(add new meetings at the top) Shortcut is http://tinyurl.com/log-pam . ***Please add items to be discussed at the next meeting(s) on Asana at the top of the OFR project***

Input for Reviewer of Bruns et al (PSI chamber - PAM comparison)

Dec-2014: Possible Group Comment on Lambe paper in ACPD

Paper and discussion at:
http://www.atmos-chem-phys-discuss.net/14/30575/2014/acpd-14-30575-2014-discussion.html

==========Final draft of comment posted 16 Jan 2015==========

This is an interesting study on the topic of the comparability of SOA studies performed in large environmental chamber studies and fast portable oxidation flow reactors (OFR). OFRs are gaining increased use in recent years in the atmospheric chemistry community. We commend the authors on their work in conducting flow reactor experiments and compiling these comparisons of chamber and flow reactor SOA formation studies, and hope that they and others will continue to explore these topics in the future.

However, there are some key aspects related to documentation of conditions, applications of experimental methods, data presentation, and data interpretations that are not well described in the paper. In our opinion these should be addressed before publication of this manuscript.

1. OH exposure:

As Referee 3 noted, the experimental section is lacking some key details. One critical aspect, in particular, is the lack of information on how the OH exposure (OH_{exp}) is calculated. The only reference to OH_{exp} calculations appears in Sect. 2.1 (p 30581, lines 8-13) as “OH concentrations were varied by changing the UV light intensity, and were quantified by measuring the decay of SO_2 and applying the known OH+SO_2 rate constant (Davis et al., 1979).” Depending on the details of how such experiments were done, there could be substantial errors in the estimated OH_{exp}. However there is not sufficient detail in the manuscript to ascertain whether this is the case or not. It would be very useful to the community and the future users of the results of this paper if more details were provided, so readers and other researchers don’t have to speculate whether disagreements may be due to errors or uncertainties in OH_{exp}.

As discussed in Ortega et al. (2013) and Li et al. (2015), high VOC concentrations (or high concentrations of other compounds that react with OH) can “suppress” OH by shifting OH to HO_2 in the reactor, resulting in much lower OH exposures than measured for the same conditions in the absence of added “external OH reactivity” (OHR_{ext}). Measurements and modeling carried out by our group (using reactors that employ either 254 nm only or both 254 + 185 nm wavelengths from mercury lamps to generate OH) suggests this “OH suppression” can

reach 1-2 orders-of-magnitude for high OHR_{ext} (100-1000 s^{-1}). Very high OHR_{ext} were indeed used in the experiments described in this paper.

With the information provided, it is impossible to know if the effects of OH suppression from high OHR_{ext} were accounted for or not in this study. Several critical pieces of information include:

- Were the SO_2 decay measurements performed only "offline", i.e. in the absence of VOC? Or were they carried out "online" (in the presence of added VOC)?
- If offline, at what range of OHR_{ext} (i.e. SO_2 concentrations)?
- What H_2O concentrations were used for the calibrations and how do they compare to those used in the VOC experiments, if those were different experiments?
- What input O_3 levels were used for the SO_2 and VOC experiments?
- Were the calibrations and SOA experiments conducted close in time? Hg lamps age with time and the same light power setting may not correspond to the same UV flux if multiple months have passed.

H_2O and O_3 concentrations will strongly affect both OH_{exp} and degree of OH suppression for a given lamp setting. If calibrations were not conducted at relevant conditions or characterization of the effects of OH suppression estimated, a discussion of possible biases should be included in the manuscript, or (better) OH_{exp} calibration experiments should be conducted under conditions representative of the OHR_{ext} of the experiments. If differences in OH suppression between calibrations and VOC experiments were corrected for, the details of such corrections should be thoroughly described in the paper.

Also, for conditions with high VOC concentrations, RO_2+SO_2 reactions may cause substantial decay in SO_2, not attributable to OH (Kan et al., 1981; Richards-Henderson et al., 2014). Therefore, if online calibrations were conducted (i.e. if the SO_2 was introduced at the same time as the VOC) this may cause a substantial overestimate in OH_{exp}. If additional high OHR_{ext} calibrations/characterizations experiments are conducted, use of an additional compound that reacts with OH but not RO_2, such as CO, would help eliminate errors arising from that cause.

2. Interpretation of SOA yield comparisons:

This concern about uncertainties in the quantitative OH exposure relates to Referee 2's comment about the authors' interpretation of Fig 5 that "It is not evident to me from Figure 5 that SOA yields at comparable OH exposures are a factor of 2 to 10 lower in the flow reactor than in chambers." For Fig 5a and Fig 5b, it appears that a decrease in OH exposure on order of a factor of ~2 would make the yields between the chamber and PAM indistinguishable for overlapping OH_{exp}. Therefore, unless the authors can demonstrate that the uncertainty in OH_{exp} exposure is substantially less than a factor 2 with their methods, this statement should be removed from the paper (especially from the abstract and conclusions, where it appears in less quantitative terms), or possibly modified to reflect only the factor of 2-3 difference for isoprene SOA under the experimental conditions of these studies (and also probably the experimental agreement for the other compounds). Such low uncertainty of only a factor of 2 in OH_{exp} is difficult to achieve in practice with a PAM in our experience, and in any case requires careful

work on this topic, something that cannot be assessed from the current version of the paper.

Meanwhile, only one chamber experiment from isoprene oxidation (in Fig 5a and Fig 6) was compared to the yield of isoprene in flow reactor experiments. However, isoprene SOA yields were also reported in other experiments, e.g., Kroll et al., (2006) found a yield range of 0.9%-3.6% for isoprene oxidation (low NO conditions) in chamber studies, which is lower than the chamber yield (~5.5%) used in this study and similar to the yield range in the PAM. A more comprehensive summary of published chamber yields should be included. Alternatively if there are reasons to exclude certain chamber studies, these should be given.

On a related point, what do the one-sigma uncertainties represent in Fig 5? Please clarify. As is, they may lead readers to assume they represent the uncertainty in the OH exposure (which is almost certainly much larger). They more likely represent ONLY the propagated variability from the measurements used to calculate it (rather than uncertainty in the offline/online calibration and/or models use to estimate OH_{exp}). An uncertainty analysis should be conducted to characterize the true uncertainties in OH_{exp}, which would help clarify whether the differences in yield in Fig 5 really have meaning.

Table 1 and Figs 1-4 show that 8 different compounds were studied, however the yields are only discussed for 3 compounds. Why? Given that the yield results will likely be of the most interest to the community from this study, it would seem useful to discuss those results. This would give a better sense of the variability in the agreement/disagreement and provide better support for any generalizations and conclusions. As is, a reader quickly skimming the abstract and figures will assume that the yield conclusions broadly apply to the relatively wide range of compounds studied, which in current form is not supported in the manuscript.

3. Other topics:

OA concentrations have a major effect on SOA yields (as the authors point out as background in Sect. 3.4). However, the OA concentrations in the PAM vs chamber experiments in Fig 5 are not discussed in terms of their effect on the measured SOA yields. At least some of the chamber studies report OA-dependent yields, and the chamber yields should be corrected to the same OA concentrations observed in the flow reactor experiments.

We suggest that Fig 7 should be plotted vs seed surface area, rather than mass, since condensation to seed aerosol or reactive uptake to an acidic seed aerosol would likely be a surface area-limited process.

Furthermore, it seems from the manuscript that the sulfuric acid (H_2SO_4) seed aerosol was produced by oxidation of SO_2 concurrent to isoprene oxidation in the flow reactor, in contrast to the atomized ammonium sulfate seed. Nucleation and atomization likely produced very different size distributions and thus very different surface area/mass ratios, potentially affecting the yields of SOA from isoprene. Also the size distribution in the nucleation experiments may lead to a

significant fraction of SOA mass being too small to be measured by the AMS. The SMPS measurements from these experiments may help answer these questions.

Comparison of the mass spectra in Fig 2 is very unclear. Larger log-log scatterplots, difference plots, or uncentered R^2 (Ulbrich et al., 2009) may be more useful. This topic was also alluded to by both referees.

Particle wall losses in the reactor are quoted as 32% +/-15%. This is much higher than in our experience, where these losses are typically 5% in mass, when using an aluminum wall chamber. We observed losses of ~30% when using a glass cylindrical chamber as used in this study. As reported in Ortega et al., (2013), we believe the increased loss is due to nearly complete loss of charged particles to walls made of insulating material such as glass, Pyrex, or Teflon. In addition, very different charged-particle loss corrections need to be used when generating (charged) particles from an atomizer or (uncharged) particles by nucleation. Freshly atomized particles tend to be highly charged leading to even higher losses, and this effect can be reduced by passing the particles through a sufficiently potent radioactive neutralizer. It should be stated whether such neutralization was done or not in this study, so that it can help compare the likely particle losses in the experiments reported here with other studies. We suggest that the authors discuss these issues in some detail, as otherwise other groups may not be aware of the difference and apply the wrong loss correction in the future, thus significantly over or underestimating these effects.

Page 30588, lines 4-12. The authors briefly discuss the time required for condensation, noting timescales of 2000-20,000 seconds, while the residence time in the reactor is 100 s. If those timescales represent e-fold timescales, that would suggest only 0.5-5% of the condensable products would condense in the reactor, rendering the PAM useless without large seed surface areas, which is clearly not the case. For example, if the isoprene yield was corrected by that condensation efficiency, SOA yields of ~60-600% would be implied. A more detailed discussion (including explicit calculation of the condensation timescales) is needed.

Seed experiments were shown only for isoprene, which is the only compound with evidence for lower yields in PAM compared to a chamber experiment. However, the authors conclude at the end of Sect. 3.5 “these measurements suggest seed particles are required in flow reactor measurements in order to more closely simulate condensation conditions in environmental chambers.” Such a general statement is not supported and should be modified accordingly.

This comment grew out of a journal club discussion in our group, and was jointly redacted by Doug Day, Brett Palm, Amber Ortega, Zhe Peng, Weiwei Hu, and Jose-Luis Jimenez.

References:

Ortega, A. M., Day, D. A., Cubison, M. J., Brune, W. H., Bon, D., de Gouw, J. A. and Jimenez, J. L.: Secondary organic aerosol formation and primary organic aerosol oxidation from biomass-burning smoke in a flow reactor during FLAME-3, Atmos. Chem. Phys., 13(22), 11551–11571,

doi:10.5194/acp-13-11551-2013, 2013.

Kan, C. S., Calvert, J. G. and Shaw, J. H.: Oxidation of sulfur dioxide by methylperoxy radicals, J. Phys. Chem., 85(9), 1126-1132, doi:10.1021/j150609a011, 1981.

Richards-Henderson, N., Ward, M., Goldstein, A. and Wilson, K.: OH-initiated heterogeneous oxidation of saturated organic aerosols in the presence of SO2: uptake kinetics and product identification, AGU Fall Meeting, Talk A11M-06, https://agu.confex.com/agu/fm14/meetingapp.cgi#Paper/20473, San Francisco, USA, Dec 2014.

Kroll, J. H., Ng, N. L., Murphy, S. M., Flagan, R. C. and Seinfeld, J. H.: Secondary organic aerosol formation from isoprene photooxidation, Environ. Sci. Technol., 40(6), 1869-1877, doi:10.1021/es0524301, 2006.

Ulbrich, I. M., Canagaratna, M. R., Zhang, Q., Worsnop, D. R. and Jimenez, J. L.: Interpretation of organic components from Positive Matrix Factorization of aerosol mass spectrometric data, Atmos. Chem. Phys., 9(9), 2891–2918, doi:10.5194/acp-9-2891-2009, 2009.

Li, R., Palm, B. B., Ortega, A. M., Hlywiak, J., Hu, W., Peng, Z., Day, D. A., Knote, C., Brune, W. H., de Gouw, J. and Jimenez, J. L.: Modeling the radical chemistry in an Oxidation Flow Reactor: radical formation and recycling, sensitivities, and OH exposure estimation equation, J. Phys. Chem. A, revised, 2015.
==========end comment to be posted==========
Internal discussion below:

The ACPD paper by Lambe et al. examines the important question of the comparability of flow reactors and atmospheric chambers.

<u>Estimation of OH exposure</u>
Main issue is their estimation of age, only say “OH concentrations were varied by changing the UV light intensity, and were quantified by measuring the decay of SO2 and applying the known OH+SO2 rate constant (Davis et al., 1979).” It would be useful to the community and the future use of their results if they gave more details, so we don’t have to speculate in our papers whether disagreements may be due to errors in OHexp on their end.

- Issue 1: they don’t specify whether OHexp cals were done online or offline, or at which (or several OHRext), nor at which H2O
- Issue 2: very large variation of OHRext, so OHexp will change accordingly
    - Zhe: “They did use very high OHRext, especially in the case of isoprene (OHRext=~1150 s-1”
    - Zhe could estimate OH suppression with his model
    - But there is also issue of uncertain OH recycling from isoprene that could play a role at these very high OHexp
    - If SO2 calibrations done offline, then there could be substantial errors in OHexp.
        - Zhe: “I just check RO2+SO2. Their k is up to 1e-14 cm3 molec-1 s-1. [RO2] is always ~1.15e13 molec cm-3. Residence time was 100 s. So it

might be possible that they calibrated an "RO2exp" as OHexp."

- Issue 3: if doing online cals, RO2 + SO2 reaction may play a role
    - Zhe: "At AGU, at least 3 people told me heterogeneous RO2+SO2 is much faster than in the gas phase. k could be 10^-13 cm3 molec-1 s-1. In online cals, SO2 might be dominantly consumed by RO2 in SOA, leading to a very large overestimation of OHexp."

Other topics

- OA concentrations have a major effect on SOA yields. However the OA concentrations in the PAM vs chamber experiments in Fig 5 are not even mentioned.
    - effect of surface area
    - Sulfate vs OA mass
- Selection of chamber data: did not include some of the Kroll et al. studies from Caltech, such as Kroll et al. (2006)
- Figure 7 should be plotted vs seed surface area, not mass. Nucleation and the atomizer may produce very different size distributions and thus very different area/mass ratios. Also the size distribution in the nucleation experiments may start being too small to be measured by the AMS.
- Comparison of MS in Figure 2 is unclear. Larger log-log scatterplots of the MS, or 87difference plots, or uncentered R2 (Ulbrich et al. 2009) may be more useful. This topic was also alluded to by one of the reviewers.
- Abstract "The studies show that seed particles increase the yield of SOA produced
- in flow reactors by a factor of 3 to 5". This has only been shown for isoprene, so the conclusion cannot be generalized to other system that have not been studied.
- Particle wall losses in the reactor are quoted as 32% +/-15%. This is much higher than in our experience, where these losses are typically 5% in mass, using an aluminum wall chamber. We observed before losses of ~30% when using a glass cylindrical chamber as used in this study. We suggest that the authors add this explanation as otherwise other groups may not be aware of the different and apply the wrong loss correction in the future.

Conclusion about yields

- we don't think it is supported

30-Sept-2014 AMS/OFR: Pedro, Doug, WW, Jason

Quantification of organic AMS (NO3 chamber study, DAQ5 vs DAQ4 vs AP240/ADQ

- Chamber studies AMS (Lab, DAQ5/ADQ) vs SMPS suggest organic overestimated by factor of 1.5-4 (only 4 if CE is as low as 0.5 for SOA)
- WW tests after chamber study (same AMS settup) show that CE AmmSulfate=0.37, whereas oleic acid has apparent CE=4 (assume Oleic acid CE=1)
- Jason tested same system with AP240/DAQ4, AP240/DAQ5, ADQ/DAQ5 and sees similar overestimate in oleic acid (+/-30% depending on card/DAQ combo).
- Compared Jason's AP240/DAQ4 spectra to UMR spectra (L_STD_Q_024), and looked ok but with much less higher m/z's. Later realized that was PSLs coated with oleic acid.

Need to compare to pure oleic acid spectra.

- Something with newer version of Squirrel? Pedro reworked data recently using recent versions of SQ and versions as old as SEAC4RS version and got same answer: Pedro add versions and what dataset here?
- Weiwei and Doug looked over chamber NO3/terpene AMS vs SMPS comparison and apparent overestimate in OA seems variable which could be partly due to changing CE. Applying a constant scaling of the AMS species based on the SMPS vs AMS total comparison would be tricky/uncertain since if AmmSulfate (seed) and organic SOA are have different scaling this means the composition-determined density is no constrained by AMS relative contributions. And simply scaling organic to match the SMPS volume ignores CE. Hopefully we can better understand the organic quantification first, before making corrections to AMS using SMPS.
-

Action Items:

- Compare Oleic acid (AP240/DAQ4 to L_STD_W_039: Allison Aiken's HToF W-mode UMR, pure oleic acid and/or L_STD_Q_080 Alfarra's Quad AMS UMR spectrum (See: http://cires.colorado.edu/jimenez-group/AMSsd/) -(Jason)
- Workup/compare AMS vs CPC oleic and squalene on LabAMS/CapVap and HIAPER/StdVap during Cap Vap expts done by WW in winter/spring 2014 (Doug to look at soon if possible as WW is off to GoA campaign tomorrow). These expts were done with AP240/DAQ4
- after new lens on HIAPER and tested, repeat oleic acid, amm. sulfate, amm nitrate with AP240/DAQ4 (Jason)
- Further look at chamber study AMS/SMPS comparisons and better generalize trends (although as noted above between CE and organic quantification issues, problem is underconstrained)
- Confirm that CE=1 for oleic acid in literature if possible (Alfarra 2004 reference in Mathews 2008 quoting CE=1 which is a PhD thesis. The Alfarra thesis is linked at the bottom of the AMS papers page: http://cires.colorado.edu/~jjose/ams-papers.html

14-July-2014 AMS/OFR: Pedro, Doug, WW, Jose, Zhe, Brett, Amber

- Discuss Bill Brune's student's measurements of flux 185/flux 254. Decide to use f185/f254 0.5% with no power dependence.
- SOAS organic nitrate comparison (TDLIF vs AMS)
- Brett's investigation into the AMS transmission curve to correct the mass added using the SMPS. Transmission curve applied will increase OFR mass added by 20% on average. However in the enhancement vs OHexp it is nearly a factor of 2 at the peak mass added.

+ For Amber she looked at this and it's only ~10% and she is missing ~⅓ of the SMPS points so we propose just showing the AMS vs SMPS mass added comparison plot and state this bias and do not correct.

10-July-2014: OFR Code (Multiplex Experiment Processor (MEP) Discussion): Jose, Doug, Brett, WW, Amber

- Discussed inputs (AMS data, Master Logger, External Meas), and desired output (enhancement plots)
- Version 2 of OFR code, to use Experiment ID.New Data Sets: implement experiment ID in Master Logger, calculate Org_allQC, Org_ratio, Org_diff, and Perturbation_all. For each experiment ID identify: 1) Reactor, 2) Name of function that performs perturbation, 3) Waves that are needed, 4) non-perturbation regions.
- In either case (future projects and past projects): Donna adds table of Perturbation Subset Selection indicating periods of interest with name, expt ID, include runs, don't include runs, and notes, and maybe a conditional statement.
- Donna will show existing housekeeping AMS tool that WW used, to model this above Perturbation Subset Selection Table

2-July-2014 AMS/OFR: Pedro, Doug, WW, Jose

- Comparison of SOAS CU and GA-Tech. 15% drifts. Check if CE
- org NO3 comparison with TDLIF. Possibility of NO2 breakthrough in TDLIF? Doug/Weiwei write email draft to Ron's group discussion possibilities
- Peakshaps and MZ cals using fluorine from SOAS; fluorine helps a bit everywhere.
- Brett on mass defect plot of PTRMS in O3 OFR.

16-June-2014 AMS/OFR: Pedro, Doug, WW, Amber, Jose, Zhe

- Agenda, action steps in Asana
- Amber on calnex AMS "missing mass" based on SMPS size distributions
- Pedro on ions at mz60
- Zhe on OFR modeling
    - internal vs external reactivity
    - OH suppr.
    - OHexp/O3exp (show different VOCs)
    - OHexp/J254, J185, Jtot
    - table of advantages, disadvantages for OFRs, chamber, etc.

10-June-2014: GECKO Tutorial @ NCAR: Doug, Jordan, Zhe, Jose, Julia Lee-Taylor, Geoff Tyndall

-Julia walks through ppt presentation. Notes are added to "note" section in Google Doc of Julia's presentation here:
https://docs.google.com/presentation/d/1VZXJZkvalTdOUzu3udquRwMfQNOcb0gZrhbhS5dm4H8/edit#slide=id.p13

- O3, NO, HCHO, isoprene

2-June-2014 AMS/OFR: Brett, Pedro, Doug, WW, Amber, Jose

Brett discusses line losses and lens cutoff for BEACHON:
AMS transmission:
- time series of SMPS mass below AMS size cut-off (size dependant transmission from Dva 40-100nm). Up to 1 ug sometimes. Often missing amount is 10-15% and sometimes up to 50%. Correlation plot with this corrections is now AMA/SMPS ~1.15. Seems to overcorrect.
- Histogram of amount corrected divided by uncorrected amount added in OFR shows a lot of points lie in 0-0.2. Large spike at -0.05 where just a little mass added to points where a little mass was lost. Will try moving the AMS transmission curve sequentially and computer R2 and slope for AMS vs SMPS comparison and see what curve optimizes the comparison.
Line Loss:
- ~5% so smaller
Composition to assign missing mass?:
Proposed function:

IF (E_SO4) > 0 and (E_OA) > 0
  Then Split missed mass proportionally
ELSE IF one of them > 0
  Then call all the missed mass that one
ELSE
  Then try 2 options: (a) Ignore and (b) call it 100% OA
END

30-May-2014 AMS/OFR Mtg: Brett, Pedro, Doug, Zhe, WW, Amber, Jose:

254/185 for Zhe's 254-only model: Can we constrain 254 using OHexp? Lab or Field? SOAS?
- Backstory - is Zhe using Rui's equation (below), the modeling results are not consistent. We are looking for ways to constrain 254 (looking for soft calibrations in lab or soft data in field with CO or PTRMS measurements).
- Brett: Follow up w Roger about PTRMS data for OFR254, then calculate OHexp and give to Zhe.

Amber on CalNex AMS/SMPS comparison (w PToF/SMPS size distributions)
- Ambient SMPS/AMS +/- 50%. Need to re-do for that ratio timeseries from Patrick's data
- chose 3 periods comparing enhancements and size distributions
- size distributions for SMPS seems like it's higher by factor of ~3 (compared to time series)
- Action items in Asana

Pedro on SEAC4RS
- C2H4O2 vs HROrg60; Cc2H4O2 is 90% which seems high compared to Cubison paper
- CO2+(org) vs HROrg44
- m/z 43 ions (HC is 20% in plumes)
- m/z 57 ions
- C2H3 vs C2H5 - strongly correlated (Manjula said they weren't correlated for her standards)

- m/z 30 iepox SOA tracer vs m/z 82 iepox tracer
- f60 vs f82 plot; shows nicely IEPOX, BBOA and background regions
- CH2O+ vs C5H6O, - C4H5+ vs C5H6O. C3H7O2 (75)+ vs C5H6O
- f44 vs f82 plots
- f82 vs SO4/tot

Brett
- final SMPS/AMS comparison
- size comparison for one period over 8/1-2 shows good agreement btw SMPS and AMS
- Doug showed size resolution paper plot, a monodisperse of 50nm has a 1sig of 17.
- Doug needs to include DMA size resolution in his paper
- To correct AMS for small particles:
- 1) Transmission (plumbing) correct SMPS size distribution
- 2) Apply AMS lens transmission low cut off (corrected by density) to SMPS size distributions (apply in Dm space)
- 3) Calculate "missing small mass" by calculating difference between SMPS (after plumbing trans corr) and AMS lens transmission curve line.
- 4) Make PToF-based time series of composition below 100nm (may be different for different campaigns, and may need to do some averaging or look at total mass) and calculate the fractional composition of each species contribution to small sizes.
- 5) Add "missing mass" of each species (esp for OFR to calculate enhancements) to AMS OFR timeseries

---

Equation for lamp fluxes: Rui 5/23/14

log(f185/f254)=-3.15+0.23*logf185

Lamp power settings (%)	Photon flux at 185nm (f185)	Photon flux at 254nm (f254)	f185/f254 (%)
0	0.00E+00	0.00E+00	0
10	7.87E+11	1.97E+14	0.4
20	4.80E+12	8.00E+14	0.6
40	2.02E+13	2.53E+15	0.8
60	4.43E+13	4.43E+15	1
2x100	8.60E+13	7.17E+15	1.2

20-May-2014 AMS/OFR Mtg: Brett, Pedro, Doug, WW, Amber, Jose

- Brett on BEACHON SMPS vs AMS, and AMS corrections
- WW: IEPOX update, SMPS vs AMS
- Amber: AMS vs SMPS
- Pedro: IEPOX summary
- GoAmazon cals etc?

