Interactive comment on “Iodine chemistry after dark” by Alfonso Saiz-Lopez et al.

We thank Dr. Louis for the insightful comments. Below we provide a detailed point-by-point answer (AC – Author Comment) to each comment on our manuscript (RC – Referee Comment).

RC:

This paper presents a very interesting study on the iodine atmospheric chemistry using two modelling approaches: one at the molecular level, one at the global level. The potential energy surfaces for three different reactions were explored for the first time by theoretical calculations: HOI + NO_2, HOI + HNO_3, and HOI + NO_3. I have several comments concerning this work. 1) Spin-orbit correction (SOC) is very important for iodine-containing species. The authors stated on page 6 line 12 that "spin-orbit splittings of -17 and -5 kJ mol-1 were applied to energies of I and IO". These values do not correspond to the well-known value for I atom (-30.3 kJ mol-1 from C.E. Moore, Atomic Energy Levels, USGPO, Vols. II and III. NSRDS-NBS 35, Washington, DC, 1971). Over the last years, my group performed theoretical calculations to get the SOC values for numerous iodine-containing species using the CASPT2/RASSI methodology. The corresponding values for I, IO, and HOI are -30.0, -14.4, and -5.9 kJ/mol (Meciarova et al., CPL, 2011, 517, 149; Khanniche et al., JPCA, 2016, 120, 1737; Sulkova et al., JPCA, 2013, 117, 771). These calculations were also validated by comparison to few available data. I recommend the authors to update their energetics according to the correct SOC values. 2) In Table 2, there are several low frequency modes for molecular complexes and transition state. Are they among them one or several which should be treated as hindered rotors? It is also interesting to compare calculated vibrational frequencies for HOI, NO3, IO, HNO3 with their available experimental counterparts. 3) Nitrogen oxides also exhibits often an instability of the wavefunction (internal or RHF -> UHF). Is-it the case here for all stationary points? This instability will affect the energetics. The Gaussian09 software includes an option to check it. 4) What is the level of theory used for the energetics? It is not clear.

AC:

Response to Comment 1: the sentence on page 6 should have read spin-orbit “corrections” rather than “splittings”. The sentence has now been rephrased to make this clear.

Response to Comment 2: we not treat the low frequency modes in the HOI-NO_3 and IO-HNO_3 complexes as hindered rotors. In our experience, this level of sophistication in RRKM calculations is only warranted if experimental rate coefficients are available, to which hindered rotor barrier heights can be fitted (ab initio barrier heights are generally not accurate enough).

We have added the following sentence on page 7, line 18 to make these points.

We have previously compared the calculated vibrational frequencies of iodine-containing molecules with available experimental data [Plane et al., 2006], and found this level of theory to be good enough for the purpose of this study.

Response to Comment 3: the nitrogen oxides of relevance to this study are HNO_3 (which does not exhibit an RHF → UHF instability at the level of theory used), and NO_2 which is a radical.

Response to Comment 4: the energetics are determined at the same level of theory as the geometry optimisations and vibrational frequency calculations. This is made clearer on page 6.

RC:

Concerning the atmospheric modelling, the reaction of NO_3 with iodocarbons is important as noticed on page 8 line 15, it could be also important to see if adding the reactivity of atmospheric VOC with iodine-containing species will affect the results because this reaction will produce iodocarbons.

AC:

As stated in the referred paragraph, there are many uncertainties about the products of these reactions, and in the case of the NO_3+CH_2I_2 reaction the rate constant is significantly slower than R4. Therefore we have decided not to include these reactions due to the lack of information in the bibliography.

Interactive comment on “Iodine chemistry after dark” by Alfonso Saiz-Lopez et al.

We would like to thank Howard Roscoe for his comments and support. Below we provide a detailed point-by-point answer (AC – Author Comment) to each comment on our manuscript (RC – Referee Comment).

RC:

This paper makes an important point about atmospheric chemistry. It is scientifically sound and rigorous except for the few items in Minor Comments, and except perhaps for the theoretical calculations in Section 3 on which I am not competent to express an opinion. It is also well written, except for the trivia listed under Editorial Comments below.

Provided it receives a satisfactory review from experts in calculation of reaction rates, I have no hesitation in recommending it for publication in ACP after minor revision.

Minor comments:

RC:

1. p14 line22 - according to the caption of Figure 11 (p39) it applies to the region 110 to 106degE and 16 to 23degN. This region just touches the southern tip of Baja California but is centred a long way to its south. It just touches a coastal region of mainland Mexico, but is never at the “coastal region” even of Mexico let alone the stated Baja California - much of the region is in what might be called the open ocean. Presumably this region is chosen because of the large pollution amounts there that we infer from Figures 7, 8 and 9; but there is no discussion of why they should be so large - is it a concentration of shipping using the Panama Canal that spreads out further north?

AC:

The text and the caption have been changed to refer to an Ocean Pacific Region at the south of Baja California, instead of a “coastal region”. As pointed out by the reviewer, that zone was selected due to the high levels of NO_3 caused by pollution outflow from the west coasts of Mexico and USA and shipping lanes.

RC:

2. p6 line21 - given the argument of p6 lines17-18, why does a transition state 110 kN/mole above the reactants allow the reaction to proceed?

AC:

Please note that in that paragraph at the end of page 6 we are not saying that reaction 3 is viable. In fact we conclude at the end of the theoretical calculation section that only reactions 1 and 4 are likely to proceed.

