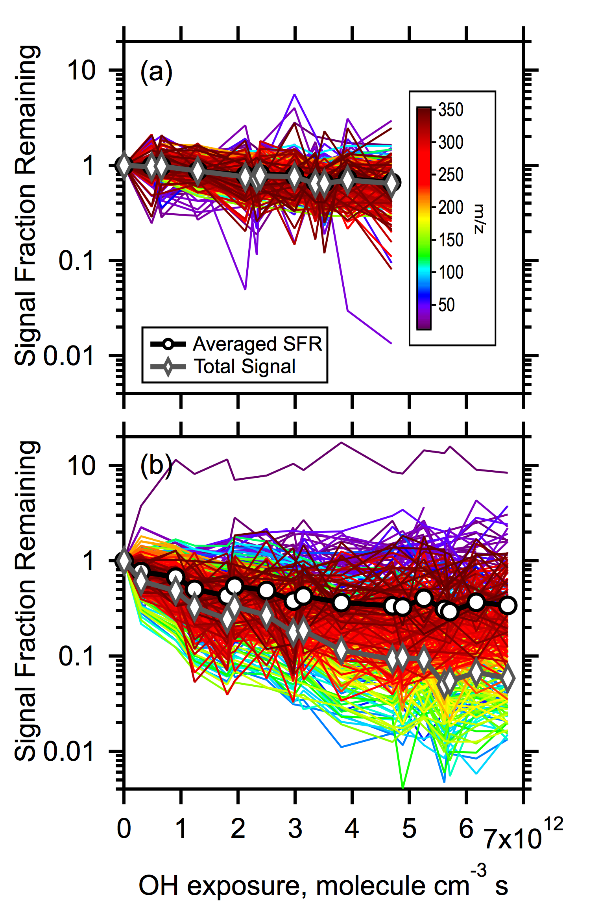
* Fig4a.csv: Signal intensity of ions with m/z = 15-350 normalized to total signal intensity at four different OH exposure at low RH
* Fig4b.csv: Signal intensity of ions with m/z = 15-350 normalized to total signal intensity at four different OH exposure at high RH



**Figure 5.** Coefficient of determination (R2) between spectra of oxidized SOA and non‑oxidized SOA as a function of OH exposure for dry (red circles) and wet (blue triangles) conditions. Spectra are filtered by excluding ions that have percentage contribution to total signal below 0.5 %. Lines are exponential fits, and presented only as visual guides.

Associated data file: Fig5.csv

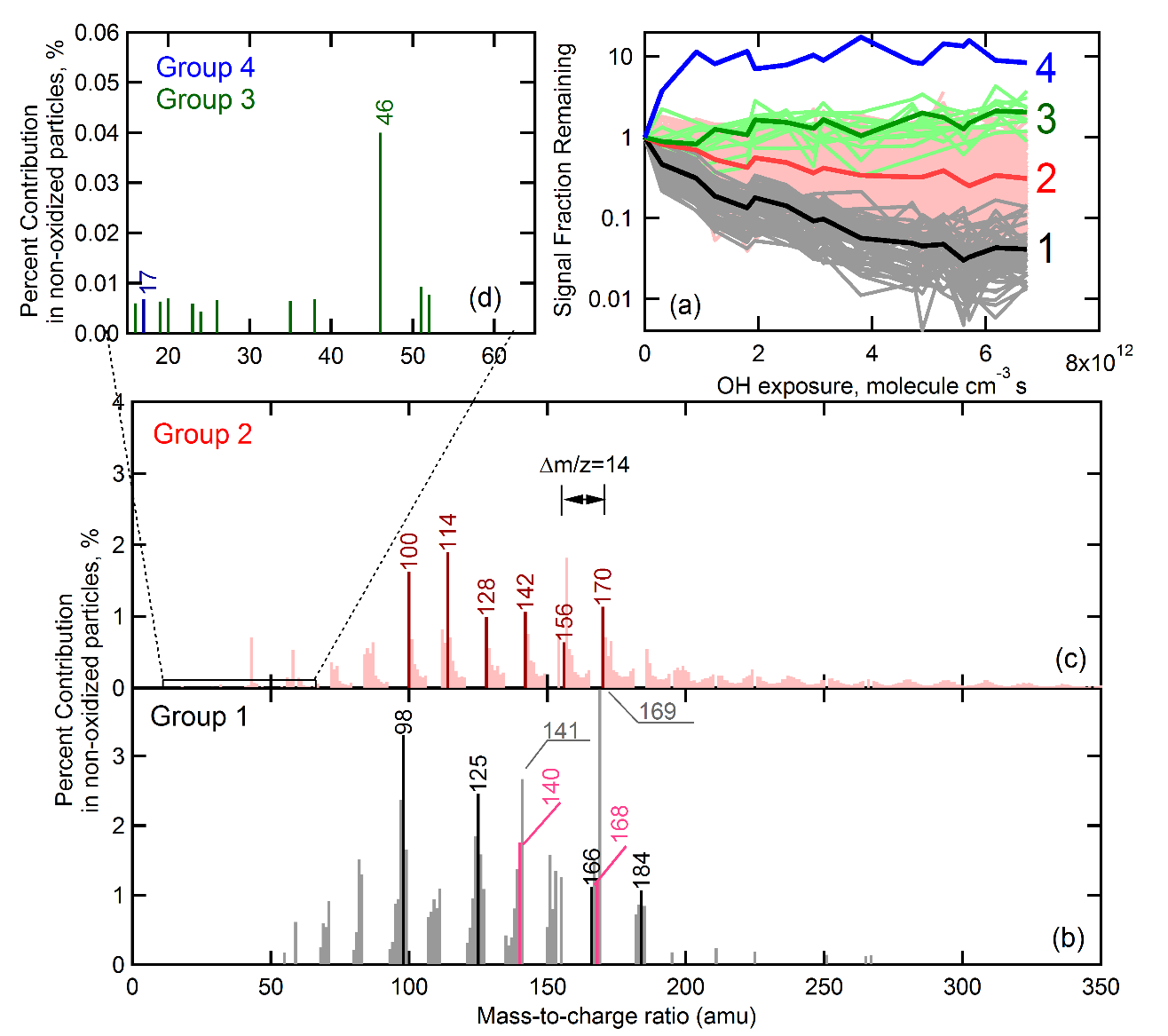
* Fig5.csv: R2 between spectra of oxidized particles and non‑oxidized particles as a function of OH exposure for low and high RH, along with exponential fits of R2