Brett on SMPS vs AMS comparison:
Ambient
- During first half of campaign when fluorine diffusion was high. AB followed temperature swings (20%) which tracked AMS/SMPS comparison. Thus affected AB but not necessarily aerosol IE. Chose to not use AB correction for first half. Pulls AMS/SMPS comparison to within ~15%.
OFR
- High AMS/SMPS during high nitrate production. Correct by assuming X% evaporates in SMPS (80%) to get good agreement.
- Consider O/C dependant density correction for OFR data
- Find a few more periods where substantial volume <60 nm and average AMS PToF together to see if an see small mode in AMS
Paper outline
- James' IVOC data seems to correlate with OFR mass produced and very similar magnitude.

Amber on SMPS/AMS comparison, CalNex
- Very often see no mass enhancement in SMPS but have in AMS. Possibly size is growing outside SMPS upper range.
- Need to make series of size distribution plots to look at more closely.

Weiwei AMS/SMPS comparison, SOAS
- At low AMS concentrations AMS/SMPS decreases a lot (~0.5)
- For OH OFR, also see high nitrate periods AMS >> SMPS
- Remake some AMS vs SMPS
- Generally the SMPS enhancement looks similar to AMS.
- Make SMPS enhancement vs OH exposure.

Weiwei IEPOX SOA
- f82 all over the map for MS database for UMR.
- calculated estimated IEPOX aging from high IEPOX period during SOAS

----------Email from Bill Brune on O3/OH ratios in the atmosphere 5/13/2014----------

“OH and O3 are not totally uncorrelated since ozone + water + sunlight is the main or at least a major OH source. I took a quick look at several past data sets. I would say that generally the midday ratio of O3 (ppbv)/OH (pptv) is in the range of 20 to 2000 but most of the ratios are in the range of 50 to 500. The ratio tends to be lower in cities and higher in forests or the free troposphere.

So in the PAM O3 is in the several 1000's of ppbv and OH is in the few 100's of pptv. In Kang et al. 2007, the ratio was typically ~15 to 100, which is on the lower end of the range of atmospheric ratios. You'll have to estimate what it is for the way that you are running the PAM chamber.”
- and -
“In the early morning or evening the O3/OH ratio was generally at the upper end of the range.”

Doug comment:
Consider OH: 1e6-1e7 and O3: 20-200ppb without any covariance, thus giving us a 100-fold range in OH/O3 roughly describes concentrations ranges, however due to the covariance of OH & O3, it pulls "typical" ratios into the 10-fold range Bill quoted.

Amber comment:
Quoted from my ACP paper
(http://www.atmos-chem-phys.net/13/11551/2013/acp-13-11551-2013.html)
“While 185 nm UV light photochemically produces both OH and O3, the OH / O3 ratio in the reactor is about 10 times daytime ambient levels. In this study, OH exposure
ranged from 1.36 × 10^10 to 6.5 × 10^11 molec. cm−3 s, and O3 exposure from 1.5 × 10^15 to 3.4 × 10^16 molec. cm−3 s.“

5-May-2014: AMS Mtg: Brett, Pedro, Doug, WW, Zhe, Amber, Jose
Agenda:
- WW on SOAS + SEAC4RS
- Look @ Sam’s AMS factor vs CIMS SOAS plots
- Pedro on PMF, Variables to be posted.

- Sam shows CIMS vs AMS factor plots
  - Do correlations with total SV-OOA (just sum the 2 together)
  - check period on 6/18/13 (especially SVOOA/Pinic acid). Possible instrumental issues? Goes up from zero to high and back down, correlations with AMS no present.
  - do correlation plots for each PMF factor

- Harald plotting tools. Correlogram of all ions. Custom design to handle external variables (standalone). Also add feature that time series and correlation plot is shown.

- Weiwei's outline on IEPOX SOA paper
    - check where the database OOA spectra that exceed background are from. Possible biogenic influence?
    - See Asana task

- Pedro shows SEAC4RS f82, PMF, etc.

2-May-2014: AMS Mtg: Brett, Pedro, Doug, WW, Zhe, Amber, Jose

Agenda:
- Brett on GoAmazon overview

GoAmazon & general campaign logistics:
- got there 4 days before, 10 days to get AMS and PAM running
- planned 95 person-day + 3 tickets, used 115 p-d + 4 tickets, not too bad
- 115 p-d / 59 campaign days = 1.95
- Donna: should come on 2nd wave, there are often bugs in SQ that surface then and are difficult to deal with otherwise

GoAmazon Brett
- Need to annotate the slides with what happened on each period, so that others can use dataset in the future after Brett has moved on
- periods where not logging O3 need to make model of H2O, T, lights to calculate O3
- Find out if atmospherically this is N or S hemisphere (just ask Paulo, Scot, Andi…), - CO background was ~100 ppb
    (NOAA CO http://www.esrl.noaa.gov/gmd/ccgg/globalview/co/co_intro.html)
- CO for OH exposure worked well
- Denuded OH OFR showed almost production (and hetero oxidation/losses) compared to standard OH OFR in parallel. Do some more of this during IOP2
- Isoprene standard addition. Made ~2ug/m3 from ~50ppb isoprene/MVK (estimated 2% yield). No evidence of IEPOX SOA (f82 goes down)
- Investigate delivering isoprene/monoterpenes with diffusion cell or otherwise maybe getting a few lecture bottles made by Apel/Reimer company for IOP2 standard addition experiments.

1-May-2014 ePToF discussion (mainly experiments to do with new ADQ card)

- Pedro, Donna, Joel, Doug D., Jose

Agenda:
+ Experiment list for ADQ card
+ Update for Richard (send data to work with? wait for ADQ data)

Tell Richard we will give him data with an ADQ that will be saved in both Tofware and AMS format. This will be after the second week of May. He can look at dynamic range by looking at different mzs.

Paper outline

Seven figures of data obtained with ADQ:

Experiment

1. Chopper wheel, signals vs particle time-of-flight in PtoF (Seq/AB) EPToF(Seq/Sig/AB)

Size Distributions

2. Size distributions of aerosol w both regular PToF and ePToF (for several m/z with PSLs)
    - Quote SNR improvement in size dist (peak height / RMS of baseline in PToF)
3. Comparison of deconvolution w matrix vs Rich's mode

Total Concentrations

4. Schematic of OLD GENALT / chopper movement and how we process signals
5. Time series of total AB and total mass concentrations for main species for MS vs total PToF vs total ePToF w/ ambient data (PTof data is DC marker corrected)
    - Quantify the change in total time series SNR
6. Schematic of NEW GENALT / chopper movement and how we process signals
7. Mass loading vs time. Demonstration of ePToF-only mode, comparison w MS mode (total signal, also HR spectrum) ePToF summed across PToF bins is "not really PToF'.
    the sqrt(2) factor should pop out

Joel wonders if we want to look at low concentration regimes

30-April-2014: PAM Mtg: Doug, Brett, Amber, Weiwei, Zhe, Rui, Jose

- GoAmazon-2 schedule discussion
- PAM lights
- Zhe's results
- GoAmazon-1 overview

Lamp flux

- Brett shows ozone vs 254nm photodiode.
    +Looks looks linear at appears that the 254/185 doesn't changes at most a factor of 2 (maybe not at all).
    + at lower light settings as temperature increases, flux increases (both wavelength). Before we saw that at high lamp settings flux decreased with increased temperature (falling over the lamp efficiency curve).

Rui shows model turning off fluxes and comparison to Pedro's flux measurements

- Agreed to retune 185nm to match ozone for lower light settings (b/c had high 254 nm before). For the lowest setting, this will cause OHexp to drop by factor of 2-3.
- Keep the f185/f254 nm range from 0.4%=>1.2% since GoA and SOAS data (O3 vs 254 photodiode) suggest range shouldn't be bigger.
-need to show explicit equation for light flux ratio (e.g. log(f185/f254) = a + b*log(F185)
- keep as percent lamp power for sizing of points for model/experiment plots

Rui's paper outline:
- Figure 6 (sensitivities plots).
    + Add additional row of H2O2 concentration
    + Add additional column with OH reactivity on the x-axis (then explore the dependence on different light settings/"internal reactivity" on following plot
    + change x-axis of "flux fraction" axis to log(F185).

Zhe's uncertainty analysis:
- shows bar graphs results (OHex, O3) for changing all parameters by 5%. Total net change is only ~20% (as opposed to ~250% if summed up all parameters*5%). Highly buffered system.
- Image plots of total reactivity (internal + external) with photon flux on y-axis and H2O on x-axis. Plots for different external reactivity.
- Image plots of OH internal cycling/OH primary production (flux, H2O). High flux, low water makes recycling much larger. Middle case, recycling is only 10% of primary production.
- Image plots of HOx lifetime (ranges from 0.1 to 10 s)
- Image plots of OH-to-HO2 conversion rate / OH total loss rate (%)
- Image plots of HO2-to-OH conversion rate / HO2 total loss rate (%)
-

28-April-2014 Update of modeling results
https://docs.google.com/document/d/1mXz-rCiNA6xzFoOnczkVKx68KFweUp_c0ORXIhZQ5ps/edit

23-April-2014 ePToF discussion
- Pedro, Doug W., Donna, Joel, Doug D.

Pedro shows slides:
MS comparisons:
- In order to deal with MS jitter (50ns), just widen sticks to make UMR (AB converges to constant value, otherwise it has a spread of value due to the mixing); definitely still scaling issues in Squirrel but Doug W suggests ignoring that for now since it will be normalized later anyway (S/N and shape of ePToF is what's important)
- Confidence limits; shows how CLs change with averaging Boulder data. Right now they don't seem right.
- S/N improvement seems to scale for AB as expected
- S/N seems different for N2 and Ar
- S/N for aerosol signal doesn't seem to quite scale properly (Boulder amm. nitrate). Need to compute Std dev using running mean b/c current method is making noise too be for MS, ePToF.
Now Size Distributions:
- Compare Reg PToF vs ePToF size distributions for Boulder mz46 data for different averaging times. Doug note: need to bin in dlog space for comparisons (when ptof and eptof different ptof

time bins)
- When comparing ePToF to MS
    factor of 2 for the fact that we use only every other PToF
    factor of 2 for the fact that the ePToF wheel is half open, half closed
    Doug wants to be sure that we are using the actual time the DAQ records within the ePToF run, you aren't making assumptions.

A wonderful idea from Joel is to compare MS Open with summed of all ePToF (in the PToF bin dimension) divided by 4 (two factors of 2)

Paper conversation: Joel thinks that data that only go into this should be with the ADQ. Use lab and ambient ADQ data. Can borrow an ADQ from someone for a week?

Bottom line is that if you have enough signal it works.

Pedro suspects that the lens had a transmission issue beginning last Nov, Dec. Doug says this a more likely explanation is it becoming dirty, bent…..not a true change in the "physics of the lens" . You can use a good telescope and fiddling to see the apperature. This would be a good topic for user mtg

21-April-2014 PAM Mtg

- Agenda:
    + Schedule/Planning for configuring/shipping/setup of HR-AMS for Reddy at DRI
    + Lamp output dependencies (new plots from Brett, Weiwei)

- Info on lights
    + What Bill tolds us ~ 5% ratio - Bill's Post-Doc's last modeling paper: http://www.atmos-chem-phys.net/13/5017/2013/acp-13-5017-2013.pdf

    + Rui's model (discuss updated results)
        - Tuning case: low H2O, OH is insensitive to F254, explains why she had to increase it so much

Action Item: Rui to do model / meas. comparison with ratio = 1.2% at high power, decreasing x3.5 at the lowest power.
    - If that matches measurements, we go with that

- SOAS 254 nm photodiode / O3 concentration (surrogate for 185nm):
    - single light ramp periods (constant temperature) the O3 vs 254nm diode looks linear and the same at different temperatures suggesting the the **185nm vs 254nm ratio does not change with lamp power setting**.
    - lamp power is affected by temperature (but not ratio). Increases by ~40% over 25-35 C

temperature range

- over the ~3-week period, it appears that the 254 photodiode response increases, approximately doubling. Thought is that the photodiode Teflon diffuser may be bleaching, becoming more transparent.

- GoAmazon 254 nm photodiode / O3 concentration (surrogate for 185nm):
  - Same as SOAS, except no drift in the 254nm diode sensitivity
  - No [H2O] dependance (only temperature which obviously sometimes correlates)

Zhe's sensitivity PAM kinetic model modeling:

- Shows bar graphs of high/low/mid lights, water, OH reactivity with the absolute sensitivity (correlation coefficient weighted by absolute value in range in error input).
- Generally only a few reactions matter. OHexp typically most sensitive to O2+hv, H2O+hv reactions (not bi/tri molecular reactions); H2O2 most sensitive to HO2+HO2, ...

- Decide to try using constant 1.2% F185/F254 ratios for Rui's model runs.
- Decide not to pursue direct measurements of F185/F254 ratio for now and push ahead with the papers acknowledging there is some uncertainty in there (Zhe's model should quantify what the uncertainty/sensitivity it presents for different conditions.

15-Apr-2014: Modeling results for cases of interest defined on 9-Apr (by Zhe)

- 5000 trajectories
- Uncertain parameters: rate constants, T, P, ratio F185/F254 (F185 fixed), residence time

- Convergence test:

  Default case:

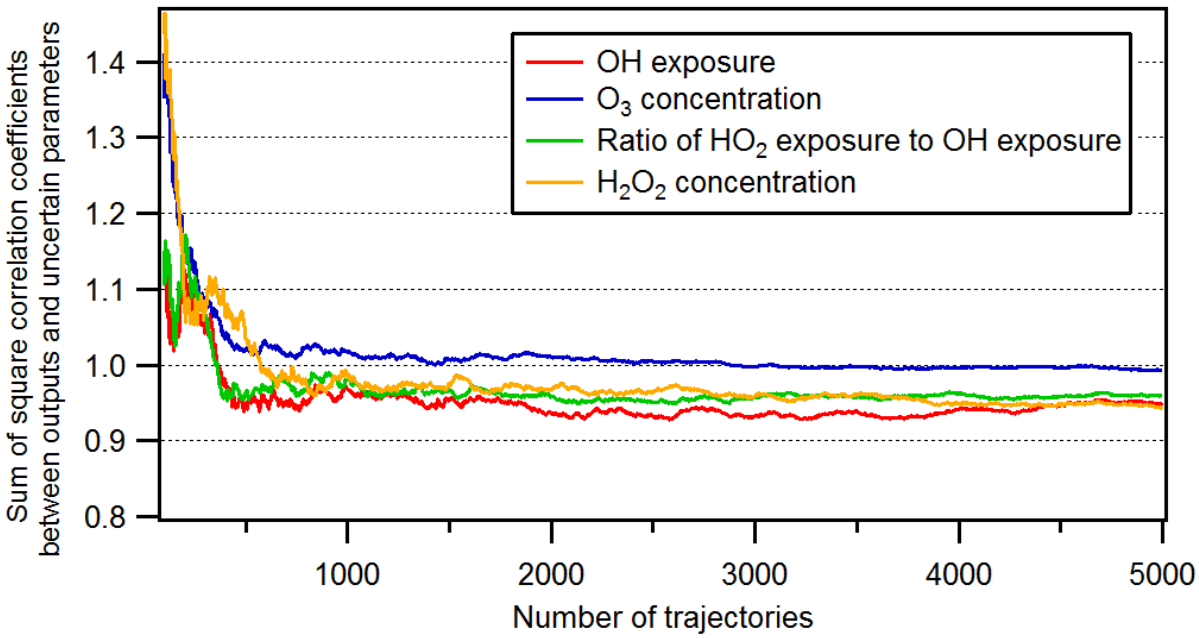
  - All outputs well converged
  - Sum of first order effects

    OHexp: ~0.95

    O3: ~0.99

    ratio HO2exp/OHexp: ~0.96

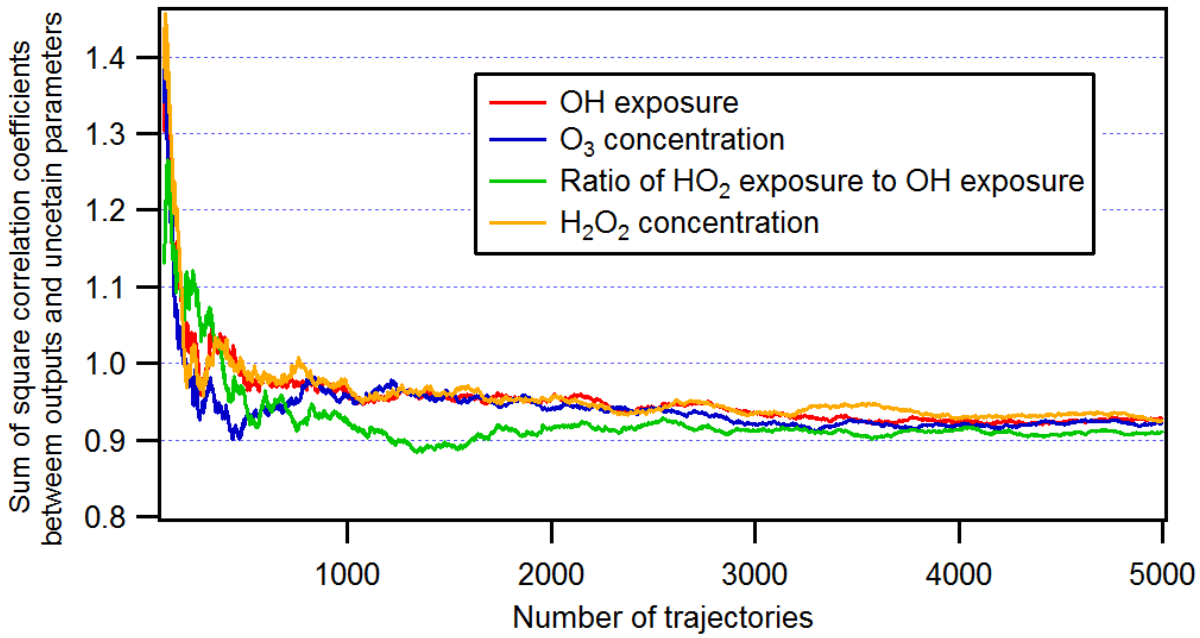
    H2O2: ~0.94



Case HHH:

- All outputs well converged
- Sum of first order effects
  - OHexp: **~0.93**
  - O3: **~0.92**
  - ratio HO2exp/OHexp: **~0.91**
  - H2O2: **~0.93**

- HDMR necessary!



- Output statistics:
  - All output distributions are approx. normal
  - **Case label: L/M/H L/M/H 0/L/H**
    H2O light OHR

Case	OHexp	F(OH exp)	O3 conc	F(O3 conc)	Ratio HO2exp /OHexp	F(ratio)	H2O2 conc	F(H2O2 conc)
MM0	1.62e12	1.18	1.01e14	1.14	7.86	1.23	2.44e12	1.30
LL0	6.77e10	1.21	1.19e12	1.13	3.69	1.19	1.54e9	1.41
LH0	1.01e12	1.18	1.12e15	1.13	19.86	1.20	4.73e12	1.37
HL0	4.98e11	1.18	9.39e11	1.15	1.82	1.24	3.16e10	1.31
HH0	9.12e12	1.20	5.57e14	1.19	6.35	1.30	1.36e13	1.30
MML	7.48e11	1.18	1.03e14	1.13	23.30	1.23	5.12e12	1.21
LLL	1.27e9	1.30	1.19e12	1.13	524.58	1.24	9.76e9	1.34
LHL	8.16e11	1.18	1.12e12	1.13	26.62	1.19	5.39e12	1.34
HLL	2.80e10	1.24	9.49e11	1.15	90.54	1.28	2.69e11	1.22
HHL	8.12e12	1.21	5.60e14	1.18	7.52	1.31	1.37e13	1.56
MMH	1.70e11	1.21	1.04e14	1.13	131.67	1.24	1.28e13	1.22

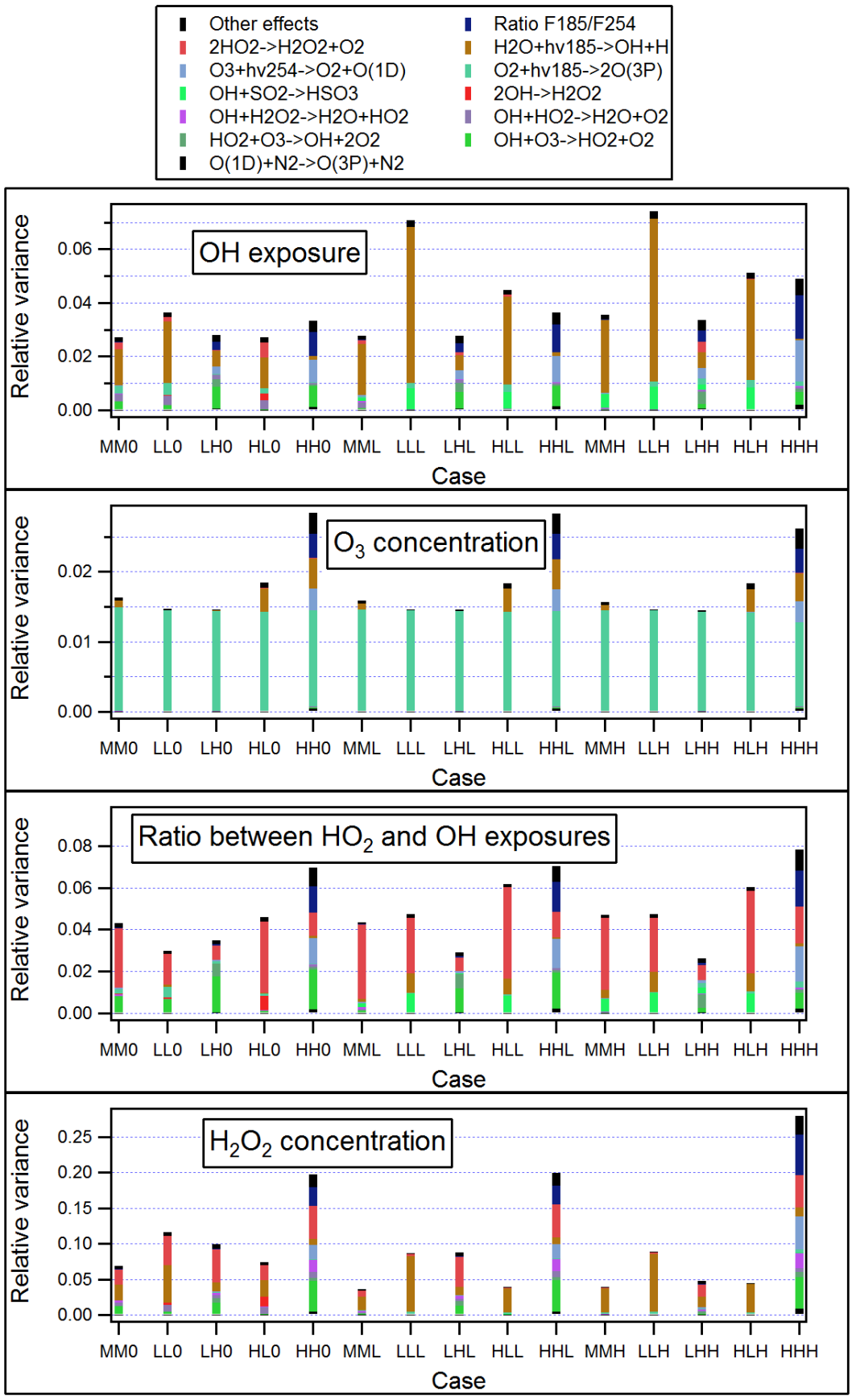
LLH	1.33e8	1.31	1.19e12	1.13	5133.17	1.24	1.02e10	1.35
LHH	3.81e11	1.20	1.13e15	1.13	69.91	1.18	1.01e13	1.24
HLH	3.23e9	1.25	9.50e11	1.14	837.44	1.28	3.14e11	1.23
HHH	4.51e12	1.25	5.98e14	1.18	17.41	1.32	1.96e13	1.70

- Uncertain parameters:

Index	Parameter	Index	Parameter	Index	Parameter
0	O(1D)+H2O->2OH	16	H+HO2->2OH	32	OH+SO2->HSO3
1	O(1D)+N2->O(3P)+N2	17	H+HO2->O(3P)+H2O	33	HSO3+O2->HO2+SO3
2	O(1D)+CO2->O(3P)+CO2	18	H+HO2->O2+H2	34	OH+HNO3->H2O+NO3
3	O(1D)+O2->O(3P)+O2	19	OH+H2->H2O+H	35	O2+hv185->2O(3P)
4	O(1D)+O3->2O2	20	2OH->H2O+O(3P)	36	O3+hv254->O2+O(1D)
5	O(1D)+O3->O2+2O(3P)	21	NO+O3->NO2+O2	37	H2O2+hv185->HO2+H
6	O(1D)+H2->OH+H	22	NO2+O3->NO3+O2	38	H2O2+hv254->2OH
7	O(3P)+OH->O2+H	23	OH+H2O2->H2O+HO2	39	HO2+hv254->OH+O(1D)
8	O(3P)+HO2->OH+O2	24	O(1D)+N2O->2NO	40	HO2+hv185->OH+O(1D)
9	O(3P)+H2O2->OH+HO2	25	HO2+NO2->HNO4	41	H2O+hv185->OH+H
10	O(3P)+O3->2O2	26	OH+HNO4->products	42	2HO2->H2O2+O2
11	H+O3->OH+O2	27	O(1D)+N2->N2O	43	T
12	OH+O3->HO2+O2	28	OH+NO2->HNO3	44	P
13	HO2+NO->OH+NO2	29	O(3P)+O2->O3	45	F185 (fixed)