RC:

3. Why do Figures 4 and 5 have time co-ordinates starting at 48 hours? Is this to allow a steady state to build up? - if so it should be discussed. And what version of time is it - time since midnight or time since noon? - a careful reading of text and figures tells us which, but it should be spelled out in the caption. And why do Figures 10 and 11 have time co-ordinates that start at 0 hours rather than 48? And although we can guess that time in Figures 10 and 11 is since midnight, is it mean solar midnight over the region, or solar midnight at the geographic centre of the region, or midnight in the local time zone at 108degE?

AC

Figure 4 and 5 represent data from the 1-D THAMO model, whereas figures 10 and 11 contain data from the 3-D CAM-Chem model. In a 1D model like THAMO 2 days of simulation are enough to reach steady conditions, so we have plotted the third day of simulation. On the other hand the 3D global model CAM-Chem needs at least 1 year to reach steady conditions throughout the marine troposphere. So we have run CAM-Chem for two years and then used the data from the second year. Figures 10 and 11 contain hourly averaged data during August and January respectively. Therefore we have used a more general local time 0-23 hours scale for Figure 10 and 11.

RC:

4. We are told in the text (p14 line2) that Figure 8 has “as in the previous figure”.. “nighttime averaged differences”, yet p13 line17 tells us that the previous figure, Figure 7, uses “midnight averages”. Which are used in which figures, and why do the captions not spell out the averaging hours as opposed to having them buried in the text?

AC:

Both Figure 7 and 8 correspond to night time averages from 0LT to 01LT. We have changed the text in p13 line17 to “nighttime averaged”. We decided not to include that data in the caption to avoid repetition of information.

Editorial comments:

RC:

p3 line3 introduces and defines MBL but it was already used without definition on p2 line15.

AC:

MBL defined for the first time in P2 line 15.

RC:

p3 line10 - surely, hyphens after “iodine” and “bromine” ?

AC:

Typo corrected

RC:

p4 line2 - delete “and”

AC:

Typo corrected.

RC:

p6 line12 - insert “of” after “energies”.

AC:

Typo corrected

RC:

p7 line13 - insert “the” after “of”.

AC:

Typo corrected

RC:

Fig4 lowest panel - the meanings of the four lines are not in the caption and their panel legends are obscure.

AC:

More information has been included in the caption to make the bottom panel clearer.

RC:

Figs 7, 8 and 9 - the captions do not say the altitude or the vertical extent of the averaging.

AC:

Included “at the surface level” at the end of the caption.

RC:

Fig10 - the right hand axis legend says “mixing ration”.

AC:

Typo corrected.

RC:

Fig10 caption - insert “the” after “at”.

AC:

Typo Corrected.

RC:

Fig11 caption - say the altitude.

AC:

Included “at the surface level” at the end of the caption.

Interactive comment on “Iodine chemistry after dark” by Alfonso Saiz-Lopez et al.

We thank the reviewer his/her time to carefully read through and for the comments. Below we provide a detailed point-by-point answer (AC – Author Comment) to each comment on our manuscript (RC – Referee Comment).

RC:

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

AC:

Even though this work is based on modelling studies, we consider that all the information contained in this manuscript is necessary to present the new proposed reaction scheme and assess its effects on nighttime chemistry. Therefore we prefer to keep the manuscript as it is, regarding number of figures. The 3D model plots constitute a helpful way to show the global effect of this nighttime chemistry, so we also prefer to keep them in the manuscript.

In detail there are the following deficiencies:

RC:

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.

AC:

We assume that the reviewer is referring to the "dawn spike" in IO, rather than NO_3 as written in the comment. While the Read et al., 2008 and the Mahajan et al., 2010 papers present the hourly averaged diurnal profiles of IO at CVAO, the observations were made at a higher temporal resolution of 30 s. The observations made at higher temporal resolution also did not detect any IO above the detection limit, which was about 1 pptv for the 30 s data. Hence we feel that this is not a case of dilution, but rather the absence of an IO spike.

RC:

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.

AC:

We are not saying in those paragraphs that R1 is hypothetical. In fact R1 was already included in the Saiz-Lopez et al., 2014 study. What we are doing is studying the feasibility of reactions R2-R4, and after checking that only R4 is viable, we study the effects of the nighttime R1 and R4 reactions using the THAMO and CAM-Chem models.

RC:

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?

AC:

Sentence changed to: "The absence of a barrier above the entrance channel, and the fact that the intermediate complexes and barrier are well below the entrance channel within their uncertainties, means that the uncertainty in k_4 principally arises from the estimated capture rate coefficient and so is likely to be no more than a factor of 2."

RC:

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.

AC:

The flux is given by the species concentration difference between the two phases.

RC:

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

AC:

Please see answer above.

RC:

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 O3/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).

AC:

This is correct. The sentence is wrong. It should be over two orders of magnitude change in K_4 leads to a factor of two change in NO_3. This has now been corrected in the manuscript.

RC:

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.

AC:

The plot is showing the difference in volume mixing ratio (for HOI and I_2) between the simulation including R1,R4 and the simulation without R1,R4.

We are showing the surface level mixing ratio averaged from 0 to ~150m altitude. The caption of figure 7 has been modified to include “at the surface level”, and the typo “vertical mixing ratio” has been corrected to “volume mixing ratio”.