**Figure 6.** Signal decay of all peaks observed above background in the mass‑to‑charge range of 15 – 350 amu as a function of OH exposure for (a) low RH and (b) high RH conditions. Colors denote mass‑to‑charge of a given peak. The black open circles and line denotes the unweighted averaged decay of all the peaks. The dark gray open diamonds and line denote the total signal fraction remaining (i.e. the signal weighted average of all peaks). Note that log scale for the y‑axis.

Associated data files: Fig6a.csv, Fig6b.csv

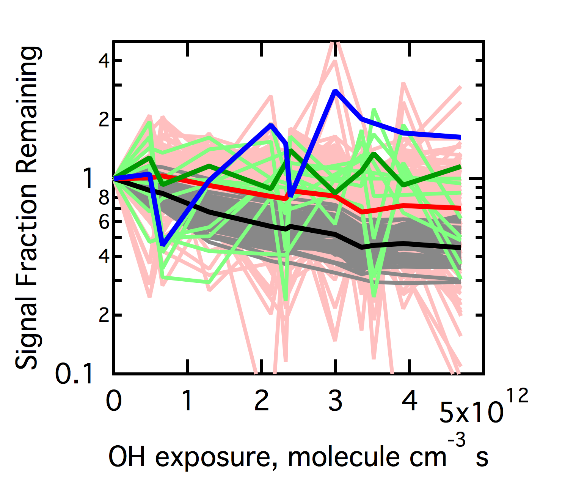
* Fig6a.csv: Normalized signal loss of 336 ions (m/z = 15-350, corresponding to columns in UMR\_matrix) and normalized mean signal loss and total signal loss as a function of OH exposure at low RH
* Fig6b.csv: Normalized signal loss of 336 ions (m/z = 15-350, corresponding to columns in UMR\_matrix) and normalized mean signal loss and total signal loss as a function of OH exposure at high RH



**Figure 7.** (a) Categorization of peaks according to their decay with OH exposure for high RH experiments. The peaks were classified into four groups. Peaks in Group 1 (gray) exhibit the fastest decay with the average shown as the solid black curve. The peaks in Group 2 (red) exhibit the second fastest decay, with the average shown in dark red curve. The peaks in Group 3 (green) exhibit negligible decay, with the average shown in dark green. Group 4 (blue) contains only one peak. (b) Spectrum of the peaks in Group 1. Group 1 contains markers from *cis*‑pinonic acid (black peaks) and pinic acid (pink peaks). (c) Spectrum of the peaks in Group 2. Group 2 contains patterns of repeating peaks separated by m/z = 14, illustrated by dark red peaks. (d) A zoomed‑in view of the peaks of Group 3 and Group 4. These peaks have very small intensities.

Associated data files: Fig7a\_1.csv, Fig7a\_2.csv, Fig7bcd

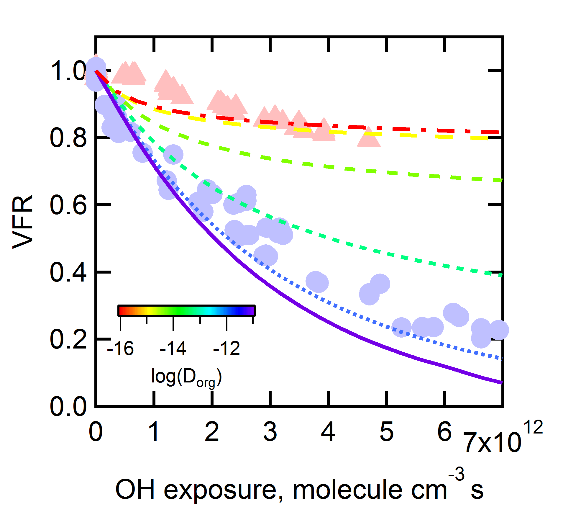
* Fig7a\_1.csv: Normalized signal loss of ions as a function of OH exposure at high RH. Four matrices correspond to four groups with each matrix only containing signal decay of ions that are clustered into that group
* Fig7a\_2.csv: Average of the normalized signal loss of ions clustered to four different groups as a function of OH exposure at high RH
* Fig7bcd.csv: Spectra of four groups of non‑oxidized particles at high RH



**Figure 8.** Signal fraction remaining of all the individual ions observed above background in the range m/z = 15 – 350 under low RH conditions. Ions are colored according to the groupings determined for the high RH conditions (c.f. **Figure 6**).