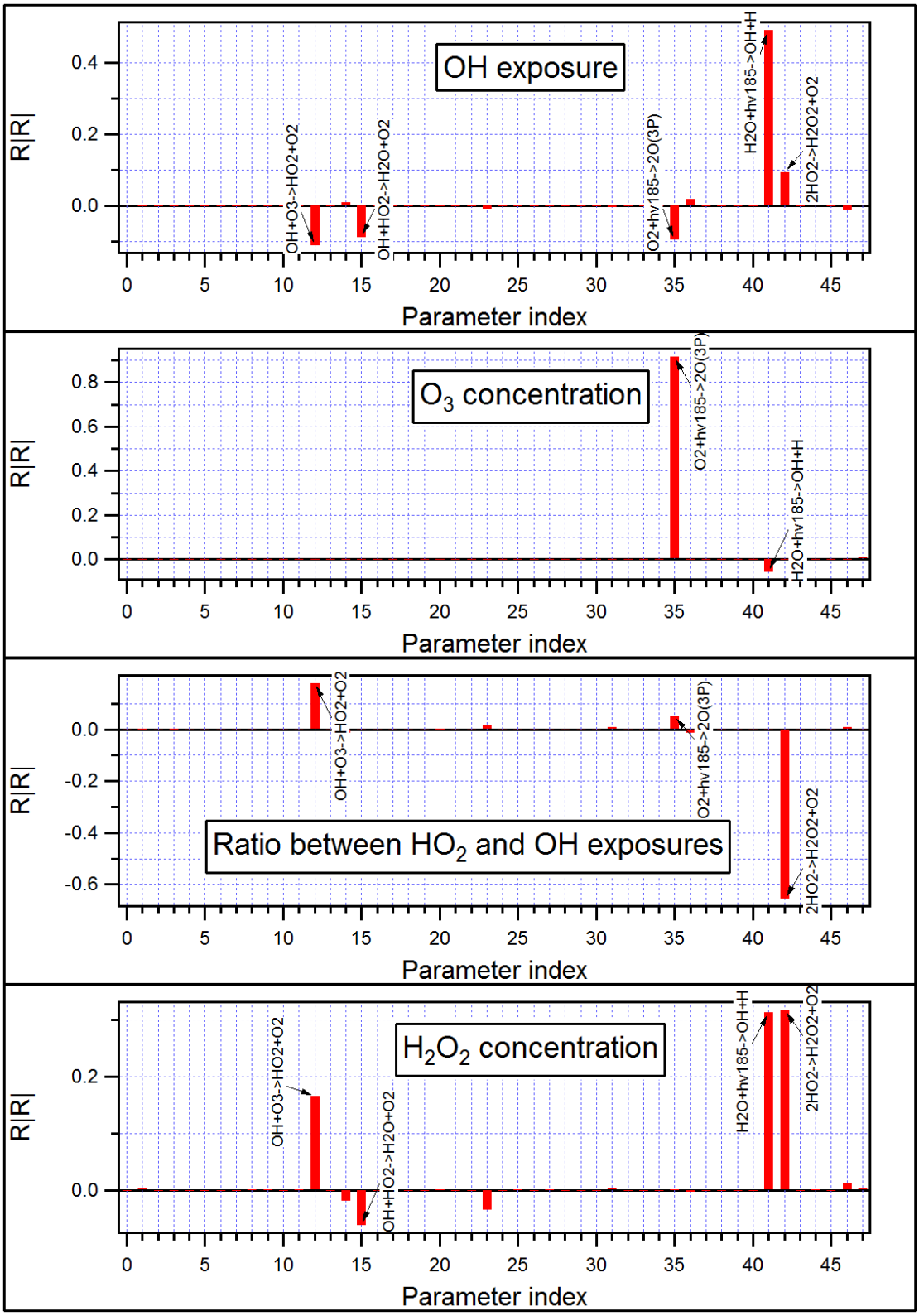
14	HO2+O3->OH+2O2	30	H+O2->HO2	46	ratio F185/F254
15	OH+HO2->H2O+O2	31	2OH->H2O2	47	residence time

- Key parameters’ contributions to output relative variances

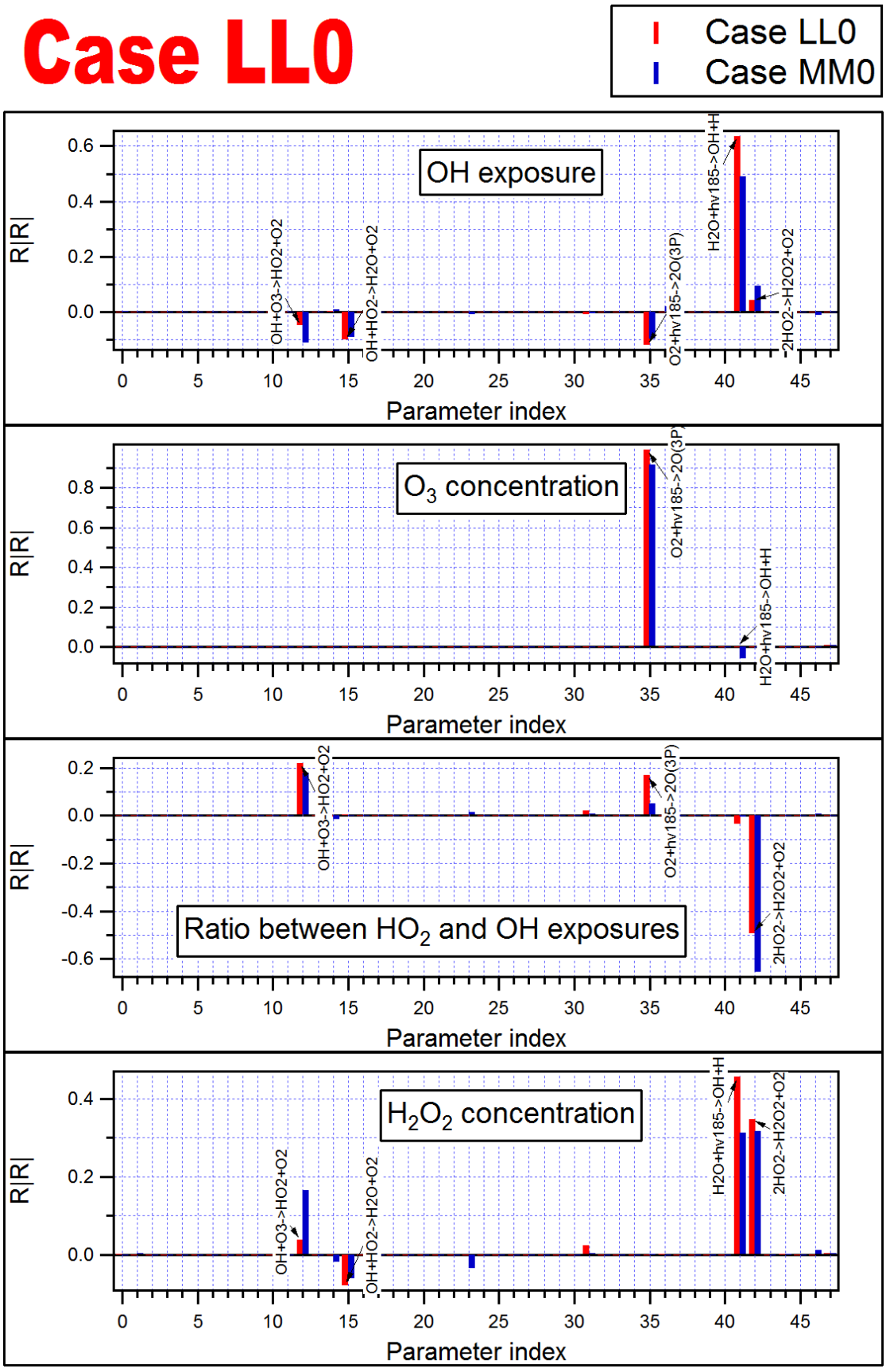

Other effects
2HO2->H2O2+O2
O3+hv254->O2+O(1D)
OH+SO2->HSO3
OH+H2O2->H2O+HO2
HO2+O3->OH+2O2
O(1D)+N2->O(3P)+N2
Ratio F185/F254
H2O+hv185->OH+H
O2+hv185->2O(3P)
2OH->H2O2
OH+HO2->H2O+O2
OH+O3->HO2+O2
OH exposure
O3 concentration
Ratio between HO2 and OH exposures
H2O2 concentration
Relative variance
Case
MM0
LL0
LH0
HL0
HH0
MML
LLL
LHL
HLL
HHL
MMH
LLH
LHH
HLH
HHH

- Correlation coefficient*|Correlation coefficient| by case

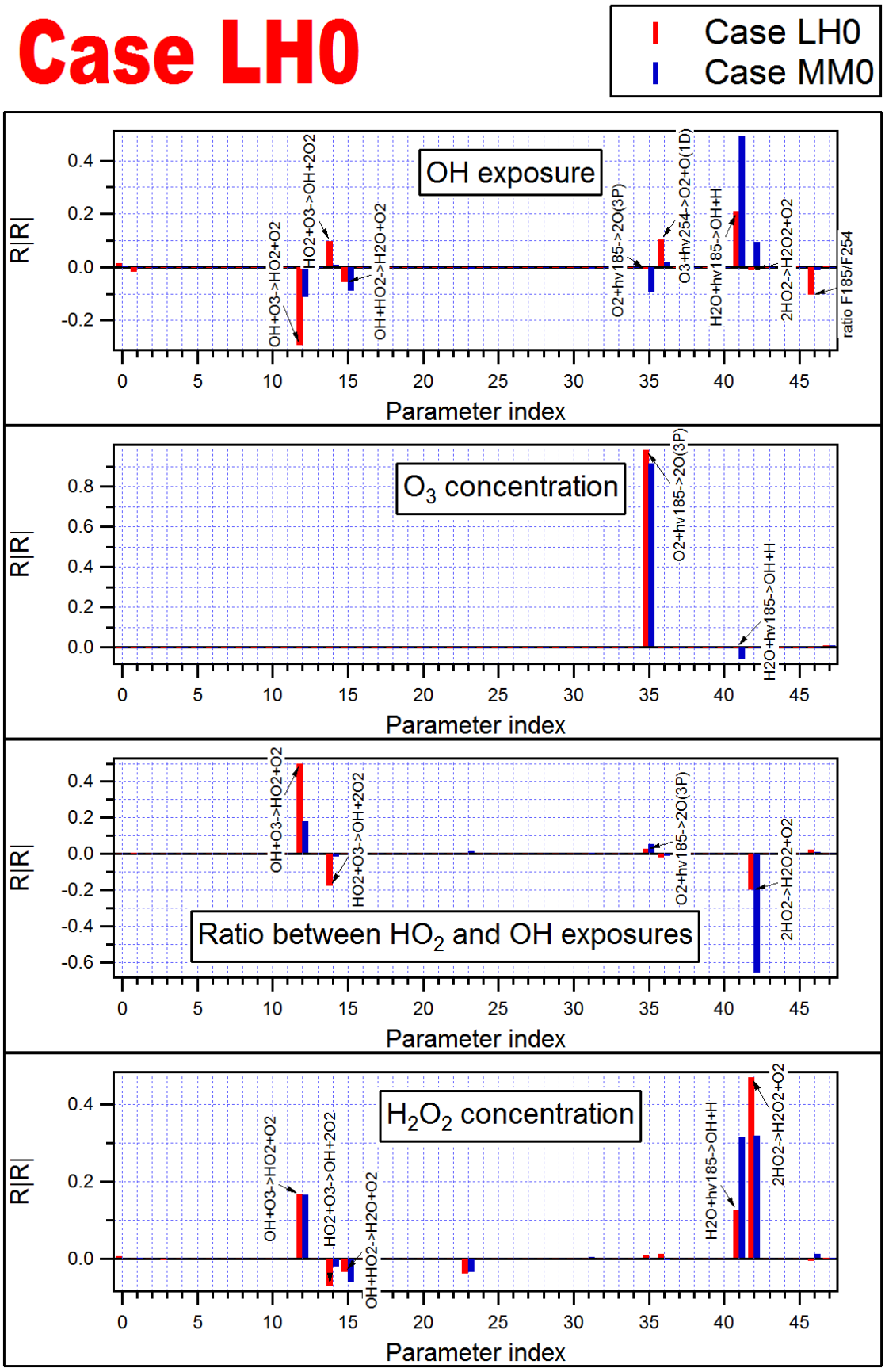
Case MM0


OH exposure
R|R|
Parameter index
OH+O3->HO2+O2
OH+HO2->H2O+O2
O2+hv185->2O(3P)
H2O+hv185->OH+H
2HO2->H2O2+O2
O_3 concentration
Ratio between HO_2 and OH exposures
H_2O_2 concentration

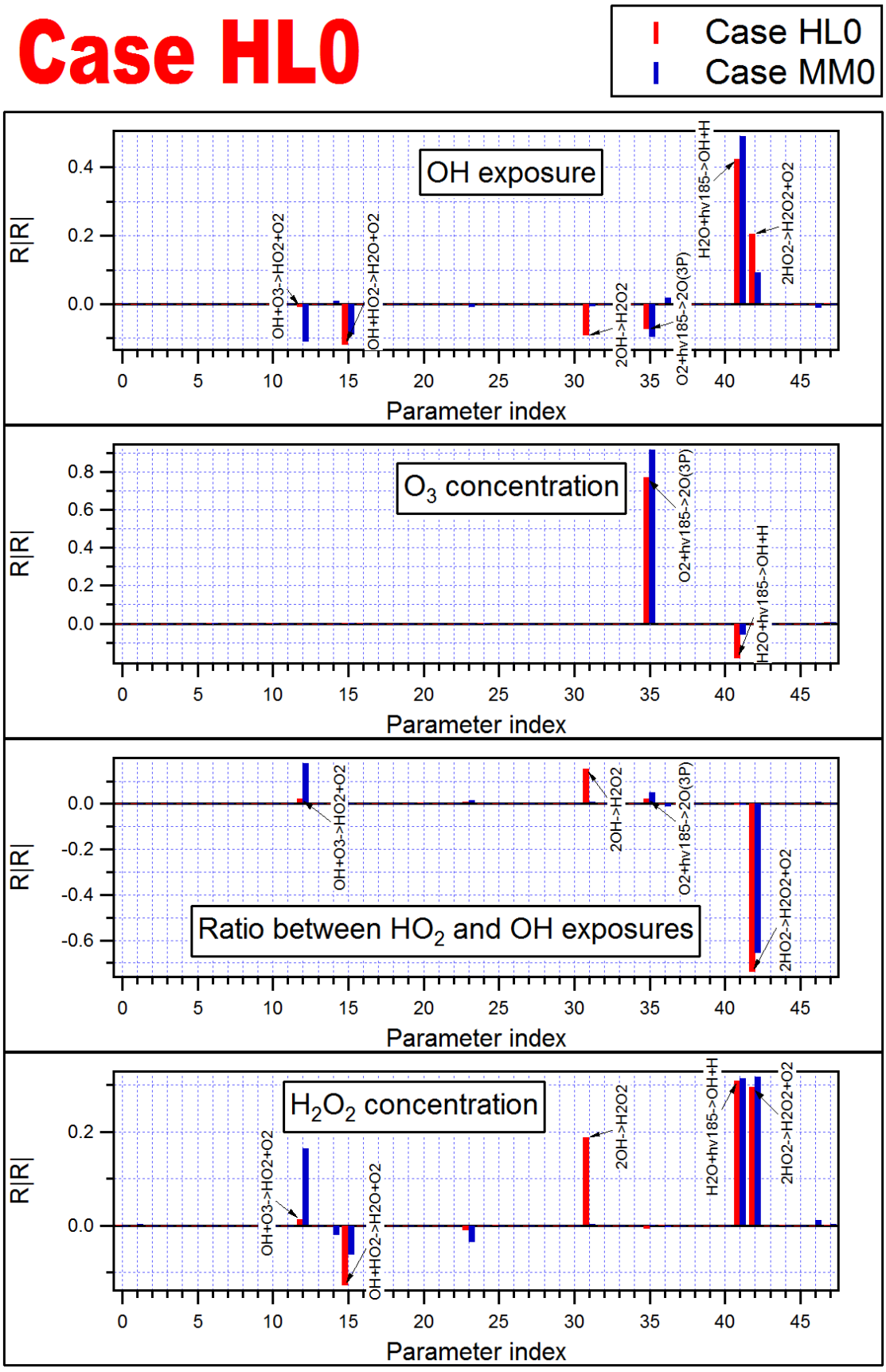
Case LL0


Case LL0
Case MM0
OH exposure
R|R|
Parameter index
OH+O3->HO2+O2
OH+HO2->H2O+O2
O2+hv185->2O(3P)
H2O+hv185->OH+H
2HO2->H2O2+O2
O3 concentration
Ratio between HO2 and OH exposures
H2O2 concentration

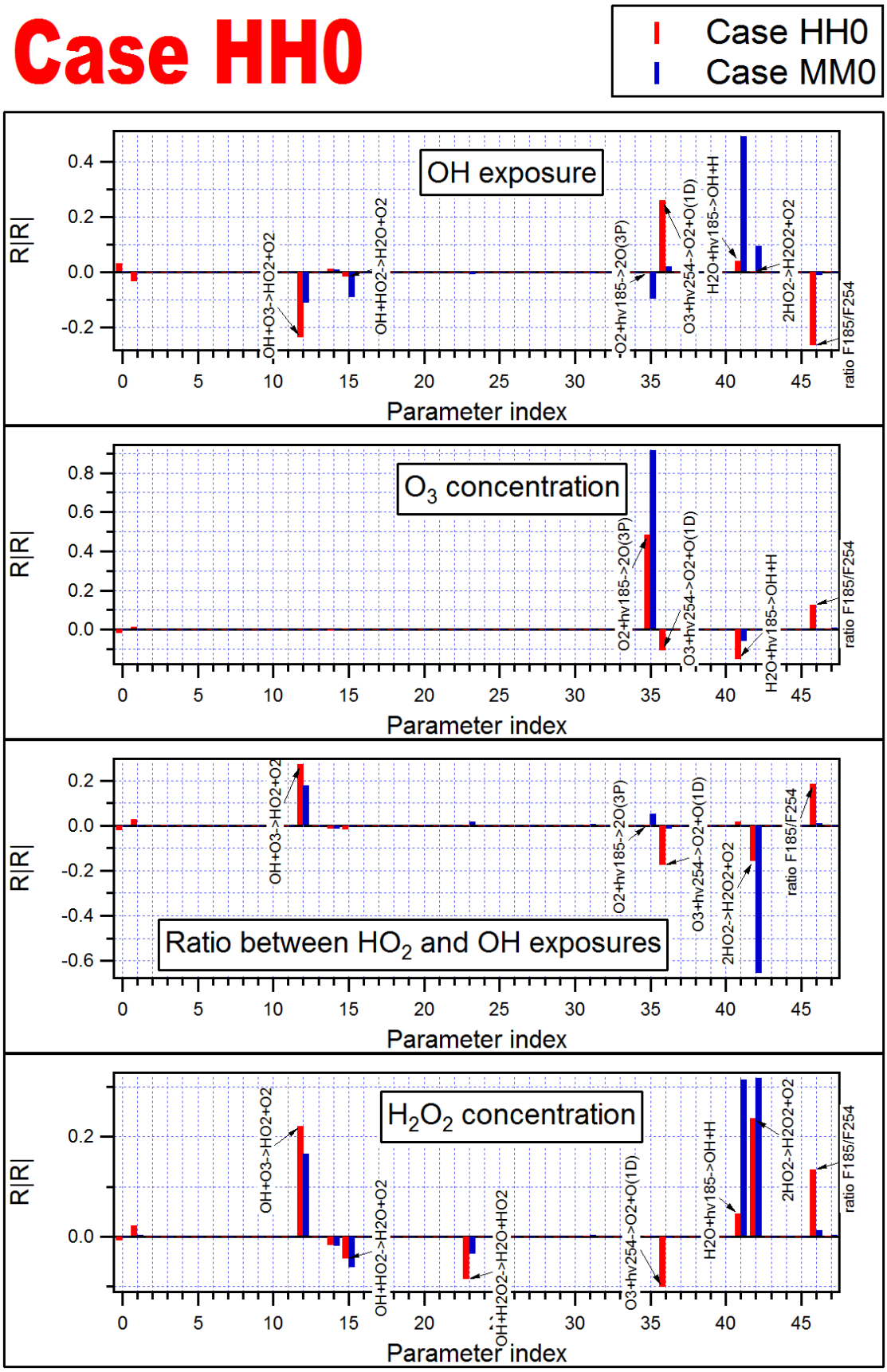
Case LH0


Case LH0
Case MM0
OH exposure
R|R|
OH+O3->HO2+O2
HO2+O3->OH+2O2
OH+HO2->H2O+O2
O2+hv185->2O(3P)
O3+hv254->O2+O(1D)
H2O+hv185->OH+H
2HO2->H2O2+O2
ratio F185/F254
Parameter index
O3 concentration
O2+hv185->2O(3P)
H2O+hv185->OH+H
Ratio between HO2 and OH exposures
H2O2 concentration

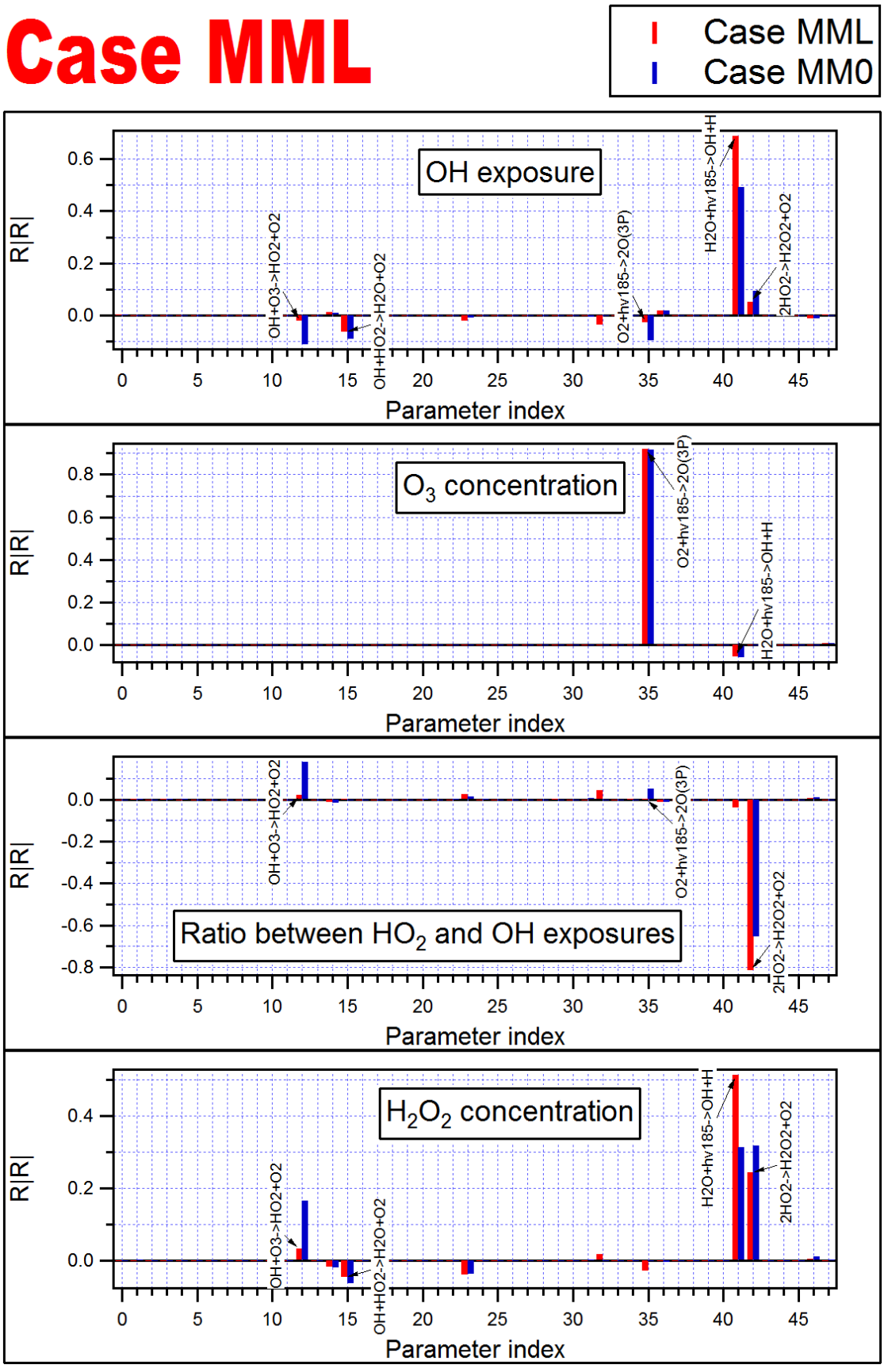
Case HL0


Case HL0
Case MM0
OH exposure
R|R|
Parameter index
OH+O3->HO2+O2
OH+HO2->H2O+O2
2OH->H2O2
O2+hv185->2O(3P)
H2O+hv185->OH+H
2HO2->H2O2+O2
O3 concentration
Ratio between HO2 and OH exposures
H2O2 concentration