RC:

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

AC:

Figure 8 is the same as figure 7 but for $IONO_2$ and NO_3. Nevertheless, for consistency we have changed in P13 line 17 “midnight averaged” for “nighttime averaged” in the reference to figure 7.

RC:

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.

AC:

Even though the effect on DMS is not the main point of this work, we consider interesting to show the possible different ramifications of the new scheme, in this case how continental pollution outflow could affect DMS levels both geographically and quantitatively. The purpose is to show that this nighttime chemistry could potentially have an important impact on the nocturnal oxidizing capacity of the MBL.

Minor points:

RC:

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.

AC:

Certainly there are too many references. We have now removed several of them.

RC:

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

AC:

Indeed they contribute ¼. Corrected to “only up to a fourth”.

RC:

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

AC:

We think this reaction is not within the scope of this work, although is part of the model´s chemical mechanism.

RC:

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.

AC:

Even though [CH_2I_2] could be higher than [HOI], the products of the reaction NO_3+CH_2I_2 are uncertain, as reported in the bibliography. So for now we have decided not to include that reaction in the models.

RC:

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

AC:

We are using the 1D and 3D models to study the nocturnal effects of R1 and R4, not just R4. Previously we have theoretically studied the feasibility of two other reactions. Nevertheless the impacts of these reactions on the nocturnal oxidizing capacity of the atmosphere in marine regions affected by continental pollution outflow is considerable, affecting the levels of NO_3, HOI, I_2 and $IONO_2$ (among others). That is why we consider it “new chemistry”. We will further clarify this point in the revised manuscript.

RC:

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

AC:

Lawler et al.; 2014 reported I_2 values of ~1 pmol mol^{-1} (ranging from 0.02 to 1.67 pmol mol^{-1}), so the results in figure 4 for the scenario including R1 and R4 are in better agreement than those for the scenario without R1 and R4. The modelled results without R1 and R4 are three times higher than Lawler et al., 2014 measurements.

RC:

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

AC:

Certainly, we have included “on aerosols” after “the uptake”.

RC:

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.

AC:

We have now moved this discussion to the end of the “Atmospheric modelling” section.

RC:

Page 12, line 11 and Fig. 5: $IONO_2$ appears to be wrongly labelled as NO3.

AC:

This has been corrected in Fig 5.

Interactive comment on “Iodine chemistry after dark” by Alfonso Saiz-Lopez et al.

We thank the Referee for his/her comments. Below we provide a detailed point-by-point answer (AC – Author Comment) to each comment on our manuscript (RC – Referee Comment).

RC:

Saiz-Lopez et al. investigate the nighttime chemistry of iodine. The study is very interesting and I recommend publication in ACP after considering several changes as described below.

- Title:

I find the expression "after dark" quite unusual for a scientific paper. Why not simply call it "nighttime chemistry"?

AC:

Thank you for the suggestion about the title change, however we prefer to keep the title as is.

RC

- Section 4:

Instead of presenting the full chemical mechanism, the authors refer to 6 previous publications. I find it quite tedious that I have to obtain and read 6 additional papers if I want to check the currently used mechansim. I suggest to provide the full mechanism (exactly as it was used in this study) together with this paper, e.g. in the supplement.

AC:

As the reviewer suggests, we have included the full iodine chemistry scheme in a supplementary information document. The scheme is referenced in page 22 line 12 in the main text.

RC:

- Page 11, line 1:

It is said that "HOI peaks during the daytime". I think a better description would be to say that it peaks just before sunset. What is the reason for the sunset peak?

AC:

We have modified that phrase to “HOI is present during daytime, due to its production through the reaction of IO with HO_2, and peaks just before sunset” as suggested by the reviewer.

The main loss channel for HOI is the photolysis to atomic iodine. Therefore before sunset the solar radiation intensity decreases and this channel is less effective. Another important loss channel for HOI is the heterogeneous reaction with halide anions on aerosols. After sunset the precursor IO is not formed, and consequently the HOI levels drop.

RC:

- Page 11, lines 13-14:

"It should be noted that during nighttime the uptake of emitted species such as I2 and HOI, and the uptake of reservoir species such as IONO2, can play a major role in the cycling of iodine."

What is meant by "uptake"? Uptake on aerosols? On clouds?

AC:

In this paragraph we are referring to uptake on aerosols. We have now mentioned in the paragraph that we are referring to aerosols.

RC:

- Page 11, line 21:

The outdated JPL recommendation Sander et al. 2006 is cited here for mass accommodation coefficients. Has it been checked if there are any updates in the current recommendation JPL 2015?

AC:

Yes, we have checked the mass accommodation coefficients but they haven’t been updated.

RC:

- Page 12, lines 16-17:

"The IO dawn spike [...] is due to a buildup of the emitted I2 and HOI [...] over the night".

I cannot see a buildup of HOI in Fig. 4.

AC:

Perhaps it is difficult to appreciate, but the levels of HOI in figure 4 for scenario 1 never drop to zero during the night. Note that at midnight the levels are between 4 and 5 pmol mol^{-1}, and from 0:00 to 6:00 hours the concentrations only drop to 3.5 pmol mol^{-1} in the lowest levels of the model. This situation is different from scenario 2, in which [HOI] at midnight is around 1 pmol mol^{-1}, and drop to values close to zero at 6:00 hours. So we believe that there is a substantial difference between the two scenarios when it comes to [HOI], with a considerable buildup of HOI during night for scenario 1.