Associated data files: Fig8\_1.csv, Fig8\_2.csv

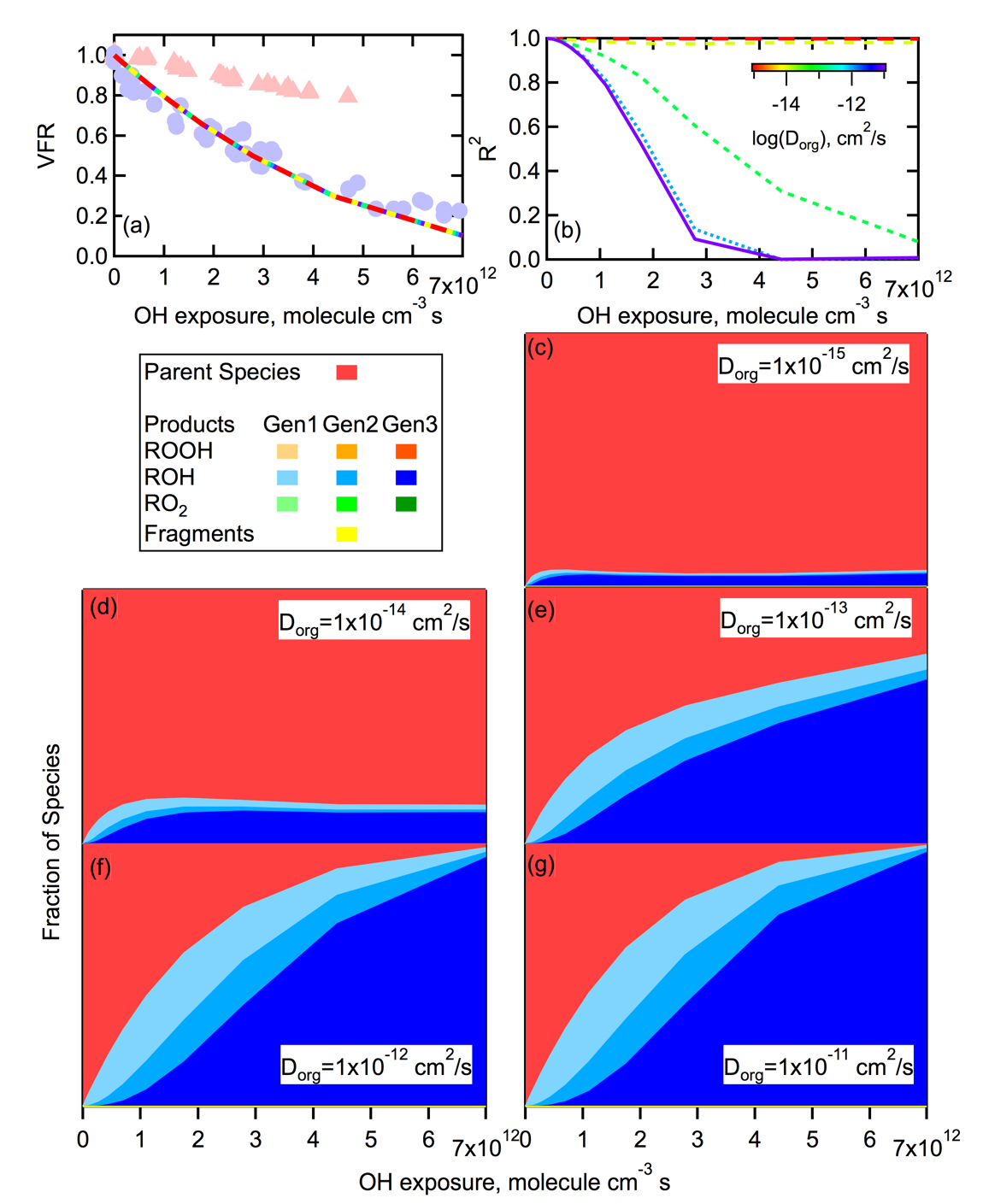
* Fig8\_1.csv: Normalized signal loss of ions as a function of OH exposure at low RH. Four matrices correspond to four groups with each matrix only containing signal decay of ions that are clustered into that group
* Fig8\_2.csv: Average of the normalized signal loss of ions clustered to four different groups as a function of OH exposure at low RH



**Figure 9.** Comparison between observations (points) and simulations (lines) at varying *D*org of the dependence of the volume fraction remaining versus OH exposure for SOA for low RH (red triangles) and high RH (blue circles) conditions. The simulations assumed  = 0.6, *p*frag = 0.5, and *k*RO2+RO2 = 310‑22 cm3 molecule‑1 s‑1. The *D*orgrange from10‑16 to 10‑11 cm2 s-1, denoted by colored lines.