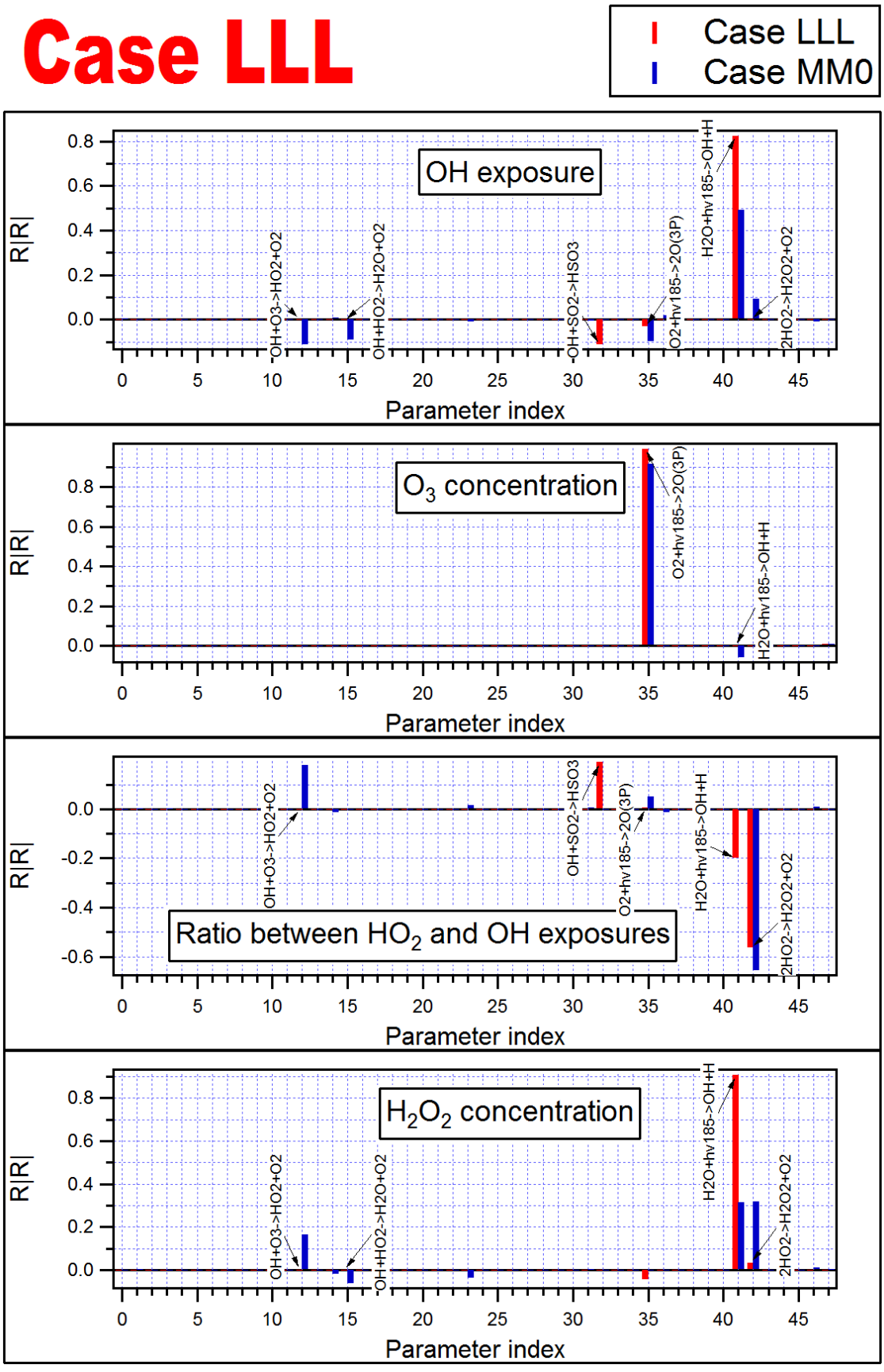
Case HH0


Case HH0
Case MM0
OH exposure
R|R|
Parameter index
OH+O3->HO2+O2
OH+HO2->H2O+O2
O2+hv185->2O(3P)
O3+hv254->O2+O(1D)
H2O+hv185->OH+H
2HO2->H2O2+O2
ratio F185/F254
O3 concentration
H2O+hv185->OH+H
Ratio between HO2 and OH exposures
H2O2 concentration
OH+H2O2->H2O+HO2

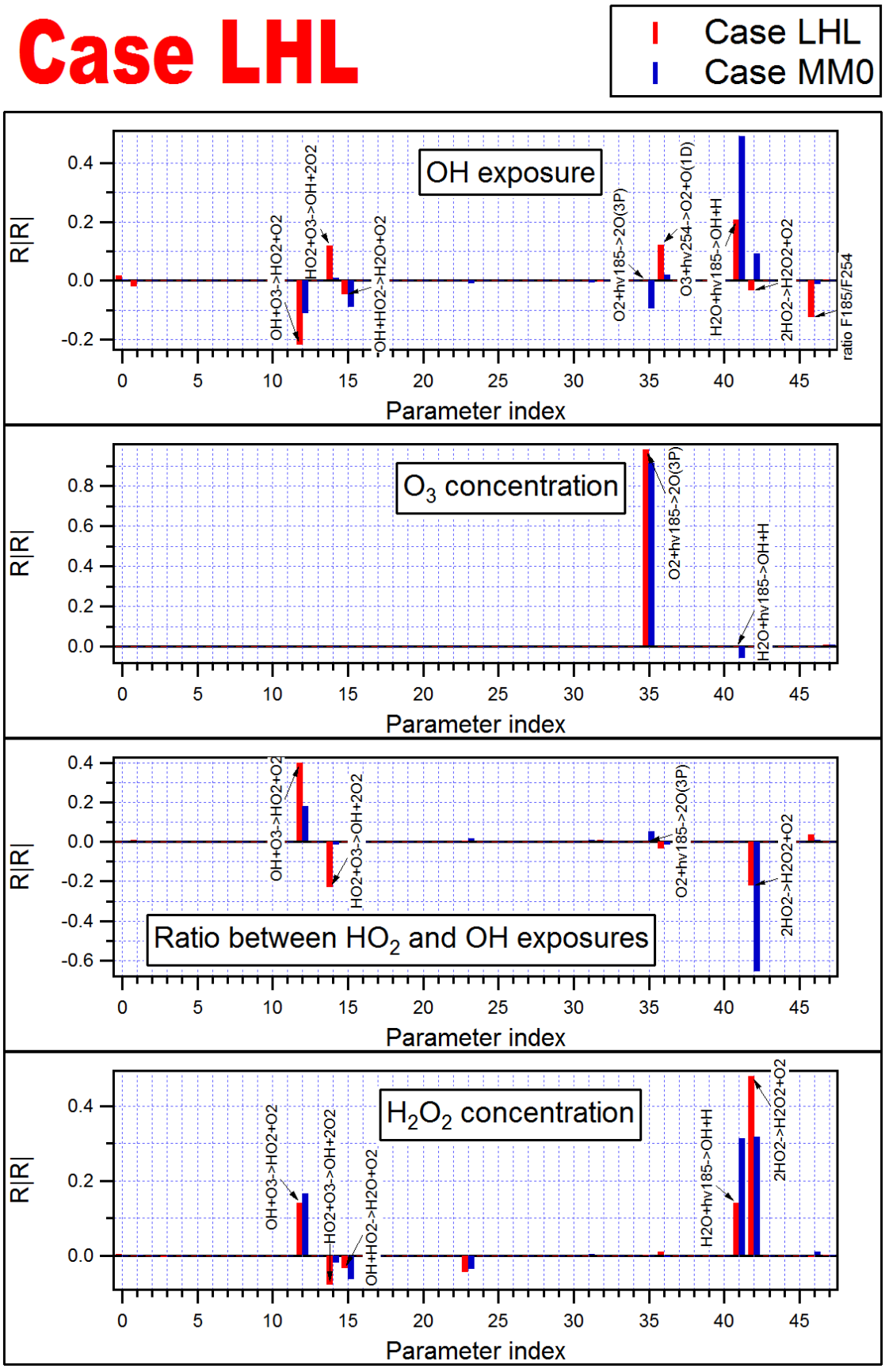
Case MML


Case MML
Case MM0
OH exposure
R|R|
OH+O3->HO2+O2
OH+HO2->H2O+O2
O2+hv185->2O(3P)
H2O+hv185->OH+H
2HO2->H2O2+O2
Parameter index
O_3 concentration
R|R|
O2+hv185->2O(3P)
H2O+hv185->OH+H
Parameter index
Ratio between HO_2 and OH exposures
R|R|
OH+O3->HO2+O2
O2+hv185->2O(3P)
2HO2->H2O2+O2
Parameter index
H_2O_2 concentration
R|R|
OH+O3->HO2+O2
OH+HO2->H2O+O2
H2O+hv185->OH+H
2HO2->H2O2+O2
Parameter index

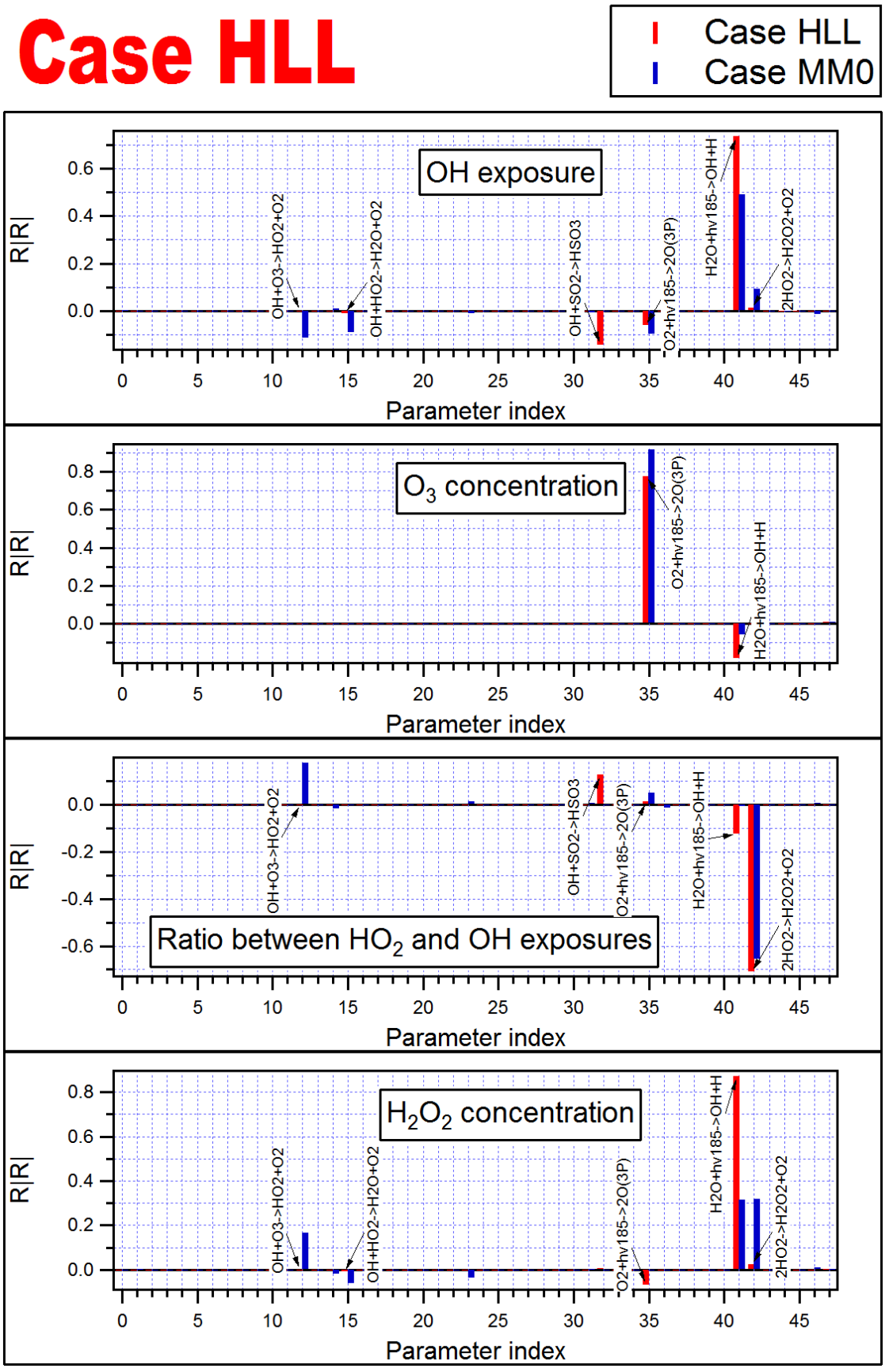
Case LLL


Case LLL
Case MM0
OH exposure
O3 concentration
Ratio between HO2 and OH exposures
H2O2 concentration
R|R|
Parameter index
OH+O3->HO2+O2
OH+HO2->H2O+O2
OH+SO2->HSO3
O2+hv185->2O(3P)
H2O+hv185->OH+H
2HO2->H2O2+O2

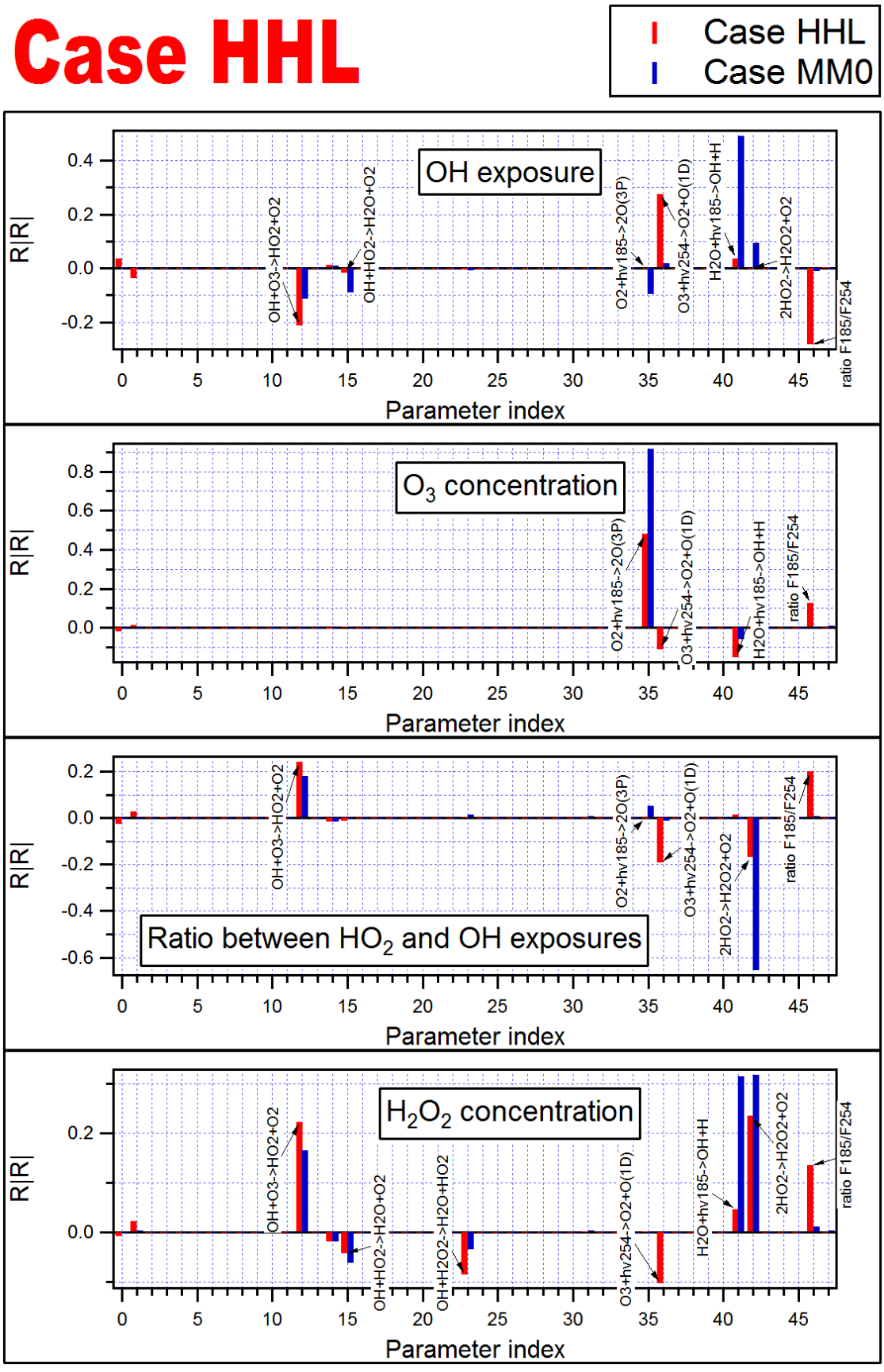
Case LHL


Case LHL
Case MM0
OH exposure
R|R|
OH+O3->HO2+O2
HO2+O3->OH+2O2
OH+HO2->H2O+O2
O2+hv185->2O(3P)
O3+hv254->O2+O(1D)
H2O+hv185->OH+H
2HO2->H2O2+O2
ratio F185/F254
Parameter index
O3 concentration
O2+hv185->2O(3P)
H2O+hv185->OH+H
Ratio between HO2 and OH exposures
H2O2 concentration

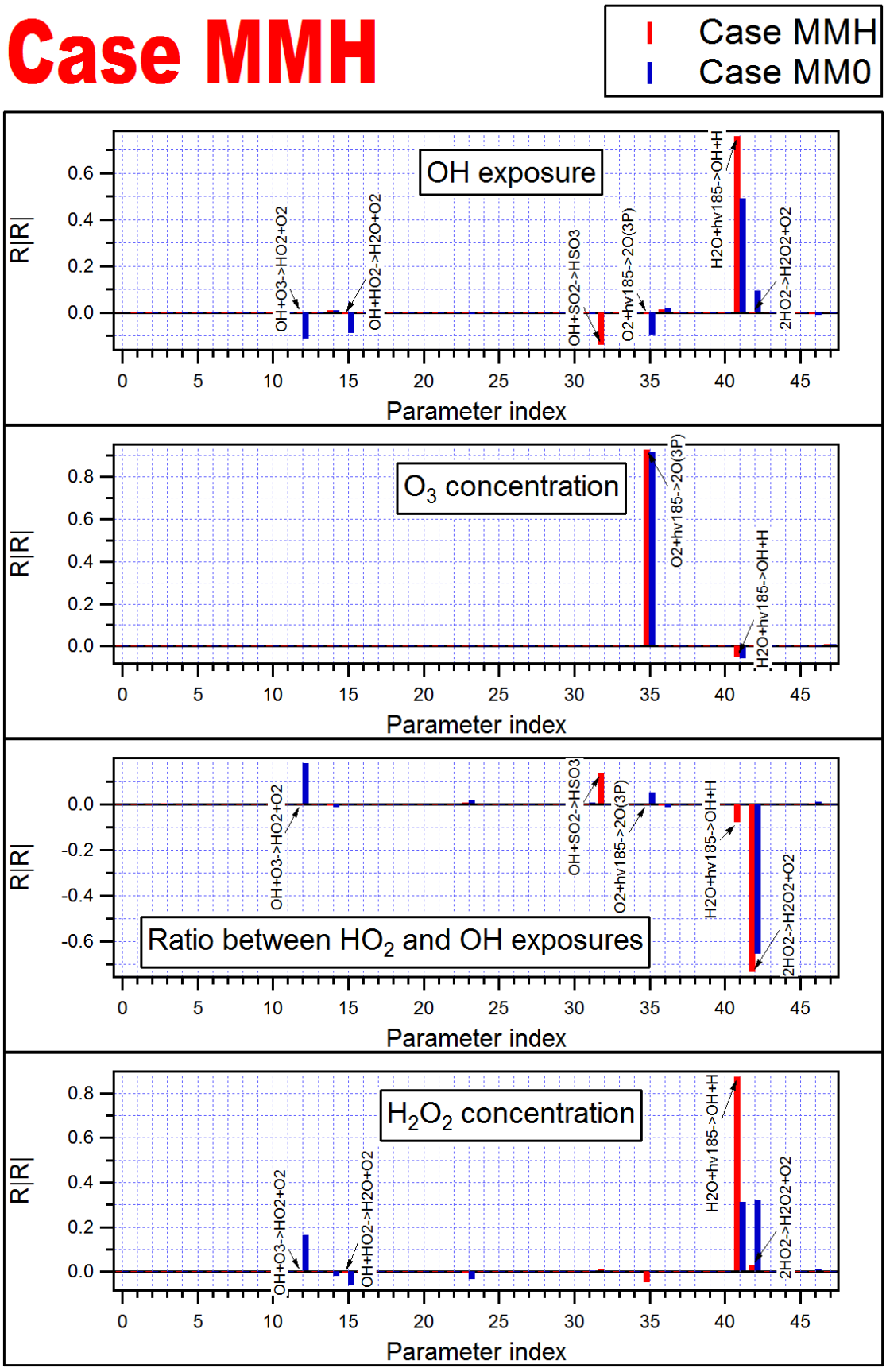
Case HLL


Case HLL
Case MM0
OH exposure
R|R|
Parameter index
OH+O3->HO2+O2
OH+HO2->H2O+O2
OH+SO2->HSO3
O2+hv185->2O(3P)
H2O+hv185->OH+H
2HO2->H2O2+O2
O3 concentration
Ratio between HO2 and OH exposures
H2O2 concentration

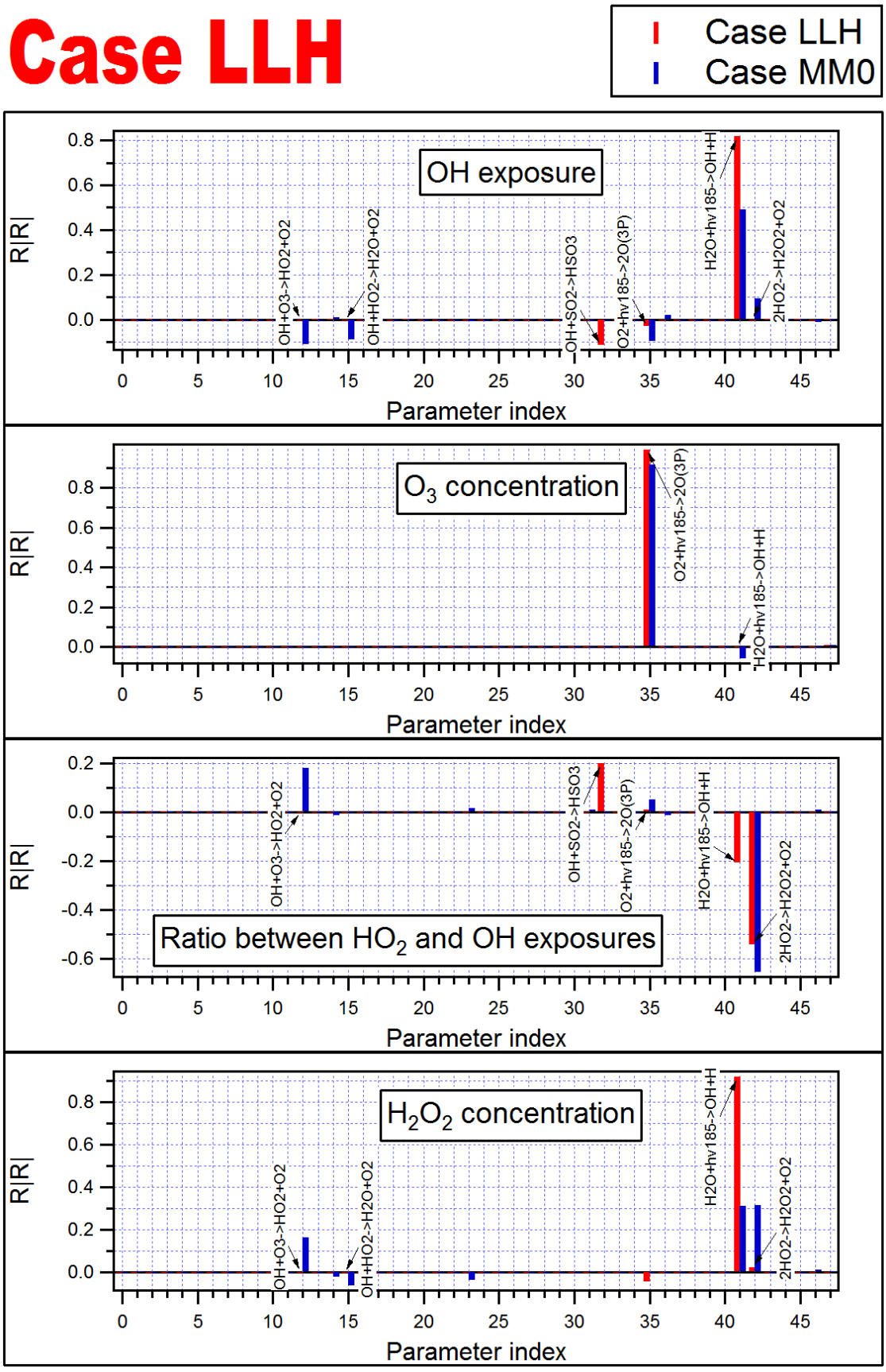
Case HHL


Case HHL
Case MM0
OH exposure
R|R|
Parameter index
OH+O3->HO2+O2
OH+HO2->H2O+O2
O2+hv185->2O(3P)
O3+hv254->O2+O(1D)
H2O+hv185->OH+H
2HO2->H2O2+O2
ratio F185/F254
O3 concentration
Ratio between HO2 and OH exposures
H2O2 concentration
OH+H2O2->H2O+HO2