RC:

- Page 12, line 21:

"Reactions R1 and R4 also reduce the NO3 mixing ratio (Fig. 4, middle panels)." Should this be Fig. 5?

AC:

Certainly, typo corrected.

RC:

- Page 13, line 17:

Please define "LT".

AC:

LT refers to Local Time.

RC:

- Table 2: The numbers listed here are probably wave numbers, not vibrational frequencies.

AC:

It is customary to quote vibrational frequencies as wave numbers. There is a mistake in the footnotes, which should be:

[a] Cartesian co-ordinates in Å. [b] In cm^{-1}. [c] In GHz. [d] In kJ mol^{-1}, including zero-point energy and spin-orbit coupling of I and IO (see text).

RC:

- Figs. 4 and 5: A color scale should be shown. Also, it would be easier to compare the left hand panels with the right hand panels if the same color scale was used.

AC:

Thanks, however we respectfully think that the figure is clear enough as is, the numbers are shown in the plots.

RC:

- Fig. 5: For consistency, the name IONO2 should be used in the plots, not INO3.

AC:

We have corrected Fig 5.

RC:

- Fig. 7: What is a "vertical mixing ratio"?

AC:

Thanks, it is a typo. Corrected in the caption of figure 7 to “volume mixing ratio”.

RC:

- Figs. 7,8,9:

"without reactions (1) and (2)"

Should this be "without reactions (1) and (4)"?

AC:

Indeed, we are referring in the caption to reaction 1 and 4. The typo has now been corrected.

Iodine chemistry after dark

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Abstract

Little attention has so far been paid to the nighttime atmospheric chemistry of iodine species. Current atmospheric models predict a buildup of HOI and I_2 during the night that leads to a spike of IO at sunrise, which is not observed by measurements. In this work, electronic structure calculations are used to survey possible reactions that HOI and I_2 could undergo at night in the lower troposphere, and hence reduce their nighttime accumulation. The new reaction NO_3 + HOI → IO + HNO_3 is proposed, with a rate coefficient calculated from statistical rate theory over the temperature range 260 - 300 K and at a pressure of 1000 hPa to be $k(T) = 2.7 \times 10^{-12} (300 \text{ K} / T)^{2.66}$ cm^3 $molecule^{-1}$ s^{-1}. This reaction is included in two atmospheric models, along with the known reaction between I_2 and NO_3, to explore a new nocturnal iodine radical activation mechanism. The results show that this iodine scheme leads to a considerable reduction of nighttime HOI and I_2, which results in the enhancement of more than 25% of nighttime ocean emissions of HOI + I_2 and the removal of the anomalous spike of IO at sunrise. We suggest that active nighttime iodine can also have a considerable, so far unrecognized, impact on the reduction of the NO_3 radical levels in the marine boundary layer (MBL) and hence upon the nocturnal oxidizing capacity of the marine atmosphere. The effect of this is exemplified by the indirect effect on dimethyl sulfide (DMS) oxidation.

1. Introduction

Active nighttime iodine chemistry was first evidenced a decade ago when it was shown that nocturnal I_2 emitted by macroalgae could react with NO_3 leading to the formation of IO and OIO, which were measured in the coastal ~~marine boundary layer (~~MBL~~)~~ at Mace Head, Ireland (Saiz-Lopez and Plane, 2004). The nitrate radical has also been recently suggested as a nocturnal loss of CH_2I_2, which helps to reconcile observed and modelled concentrations of this iodocarbon over the remote MBL (Carpenter et al., 2015). However, most of the work on reactive atmospheric iodine has focused on the use of daytime observations and models to assess its role in the catalytic destruction of ozone and the oxidizing capacity of the troposphere (e.g. Saiz-Lopez et al. (2012b) and references therein). In the MBL, iodine, along with bromine, catalysed ozone destruction contributes up to 45% of the observed daytime depletion (Read et al., 2008; Mahajan et al., 2010a), although this contribution shows large geographical variability (Mahajan et al., 2012; Gómez Martín et al., 2013; Prados-Roman et al., 2015b; Volkamer et al., 2015). Iodine compounds have also been implicated in the formation of aerosols, although the mechanisms and magnitudes of these processes are not fully understood (O'Dowd et al., 2002; McFiggans et al., 2004; Saunders and Plane, 2005; Pechtl et al., 2006; Saiz-Lopez et al., 2006; Mahajan et al., 2009a; Hoffmann et al., 2001; Gomez Martin et al., 2013; Sommariva et al., 2012; Allan et al., 2015; Roscoe et al., 2015). Reactive forms of inorganic iodine may also contribute to the oxidation of elemental mercury over the tropical oceans (Wang et al., 2014). In recent years, iodine sources and chemistry have also been implemented in global models demonstrating the effect of iodine chemistry in the oxidation capacity of the global marine troposphere (Ordóñez et al., 2012; Saiz-Lopez et al., 2012a; Saiz-Lopez et al., 2014; Sherwen et al., 2016).