Associated data file: Fig9.csv

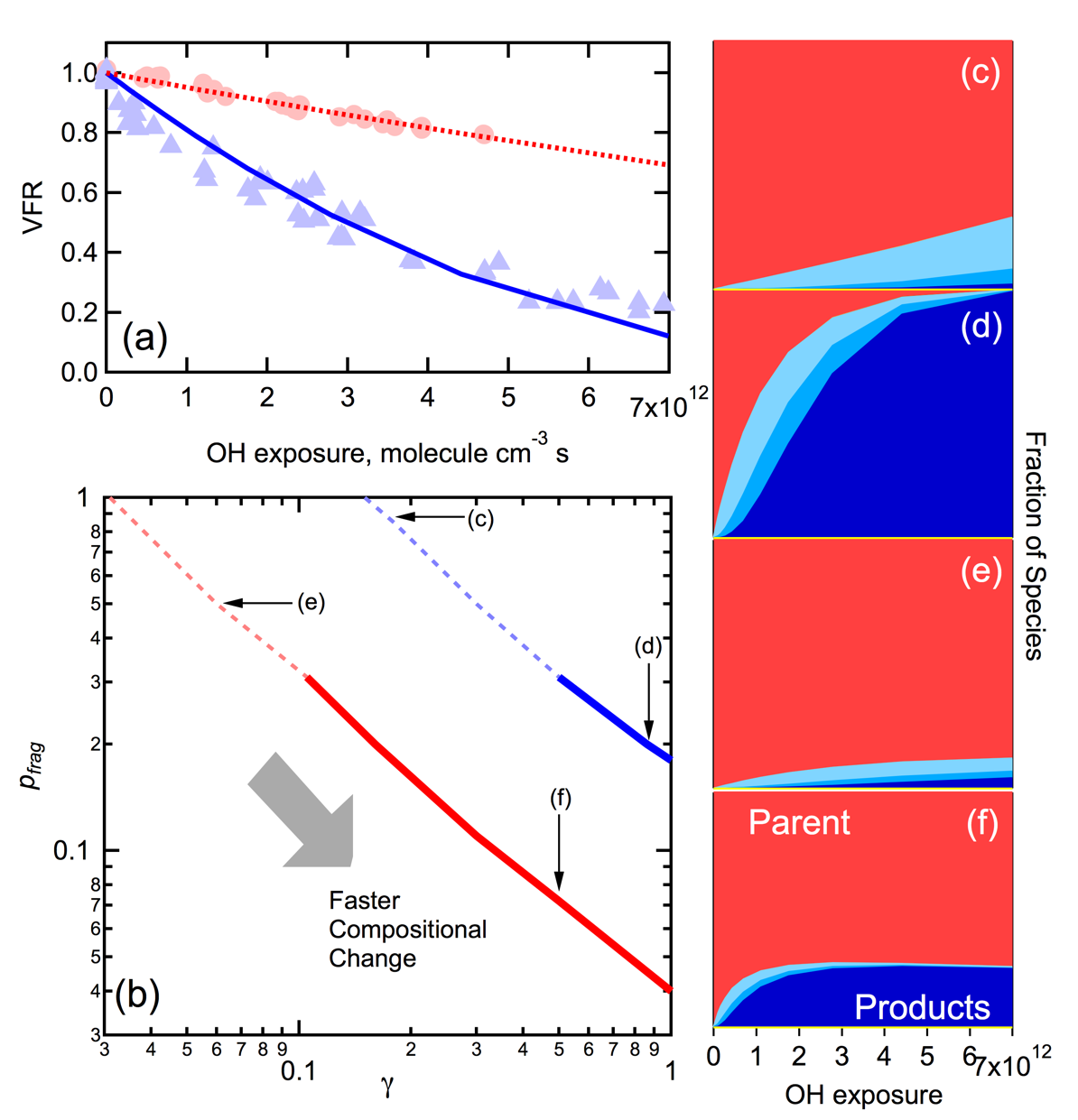
* Fig9.csv: Observed normalized volume loss of particles as a function of OH exposure for four independent experiments, two at low RH and two at high RH (same as Fig3a.csv) along with simulated VFR as a function of OH exposure using six *D*org different by orders of magnitudes



**Figure 10.** Simulated effect of variations in the diffusion coefficient on mass loss and compositional change. For these simulations, the *D*org is allowed to vary from 10‑11 to 10‑15 cm2 s‑1 while all other parameters are held constant and chosen to give good agreement with the high RH observations ( = 0.50, *p*frag = 0.31). (a) The simulated volume fraction remaining versus OH exposure. Observations (symbols) are shown for reference for low RH (red triangles) and high RH (blue circles) conditions. The simulation results overlap because diffusivity has no effect on bulk mass loss. (b) The calculated coefficient of determination (R2) between the molecular density of all simulated species as a function of OH exposure, referenced to the no oxidation case. The *D*org is indicated by the line color, with the purple solid line denoting the fastest diffusion. (c-g) Simulated fractional concentrations of each species as a function of OH exposure for different *D*org. Colors indicate different species and generation (see legend). Only the ROH species are readily visible.