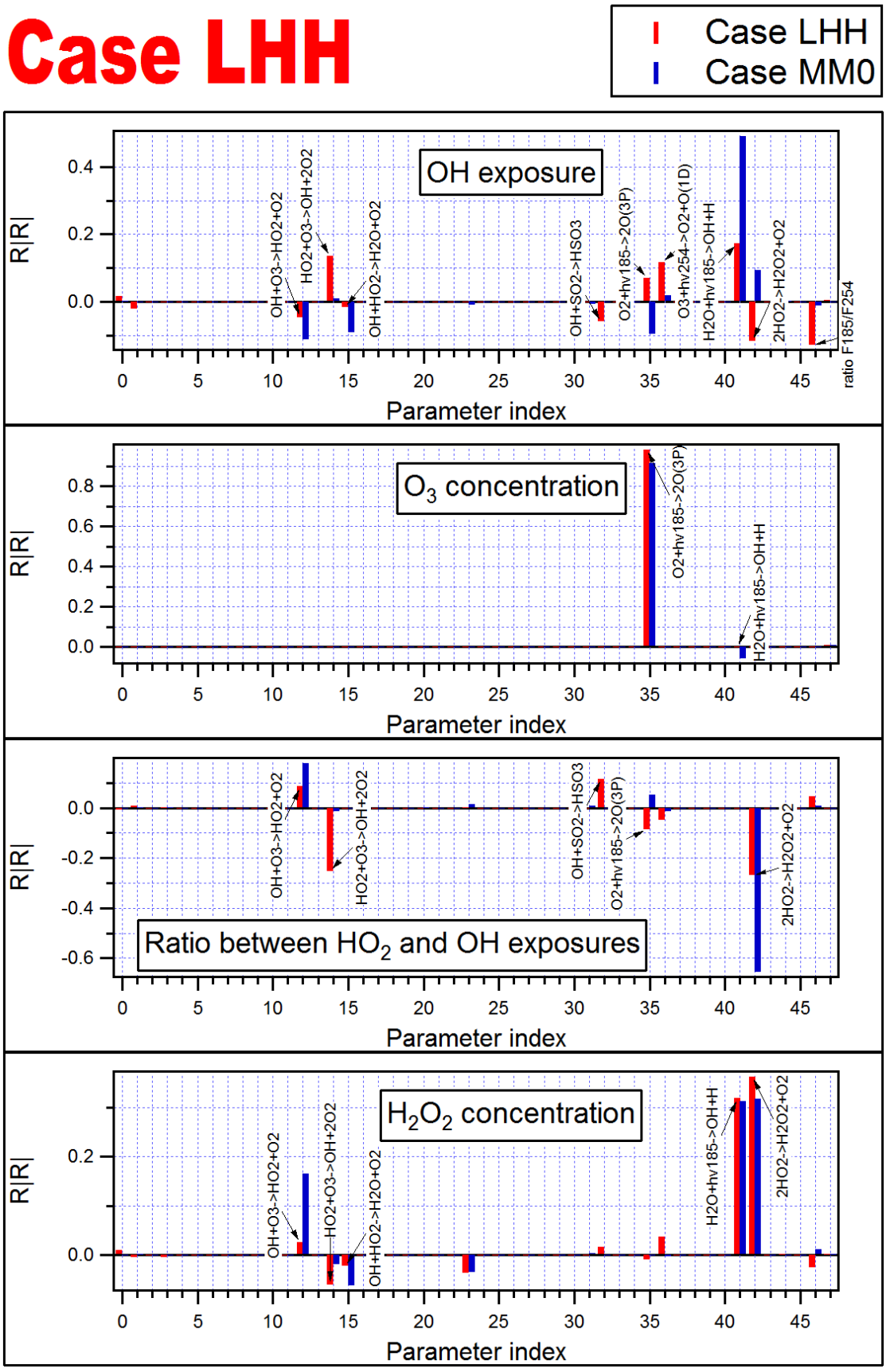
Case MMH


Case MMH
Case MM0
OH exposure
R|R|
Parameter index
OH+O3->HO2+O2
OH+HO2->H2O+O2
OH+SO2->HSO3
O2+hv185->2O(3P)
H2O+hv185->OH+H
2HO2->H2O2+O2
O3 concentration
O2+hv185->2O(3P)
H2O+hv185->OH+H
Ratio between HO2 and OH exposures
H2O2 concentration

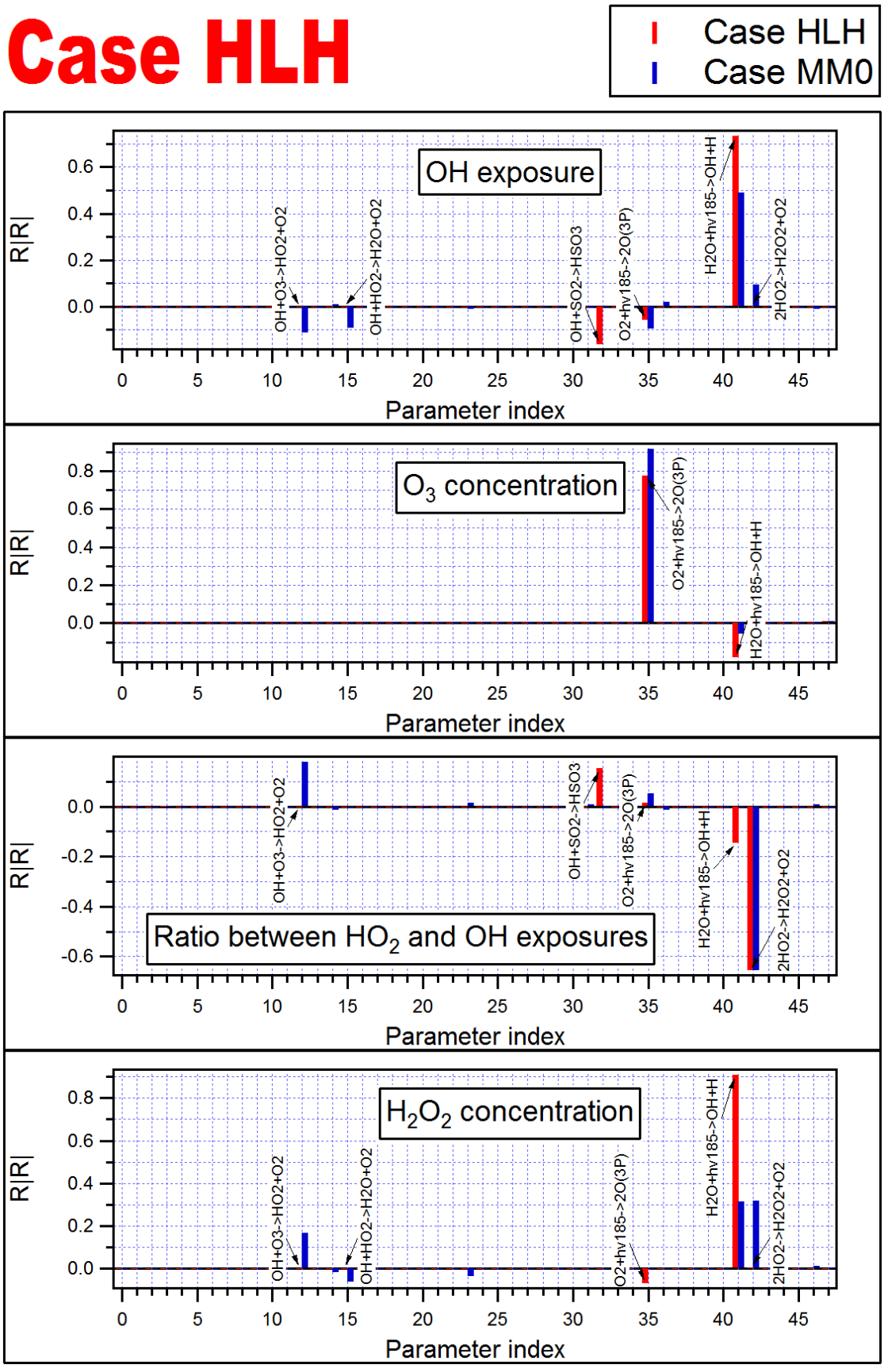
Case LLH


Case LLH
Case MM0
OH exposure
R|R|
OH+O3->HO2+O2
OH+HO2->H2O+O2
OH+SO2->HSO3
O2+hv185->2O(3P)
H2O+hv185->OH+H
2HO2->H2O2+O2
Parameter index
O3 concentration
O2+hv185->2O(3P)
H2O+hv185->OH+H
Ratio between HO2 and OH exposures
H2O2 concentration

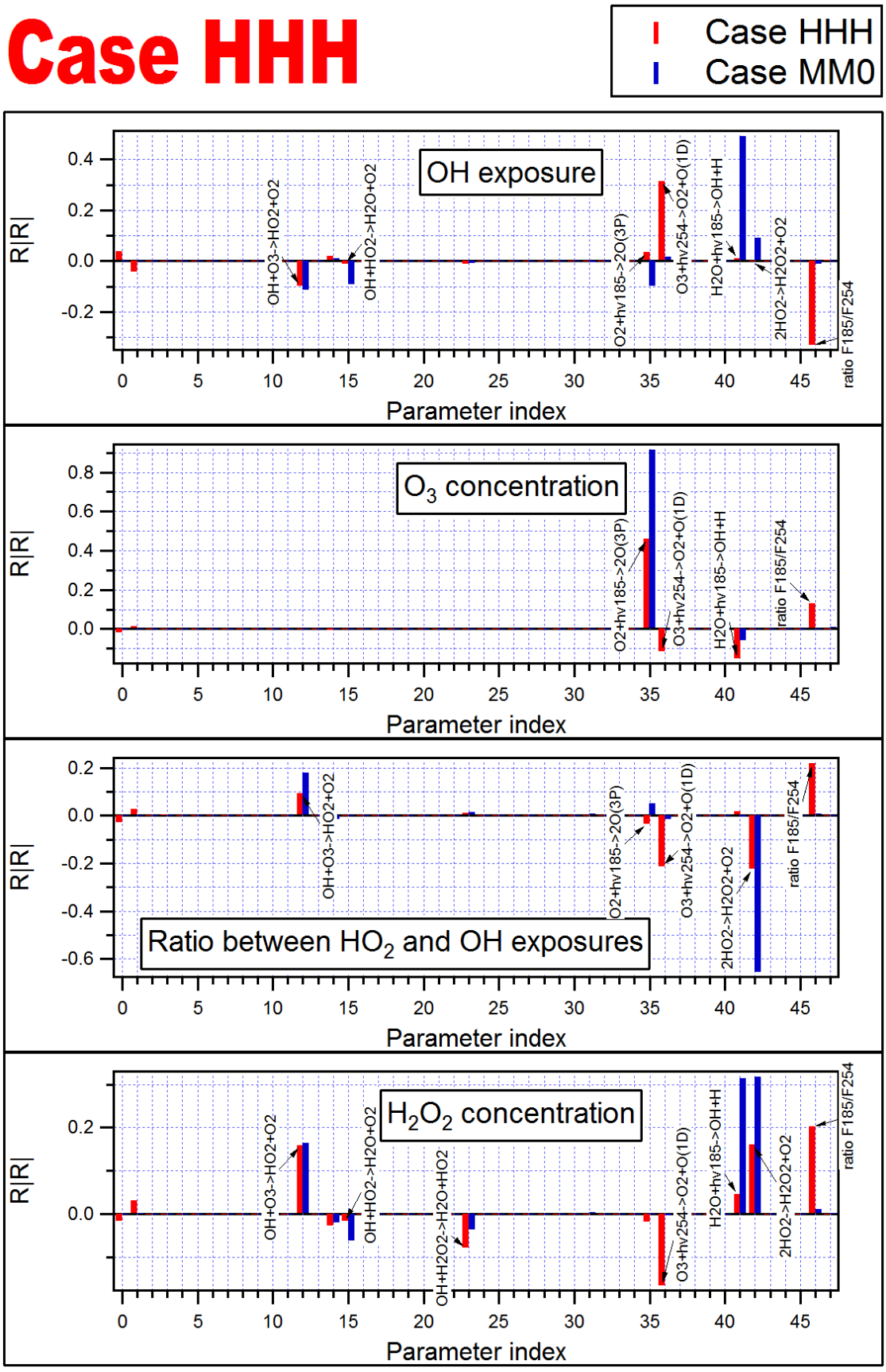
Case LHH


Case LHH
Case MM0
OH exposure
R|R|
Parameter index
OH+O3->HO2+O2
HO2+O3->OH+2O2
OH+HO2->H2O+O2
OH+SO2->HSO3
O2+hv185->2O(3P)
O3+hv254->O2+O(1D)
H2O+hv185->OH+H
2HO2->H2O2+O2
ratio F185/F254
O3 concentration
O2+hv185->2O(3P)
H2O+hv185->OH+H
Ratio between HO2 and OH exposures
H2O2 concentration

Case HLH


Case HLH
Case MM0
OH exposure
R|R|
Parameter index
OH+O3->HO2+O2
OH+HO2->H2O+O2
OH+SO2->HSO3
O2+hv185->2O(3P)
H2O+hv185->OH+H
2HO2->H2O2+O2
O3 concentration
O2+hv185->2O(3P)
H2O+hv185->OH+H
Ratio between HO2 and OH exposures
H2O2 concentration

Case HHH


Case HHH
Case MM0
OH exposure
R|R|
OH+O3->HO2+O2
OH+HO2->H2O+O2
O2+hv185->2O(3P)
O3+hv254->O2+O(1D)
H2O+hv185->OH+H
2HO2->H2O2+O2
ratio F185/F254
Parameter index
O3 concentration
Ratio between HO2 and OH exposures
H2O2 concentration
OH+H2O2->H2O+HO2

9-Apr-2014: Topics for discussion

- Zhe: summary of his work
    + Decisions to make:
    (1) Which are the uncertain INPUT parameters and their ranges
        - Current ones w these changes
            + remove F254 +/=10%. Keep F254 constant.
            + Keep F185/F254 = 5% (value) +/-20% (uncertainty) for now
            + Add flowrate +/-1% uncertainty
            + We decide to NOT include H2O
    (2) Which OUTPUT parameters do we consider?
        - So far: OHexp (molec cm-3 * s) and O3 concentration out
        - HO2_exp/OH_exp & H2O2 output
        - Here we have defined a master plot (8 plots for S & U for 4 outputs + N inputs)
    (3) At which locations of the space (Flux, H2O, OHR), and how do we explore the space?
        - Rui: 5 cases: low H2O + low F… + mid everything
        - Max: 5 cases of Rui for OHR_ext = 0, 10, 100 s-1
        - Initial cases:
            + Central case w OHR = 0, 10, 100 (3 cases)
            + “4 corners” w OHR = 100 (4 cases)

Emerging issue
    + What is the ratio F185/F254 that we should use for the modeling papers?
        - Specifications in http://www.bhkinc.com/literature/AnlmpDS_101010.pdf state ~ 50%
        - A while ago we tried that and model results didn’t make a lot of sense. Bill Brune told us to use 5% instead based on his experience
        - Rui has tuned the model to match SO2 experiments with R ~ 0.01% to 1%. Is this legitimate?
    + Piece of evidence:
        - Plot O3 vs F_254 measurement for SOAS and GoAmazon, we should get an idea of whether the ratio is approx constant with light voltage or not. Because O3 produced is proportional to F_185, while F_254 has only a weak impact on O3, while OHexp is proportional to F_254. Basically plotting O3 vs F_254 is an approximation of plotting F_185 vs F_254.

Added by Amber after meeting: Check out pg 5 and 7 in this document (I got this doc in an answer, from asking about this on ResearchGate) - http://www.heraeus-noblelight.com/media/webmedia_local/media/pdf/uv/b119_lampflyer_e_final.pdf

Action items
    - Rui to run model with 5% ratio and compare to current tuned ratio

- Rui & Zhe (and Amber if time): look up how mercury lamps (fluorescent lamps) work
- Zhe to run above tasks w/ 5% ratio for now
- WW + Brett to plot O3 vs F_254
    + Make plot only w/ final 5 min (remove transients) and separate plot /symbol for each light setting & color by time during the campaign.
    + Plot diurnal cycle of both variables for each light setting (Over shorter period)

4-Feb-2014: WW, Amber, Doug, Jose

- *SMPS data finalized ? -Weiwei*
- *Amber - code for SMPS*
    - *plot ratio & difference between ambient and pam at lights off as a time series*
    - *make same plots as standard PAM plots for SMPS < 40nm*
    - *fraction of enhancement that is less than 40*
    - *for enh. vs PCA overlap SMPS with AMS*
    - *Add mass enhancement of SMPS vs AMS mass enhancement*
    - *Color/marker the above plot by under 40 nm, as well as SMPS vs AMS total mass conc.*

21-Jan-2014: AMS + PAM Mtg

- Agenda:
    + Filter schedule, storage, shipping (see email from Brett 1/15/14)
    + Other GoA14-related matters?
        - Donna needs to work on software some
    + Amber: Soft vs hard for CalNex

+ Notes for Amber
    - Plot day and night separately on OA/D_CO vs phot age

Soft:
- update frag for O in soft OH
- look at MS for UMR
- look at TS in UMR not using ABcorr
- look at the field log for soft
    - Write $OH_{185+254}$ and so on, to make clear that it is OH, the wavelengths are a less important detail
    -mass defect plot of delta-org for hard and soft, using open circles for decay, closed for increase, do it for the point where they overlap in OHexp.
    - plot delta-ion soft vs delta-ion hard with markers as chem form.
    - enhancement plot of families, use co2+ as a separate family
    - also check out F100 (mass above m/z 100)
- ***Look at OHexp for soft and hard make sure they overlap. 1st plot org enhance of hard and soft together***
-

SMPS:

- volume under and over 50 nm, enhancements
- SMPS enhancements vs OHexp, total and below 50nm
- Time series of SMPS and AMs total, SMPS for under 50nm as well.

WW+ DD:

- Capture Vaporizer expts before Brazil

7-Jan-2014: AMS + PAM Mtg

- Agenda:
  + Brazilian visa for WW
  + Rui: results of OHexp vs OHR vs other conditions
  + IEPOX-SOA aging (WW)
- Submeetings later
  + WW paper
  + NASA proposal

- Rui OH exposure from model
  + Added OHR to model, it produces the desired effect

  OHex = a + b * O3

  = (y0 + A * H2O^pow) + (a+b*H2O) * O3

  = -7.8e10 + 2.2e9*H2O^0.094 + 0.00068*O3 + 2.1e-20*H2O*O3

  + Next task: Rui to try to fit OHexp = f(O3, H2O, OHR)
    - Idea: OHexp = OHprod / OHdest
      - OHprod = A * H2O + B * O3 * H2O
      - OHdest = C * OHR + D * O3^2
  - Alternative is to fit just OHsupp = OHexp/OHexp_0 (_0 means with OHR = 0)
    - Rui will try to see how this is fittable
  + WW and Rui to plot O3 and OHexp vs relative light intensity for SOAS conditions

- IEPOX-SOA aging
  - we see it in ambient, but it is NOT a factor in PAM. That means it is reacting away. We should quantify how quickly.
  - WW to quantify IEPOX-SOA (also SV-OOA?) aging using the f44-f82 diagram, and using ME-2
  - Add standard HOA, BBOA… from Sally's paper (in database) to the plot
  - Plot f53 vs f82 and f91 (MT + ARO) vs f82

20-Dec-2013: PAM "working" OHexp Meeting: Brett, Rui, Amber, Doug, Jose

- Agenda: Examining functional form of OHexp for use in field projects, by combining field, lab, and model results.

- Rui's functional form works at high O3 compared to lab/field results. It doesn't work at lower O3 (Ohexp lower than 1e12) ...perhaps it's suppression at lower O3 that shifts the model.

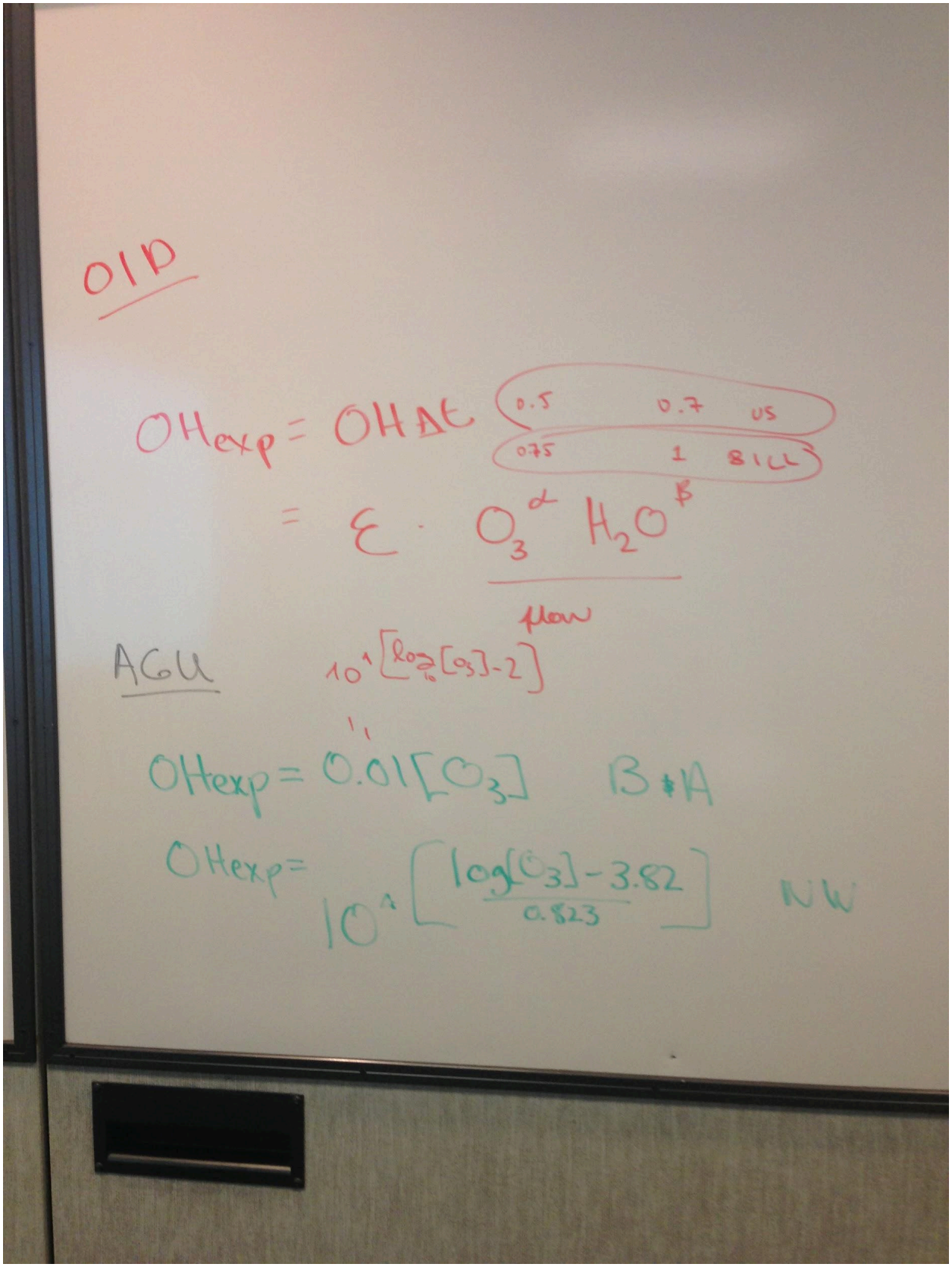
- Action steps for Rui

(1) Run model and plot OHexp/OHexp_0 = OHSupp, vs OHR in range 0 to 150 s-1 for 5 key datapoints: O3, H2O

+ test under CORNER points, extreme regimes of O3 (30 ppb - 30 ppm or 1e12-1e15), H2O (1e16 - 1e18); then in the middle of these ranges for both O3 and H2O (CENTER 4 ppm O3, 1%H2O or 1e14 O3, 2e17 H2O)