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Iodine is emitted into the atmosphere from the ocean surface in both organic and inorganic forms. The main organic compounds emitted are methyl iodide (CH_3I), ethyl iodide (C_2H_5I), and propyl iodide (1- and 2-C_3H_7I), chloroiodomethane (CH_2ICl), bromoiodomethane (CH_2IBr), and diiodomethane (CH_2I_2) (Carpenter, 2003; Butler et al., 2007; Jones et al., 2010; Mahajan et al., 2012). However, these organic compounds contribute only up to a fourth~~third~~ of the MBL iodine loading (Großmann et al., 2013; Mahajan et al., 2010a; Jones et al., 2010; Prados-Roman et al., 2015b). Inorganic emissions of HOI and I_2, which result from the deposition of O_3 at the ocean surface and subsequent reaction with I^- ions in the surface microlayer, account for the main source of iodine in the MBL (Carpenter et al., 2013). Recent laboratory experiments have shown that HOI is the major compound emitted, and provided parameterizations of the fluxes of both species depending on wind speed, temperature, and the concentrations of O_3 and I^- (Carpenter et al., 2013; MacDonald et al., 2014). These parameterized fluxes of HOI and I_2 have then been used in a one-dimensional model to study the diurnal evolution of the IO and I_2 mixing ratios at the Cape Verde Atmospheric Observatory (CVAO) (Carpenter et al., 2013; Lawler et al., 2014). The model simulations replicate well the levels and general diurnal profiles of IO and I_2, although an early morning 'dawn spike' in IO is predicted by the models, but has not been observed (Read et al., 2008; Mahajan et al., 2010a). The morning peak predicted by current iodine chemistry models is due to a buildup of the emitted I_2 and HOI (which is converted into I_2/IBr/ICl through heterogeneous sea-salt recycling) over the course of the night, followed by rapid photolysis at sunrise.

Traditionally it has been thought that iodine chemistry has a negligible effect on oxidizing capacity of the nocturnal marine atmosphere. As a consequence, unlike the demonstrated effect of iodine on the levels of daytime oxidants, the impact of active iodine upon the main nighttime oxidant, NO_3, remains an open question. This is important given that in many parts of the ocean the NO_3 + DMS reaction is at least as important as OH + DMS in oxidizing DMS (Allan et al., 2000), and hence a reduction of NO_3 may have an effect in the production of SO_2 and methane sulfonic acid (MSA). Here, we discuss possible mechanisms of nighttime iodine radical activation and their potential effect on nighttime iodine ocean fluxes and the currently modeled dawn spike in IO. A new reaction of HOI with NO_3 is proposed, supported by theoretical calculations. We explore the implications of this new reaction both for iodine and NO_3 chemistries.

2. Nocturnal iodine radical activation mechanism

We use the reaction mechanism that has recently been described in a global modelling study by Saiz-Lopez et al. (2014)(see supplementary information). In addition to the reactions included in that scheme, we also include nighttime gas-phase reactions based on the theoretical calculations described below. The additional reactions are listed in Table 1 and a scheme with this new nocturnal chemistry is included in Figure 1.

To the best of our knowledge, reactions of HOI specific to night time have not been studied, either theoretically or through laboratory experiments. Currently, HOI is thought to build up overnight until sunrise, with only heterogeneous uptake on seasalt aerosol as a nighttime loss process (Saiz-Lopez et al., 2012b; Simpson et al., 2015). In addition to the well known I_2 + NO_3 reaction (R1) (Chambers et al., 1992), here we consider several possible HOI reactions that could occur at night, in the absence of photolysis and OH:

$$HOI + NO_2 \rightarrow I + HNO_3 \qquad (R2)$$

$HOI + HNO_3 \rightarrow IONO_2 + H_2O$ (R3)

$HOI + NO_3 \rightarrow IO + HNO_3$ (R4)

3. Theoretical calculations

In order to explore the feasibility of reactions 2–4 taking place under the conditions of the lower troposphere, we carried out electronic structure calculations using the hybrid density functional/Hartree-Fock B3LYP method from within the Gaussian 09 suite of programs (Frisch et al., 2009), combined with a G2 level basis set for I (Glukhovtsev et al., 1995) and the standard 6-311+g(2d,p) triple zeta basis set for O, N and H. Following geometry optimizations of the relevant points on the potential energy surfaces, and the determination of their corresponding vibrational frequencies and (harmonic) zero-point energies, energies relative to the reactants were obtained at the same level of theory. Spin-orbit corrections ~~splittings~~ of -17 and -5 kJ mol^{-1} were applied to the energies of I and IO, respectively; these were estimated by comparing the theoretical and experimental bond energies of I_2 and IO, calculated at the level of theory used in the present study, with available experimental data (Plane et al., 2006; Kaltsoyannis and Plane, 2008).

Reaction 2 is endothermic by 9 kJ mol^{-1} and so, within the expected error of ±10 kJ mol^{-1} at this level of theory, might be reasonably fast. However, the transition state of the reaction, which is illustrated in Figure 2(a), is 73 kJ mol^{-1} above the reactants and so this reaction will not occur at tropospheric temperatures. Reaction 3 is exothermic by 11 kJ mol^{-1}. An HOI--HNO_3 complex first forms (Figure 2(b)), which is 21 kJ mol^{-1} below the reactants. However, this complex rearranges to the IONO2 + H_2O products via the cyclic transition state shown in Figure 2(c), which is 110 kJ mol^{-1} above the reactants.

