

Interactive comment on “Controlled nitric oxide production via O(¹D)+N₂O reactions for use in oxidation flow reactor studies” by Andrew Lambe et al.

Anonymous Referee #1

Received and published: 6 February 2017

The manuscript, "Controlled nitric oxide production via O(¹D)+N₂O reactions for use in oxidation flow reactor studies" by Lambe et al. presents a creative concept for generating and maintaining a more realistic level of NO in atmospheric simulation experiments. The work is presented neatly, figures constructed meticulously. The idea presented here would be useful for the atmospheric chemistry community, but in the way the technique is currently described, the advantages gained from this technique over previous ones do not seem like significant progress. The work deserves publication following some revisions and clarifications.

The main issue I find with this work is that it completely missed the opportunity to demonstrate the effectiveness of this newly proposed technique with actual measure-

C1

ments of NO and N₂O. This seems particularly egregious given the moderate range of NO modeled here (figure 1) that is not difficult to measure directly. Was a NO instrument not available when this work was conceived? Wasn't producing and maintaining a predictable amount of NO the objective here? Why not show that you achieved this with observations, in addition to model? Moreover, measurement of N₂O, specifically, the decrease in N₂O mixing ratio with increasing radiation intensity would have been helpful to ensure that N₂O reaction and photolysis were indeed the reason for the observed changes in CIMS spectra. These two measurements of NO and N₂O would have been more convincing than the results from the CIMS, which I find less than convincing, if not, altogether unnecessary.

The level of O₃ (500 ppb to 50 ppm) required to generate enough O(¹D) is still much too high to simulate anything that resembles atmospherically realistic conditions. Limitations are two-fold that I can think of: (1) Given ppm levels of O₃, oxidation by ozonolysis can compete with OH oxidation making systematic study of one oxidation pathway versus the other difficult. (2) NO to NO₂ ratio also deviates from ambient, such that oxidation by NO₃ radical becomes non-negligible (along with production of HNO₃, peroxyacetyl nitrates, etc.). This, the authors note could be as high as 40% of the total oxidation by OH, O₃ and NO₃ combined. Perhaps the BVOC products from OH vs O₃ vs NO₃ can be separated using CIMS data, but the presence of different RO₂ isomers resulting from each oxidant that may react with one another (RO₂+RO₂) may mean this simple attribution may not be possible, particularly if the products possess different functional group but same molecular composition. The ppm O₃ levels used here also seem at odds with statements in the abstract and elsewhere in the manuscript that seem to suggest that ppm levels of O₃ are bad (lines 1-5), and that this proposed technique doesn't require ppm O₃ levels. In any case, have the authors attempted to run the chamber without O₃? What is the highest level of NO achieved by percent levels of N₂O due to direct photolysis? Given that most suburban+rural+remote regions experience highest NO levels less than 0.5 ppb, perhaps just N₂O and ambient level of O₃ would suffice? This approach may not be suitable for flow reactors, but it may be

C2

for the more traditional atmospheric simulation chamber studies.

The CIMS data show that, yes, as you increase NO, the level of organic nitrates increase, and levels of most organics without a nitrate decreases. This is not surprising. What is missing is that this method of NO generation by N₂O in the flow reactor can demonstrate atmospherically relevant chemistry. If CIMS is the instrument of choice, the authors need to compare CIMS spectra of the flow reactor and one that was obtained from ambient atmosphere.

The discussion sections on the types of oxidation products observed are less than convincing, lacking the detailed mechanism discussions typically included in such studies. As such, these sections read more like speculation. Does the model account for RO₂ chemistry? Is there a model output for the various organic molecular compositions observed or at least groups of organics (i.e. Krechmer 2015 ES&T)?

How much of NO:HO₂ changes (x-axis; figures 4 and 5) are due to the reaction of NO with HO₂? Is RO₂ accounted for in the calculation of NO and HO₂?

Figure 2, judging from the y-axes, much higher signal levels are observed at higher I254. Is this the result of production of later-generation oxidation products? Or just more complete oxidation? Was the amount of parent BVOC oxidized measured?

Figure 4 is misleading. From what I understand, the CIMS identifies molecular compositions but cannot assign structure/isomer/functional groups. What is the source of the drawings on top of figure 4? How were they determined?

Interactive comment on Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2016-394, 2017.