+ One more point for OHexp vs O3 "Master Plot": O3 = 100 ppb = 2.5e12; H2O = 2e17, w/ OHR = 20 and 0

- Brett, Amber, WW: keep using AGU-2013 equations for now. Once Rui produces above plots and we discuss, they may adopt model-based functional forms for cal equation


O1D
OHexp = OH ΔC
0.5 0.7 US
0.75 1 BILL
= ε · O3^α H2O^β
flow
AGU
10^1[log10[O3]-2]
OHexp = 0.01[O3] B#A
OHexp = 10^1[log[O3]-3.82 / 0.823] NW

$$OH_{exp} = Y + A \cdot H_2O^{a_1} \cdot O_3^{a_2}$$

For low O_3:

$Y = 0$

$A =$

$a_1 =$

$a_2 =$

power

$\Downarrow$

$OH_{exp} = A \cdot H_2O^{a_1} \cdot O_3^{a_2}$

For high O_3:

$Y =$

$A =$

~~$a_1 =$~~

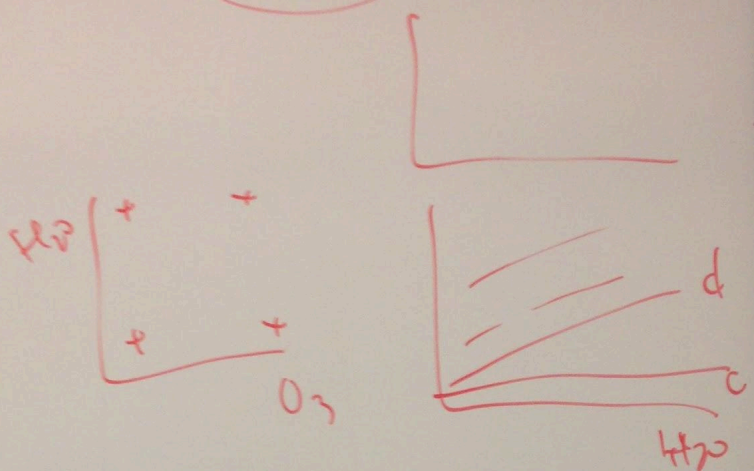
$a_2 = 1$

$\Downarrow$ linear

$OH_{exp} = Y + A \cdot O_3$

$= \left(c + d \cdot H_2O^{-1.4}\right) + \left(e + f \cdot H_2O\right) \cdot O_3$

HIGH



$$c' + d \cdot H_2O^{0.45} + (e + f \cdot H_2O) \cdot O_3$$

CO data / model - high

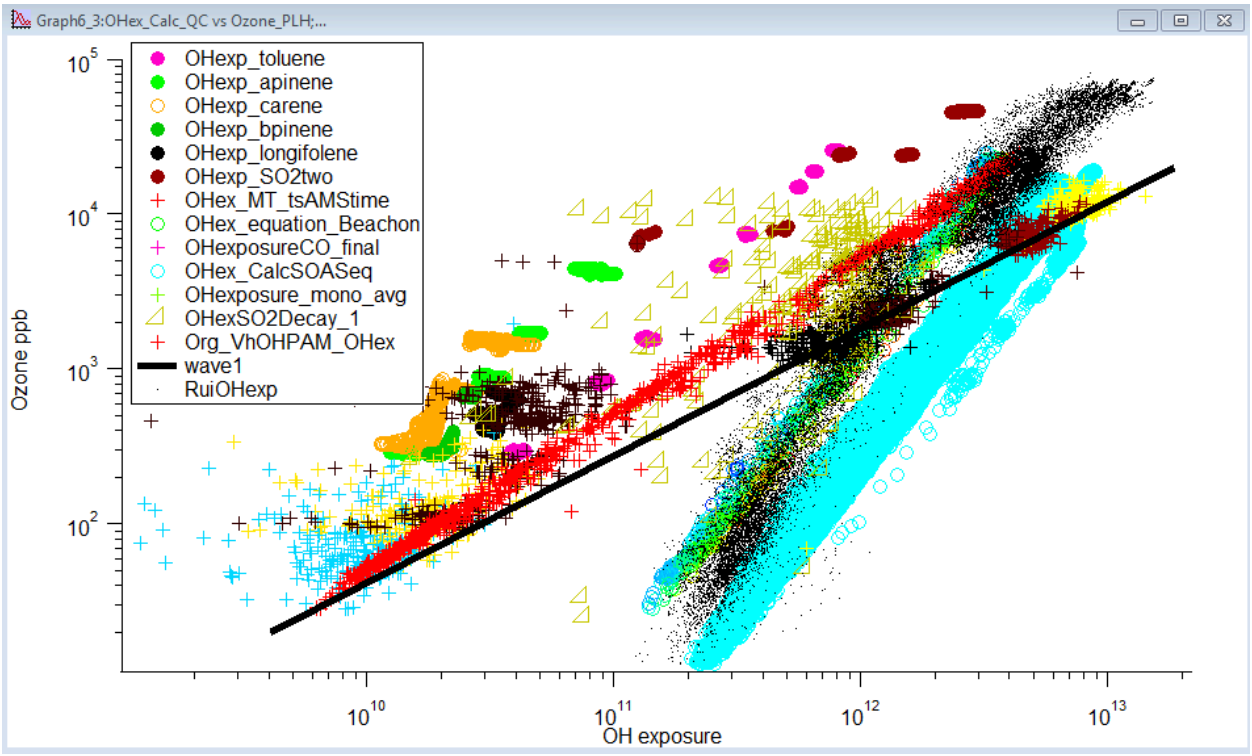
$$= c + d \cdot H_2O^{1.4} + e \cdot O_3 + f' \cdot H_2O \cdot O_3$$

LOW

$$OH_{exp} = \left[A + H_2O^{0.37}\right] \times O_3^{c + d \cdot H_2O^{0.025}}$$

$$= A \cdot O_3^{c + 0.13 \cdot H_2O^{0.025}} + H_2O^{0.37} \cdot O_3^{c + 0.13 \cdot H_2O^{0.025}}$$

$$= A \cdot O_3^{0.35} + B \cdot O_3^{0.35} \cdot H_2O^{0.37}$$



11-Dec-2013: PAM Users Meeting

- Andy Lambe: overview of PAM applications

+ Plot of max OSc chamber ~ min OSc PAM (Lambe et al, in prep) for different precursors

- Argue that chambers and PAM are “making the same stuff”

+ Andy presents titles and author lists of recent papers w/ PAM

+ Recent paper: O/C vs optical properties of SOA (Andy’s AGU talk)

+ Pajunoja et al, in prep: bounce fraction vs RH, sees bounce fraction goes down to 0 at high RH

+ Chhabra et al in prep: acetate CIMS w PAM

+ Tkacik et al in prep: SOA formation from tunnel emissions (ACSM). Plot very similar to Amber’s.

- Bill Brune

+ Propose to make model available to the community

+ Flowtubes: impact of walls. Idea of chamber is to avoid walls

- SO2 → SO4 is more like 60% for current PAM, Kang was at 90%

- MOPS: different shape, a little bit of T control to make flow stable, he thinks he is much more wall-less. He wants to test it w SO2 → SO4.

+ Lights: some 365 nm LEDs that are powerful enough and can make it. His experience is that if there is a light that makes OH, OH will win. Just doing it.

+ Lengthened and increased the flow for MOPS to improve the flow characteristics

Presentation from our group

+ Discussion of the plate presentation from WW: Bill: plate w many holes, may reduce the impact of the wind, they are doing that for the MOPS. Can discuss afterwards.

+ Bill: HO2 + O3 is the reaction that OH exposure is sensitive to. So there may be errors in that rate.

Ellie from MIT

- Looking at BC aging, chemical and optical changes, SIA and SOA coatings. Isopentane as an OH tracer. 100 ppb w hexane. Haven't done any experiments yet. CPMA to select BC mass.

- Discussion

- Bill: results seem to be similar to the atmosphere. Not sure about the processes

+ OH and HO2 processes do scale

+ Microphysical time constants may not scale

+ Surface reactions

+ Bill: run into trouble by running to higher reactant levels

+ Agree to do a-pinene yield @ 100 ppb

27-Nov-2013: Rui + Jose on Model Updates

- Rui has updated some reactions from the JPL that were missing.

+ e.g. O + O3 → 2 O2, which seems to be 10% of the fate of O

+ Some other photolysis etc

+ Calculated H, O, O1D, assuming steady state for all

+ Now using RK4 (from Christoph Knote, time step 5 ms)

- Next steps

(a) Model cleanup

+ Test time step by dividing it x3, comparing concentrations and time series of all species

+ Add H2 reactions by searching JPL (photolysis??)

+ Redo diagram and time series plots for new model

+ Redo sensitivity plot

+ Compare these for "base case hard OH"

+ For now f185 = 5% * f254

(b) Model comparison w meas @ OHR = 0

+ Run for multiple values of f254 as f(H2O) have many curves in graph. Plot results on OHex vs O3 & O3 vs H2O. Zoom (separate plot) on small values

+ Run for fixed H2O as f(flux), put those experimental points there

+ For central value of f254, change f185 x2 and div by 2

(c) Undestand cal equation

+ For the 2 regimes, plot a flux diagram and explain why there are 2 regimes

5-Jul-2013: Conference call while in the field for SOAS: Weiwei, Amber, Suzane and Jose in Tuscaloosa, Pedro and Doug in Boulder For experiments we need to do

- Topics for discussion

Calibration Type Experiments

- Schedule & responsibilities for calibration day tomorrow
  - ~~Cal our AMSs in the morning~~
  - ~~Roll call cart around to participating groups (so far replied: ACSM Provat; AMS Yu Jung)~~
    - ~~Do Bitwise (28 sat? 40/28?), check peak shape, resol, AB.~~
    - ~~Do BFSP 200 part, Use new CPC, 300/400nm, do Amm.Sulfate (make sure to take the NH4NO3 in low concentration for IE cal)~~
    - ~~Check vaporizer V&A on all AMSs + ACSM~~
    - ~~Ask about flow cal + bring Drycal~~
    - ~~Ask to see lens alignment data~~
    - ~~DP transducer to monitor flow or P sensor in DMA or rotameter~~
    - Do data analysis together with other groups
  - ~~Setting up 3rd PAM lines etc. in roof~~
  - PAM tests with CIMS? (need to discuss w CIMS folks)
  - ~~CPC intercomparison @ 4pm in trailer 5 (intercompare our CPCs in our trailer, then bring only the one in cal cart)~~
  - ~~Mass IE calibration on the AMS2~~
  - ~~RIE for the (NH4)2SO4~~
- Signal dropping in the AMS1 and AMS2: ~~up MCPs in cal day calibration~~
- Simulate AMS problem by changing voltages, then plot AB w m/z 69, AMS species (do back in Boulder)
- Work up/share results from fast valve switching with constant light settings (cover off?)
  - Weiwei will process these data.
  - Run 3rd PAM with hard OH w plate on, then off (Weiwei) - CO injection in new only for a while.
  - Look at FLAME-3 data and see if O3 changed w plate on and off (Amber)
- ~~Background of OH PAM using zero air.~~
  - Do 2 cycles, one w CO and one w/o CO
- NaNO3 (Heater scans, possibly just for new vaporizer): ammonium sulfate instead, doesn't need to be tomorrow (can do back in the lab)
- Bring RONALD to NO3 PAM -- Julie et al working on that
- PSL

Scientific Additional Experiments

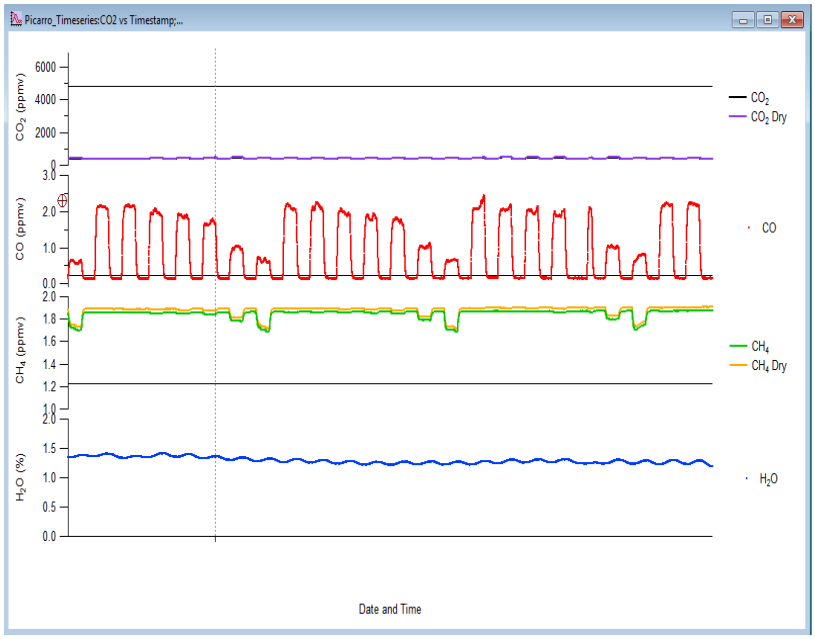
- Set up Delphine's PAM (if for CIMS hard OH, use lamps currently in NO3 PAM; Is it easy to take out the lamp from generator ?)
- TD after hard OH PAM at max SOA light setting?
    - Do it at max SOA and max OH exp (2 settings)
- hook up the Washenfelder optical measurements to a PAM reactor
    - Talk to Rebecca & Alexis - could test tomorrow (probably not)
    - ~~Email Troy about PAM work tomorrow~~
    - Jose will email Gabriel and see about a PAM test (next campaign)
    - D + P to search for metal filter hold and teflon filters
    - ~~AL crew to search for teflon filters~~, could put in front of O3 instrument

Data analysis in the field for quality checking & calibration:

- enhancement in the OH, O3 and NO3 PAM vs exposure (Weiwei + Amber)
- AMS1 and AMS2 comparison (Amber)
- AMS2 calibration analysis (Amber)
- TD-data processing & participation in intercomparison (Amber)
- Diagnostic plots for both AMS (Amber)
- Update LV control panel with ability to control more valves (Pedro, Weiwei to follow up w him)
- Plot photodiode data from OH PAM (Amber plot w T & O3 & RH, lamp settings)
- Continue intercomparisons with other composition & SMPS instruments (Suzane)
- ask Bill Brune about photodiode and lamp calibration
    - Saewung has contraption for calibration, maybe Bill as well, could maybe work with them to cal our diode? (Brett when he comes back, Amber, update - Bill Brune's group doens't bring their photodiode calibrator to the field)

Data analysis for scientific purposes

- Check the K+ detection in the AMS system (Weiwei + Amber - HR looks like sfc ionization, can plot up diff K+)
- EPTOF, PTOF comparison, update the PTOF DAQ version -- can be done after field(Data delay to zero) (weiwei)
- look at nucleation in O3 and NO3 PAMs (maybe versus OH pam) -- not urgent, will do after campaign
- Do Pika analysis on NO3 PAM (and Amb) data to look for RONO2 production, and see if we can find ways to improve our NO3 PAM methods
    - Look for standards of nitrates (jose will ask around)
- OH exposure calculation
    - From CO experiments
    - From VOCs (need to push Lina)



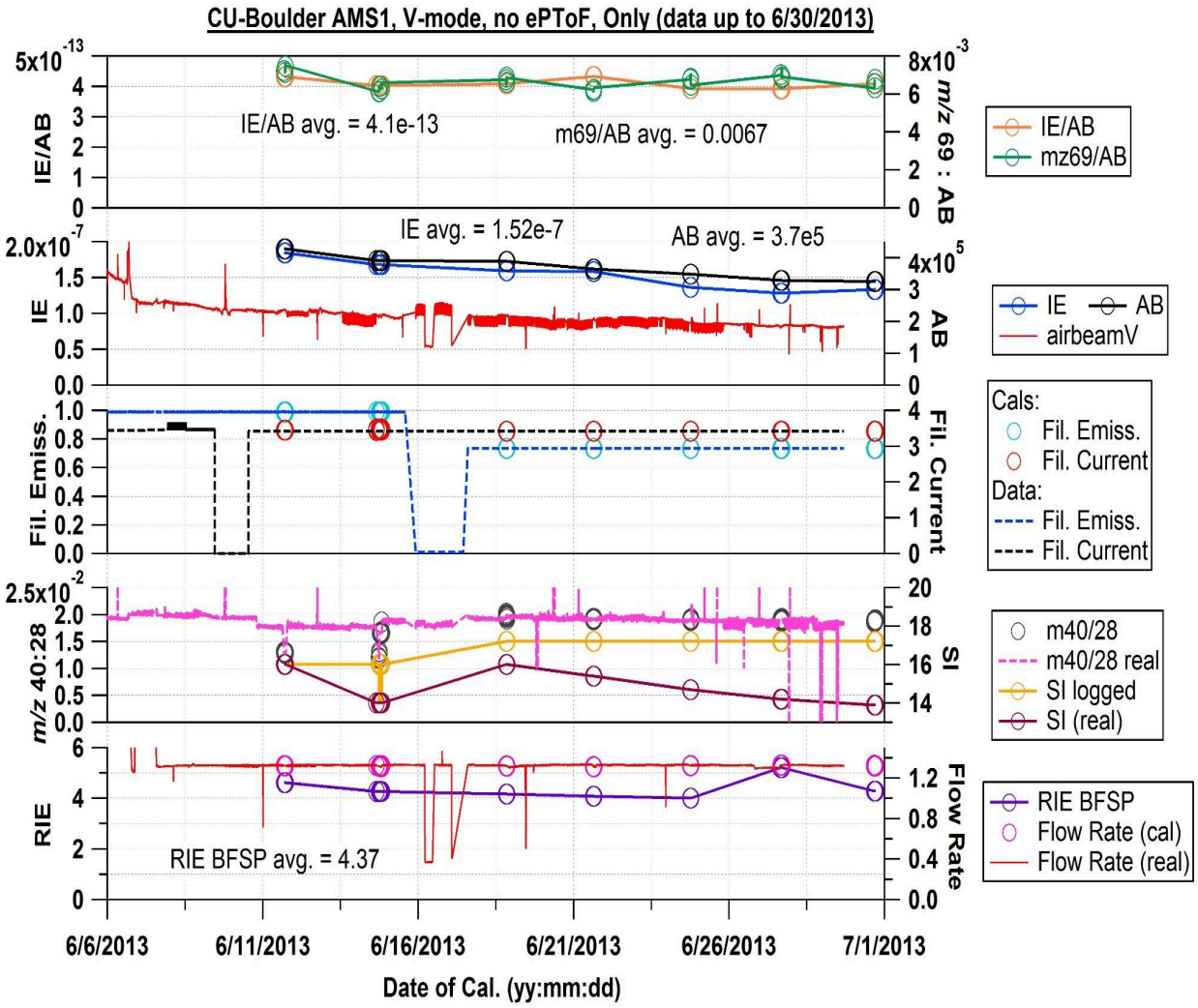
Other:

- ~~Pack the SEAC4RS box~~ (Amber-done)
- ~~Cutting the interlock cables for HIAPER (or CTOF) interlock cable~~ (Jose + WW- done)
- ~~Gas tank order: think about UHP zero air order - Weiwei~~

Small things do not need to discuss or can chat a little bit:

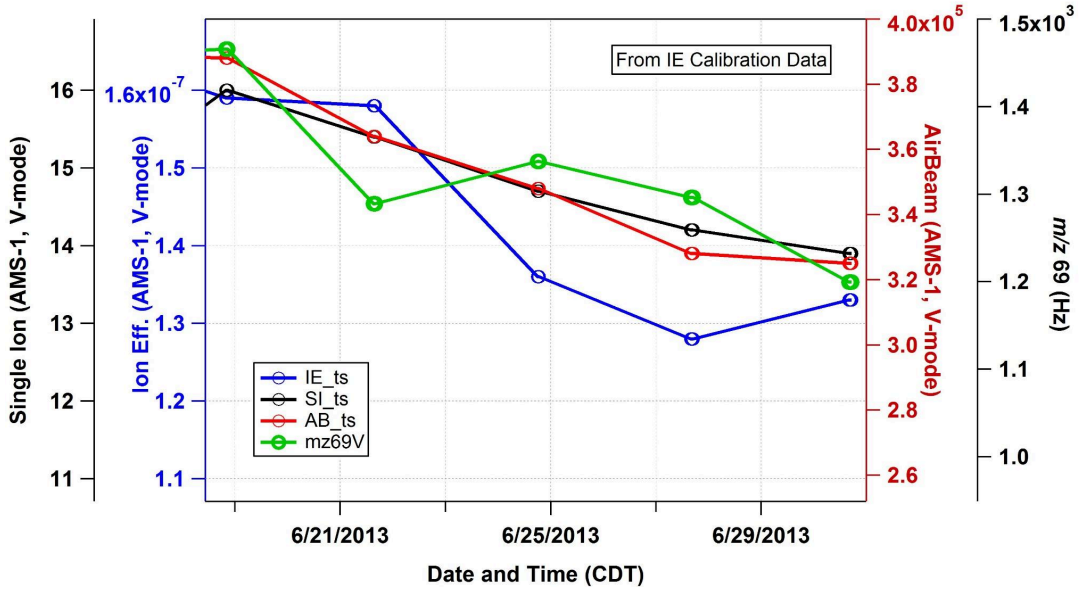
- set up the RH 2 sensor and record the data in the OH-PAM line (Aki) - Amber
- *reverse L1 and L2 scheme in PAM - not yet, let's look @ data and decide*
    - Brett did it ~17-June, should be recorded
- *Particle losses in the 10 l/min nafion - Jose thinks this can be done in the lab*
    - WW to look at the test done earlier in the campaign
- *Spreasheet for the Filter*

Recent Diagnostic Plots (Amber):



- ~~Add regular RIE~~ (Amber)
- ~~Add RIE of SO4~~ (Amber)
- Do ~~RIE of SO4 tomorrow~~ & end of campaign (WW)

IE Cal for AMS1 plot (Amber):



14-May-2013: Patrick, Pedro, Doug, Amber, Jose

- Topics
    + Pedro: detection limits and 1 min to 1sec
    + HR calculator

2-April-2013: Rui, Pedro, Doug, Weiwei, Jose, Patrick, Brett. Amber

- Rui's experiments:
    + Plan for Cals, no CO and 50 s-1 OHR, varying H2O and lights
    + Did OHR w SO2
    + CO precision 6-10 ppb @ 1-2 sec
    + Tune 185 flux to match O3, tune 254 to match OHex; Ratio of 185/254 increases with increasing voltage. Get larger numbers than we had in model (esp. 254). Then apply to other experiments
        - model tuned @ 45% RH @ OHR 50 s-1 CO (10ppm CO), not bad performance, but some RH dependence (model high in OHex @ high RH, low @ low RH. O3 is better
        - Could do experiments w very low reactivity
        - $Na_2(S_2O_3)$ works really well, see 30 ppb @ max settings
        - Weiwei to order some for SOAS and later
        - CO reacted ~few % to ~80%
    + OH suppression matches well between model/measurement for 3.5% RH (trend and abs. value). At 20% RH trend in the model is steeper than the measurements.
    + SO2 + H2O on walls (initiated by oxidants - i.e. O3)?
    + shows plot with OHexp vs cal equation with O3^(0.495-0.0003OHR)xH2O^(0.7)/flow. Remaining variability is higher OHR has lower OHexp AND Brett and Ambers are higher. Range ~factor of 3.

- Possible ways forward for Rui's experiments
    - Main issues
        + Absolute and ratio of fluxes higher than we thought (but f_254 is same as Bill had, so maybe ok)
        + w SO2 at highest fluxes, OHex higher in model and O3 is lower
        + Rui's points don't line up with Amber + Brett's by x3
    - CO and SO2 simultaneously
    - 185/254 ratio with diodes OR relative changes of one wavelength with light settings
    - 254 photolysis of substituted aromatics, etc.
    - Rui action items:
        + plot remainder of the experiments.
        + Run wide range of conditions w model and see if she can identify a good functional form for the calibration equation.
        + Think about additional experiments that could shed light (CO + SO2 together?) photolsyis?)

+ Action items for Weiwei with Doug/Pedro help:

+ Set up entire system for SOAS (Weiwei)
+ Set up CO addition (and maybe SO2) for continuous OHexp meas. Possible compare open flow vs front plate (closed flow) (Weiwei)
+ Install 254nm sensors and test different light intensities (Pedro/Weiwei)
+ Do sulfate transmission experiment with more than one neutralizer in series (perhaps not enough charges to neutralize all the particles)
+ Do seeded experiment for with monodisperse sulfate
*** Current cal equation: OHex = 7.21e-7*(ozone^(.495-0.0003*OHR))* (H2O^0.7)/Flowrate units are molec/cc, sec-1, and lpm

Eunha's thesis to: http://cires.colorado.edu/jimenez-group/EunhaKang_dissertation_final.pdf

5-Mar-2013: Rui, Pedro, Doug, Amber, Brett, Weiwei, Jose

- Discusss Rui's experiments: next steps are testing Na2S2O3 and Na2SO3 . Also MnO from RuShan, Also test SO2 and see if we can do it with that.
- Brett: BEACHON: exploring the dataset. B to prepare improved outline w graphs
- Pedro: aero-PAM: P to prepare response to Frank

4- Feb-2013: Jose and Weiwei

- Experiments for calibration of HOx model start in Feb or early March. Experiments during March, April. Then in May packing for SOAS, need to ship for SOAS on May 23 or so.