Associated data files: Fig10a.csv, Fig10b.csv, Fig10c.csv, Fig10d.csv, Fig10e.csv, Fig10f.csv, Fig10g.csv

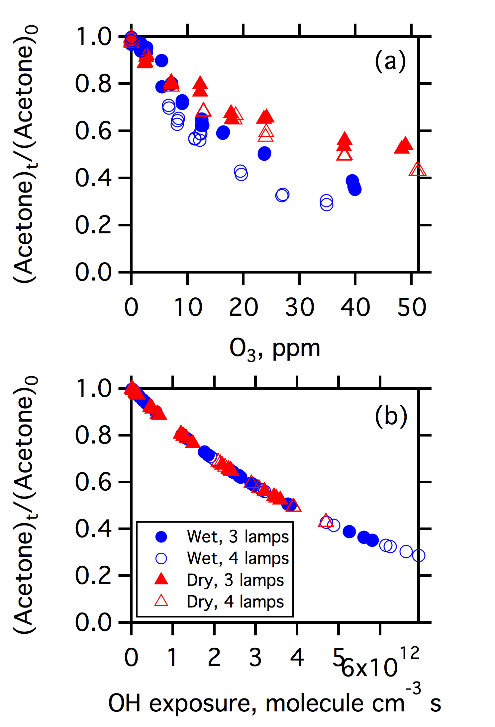
* Fig10a.csv: Observed normalized volume loss of particles as a function of OH exposure for four independent experiments, two at low RH and two at high RH (same as Fig3a.csv) along with simulated VFR as a function of OH exposure using five *D*org different by orders of magnitudes
* Fig10b.csv: Model calculated R2 between the molecular density of all simulated species as a function of OH exposure using five *D*org different by orders of magnitudes
* Fig10c.csv: Simulated molecular fraction of all the 11 species as a function of OH exposure using *D*org = 10‑15 cm2 s‑1
* Fig10d.csv: Simulated molecular fraction of all the 11 species as a function of OH exposure using *D*org = 10‑14 cm2 s‑1
* Fig10e.csv: Simulated molecular fraction of all the 11 species as a function of OH exposure using *D*org = 10‑13 cm2 s‑1
* Fig10f.csv: Simulated molecular fraction of all the 11 species as a function of OH exposure using *D*org = 10‑12 cm2 s‑1
* Fig10g.csv: Simulated molecular fraction of all the 11 species as a function of OH exposure using *D*org = 10‑11 cm2 s‑1



**Figure 11.** (a) Observed (points) and modeled (lines) VFR versus OH exposure for the best‑fit models for both low RH (red) and high RH (blue) conditions. (b) Illustration of the relationship between  and *p*frag that allow for a good fit to the observed VFR decay for low RH (red) and high RH (blue) conditions. The dashed lines show the full relationship, and the solid lines the best-estimate range. Four specific combinations of  and *p*frag are indicated for consideration of the associated composition change. (c-f) Simulated normalized composition change as a function of OH exposure for the  and *p*frag combinations indicated in panel (b). The colors correspond to different species with red indicating precursor (parent) species and other colors indicating various oxidation products (c.f. **Figure 10**). Greater compositional changes for a given OH exposure result from combinations with larger  and smaller *p*frag for a given RH condition.

Associated data files: Fig11a.csv, Fig11b.csv, Fig11c.csv, Fig11d.csv, Fig11e.csv, Fig11f.csv

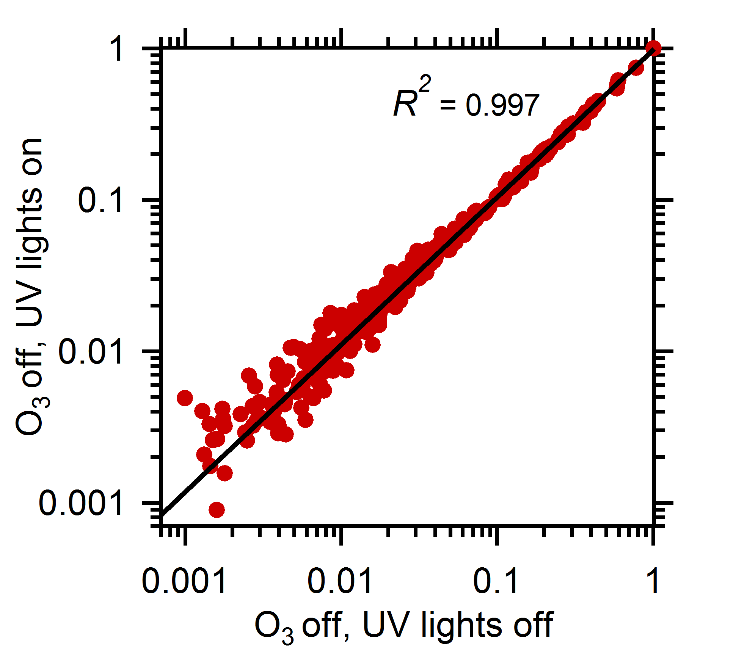
* Fig11a.csv: Observed normalized volume loss of particles as a function of OH exposure for four independent experiments, two at low RH and two at high RH (same as Fig3a.csv) along with simulated VFR as a function of OH exposure with best model‑measurement agreement for low and high RH
* Fig11b.csv: Combinations of  and *p*frag used in the simulations that produce the same best model‑measurement agreement for low and high RH
* Fig11c.csv: Simulated fraction of all the 11 species as a function of OH exposure using  = 0.18, *p*frag = 0.85
* Fig11d.csv: Simulated fraction of all the 11 species as a function of OH exposure using  = 0.86, *p*frag = 0.20
* Fig11e.csv: Simulated fraction of all the 11 species as a function of OH exposure using  = 0.06, *p*frag = 0.50
* Fig11f.csv: Simulated fraction of all the 11 species as a function of OH exposure using  = 0.50, *p*frag = 0.072