The stationary points on the potential energy surface (PES) for reaction 4 are illustrated in Figure 3. HOI and NO_3 associate to form a complex which is 24 kJ mol^{-1} below the reactant entrance channel. H-atom transfer involves a submerged transition state to form a IO--HNO_3 complex, which can then dissociate to the products IO + HNO_3. Overall, the reaction is exothermic by 11 kJ mol^{-1}. The vibrational frequencies, rotational energies and geometries (in Cartesian co-ordinates) of these intermediates are listed in Table 2.

The rate coefficient for reaction 4 was then estimated using Rice-Ramsperger-Kassel-Markus (RRKM) theory, employing a multi-well energy-grained master equation solver based on the inverse Laplace transform method - MESMER (Master Equation Solver for Multi-well Energy Reactions) (Roberston et al., 2014). The reaction proceeds via the formation of the excited HOI--NO_3 complex from HOI + NO_3. This complex can then dissociate back to the reactants or rearrange to the IO--HNO_3 intermediate complex over the transition state, which can in turn dissociate to the products IO + HNO_3. Either of the intermediates can also be stabilized by collision with the third body (N_2). The time evolution of all these possible outcomes is modelled using the master equation.

The internal energies of the intermediates on the PES were divided into a contiguous set of grains (width 10 cm^{-1}), each containing a bundle of rovibrational states calculated with the molecular parameters in Table 2. It should be noted that the HOI-NO_3 and IO-HNO_3 complexes both have low frequency vibrational modes (< 100 cm^{-1}) which should more correctly be treated as hindered rotors rather than vibrations. However, in our experience this is not worth doing this until experimental rate coefficients are available to fit the rotor barrier heights. In any case, the energies of both complexes are far enough below the energy of the entrance channel (figure 3) that relatively small changes in their densities of states will have a minor effect on the overall rate coefficient. Each grain was then assigned a set of microcanonical rate coefficients linking it to other intermediates, calculated by RRKM theory. For dissociation to products or reactants, microcanonical rate coefficients were determined using inverse Laplace transformation to link them directly to the capture rate coefficient, k_{capture}. For reaction 4 and the reverse reaction IO + HNO_3 involving neutral species, k_{capture} was set to a typical capture rate coefficient of 2.5×10^{-10} $(T/300\ \mathrm{K})^{1/6}$ $\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$, where the small positive temperature dependence is characteristic of a long-range potential governed by dispersion and dipole-dipole forces (Georgievskii and Klippenstein, 2005).

The probability of collisional transfer between grains was estimated using the exponential down model, where the average energy for downward transitions was set to $\langle \Delta E \rangle_{\mathrm{down}} = 300\ \mathrm{cm^{-1}}$ for N_2 as the third body (Gilbert and Smith, 1990). MESMER determines the temperature- and pressure-dependent rate coefficient from the full microcanonical description of the system time evolution by performing an eigenvector/eigenvalue analysis (Bartis and Widom, 1974). The resulting rate coefficient over the temperature range 260 - 300 K at a pressure of 1000 hPa is $k_4(T) = 2.7 \times 10^{-12}\ (300\ \mathrm{K} / T)^{2.66}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$. Because the intermediate complexes are not strongly bound, and the transition state and products are below the entrance channel, the only products formed in reaction 4 under atmospheric conditions are IO + HNO_3. The absence of a barrier above the entrance channel, and the fact that the intermediate complexes and barrier are well below the entrance channel within their uncertainties, means that the uncertainty in k_4 principally arises from the estimated capture rate coefficient and so is likely to be no more than a factor of 2.

Note that NO_3 also reacts with CH_2I_2 with a rate constant ~2-4×10^{-13} cm^3 $molecule^{-1}$ s^{-1}, which can have a significant effect on nighttime CH_2I_2 concentration (Carpenter et al., 2015). However the products of this reaction are still uncertain (Nakano et al., 2006; Carpenter et al., 2015) and its rate is considerably slower than that of R4.

In summary, the only likely gas-phase reactions that I_2 and HOI undergo in the nighttime troposphere are R1 and R4, respectively. These are included in the model reaction scheme to examine their impacts on the evolution of iodine species in the atmosphere.

4. Atmospheric modelling

We use two atmospheric chemical transport models to study *i*) the impact of this new chemistry on the nighttime chemistry and partitioning of iodine species, and *ii*) the resulting geographical distribution of nocturnal iodine and impact on NO_3 within the global marine boundary layer.

The first model, Tropospheric HAlogen chemistry MOdel (THAMO), is used for a detailed kinetics study of the impact of the different reactions shown in Table 1 as well as to assess which uptake rates best reproduce observations from a field study at the CVAO (Carpenter et al., 2011). THAMO has been used in the past to study iodine chemistry at the CVAO and further details including the full chemical scheme can be found elsewhere (Saiz-Lopez et al., 2008; Mahajan et al., 2009b; Mahajan et al., 2010b; Mahajan et al., 2010a; Lawler et al., 2014; Read et al., 2008). Briefly, THAMO is a 1-D chemistry transport model with 200 stacked boxes at a vertical resolution of 5m (total height 1 km). The model treats iodine, bromine, O_3, NO_x and HO_x chemistry, and is constrained with typical measured values of other chemical species in the

MBL: [CO]=110 nmol mol^{-1}; [DMS]=30 pmol/mol; [CH4]=1820 nmol mol^{-1};[ethane]=925 pmol/mol; [CH3CHO]=970 pmol/mol; [HCHO]=500 pmol/mol; [isoprene]=10 pmol/mol; [propane]=60 pmol/mol; [propene]=20 pmol/mol. The average background aerosol surface area (ASA) used is $1x10^{-6}$ cm^2 cm^{-3} (Read et al., 2008; Read et al., 2009; Lee et al., 2009; Lee et al., 2010). The model is initialized at midnight and the evolution of iodine species, O_3, NO_x and HO_x is followed until the model reaches steady state.