1-Feb-2013: Rui + Jose

- We implement calculation of O1D and O steady states per Bill's code. For default case we get O1D ~ 200 atoms cm-3 and O ~ 1e7 a cm-3
- There are some missing reactions:
+ O + O3 → O2 + O2 k = 8e-15 R = k * O * O3 = 8e-15 * 1e7 * 5e13 ~ 1e7. This is much smaller than formation 61e10 or destructions ~2e10, so ok to neglect for base case
+ O + OH → O2 + H k = 3.3e-11 R = 3.3e-11 * 1e7 * 1e10 = 3e6. This is much smaller than rates that form or destroy OH or HO2
+ O + HO2 k = 6e-11 R = 6e-11 * 1e7 * 1e11 = 6e7. Again small.
+ O + H2O2 k = 1.7e-15 R = 1.7e-15 * 1e7 * 1e12 = 1.7e4. much much smaller
- O1D for CH4
+ O1D + CH4 k_tot = 3e-10 R = 3e-10 * 1e2 * 0.3e10 = 100 molec cm-3 s-1
+ OH + CH4 k = 6e-15 R = 6e-15 * 1e10 * 0.3e10 = 1.8e5
+ conclusion is that OH is 1e3 times faster than O1D

- For Rui
+ add comments to rates that are slow
+ add simple display of O1D and OSS in both graphs
+ Make time step big + run
+ name as v2.4 (mark in comments)

+ distribute

Next task for Rui: email from Bill
The rate coefficient that I changed to get better agreement with our CO results is OH+O3:
% OH + O3 + O2 -> HO2 + 2O2
*k_oh_o3 = 1.7e-12*exp(-940./T)*
k_oh_o3 = 1.28e-13

The first one is the JPL value, which gives about 7e-14 at room temperature; the second is the one that gives the best fit to the O3, OH exposure as a function of CO addition.

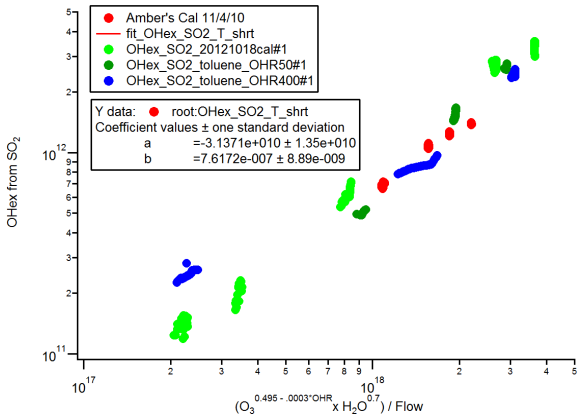
I discovered this problem when I ran the temperature to about 350K in the model and noticed that the observations and model were in much better agreement. Then I set the temperature at 300k and one-by-one changed the individual rate coefficients to their value at 350K. All of these changes did essentially nothing, but changing only O3+OH to about its 350K value made the measurements and model come into much better agreement. I have since fine-tuned the rate coefficient to 1.28e-13 to get the best visual fit.

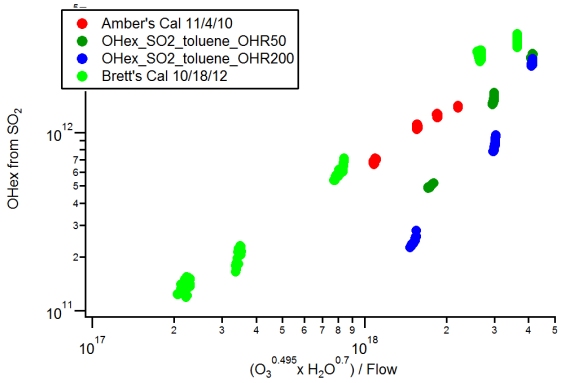
See what happens when you do this. Hopefully we can talk on Wednesday.
- Task: re-run sensitivity study with new rate and plot on top of old rate

17-Jan-13 Amber, Brett, Rui, Doug, Jose
- HOx model
    - V2.3 distributed to everyone
    - Jose mentions Runge-Kutta implementation on HOx model. Jose to follow up with Rui and Christoph
    - Rui to test N2 + H2O in model and compare. We realize that the model is making assumptions about reaction of H + O2 → HO2 being very fast. We would need to review and update the reactions before being able to study this case. That may also make the system be stiff numerically, and we would need to deal with that. We agree that this is not a high priority right now. Should discuss again in 3 months once we have done much more work with the model and experiments.

- We discuss “low ages in PAM”, Brett is done with updating age. Amber to update CalNex using SO2.

- Brett’s new cal seems to work well:





+ Functional form that captures OHreact. Rui to test whether it works in model later.

- Brett shows spectra of enhanced mass with the different PAMs. B to add them to his outline.

- Amber to plot O/C vs PhAge both absolute and relative (absolute to compare w/ Patrick. ALso plot Delta_O/C (and H/C) vs age, to see whether delta increases or decreases with O/C (in FLAMe it increases, here we think it should decrease). Also O/C vs PAge_abs (compare w http://www.geosci-model-dev.net/4/901/2011/gmd-4-901-2011.pdf)

- Brett working on paper, high priority, trying to target SOAS
- Rui working on paper, Joost gave feedback, she is digesting it.

17-Jan-13 email from Doug on HOx recycling from OH + NO2:

Regarding the recycling of HOx from OH reactivity from NO2 (OH + NO2):

JPL had rate constants for both reactions:
OH + NO2 (+M) → HONO2 (nitric acid)
OH + NO2 (+M) → HOONO (pernitrous acid)

See page 188 of pdf at:
http://jpldataeval.jpl.nasa.gov/pdf/JPL%2010-6%20Final%2015June2011.pdf

The evaluation of a handful of seemingly uncertain experiments says that the HOONO reaction is 5-15% of the sum of the two reaction channels (see link to notes after reaction in table in link above).

However, the equilibrium constant Keq(298) = 2.2e-12 for OH + NO2 <=> HOONO. So for our highest OH ~ 2.5e10 molec/cc the HOONO/NO2 ratio would be only 0.055. And I get a lifetime of 1s or 20s depending on whether you use the high or low pressure limit for the formation reaction, respectively (Kdecomp = kformation/Keq). So quickly the NO2 would be recycled and quickly react with OH ultimately forming HNO3 (if slightly delayed by the HOONO "intermediate"

step). So it appears that any formation at typical conditions would quickly decompose. Also, photolysis could also play a role in decomposing HOONO, but I couldn't find anything on that.

Thus, it appears that we can consider that we can either use the OH + NO2 (+M) → HONO2 (nitric acid) rate constants and assume that recycling = 0.0 OR the combined rate constant of the nitric acid and pernitrous acid formation and assume recycling of 0.1. However the recycling is directly to OH, not HO2 so that would need to also be accounted for in the model. Thus it seems the simplest thing to do is just use the nitric acid formation rate constant and set HOx recycling to zero.

Accounting for the minor pathway may be important in modeling the atmosphere for the purpose of taking into account that the NO2+OH doesn't entirely go to nitric acid and at colder temperatures the lifetime of HOONO is longer.

We can, of course poll Steve Brown at some point if we want an expert opinion since he spend a couple years of his life thinking about this.

-Doug

See also the Science paper from the Caltech group:
http://www.sciencemag.org/content/330/6004/646.abstract
They note the HOONO path is not directly important under boundary layer conditions since it will rapidly decompose and for atmospheric modeling it is important in respect to the need to know the HNO3-forming reaction rate well (not the sum of the two reactions). They show a branching ratio for HOONO of 12-13% at atmospheric pressures and model the effect of using their new lower HNO3-forming reaction rate on BL ozone production in LA (higher O3 by up to 5-10 ppb b/c less OH+NO2=>HNO3 leads to higher OH which leads to higher O3, kind of like the weekend effect from NOx changes).

9-Jan-13 email from Jose on HOx recycling from different compound classes with OH:
See attached the experiment with the OH reactivity for CalNex from Jessica. We can use this to estimate the actual value of the recycling coefficient (1 for CO and SO2, 0 for NO2 -- or maybe 0.1, Doug?, estimated at 0.9 for all organics). We can discuss next week if this is not clear.

8-Jan-13: Rui, Amber, Brett, Doug, Joost, Jose

- Photolysys:
    + O2 photolysis → O3 production
    + Other precursors: substituted aromatics, cresols @ 254
    + 184: limonene 4.5e-17: 15% photolysis at highest lights (so we may not see enough
        - Cross section of acetone: 2.5e-18 @ 185, not high enough

- Calibrations:
    + Rui does sensitivity to different parameters: light and H2O are the most important. T &

P have some effect @ 10% level. Residence time is pretty linear. O3 is a good measure of the total flux.

- Big picture procedure:
    (1) validate model
    (2) Explore sensitivities w model
    (3) Improve cal equation

- Plan of action
(1) Quantify 185 and 154 effective fluxes
    + measure O3 output w/ 185+254 w/o H2O: calibrate 185 flux (start immediately)
        - Do each light at different levels, and then one light max and other one at different levels
    + calibrate 254 nm flux. O3 not sensitive, need a different method. benzaldehyde photolysis with leak detector as detector. Otherwise cresols but a little more unhealthy. (Could collect frozen O3 and then put it in N2, but dangerous)

Leak detector (Pedro): sum of air ions is 1e-6 Torr signal. Detection limit is ~ 1e-13 Torr (per specficiations). Therefore the detection limit is ~ 100 ppb in air. If we added 10 ppm of benzaldehyde, that should be enough signal. Optical depth = 7 cm * 2.5e14 molec cm-3 * 2e-17 cm2 molec-1 = 3e-2 = 0.03. It would only attenuate the light by 3%.
    + If we put 100 ppm, then attenuate light by 30%
    + Alternative is AMS, but that's dangerous for the AMS.
    + Rui to bring benzaldehyde from NOAA (nitrobenzene and nitrotoluene have similar cross sections 2e-17 @ 254 nm, similar health). We decide later that the nitrobenzene cross section is much better known per the Mainz database, therefore better to work with that one.
    + Pedro to look at leak detector and help Rui with first measurements

Separate item: Pedro to explore whether we could get some permanently mounted diode for monitoring lights in field

(2) Run the toy model as if it had been verified and produce that part of the paper
(3) Do the OH reactivity quantification experiments in March (Rui is back and Weiwei is here). Also need CO tank.

Outline in Google Presentations:
https://docs.google.com/presentation/d/1M-xK1aiUtWYVe3ujRBcJ-tLg2tk1BBC3050COu4dyRk/edit#slide=id.g665b9275_4_7

07-Jan-2013 Mon: Discussion w/ Amber & Rui

Outline PAM Toy Model Paper (A.O.& R.L. 1/7/2012), *additions to outline in italics*:
(1) important sources, sinks, recycling, how do they vary with method (hard, 185+254) and level

(light, O3) and environmental variables (T, H2O, P). **No reactivity, all Hard OH**.

+ experimental verification vs light and H2O

+ Evaluation of the calibration equations

+ Show what the model does as T & P vary (also flowrate). (Could evaluate T / RH effect from BEACHON and CalNex)

Figures:

- *Arrow Plots: Discuss which to show from above variables (Rui)*
- *Panel of all variables: Table and Plots: T, P, H2O, Flux, ResT (Rui)*
  (most variance observed in order of H2O, Flux, ResT, Temp, Press)

(2) Cal equation @ 0 reactivity: we assume model is perfect, how do we estimate OHexp = f(O3_end, H2O_molec_cm-3, Flow)

- *Cal Eqn. with Model Plots: (Amber)*

(3) Effect of increasing OH reactivity

+ Character of the chemistry

+ Suppression vs calibration equations

+ New calibration equations that take supression into account

Figures:

- *Panel Table/Plots w/ reactivity: (Rui)*
- *Arrow Plots: Same with Reactivity (Rui)*
- *Expt vs Model Plots: Expts with OHR compared to Model with OHR (Amber)*
- *Cal Eqn. with Model Plots: Comparing Cal eqns derived from model suppression vs none (Amber)*

Experimental verification

- *Expt vs Model Plots: (Amber)*
- *Ambient T/P variation Plots: CalNex (Amber) and BEACHON (Brett)*

Other Topics

(3) Quantification of photolysis w simple examples:

- *Table of photolysis and plot of 1-2 examples? (Doug/Brett)*

(4) Fate of NOx: could add reactions and document what the model does. (expts w/ NOx box?)

(5) Document Non-uniformity effects

+ Different paths (distribution of residence times):

- *Flow Model Figures: residence times, how this effects precursors (Amber)*

+ Different light exposures (cross section): *(Doug?)*

27-Dec-12 Thu: Meeting w/ Joost, Rui, Doug, Amber, Jose, on possible PAM toy model paper

- Jose shows slides from PAM users' meeting + PAM wiki

- Outline

+ HOx radical chemistry:

(1) important sources, sinks, recycling, how do they vary with method (hard, 185+254) and level (light, O3) and environmental variables (T, H2O, P). No reactivity.

+ experimental verification vs light and H2O

- Evaluation of the calibration equations

- Show what the model does as T & P vary (also flowrate). (Could evaluate T / RH effect from BEACHON and CalNex)

(2) Quantification of photolysis w simple examples

(3) Effect of increasing OH reactivity

+ Character of the chemistry

+ Suppression vs calibration equations

+ New calibration equations that take supression into account

(4) Fate of NOx: could add reactions and document what the model does. (experiments w/ NOx box?)

(5) Document Non-uniformity effects

- Different paths (distribution of residence times)

- Different light exposures (cross section)

- Schedule

+ Utah work for Rui: potentially mid-Jan till end of Feb

+ Weiwei arrives 1-Feb-13

+ Do experiments when Rui back from UT, then Weiwei here. Amber also involved, as she may do 254 nm paper later on. Brett and Doug as advisors to setup.

+ start with modeling

- Action Items

+ Rui and Amber to put together a Google Doc or presentation with plots and outline, to be discussed when it is ready.

+ Rui and Amber to propose an experimental matrix (5 light levels, 5 H2O levels, both spaced “logarithmically”). Also 5 reactivity levels for ~3 light-H2O combinations.

- In actual experiments, always increase light, H2O (decrease reactivity?)

+ Doug to decide what CO level to use, and order the tank

+ Additional topics for future papers

- Soft OH (254 nm)

- More detailed modeling of VOCs, yields or MCM with this chemistry

26-Nov-12 Mon: Call w/ Drew Gentner: Possible PAM Volatility Inlet for SOAS

- Drew, Jose, Doug, Pedro, Brett, …

- Drew walks us through his slides (“PAM Inlet Design.pdf”)

- Discussion of gathering enough stats. Maybe chose one OH level where production peaks (or

maybe two).
- Volatility resolution? Primarily volatility, maybe a little polarity effects.
- Maybe aim for 2-3 C* bins/temperature step?
- Initial tests in lab ideally with PTRMS and looking at transmission/adsorption via inlet.
- Appears this design will remove most particles. Can we do it more like a diffusion drier rather than completely “blocked” config.
- Maybe drop down a little below ambient
- May want to consider using multiple (4?) types of adsorbents rather than scan temperatures
- 1/10 mm diameter adsorbent beads, quartz wool

6-Nov-12 Tue: Meeting w/ Bill (Amber, Doug, Brett, Rui, Jose) in Boulder
- See notes in log shared with him:
https://docs.google.com/document/d/1R2Fz_fMksjgC6XioODynf14WoiShVey7nnmxiJyvYKg/edit

26-Oct-12 Fri: Emails w/ Bill about T-dependence of Chemistry

Email from Bill

Sorry for the delay. From a few runs of the toy model, changing the temperature from 283 K to 323 K changes the final O3 from 37.7 ppm to 35.7 ppm and the OH exposure from 3.0e12 to 2.6e12 cm^-3 s. So the large decrease does not seem to be in the non-linear gas-phase chemistry. I played with adding different levels of gases and changing the lamp flux, and the O3 sensitivity to T changes did not differ very much from what I have here.

For it may be that the lamps are getting too hot during the day and are losing flux and then are cooler at night and are gaining flux. Your curves suggest that you could easily get a factor of two change.

I was also thinking about wall loss of ozone, but it would get worse at lower temperatures and higher relative humidity, which is just the opposite of what you are seeing. So I think we can say that temperature-dependent wall loss is not responsible.

P.S. I'll send you the new version of the toy model that includes NOx in a week or so. I need to verify that it works by comparing it to the full model and to some observations. So far, it seems to work pretty well for the limited cases I have run it on.

Reply from Jose:

(1) Dependence on T

I was running the toy model too, see attached slides. When I sent the emails yesterday we thought that the toy model may not have the T-dependence of the chemistry, but we verified later that it does. I only ran with zero OH reactivity and 185+254 (formerly known as "hard OH"),

since that's what I had done by the time your email arrived.

See attached presentation, when T goes from 273 to 303 to 323 (0 to 50C) we get:

- O3 barely changes, but it INCREASES ~2% rather than decrease when it gets warmer. (This is different than for Bill where O3 decreases a little. Bill, are you running with 185+254 or only 254? And are you sure you wrote the results correctly in your email, and not backwards?)

- OH exposure does DECREASE 25% for this large temperature change (the sign and magnitude of this are similar to Bill's results). For the more typical range of 15-20 K day to night in the field, OH exposure will change maybe 10% due to this effect. The calibration equation WILL NOT pick up this effect according to the toy model since H2O is the same and O3 doesn't change. However the actual change in O3 is much larger, so that's what we need to constrain better.

- HO2/OH ratio increases x2 from 0 to 50C. This may not matter very much since HO2 is so high anyway and will dominate the RO2 reactivity.

This T effect is something we should report in the paper about the kinetics. However, what the model does NOT have yet is T-dependence of the photolysis cross sections. Bill, do you have some previous info on those?

If the temperature effect is due to a change of the lamp flux with T (which is our dominant hypothesis per Bill's email and this discussion), then the cal equation should pick that up since we used the measured O3 which is larger at night. But that will cause more aging during the night than during the day for the same OH exposure.

(2) OH suppression

Yesterday we determined that according to the toy model, the cal equation also doesn't pick up the OH suppression due to increased reactivity. O3 actually increases as you add reactivity because the reduced OH leads to less destruction of O3 via O3 + OH which is fast. HO2 increases but HO2 + O3 is slower. So we need a term in the cal equation which decreases OHexp as a function of OH reactivity.

But on that note, not all reactivity is created equal, reactivity with SO2 regenerates HO2 and does not destroy HOx, while reactivity with NO2 does destroy OH. Reactivity with organics will mostly re-generate radicals and be more similar to SO2, but some fraction of the reactions do lead to stable products without regeneration of radicals. This is again something to look at with the toy model (which at least I are finding extremely useful to learn about this chemistry and hence the push towards a paper on it).

All of these complexities reinforce my belief that we need reliable monitoring of OHexp all the

time in the field and also in lab experiments. We are buying a cavity-ringdown CO instrument that is nominally part of the new chamber, but I think we'll use it with PAM in the lab and also the field. Since there is always CO out there, that may be the best way to do the monitoring all the time and gain more certainty on these issues.

(3) We look forward to the NOx chemistry. Doug Day was going to implement that, but if you have done that already he can work on double-checking it instead.

Cheers,
-Jose

25-Oct-12 Thu: Doug, Amber, Brett, Jose

- NPF results for Doug DOE Mtg: Amber will provide a couple of slides. Doug will present on "A screening tool for new particle formation potential in ambient air and show (a) PAM + AMS-SMPS diagram (b) results from Brett (slide from before) and (c) time series + SMPS/AMS size distribution for sulfate/organic from Amber.
    - A & B: plot O3 at lowest and the highest light setting vs ambient T (color by absolute H2O)
    - A & B: plot N_PAM - N_amb for each light setting vs time, and also for O3 and NO3 PAM (even if zero). Make diurnal cycle, look for correlations.

Oil experiments: Rui is back on Mon Oct 29th. She should lead this. Brett will recover AMS from Maggie's group, and also run SMPS. The light source time ends Nov 13, should get them the filters a week before then.

- Amber's paper: Doug 40% through. Plan: Doug finishes, then Amber digests and then Jose reads.
    + Amber to add in next version a short text on what happened when putting a plate and/or inlet in front of PAM. Also to investigate what was done in CalNex, should report if we did something.

- Amber's new plots, comparing with the frag vs func kink of Andy Lambe
    + Kink is not obvious on our plot

+ New questions for hard OH w toy model:
    (a) Amber: redo toy model cal equation to see effect of T in chemistry. Our relevant range (BEACHON, CalNex) is 10-30C. Maybe do 0C, 20C, 40C to have more sensitivity (do cal of hard OH, same as before)
    (b) Does the calibration equation at least partially capture OH supression? In hard OH, per the toy model, O3 actually increases ~10% as OH supression goes 0 to 200 s-1, so calibration doesn't account for suppression at all. Suppression needs a new term on the cal equation.

- Brett

+ When adding TOL, O3 increases, so cal equation would give MORE rather than less OH exposure

+ Brett needs to think some more about the SO2 cals, there may be an issue with the SO2 monitor.

+ In future and for publications, add factor to OHex eqn for lights, on = 1, off =0 (so we don't calculate OHex when lights are off, while O3 is still decaying). Amber: update this to revisit CalNex OHex and ERoa: OHex = L * (O3^x * H2O^y) / Flow / (a+OHR)^z. Doug thinks that this functional form won't work, we may need to modify O3 exponent as Brett did.

19-Oct-12 Fri: Doug, Amber, Brett, Jose

- We discuss the PAM users meeting

+ Doug will get CO, NOx, THC analyzers

+ Publication of first field paper is important

+ Amber to summarize Whistler paper in next mtg

+ Amber and Brett to think about kink in VK, put lines from Lambe's ES&T paper. Plot O/C and H/C vs photochemical age.

- Yields vs papers

+ Brett will finish analyzing recent MOCCS experiments

+ No more experiments for yields in near future, maybe later. For now we will use the published chamber yields.