**Figure S1.** **(a)** The observed decay in the tracer compound (acetone) as a function of [O3], which is the precursor for OH radicals. **(b)** The relationship between the decay of acetone and the OH exposure calculated from Eqn. 1 in the main text. In both panels, results are shown for low RH (red triangles) and high RH (blue circles) conditions and solid and open markers denote experiments using different photon flux for radical production, with open markers indicating larger photon flux. In panel (a), a greater loss of acetone (i.e. smaller (Acetone)t/(Acetone)0) occurs for the same [O3] for high RH experiments compared to low RH experiments (red). For a given RH condition, greater loss of acetone is observed at a given [O3] for larger photon flux. These are in accordance with reactions R1 and R2 in the main text. In panel (b), the acetone decay/OH exposure relationship is independent of RH and photon flux.

Associated data files: FigS1a.csv, FigS1b.csv

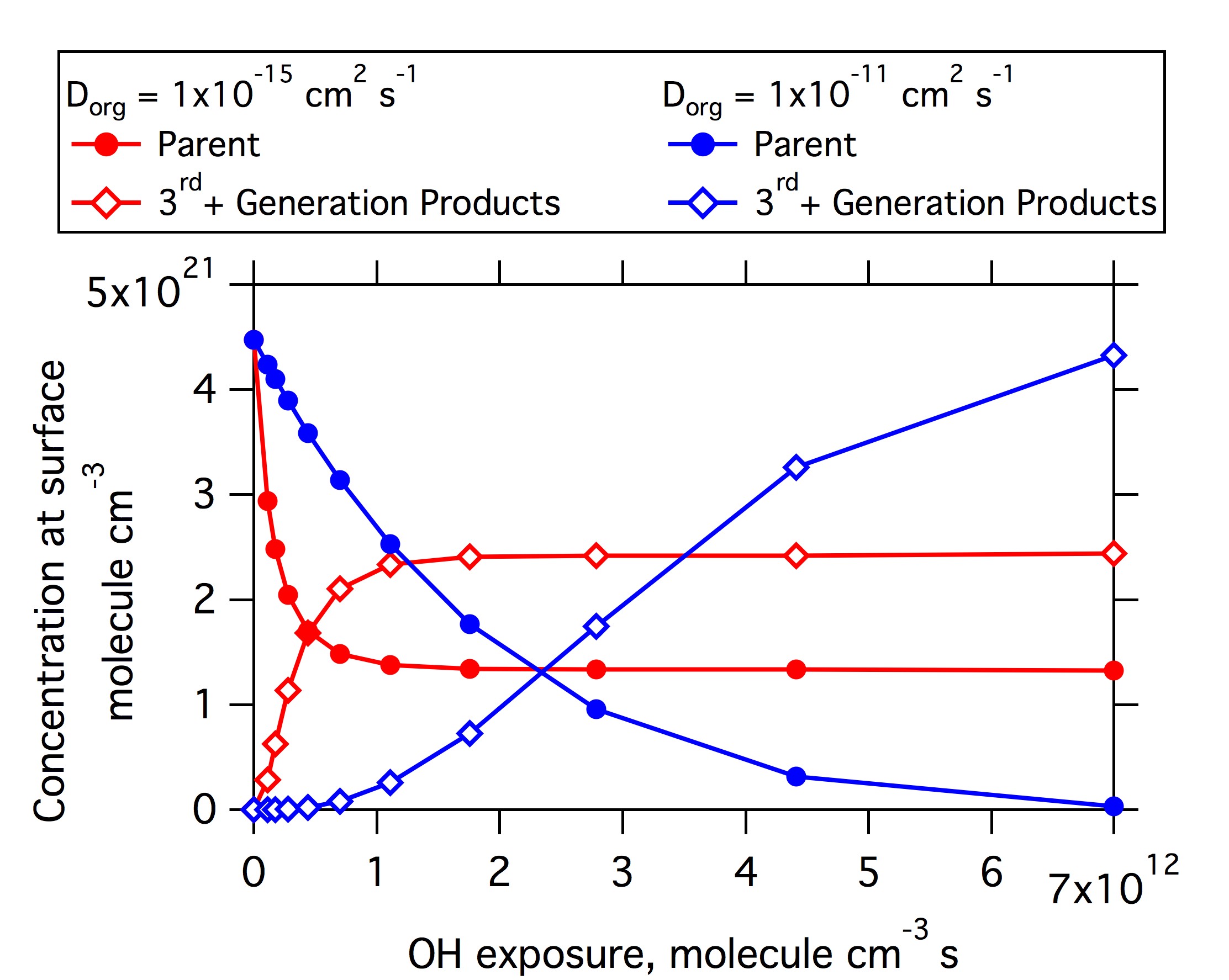
* FigS1a.csv: Normalized acetone concentration at the outlet of the reaction flow tube as a function of input O3 concentration (before dilution) for four independent experiments, two at low RH and two at high RH
* FigS1b.csv: Normalized acetone concentration at the outlet of the reaction flow tube as a function of calculated OH exposure for four independent experiments, two at low RH and two at high RH



**Figure S2.** Scatter plot of the averaged mass spectrum of non‑oxidized particles observed with no O3 in the reaction flow tube and the UV lights on compared with the spectrum of non‑oxidized particles observed with no O3 in the reaction flow tube and the UV lights off. A linear fit yields *R2* = 0.997 and the slope from orthogonal distance regression is 0.974, which indicates no difference between two test conditions and a negligible impact of photolysis.

