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Interactive comment on "Iodine chemistry after dark" *by* Alfonso Saiz-Lopez et al.

Anonymous Referee #3

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Review of the Manuscript entitled: Iodine chemistry after Dark By A. Saiz-Lopez et al.

The manuscript describes new model calculations on the atmospheric chemistry of reactive iodine species encompassing a hypothetical reaction (R4) NO3 + HOI → IO + HNO3. The possibility of R1 actually occurring is investigated by molecular structure reactions. Moreover some possible discrepancies between observations and model calculations based on "conventional" I-chemistry may be solved by including R1.

The bulk of the manuscript is devoted to a comprehensive study of the consequences of introducing R4 (along with the earlier suggested reaction R1) in two models (1D and 2D). While one may ask whether a study based on a hypothetical reaction is warranted, I feel that the manuscript contains valuable material, which is within the scope of ACP and of interest to the scientific community. However, the manuscript contains a number of errors and unclear points (see list below) which must be corrected before publication. Also, given its speculative nature the manuscript is much too long and should be

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shortened considerably. This could be done by for instance removing most of the plots based on the 2D model calculations.

In detail there are the following deficiencies:

1) Page 4, lines 16, 17: Dawn spike of NO_3 not seen in measurements: Are these data conclusive? The spike is only short and the quoted measurements had comparatively poor temporal resolution. It should also be noted that atmospheric stability over the ocean is low at night because the atmosphere cools radiatively while the ocean surface temperature stays virtually constant (this is quite opposite to land conditions). Thus the IO precursors might simply be diluted during the night. Since much of the manuscript hinges on the absence of the IO spike these points must be discussed.

2) Page 5, first two paragraphs of section 2: Here the description is not sufficiently clear, the way this reviewer understands it is: R1 is hypothetical, but its consequences were investigated earlier. In this work R2 – R4 are studied by molecular modelling finding that only R4 might play a role. In the rest of the manuscript, therefore the effects of including R1 + R4 are studied in detail.

3) Page 8, lines 9 to 13: How can the rate constant of R4 be only uncertain by a factor of 2 when the overall exothermicity of R4 is 11 KJ/mole (page 7, line 4) while the (one sigma?) uncertainty in the overall energy is 10 KJ/mole (page 6, line 15) and thus may be as low as 1 KJ/mole?

4) Page 11, lines 10-12: The "significant increase of the sea-air flux of HOI and I2" might simply be an effect of the parameterisation of the process: Is the flux of the two species just given by the concentration difference between the two phases or is it (partly) determined by the rate of formation of the species? If the latter is the case then the flux might not change at all (or less than assumed by the model). This point needs discussing.

5) Page 12, lines 14 to 15: See comments about the "dawn spike" above.

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6) Page 13, lines 8 to 11 and Fig. 6: It is not clear how the authors come to this conclusion: Fig. 6 is drawn on a semi-log scale and shows that (delta NO3/NO3) / (delta k4/k4) is about 1/300. In other words a factor of 2 change in the rate constant of R4 has negligible effect (less than 1% change) on the NO3 concentration (or mixing ratio).

7) Page 13, lines 15 to 16 and Fig. 7: It is unclear what exactly is plotted in Fig. 7. (a) is it (calculated mixing ratio without R1, R4) minus (calculated mixing ratio including R1, R4). (b) Which mixing ratio is actually shown? Is it the surface value or the vertically averaged (over which altitude range?) mixing ratio? The caption of Fig. 7 uses the term "vertical mixing ratio", which is unknown to this reviewer.

8) Page 14, line 1 and Fig. 8: See comment to Fig. 7. Also, here the text refers to "nighttime averaged differences" as opposed to 0AM to 1AM differences referred to in the explanation to Fig.7. This must be clarified.

9) Page 14, lines 9 to 11: The calculations about changes in NO3 levels are already speculative, to calculate changes in DMS (and other species) appears to be even more speculative (and not unexpected if one believes in the results regarding NO3). Therefore Fig. 9 adds little information and distracts from the main thrust of the manuscript, it should be removed.

Minor points:

Page 3, lines 15-18: This appears to be too many reference for a topic (iodine particle formation) that is not mentioned later in the manuscript.

Page 4, line 5: Organic precursors contribute 1/3?

Page 5, line 2 and following: What about BrO + DMS? The role of this reaction is neither mentioned nor discussed in the manuscript.

Page 8, lines 14 to 17: The NO3 + CH2I2 reaction can not be ruled out on the basis of the rate constant of NO3 + CH2I2 being smaller than that of R4 since the concentration of CH2I2 may be higher than that of HOI.

Page 9, line 2: Clarify that “this new chemistry” only means the introduction of R4.

Page 11, line 7: How much better is the agreement?

Page 11 line 13: The term “uptake” means aerosol uptake?

Page 11 line 13 to page 12, line 10: The discussion of aerosol uptake appears to be out of place in the results and discussion section.

Page 12, line 11 and Fig. 5: IONO2 appears to be wrongly labelled as NO3.

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