The second model is the global 3D chemistry-climate model CAM-Chem (Community Atmospheric Model with chemistry, version 4.0), which is used to study the impact of reactions 1 and 4 on a global scale. The model includes a comprehensive chemistry scheme to simulate the evolution of trace gases and aerosols in the troposphere and the stratosphere (Lamarque et al., 2012). The model runs with the iodine and bromine chemistry schemes from previous studies (Fernandez et al., 2014; Saiz-Lopez et al., 2014; Saiz-Lopez et al., 2015), including the photochemical breakdown of bromo- and iodo-carbons emitted from the oceans (Ordóñez et al., 2012) and abiotic oceanic sources of HOI and I_2 (Prados-Roman et al., 2015a). CAM-Chem has been configured in this work with a horizontal resolution of 1.9º latitude by 2.5º longitude and 26 vertical levels, from the surface to ~40km altitude. All model runs in this study were performed in the specified dynamics mode (Lamarque et al., 2012) using offline meteorological fields instead of an online calculation, to allow direct comparisons between different simulations. This offline meteorology consists of a high frequency meteorological input from a previous free running climatic simulation.

It should be noted that during nighttime the uptake on aerosols of emitted species such as I_2 and HOI, and the uptake of reservoir species such as $IONO_2$, can play a major role in the cycling of iodine. Observations at CVAO show that I_2 peaked at about 1 pmol/mol during the night and that

ICl was not detected above the 1 pmol/mol detection limit of the instrument (Lawler et al., 2014). In order to match these observations, we need to reduce the uptake and heterogeneous recycling of iodine species. The uptake rates of chemical species on the background seasalt aerosols are determined by their uptake coefficients (γ). The database of mass accommodation and/or uptake coefficients is rather sparse and essentially limited to I_2, HI, HOI, ICI, IBr on pure water/ice and on sulphuric acid particles (Sander et al., 2006). Other iodine species which are likely to undergo uptake onto aerosol are OIO, HIO_3, INO_2, $IONO_2$, I_2O_2 (Saiz-Lopez et al., 2012a; Sommariva et al., 2012). Uptake of HOI is very uncertain, with γ(HOI) ranging from 2×10^{-3} to 0.3 depending on the surface composition and state (Holmes et al., 2001). Sommariva et al. (2012) assumed γ(HOI) to be 0.6, similar to the value for HOBr measured by Wachsmuth et al. (2002). In the case of $IONO_2$, the uptake coefficient has not been measured, with most models using values of 0.1 (Lawler et al., 2014; Leigh et al., 2010; Mahajan et al., 2009; Mahajan et al., 2010a; Mahajan et al., 2010b; Saiz-Lopez et al., 2008; Sommariva et al., 2012; von Glasow et al., 2002). The modelled levels of I_2 and ICl change with different values of uptake coefficients. To match the CVAO I_2 and ICl observations (Lawler et al., 2014), we have used $\gamma = 0.01$ for HOI and $IONO_2$, which is within the uncertainty in the literature, and assumed that 80% is recycled as I_2. Further measurements of these dihalogen species are needed to better constrain their heterogeneous recycling on seasalt aerosols.

5. Results and discussion

Of the possible nocturnal iodine activation reactions involving the inorganic iodine source gases I_2 and HOI, only reactions R1 and R4 appear to be likely candidates (see Section 3). We therefore designed two modelling scenarios: Scenario 1 (S1), without nighttime reactions of I_2 or HOI with NO_3; and Scenario 2 (S2), including reactions R1 and R4 for the degradation of HOI and I_2 by NO_3. In the one-dimensional model THAMO, the I_2 and HOI are injected into the atmosphere from the ocean surface using the flux parameterizations derived from laboratory experiments (MacDonald et al., 2014; Carpenter et al., 2013). Figure 4 shows the resulting diurnal evolution of the HOI and I_2 mixing ratios in the two scenarios. The I_2 mixing ratio peaks during the night in both the scenarios due to quick loss by photolysis during the daytime. By contrast, HOI is present during daytime due to its production through the reaction of IO with HO_2, and peaks just before sunset ~~during the daytime due to its production through the reaction of IO with HO_2~~. In the first scenario, without the inclusion of reactions R1 and R4, Figure 4 (right-hand side panels) shows that HOI and I_2 both build up during the night, reaching a concentration peak just before dawn. This is especially noticeable for I_2 as the daytime concentrations are much lower than during the night. For both species, inclusion of reactions with NO_3 causes a decrease in their respective nocturnal concentrations (Fig. 4, left-hand side panels). The inclusion of reactions R1 and R4 also leads to a modelled I_2 concentration which is in better agreement with the observations of the molecule made at CVAO (Lawler et al., 2014), reaching peak values of about 1 pmol/mol, as compared to about 3 pmol/mol for the scenario without nighttime reactions. An additional consequence of including reactions R1 and R4 is the significant increase of the sea-air fluxes of HOI and I_2 at night due to their atmospheric removal by NO_3 (Fig. 4, bottom panel).