Associated data file: FigS2.csv

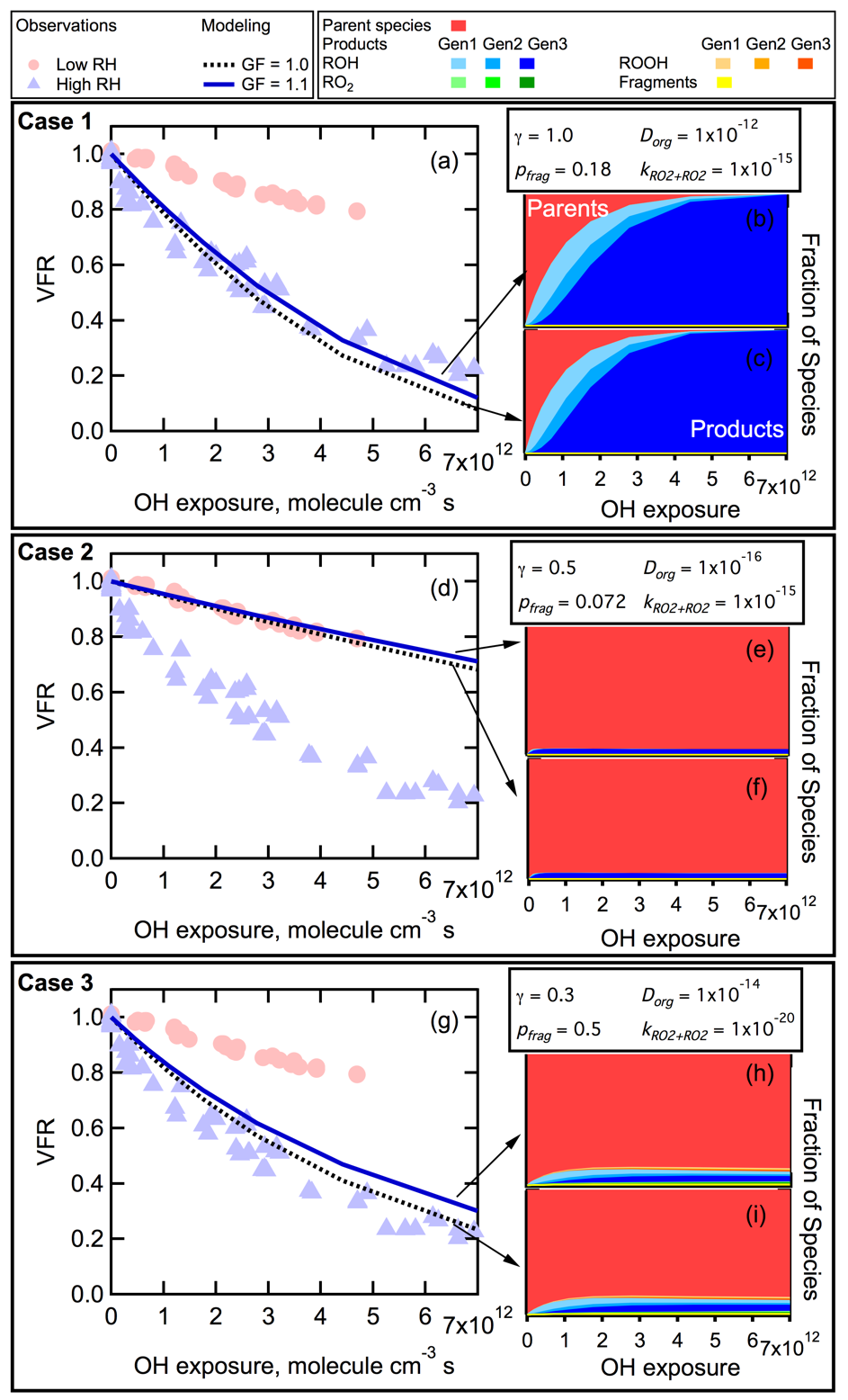
* FigS2.csv: Signal intensity normalized to the max ion for non‑oxidized particles measured with no O3, UV lights on and no O3, UV lights off in the reaction flow tube at low RH



**Figure S3.** Variation in the concentration of the parent species (filled symbols) and 3rd and higher generation species (open symbols) in the surface layer for low-RH/small-*D*org simulations (red lines/points) and for the high-RH/large-*D*org simulations (blue lines/points). These are example results for simulations assuming  = 0.5, *p*frag = 0.31, *GF* = 1.0 and *k*RO2+RO2 = 110‑15 cm3 molecule‑1 s‑1 (same conditions as Figure 10).