- Amber to follow up on nice correlation of O/C_end vs O/C_start. What is the cause. She'll plot O/C_start and Delta_O/C vs OH reactivity

Updated OHR Literature (from Amber):

				OH Reactivity			
Project	Type	Location	Year	Min	Max	Ave.	Reference
PROPHET2000	Forest	Michigan	2000	0.2	12	6.1	Di Carlo et al., 2004
TEXAQS2000	Urban/Industrial	La Porte, TX	2000	10	17	13.5	Mao et al., 2010
TRAMP2006	Urban/Industrial	Houston, TX	2006	15	30	22.5	Mao et al., 2010
MCMA2003	Megacity	Mexico City	2003	20	125	72.5	Mao et al., 2010
	Urban	Nashville, TN	1999	11		11.3	Kovacs et al., 2003
NYC2001	Megacity	NYC	2001	19		19	Ren et al., 2003b
	Winter	NYC	2004	20		20	Ren et al., 2003b
		Tokyo	2003	20		20	Yoskino et al., 2006
FLAME-3	Biomass Burning	Missoula, MT	2009	5	540	272.5	Gilman AGU talk 2011
BEACHON ROCS	Forest	Manitou, CO	2011	7	16	11.5	Kim et al., 2012 (ACPD)
MEGAPOLI	Megacity	Paris, France	2010	10	130	70	Dolgorouky et al., 2012 (ACPD)

10-Oct-2012 - PAM Users Meeting - Jose's notes

- Andy Lambe: review of past work: will post
- Bill Brune
  + Thinking about other flowtube designs? Other light sources?
  + Wall-less? Heating at the top? Converging walls, acceleration may suppress the meandering?
  + New chamber is flat-top, to avoid translating convection into horizontal motion
  + Gold standard: put SO2, convert to SO4 (can't have wall loss if that works)
    - BC: 30-40% loss of SO2 vs SO4 conversion
    - Eunha's original chamber had much lower losses
  + CO --> CO2 may be better for OH exposure, because no wall interaction. But need cavity ringdown
  + Nothing magical about SO2. Want something slow.
  + formic or acetic acid, to detect w acetate CIMS (Andy, rates similar to SO2)
  + PSI Chamber: d9-butanol, can measure well w PTRMS

To do

- look @ paper about OH*dt from Geoffrey Smith in ACP

3-Oct-12 Wed: Doug, Brett, Amber, Jose

- Agenda:
    + AAAR PAM Prez, PAM Users Mtg
    + DOE highlights: we work through them, Jose will clean up and send to DOE
- To-do:
    + A will do the Df44 vs Df43 for FLAME and Calnex, the way Pedro did it below
    + A to plot O/C_end vs O/C_start for all burns. Also Delta_O/C vs O/C_start. Same 2 plots w/ f44
    + B and A to start measuring yields vs OH exposure and OA for 1 precursor. Start with toluene & hard OH. By the end of the year (when we lose MOCCS) we need to have done 3 terpenes (BEACHON) and toluene, TMB, pentadecane (CalNex). Next most useful would be MBO w seed (BEACHON), and isoprene w seed (SOAS). For both soft and hard (probably do in parallel w both PAMs).
    + B and A, make mixing/dispersion inlet for PAM: measure, schematic, talk to Don David and Pedro

25-Sep-12: Doug, Brett, Amber, Jose

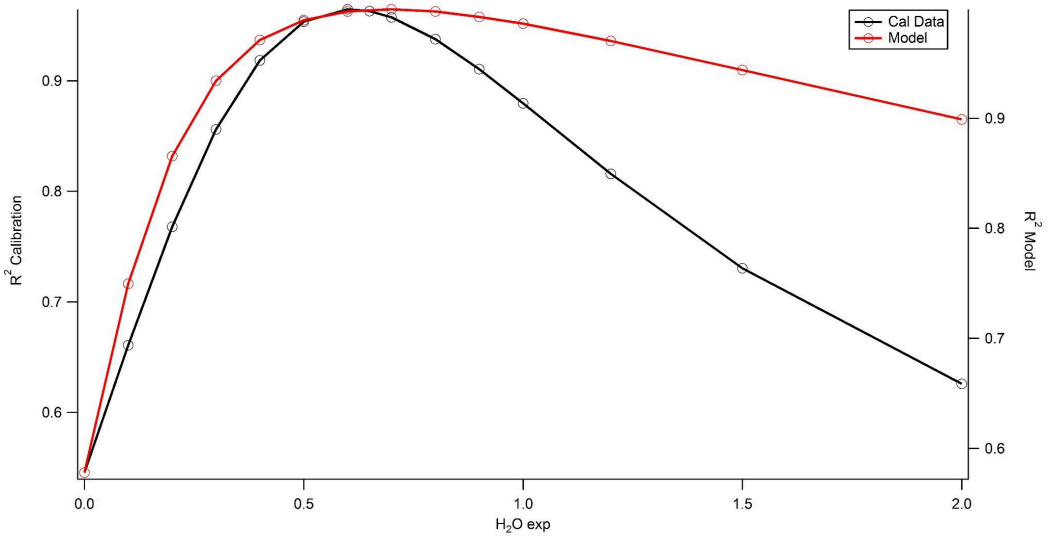
- Agenda
    + Jose emails Rui asking her to combine both graphs into 1.
    + H2SO4 PAM?
- Amber's Toy model results (see tasks on 5-Sep-12 notes)

- Amber's CalNex
    + PAM CE using NO3 part of Middlebrook algorithm. Aerosol is neutralized after PAM per the NH4 balance. Many points with 0.5 < PAM CE < 0.7.
        - CE difference between adjacent ambient and PAM points is at most 10% (per Middlebrook), so PAM changes in concentrations have to be the result of chemistry and cannot be the result of changes in CE.
    + Further ways to look at CE for CalNex PAM
        - Estimate potential SO4 from SO2? Amber will follow up and make this plot (calculate and include traces that correct for missing AMS mass and expected SO2 oxidation based on OH exposure)
        - Compare SMPS vs AMS enhancement: Amber will follow up and make this plot

- Amber's Toy Model
    + Used fluxes from Rui, 6e14, 3e13 max.
    + Hard OH: OHex vs H2O approx linear (for H2O > 0.5%)
        - Exponent of O3 should be ~0.5 (varies 0.53-0.55). Actual calibrations ~-0.49-0.53. **Toy model DOES reproduce the functional dependence of OHex on O3_out**
        - Exponent for H2O: 0.7 works best. This was w/ 30 ppb SO2 and fluxes above
        - Followup questions:

(1) Does the model have the same exponents w/ different OHR (= SO2) and different flux ratios 254/185. If yes, the functional form O3^0.5 * H2O^0.7 would seem quite general. If the exponents change a lot, then the form of the cal equation is not very robust as conditions change. Especially OHR does change, even if 254/185 is more constant for this type of lamps. To test for this A will redo the procedure for 254/185 = 5 and 50 (w SO2 = 30). Also redo for SO2 spanning range of OHR = [10, 100,1000] for default flux_max (add 4 more curves to figure below, but check before that O3 dependence is ~ ^0.5, and also check dt lack of dependence for extreme cases).

(2) Can we tell which H2O exponent is better from the actual cals? Is there enough H2O variation to tell whether H2O^1 or H2O*0.7 leads to better cals? Amber does this and it seems that 0.7 also works best: Figure below.



- Brett: plot time series of SMPS mass below 40 nm, compare with expected SO4 from SO2 loss (from SO2 monitor and OH exposure) for BEACHON. (Amber will do it for CalNex later)

- Amber FLAME: NH4 balance shows much more predicted than measured. Suggests influence of K. Amber will add the K to the measured cations and see if that closes the gap (keeping in mind that RIE may be > 1).

21-Sep-12: Meeting Canceled, some updates

- Jose met w Alma yesterday and discussed comparing the toy model to GECKO. There were several errors in how GECKO was setup for the photolysis rates, and the comparisons should allow us to identify any other discrepancies. See details on that shared document: https://docs.google.com/document/d/1Jzg-QZb7M3CMuOeIQIArpCYjMDEhwV435aNDJXXWOGo/edit

- Items for next meeting:

    - Amber to complete toy model task by then

- Amber to be ready to show / discuss the paper (if you not yet sent to J&D for comments)

- Also, to be ready to discuss the PAM CalNex CE implications, although that can be postponed to the next meeting, if that's too much to prepare

18-Sep-12: Doug, Jose

Rates:

+ OH range in hard OH PAM is 1e9-1e10. HO2 is ~100x that, so 1e11-1e12. Maybe be able to go lower with soft OH PAM, if we inject less O3

+ RO2 + HO2: 5-9e-12

+ RO2 + NO: 7e-12 (CH3O2)

+ HO2 + NO: 8e-12

+ O3 + NO: 2e-14

+ RO2 + RO2: 3.5e-13

+ HO2 + HO2: 1.5e-12

+ Rates of RO2 are similar w/ HO2 or NO, so that we can compare those concentrations. We have 4-40 ppb of HO2, so we would need at least that much, preferably 3x or 10x more NO. We can inject a lot of NO (1 ppm), that will supress O3 temporarily in hard OH and make NO2 (eventually system makes 10s of ppm of O3). If we have 1 ppm of O3, lifetime of NO is 1s. Photolysis of NO2 is almost negligible (~2% over residence time @ 185 nm, negligible @ 254 nm, per calculations below), and HNO3 is also very slow.

- It seems that we cannot have high NO under ambient air, because O3 is formed from O2 photolysis. Unless maybe we injected 50 ppm NO to supress O3 formation completely.

- Another idea is to put a small blacklight for NO2 → NO, same cross section at 350 nm as @ 185, ~4e-19. Seems too little to matter, unless UV light flux of blacklight is much higher than for PAM lamps.HNO3 cross section in the 350 and visible is negligible.

11-Sep-12: Rui, Brett, Amber, Doug, Jose

- Agenda:

+ updated poster graphs from Rui

- fx from AMS

+ toy model calcs from Rui

+ toy model calcs from Amber

+ Updates in toy model rates and graphing from Rui

- Updated poster:

+ Add literature yields for n-alkanes to the graph:

+ Use http://pubs.acs.org/doi/pdf/10.1021/es300409w for relative yields to C12, and use C12 yield as 0.15 per Presto: http://pubs.acs.org/doi/pdf/10.1021/es903712r

+ Other literature references:

(GECKO yields for n-alkanes: Fig 5 in http://www.atmos-chem-phys.net/12/7577/2012/acp-12-7577-2012.pdf, also Lim and Ziemann, maybe CMU)

Lim and Ziemann 2009 (yields): http://pubs.acs.org/doi/pdf/10.1021/es803389s
Ziemann 2011 Review (Alkanes, Alkenes)
www.tandfonline.com/doi/abs/10.1080/0144235X.2010.550728

+ Eventually you can do a forward model using literature yields, and see how different it is from the fitting results. This is probably the cause of the large variation on the fit results depending on what period in the experiment we include.

+ OH supression in model?

+ Model cleanup

(1) Group and color reactions by radical generation, propagation, and destruction in the flux diagram

(2) HOx - only flux diagram

(3) Long plane ride... Rui is bored... let me read the JPL! :-)

- Send us the best version when you leave, ideally with #1

Amber: Toy model results

- Simulating cals w/ toy model
- Soft OH:

+ (1) estimating the flux from DO3, flux varies with H2O and for the different cases. Toy model overpredicts OH exposure then by x3

+ (2) plotting OHex vs DO3/O3 works well, for O3 > 1 ppm. 100 ppb results are lower. There must be some different chemistry that's important for the 2 regimes.

+ Model seems to have a different H2O dependence than measurements.

- Hard OH

+ (3) used flux_254 as f(H2O)

+ Really not useful at present

+ Need to redo with average flux_254 vs light, then tuning flux_185/flux_254. Results don't make a lot of sense. Amber needs to keep thinking about it.

+ Redo this (question #4 below) for the default fluxes 6e14 / 3e13

Rui: OH suppression in Toy model

- Only have results for soft OH

- We calculate OH suppression: very strong suppression at low O3 (99% at 100 ppb), less suppression (few 10%) at 10-100 ppb O3

This much greater suppression for low O3 seems to be largely due to the fact that that HOx-O3 OH reactivity is very small for low ozone and the additional reactivity from the SO2 quickly overwhelms the HOx cycling chemistry (for example for H2O=1.5%: HOx-O3 reactivity for 10ppm O3, OHR=21 s-1; for 100 ppb 0.26 s-1); Thus OH=>=>HO2 but regeneration of OH is small.

7-Sep-12: Rui, Brett, Amber, Doug, Joost, Jose

- Rui: updates on yields and poster
    + Need to add 1-MN Chan yield to plot
    - discussion if plotting vs VOC reacted (instead of SOA) for comparison
    - spit up MN and Toluene curves into 2 plots
- Rui: walks through IGAC conference posterx
    + Rui: will plot bar graph of species amount, yield, and SOA vs c* (3x bar graph)
    + Brett: add f44, f43, f57 vs time in the oil experiment (sum all species into OA) for poster
    + Rui: other oil experiments: show results with different volatility distributions
    + Rui will extract OH supression vs OH reactivity for the oil evaporation experiment

- Possible paper on PAM chemistry
    + OH cals: data vs toy model
    + OH supression w validated toy model, and vs data
        - Detail: OH vs O3 exposure
    + photolysis with validated fluxes: prob of photolysis vs cross section, also for important species
    + Non-uniformity effects
        - Different paths
        - Different light exposures (cross section)
    + Followup: discuss @ next meeting

- Amber: draft of FLAME paper by 14-Sep-12

For Next Time

- Rui to update reaction rates from Tiffany's
- Group reactions in legend, and color, by type (automate arrow size)

5-Sep-12:

- Agenda: Follow up on action items from last time
    + Reply to Bill's email -- done
    + Followup on toy model plots and interpretation - Rui
    + Toy model calibration with OH_exp and O3_out - Amber
    + Updated yield plots - Brett and Rui

- Brett: George and Abbat TPOT het ox points are consistent with our data

- Rui et al: playing w toy model
    + implement updated H2O and H2O2 photolysis, and attenuation of 185 and 254
    + new default 254 is 6e14 at full power w 2 lights
    + Soft OHexp in toy is proportional to DO3/O3 as in cal equation. Numbers appear to be in the ballpark of Amber's exp.
- Amber compiled OH reactivity:

				OHR	OHR	OHR	
Project	**Type**	**Location**	**Year**	**Min**	**Max**	**Ave.**	**Reference**
PROPHET	Forest	Michigan	2000	0.2	12	**6.1**	Di Carlo et al., 2004
TEXAQS	Urban/Ind.	La Porte, TX	2000	10	17	**13.5**	Mao et al., 2010
TRAMP	Urban/Ind.	Houston, TX	2006	15	30	**22.5**	Mao et al., 2010
MCMA	Megacity	Mexico City	2003	20	125	**72.5**	Mao et al., 2010
	Urban	Nashville, TN	1999	11		**11.3**	Kovacs et al., 2003
	Megacity	NYC	2001	19		**19**	Ren et al., 2003b
	Winter	NYC	2004	20		**20**	Ren et al., 2003b
	Megacity	Tokyo	2003	20		**20**	Yoskino et al., 2006
FLAME-3	Bio. Burning	Missoula, MT	2009	5	540	**272.5**	Gilman et al., 2011 (AGU)
BEACHON ROCS	Forest	Manitou, CO	2011	7	16	**11.5**	Kim et al., 2012 (ACPD)

+ Followup for Rui:
    - email v2.1 of toy model to everyone
    - color labels and update case label automatically
    - draw simplified diagram with HOx as one species
    - Look @ JPL No 17 for any reactions that we may be missing
    - Plot OH_supression vs OH_react (0,1,10,100,1000 OHR_0 = k_OH_SO2 * SO2_mol_cm3 for soft & hard (typical conditions H2O =0.1,0.5...2.5% O3_0 = 0.1,1,10,100 ppm & flux254 = 6e14, 50%, 25%, 10%, 5% & flux185 = 3e13/6e14 * flux_254)
        + soft: H2O, O30, flux, SO2 → OHR
        + hard: H2O, flux, OHR

+ Followup for Amber (w updated toy model v2.1 from Rui)
    (1): For SOFT OH, for each cal experiment, use H2O, DO3 to determine flux_254. With that flux, calculate OHex_toy and compare to OHex_SO2.
        - Also plot flux254 vs lamp_V
    (2) For SOFT OH, run toy model for H2O = 0.1 to 2.5 in steps of 0.4, and initial O3 of 0.1 to 100 ppm (0.1,1,10,100) and flux254 = 4 lamp settings, and plot OHex_toy vs DO3/O3 (testing how well cal equation works according to toy model)

- Plot experimental data in the same way

(3) For HARD OH: use the flux_254 determined for the same lamp settings using soft OH (assume sleeve change doesn't matter). Then tune flux185 for the cals (a) to get OHex right (b) to get O3_end right. Then compare those flux185

- Plot constrained flux_185 vs flux_254

(4) For HARD OH: use the average flux185 from above and then test cal equation w toy model. Run for the toy model for H2O steps as above, flux steps as above. Then plot (all for toy) OHex_avg vs (O3^0.5 * H2O)/FR. How linear is this? What is K? Plot experimental data on top.

29-Aug-2012: Doug, Brett, Rui, Amber, Jose

Photolysis Rates Calc

- Using specs from 1" and 2" lamps:
  + @ 185 nm = 1.49e13 photons / cm2/s @ 20 cm, or 2.3e15 total photons per inch (assuming cylindrical, lower limit) or 7.8e16 total photons/inch (assuming spherical, upper limit)
  + @ 254 nm = 3.8e13 photons /cm2/s @ 20 cm, or 6.27 e15 total photons per inch
- If we use 10 cm as a typical path, and correct by 1/r^2, the fluxes are:
  + @ 185 nm = 7.96e13 photons / cm2/s
  + @ 254 nm = 15.2e13 photons / cm2/s
- Geometric effect: assume that each 2 inch element is the same as specified, Doug does calculation and we estimate that increases flux x3
  + @ 185 nm = 2.4e14 p/cm2/s
  + @ 254 nm = 4.56e14 p/cm2/s
- Need to account for & oxygen attenuation @ 185 nm
  + O2 cross section = 1.1e-20 cm2/molec
  + Beer's law, I/I0 = exp(-sigma * L * N), where the product is the optical depth, which is 1.1e-20 * 10 * 0.5e19 = 0.58
  + @ 185 this would reduce the flux to 1.3e14
- (Update) Account for H2O attenuation
  + JPL s = 6.75e-20, optical depth = 6.75e-20 * 10 * (1.5/100 * 2.5e19) = 0.25
  + We look @ geometry and decide 7 cm is better than 10 cm
  + This will depend on H2O
- (Update) O3 attenuation @ 254 nm?
  + s = 1.15e-17, so optical depth = 1e-17 * 7 cm * 7e-5 * 2.5e19 = 0.13 (70 ppm hard OH)
  + With hard OH, O3 = 20 ppm, OD = 0.03
  + So 254 is attenuated some, but less than 185
- What's on the toy model
  + @ 185 nm = 2e13 photons / cm2 /s
  + @ 254 nm = 2e14 photons / cm2 /s

Absorption Cross sections

- Absorption cross section of O2 @ 185 (>> than O3)

+ *Bill is using: 1.1e-20*
+ Mainz database: 3e-21 @ valley to 1.3e-19
http://www.atmosphere.mpg.de/enid/fe583030ac1819fa021d4447742ff0a4,0/Spectra/Catalogue_Spectra_5p4.html
+ Brasseur and Solomon: 2e-22 to 2e-20

- Cross section of H2O @ 185 nm
+ Bill is using 7.01e-21
+ *JPL evaluation = 5.5e-20 (same as Mainz database)*
+ Yung book = 1e-20
+ Brasseur + Solomon = 3e-20

- Amber calculates the default case w both H2O cross sections:
+ OHexp = 1.3e12, O3 = 15 ppm
+ OHexp = 2.8e12, O3 = 14 ppm
+ If she also uses 4e13 p/cm2/s for 185 nm, she gets OHexp = 3.4e12 & O3 = 27.5 ppm

Email to Bill

Hi Bill,

We are working on the toy model and comparing to experiments, lamp fluxes etc. and have a few quick questions. In particular the toy model produces 5 times lower OH exposure than Amber's calibration equation.

(1) The toy model uses Flux_185 = 1/10 * Flux_254. However the lamp has power_185 = 50% * power_254 (http://www.bhkinc.com/literature/AnImpDS_101010.pdf). We estimate from the O2 absorption that the optical depth at 10 cm is 0.58, so the effective power should be 30%, not 10%. Comments?

Also, did you measure the light fluxes? Calculating from the lamp specs and a typical distance of 10 cm, we estimate the fluxes at 185 and 254 as: 2.4e14 and 4.6e14 photons/cm2/s, while you are using 2e13 and 2e14. A slightly higher flux at 185 would produce results more consistent with the observations.

(2) Do you know the width of the emission line of this lamps? (Even better, do you have that spectral shape?) This matters in terms of determining the actual photolysis rate for O2, since the spectrum is highly structured in this region:

http://www.atmosphere.mpg.de/spektrum_image3.php?subkat=&kat=Oxygen&file=O2_SchumannRunge%2812-0%29+to+%289-0%29_lin.JPG

(3) For water you have a cross section of 7e-21 cm2, but the JPL and MPI datasets indicate 5.5e-20. If we use the JPL value, the model produces higher OH and the same O3, and it gets closer to our calibration equation. E.g. see:

http://www.atmosphere.mpg.de/spektrum_image3.php?subkat=&kat=Hydrogen%2Bwater&file=H2O_180-200nm_log.JPG
http://jpldataeval.jpl.nasa.gov/pdf/JPL%2010-6%20Final%2015June2011.pdf

(4) Have you evaluated the toy model against Eunha's or other measurements?

Photolysis of other species

- For 254 nm a given molecule with a cross section of 1e-17 cm2 (max in practice), times a flux of 5e14 p/cm2/s, the photolysis lifetime is 200 seconds. At 1e-19, it is 20000 s.
    + @ 254 nm, HNO3 = 1.95e-20; CH2O = 3.4e-21; acetaldehyde = 1.57e-20; other aldehydes and ketones (FP) ~ 1e-20; H2O2 = 8e-20; TBP 2e-20; NO2 = 1.05e-20
        - All of these have a lifetime of many hrs under our conditions

- For 185 nm the flux is likely more 2e13, lifetime is 5000 seconds for 1e-17
    - Residence time is 180 s, so only 4% would be photolyzed
    + Anything with a lower cross section is reduced proportionally
    + @ 185, HNO3 = 1.4e-17; NO2 = 5e-18; H2O2 = 1.1e-18; TB peroxide = 4.2e-19; CH2O = 4.2e-18; acetaldehyde = 1.0e-17
    + Doug should find MHP and any other peroxide cross sections

http://www.atmosphere.mpg.de/enid/7dc0bd0a0dcf47ecdfc3217c28c2a135,2e82695350454b5452554d5f6b6174092d095065726f7869646573093a095f7472636964092d093531363939/Spectra/Catalogue_Spectra_5p4.html

Examples:

Peroxides sigma:	254 nm	185 nm
H2O2	8E-20	9.0E-19
methyl hydro peroxide	3E-20	??
tert-butyl peroxide	2E-20	4.2E-19
dimethyl peroxide	1.6E-20	??
di-tert-butyl peroxide	2.4E-20	??
HMHP	3.0E-20	??

(HMHP = hydroxymethylhydroperoxide)

Per further discussions with Bill, AAAR PAM meeting, etc. considering photolysis at 254, it was pointed out that substituted aromatics may have some of the largest 254nm cross sections (e.g. Trost et al. '97). A few seem to photolyze as much as 10-90%; however, it can be shown that probably under all conditions of the PAM OH photolysis is >10x's faster still (see Excel spreadsheet that Doug sent to group demonstrating this: "PhotOxInPAM_121012.xlsx").

Cross sections for aromatics at 185nm:
There is strong absorption of aromatics centered right around 185nm. Cross sections for benzene, toluene, xylenes, TMB are around 1e-17 to 1e-16. So we may want to keep on eye on that as we think about this.

The phenolic aromatics (e.g. phenol, p/m/o-cresols) that were discussed with the other PAM folks in this email thread have cross sections of ~1e-17 which can lead to up to 10-90% loss in

PAM, however we as discussed, it appears that for probably all conditions, OH oxidation is always >10x's faster.

Thus, the same logic should apply for the 185nm photolysis at ~1e-16
cross sections since the 185nm flux is 10x's less than that at 254nm.

Non-phenolic aromatic VUV cross sections:
http://www.atmosphere.mpg.de/spektrum_image3.php?subkat=Benzene&kat=Aromatic+compounds&file=C6H6_VUV_log.JPG
http://www.atmosphere.mpg.de/spektrum_image3.php?subkat=Alkyl-%2Cvinylbenzenes&kat=Aromatic+compounds&file=%28CH3%29C6H5_VUV_log.JPG
http://www.atmosphere.mpg.de/spektrum_image3.php?subkat=Alkyl-%2Cvinylbenzenes&kat=Aromatic+compounds&file=p-%28CH3%292C6H4_VUV_lin.JPG
http://www.atmosphere.mpg.de/spektrum_image3.php?subkat=Alkyl-%2Cvinylbenzenes&kat=Aromatic+compounds&file=m-%28CH3%292C6H4_VUV_lin.JPG
http://www.atmosphere.mpg.de/spektrum_image3.php?subkat=Alkyl-%2Cvinylbenzenes&kat=Aromatic+compounds&file=o-%28CH3%292C6H4_VUV_lin.JPG
http://www.atmosphere.mpg.de/spektrum_image3.php?subkat=Alkyl-%2Cvinylbenzenes&kat=Aromatic+compounds&file=1%2C2%2C4-%28CH3%293C6H3_VUV_lin.JPG

Rui runs toy model w/ arrow diagram
- Hard OH default:
    + radicals fed by J_H2O -> OH + HO2, then by O3 photolysis. Both important

(Lots of discussions on toy model)

Action Items from meeting
- Jose will ping Bill if he doesn't reply to our email
- Doug will look for additional absorption cross sections for peroxides and other organics
- Rui will update the plots of the toy model as discussed, then send to Jose
- Amber will dig conditions and results of calibrations (SO2 decay, O3 output) for calibration of the toy model

Points of discussion for next time
- Is water cross section wrong? (per email to Bill)
- How to tune toy model with observations? Use O3 formation to constrain flux_185 while SO2 constrains OH exposure

Topics for PAM gas-phase kinetic paper:

- Temperature dependence of lamps (x2 more O3 observed at night in BEACHON and CalNex);

this temperature dependence should be picked up in cal equation but not T-dependant chemistry (see below)

- OH reactivity:

- the cal equation also doesn't pick up the OH suppression due to increased reactivity. O3 actually increases as you add reactivity because the reduced OH leads to less destruction of O3 via O3 + OH which is fast. HO2 increases but HO2 + O3 is slower. So we need a term in the cal equation which decreases OHexp as a function of OH reactivity.

- all reactivity not same (i.e. organics vs NOx: NOx directly destroys HOx, organic mostly recycle

- Temperature dependant chemistry (see Jose's email to Bill et al 10/26/12):

- For "hard OH" increasing T results in very small O3 change, but it INCREASES ~2% rather than decrease when it gets warmer.
- OH exposure does DECREASE 25% for this large temperature change (the sign and magnitude of this are similar to Bill's results). For the more typical range of 15-20 K day to night in the field, OH exposure will change maybe 10% due to this effect. The calibration equation WILL NOT pick up this effect according to the toy model since H2O is the same and O3 doesn't change. However the actual change in O3 is much larger, so that's what we need to constrain better.
- HO2/OH ratio increases x2 from 0 to 50C. This may not matter very much since HO2 is so high anyway and will dominate the RO2 reactivity.
-the model does NOT have yet is T-dependence of the photolysis cross sections. Bill, do you have some previous info on those?