Associated data file: FigS3.csv

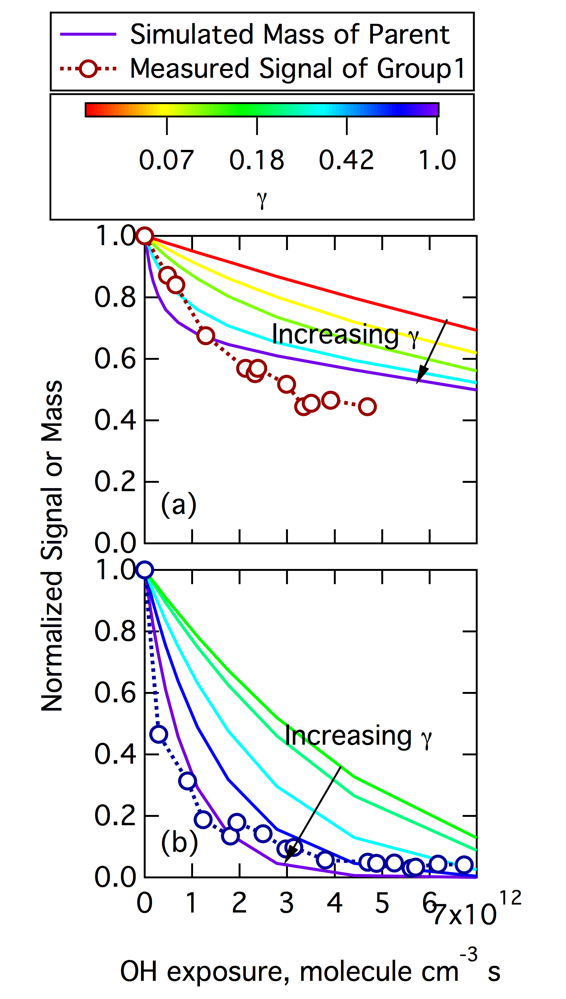
* FigS3.csv: Simulated concentrations of parent species and 3rd and higher generation species in the surface layer as a function of OH exposure using large and small diffusivity, corresponding to high and low RH conditions, respectively.



**Figure S4.** Comparison of simulation results using an RH‑dependent *GF* with various combinations of RH‑independent *D*org, , *p*frag and *k*RO2+RO2. Three cases (unique combinations of *D*org, , *p*frag and *k*RO2+RO2) are shown as examples. (Parameter values are in the figures. *D*org has unit of cm2 s‑1 and *k*RO2+RO2 has unit of cm3 molecule‑1 s‑1.) For each Case, three panels are shown. **(a, d, g)** Simulated volume loss with *GF* = 1.1 (blue solid line) or *GF* = 1.0 (black dashed line) compared to observation for high RH (blue triangles) and low RH (red circles). **(b, e, h)** Simulated compositional change with *GF* = 1.1. Parent species are shown as red and product species are shown as blue/orange/green shades. **(c, f, i)** Simulated compositional change with *GF* = 1.0. There is negligible difference between *GF* = 1 and *GF* = 1.1for all cases indicating small impact of hygroscopic growth on composition evolution.

Associated data files: FigS4a.csv, FigS4b.csv, FigS4c.csv, FigS4d.csv, FigS4e.csv, FigS4f.csv, FigS4g.csv, FigS4h.csv, FigS4i.csv

* FigS4a.csv: Observed normalized volume loss of particles as a function of OH exposure for four independent experiments, two at low RH and two at high RH (same as Fig3a.csv) along with simulated VFR as a function of OH exposure using *GF* = 1.0 (no water) and 1.1 (water uptake)
* FigS4b.csv: Simulated molecular fraction of all the 11 species as a function of OH exposure when water uptake is considered
* FigS4c.csv: Simulated molecular fraction of all the 11 species as a function of OH exposure when water uptake is not considered
* FigS4d.csv: Observed normalized volume loss of particles as a function of OH exposure for four independent experiments, two at low RH and two at high RH (same as Fig3a.csv) along with simulated VFR as a function of OH exposure using *GF* = 1.0 (no water) and 1.1 (water uptake)
* FigS4e.csv: Simulated molecular fraction of all the 11 species as a function of OH exposure when water uptake is considered
* FigS4f.csv: Simulated molecular fraction of all the 11 species as a function of OH exposure when water uptake is not considered
* FigS4g.csv: Observed normalized volume loss of particles as a function of OH exposure for four independent experiments, two at low RH and two at high RH (same as Fig3a.csv) along with simulated VFR as a function of OH exposure using *GF* = 1.0 (no water) and 1.1 (water uptake)
* FigS4h.csv: Simulated molecular fraction of all the 11 species as a function of OH exposure when water uptake is considered
* FigS4i.csv: Simulated molecular fraction of all the 11 species as a function of OH exposure when water uptake is not considered



**Figure S5.** Simulated decay of the molecular density of parent species in the condensed phase as a function of OH exposure for varying  (solid lines) compared to observed decay of the fractional contribution of Group 1 ions signal to total signal (symbols and dashed lines) for low RH (a) and high RH (b). The  used for simulations are denoted by colors with purple indicating  = 1.0 (see legend; note log scale for ). For each condition (low or high RH), *p*frag are chosen in the simulations to produce best model‑measurement agreement according to the ‑*p*frag relation in Figure 11b, while all the other parameters are held constant. These results show that decay of parent compounds is faster with increasing  for both RH conditions

Associated data files: FigS5a.csv, FigS5b.csv

* FigS5a.csv: Normalized mass loss of parent species as a function of OH exposure from simulations using five different ‑*p*frag combinations along with observed average decay of signal intensity of Group 1 ions as a function of OH exposure at low RH
* FigS5b.csv: Normalized mass loss of parent species as a function of OH exposure from simulations using five different ‑*p*frag combinations along with observed average decay of signal intensity of Group 1 ions as a function of OH exposure at high RH