Con formato: Subíndice

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~~iodine species. The uptake rates of chemical species on the background seasalt aerosols are determined by their uptake coefficients (γ). The database of mass accommodation and/or uptake coefficients is rather sparse and essentially limited to I_2, HI, HOI, ICI, IBr on pure water/ice and on sulphuric acid particles (Sander et al., 2006). Other iodine species which are likely to undergo uptake onto aerosol are OIO, HIO_3, INO_2, $IONO_2$, I_2O_2 (Saiz-Lopez et al., 2012a; Sommariva et al., 2012). Uptake of HOI is very uncertain, with γ(HOI) ranging from 2×10^{-3} to 0.3 depending on the surface composition and state (Holmes et al., 2001). Sommariva et al. (2012) assumed γ(HOI) to be 0.6, similar to the value for HOBr measured by Wachsmuth et al. (2002). In the case of $IONO_2$, the uptake coefficient has not been measured, with most models using values of 0.1 (von Glasow et al., 2002; Saiz-Lopez et al., 2008; Mahajan et al., 2009b; Mahajan et al., 2010b; Mahajan et al., 2010a; Leigh et al., 2010; Sommariva et al., 2012; Lawler et al., 2014). The modelled levels of I_2 and ICl change with different values of uptake coefficients. To match the CVAO I_2 and ICl observations (Lawler et al., 2014), we have used γ = 0.01 for HOI and $IONO_2$, which is within the uncertainty in the literature, and assumed that 80% is recycled as I_2. Further measurements of these dihalogen species are needed to better constrain their heterogeneous recycling on seasalt aerosols.~~

Figure 5 shows the diurnal evolution of IO, NO_3 and $IONO_2$ in both model scenarios. Although the daytime peak values of IO are well reproduced in both scenarios, reaching about 1.5 pmol/mol around noon similar to the ground-based observations (Read et al., 2008), the inclusion of reactions R1 and R4 leads to the removal of the dawn spike in IO, which is predicted by current iodine models but was not observed at CVAO (Read et al., 2008; Mahajan et al., 2010a) . The IO dawn spike predicted by models is due to a buildup of the emitted I_2 and HOI (which is converted into I_2/IBr/ICl through heterogeneous recycling) over the night, followed by rapid photolysis after first sunlight. However, due to the considerable removal of HOI and I_2 through the night due to reaction with ambient NO_3, this spike does not appear in the second scenario, leading to a modification of the diurnal profile of IO that better matches with observations.

Reactions R1 and R4 also reduce the NO_3 mixing ratio (Fig. 5~~4~~, middle panels). In scenario 1, the NO_3 is modelled to peak at about 14 pmol/mol just before dawn. However, the inclusion of reactions R1 and R4 leads to near complete depletion of NO_3 close to the surface, with the peak level at the surface reaching only 2 pmol/mol, since reactions R1 and R4 become the main atmospheric loss processes for NO_3 in the lower MBL. These reactions lead however to the buildup of $IONO_2$ during the night (Fig. 5, bottom panels). In the absence of reactions R1 and R4, significant levels of $IONO_2$ are seen only at dawn and dusk since no other reactions produce $IONO_2$ at night, and during the day $IONO_2$ is removed by photolysis. However, with continuous conversion of I_2 and HOI to $IONO_2$ by reactions R1 and R4 in scenario 2, $IONO_2$ is modelled to reach up to 3 pmol/mol in the nocturnal MBL.

Given the associated uncertainty in the theoretical estimate of the k_4, we used THAMO to assess the sensitivity of surface NO_3 to k_4. Figure 6 shows that NO_3 is in fact highly coupled to k_4, with the expected uncertainty in k_4 of one order of magnitude~~a factor of 2~~ (see above) giving rise to a factor of two change~~similar uncertainty~~ in NO_3. A laboratory measurement of $k4$ should therefore be undertaken in the future.

We now implement the nighttime reactions in the 3D global model (CAM-Chem) to assess the resulting geographical distributions and impacts of these reactions. We have also run two different scenarios in CAM-Chem, the first without R1 and R4 in the chemical scheme, and the second including the new nighttime iodine chemistry. Figure 7 shows how the inclusion of R1 and R4 reduces globally the nighttime concentrations of I_2 and HOI. The plots correspond to the nighttime~~midnight~~ averaged (from 00LT to 01LT) differences between the model scenarios. Considerable reductions of up to 0.5 and 10 pmol/mol (i.e. up to 100% removal) are observed for I_2 and HOI, respectively, particularly over coastal polluted regions where continental pollution outflow leads to higher levels of NO_3 in the nighttime MBL. Major shipping routes also show strong nocturnal iodine activity due to the characteristically high NO_x, and resulting NO_3, associated with shipping emissions.

Figure 8 shows the effect of this nocturnal chemistry on the concentrations of $IONO_2$ and NO_3. As in the previous figure, the plots correspond to the nighttime averaged difference between the second and the first scenarios. The maps show an increase of $IONO_2$ of up to 15 pmol/mol (~600%) over polluted coastal areas, due to efficient conversion of NO_3 into $IONO_2$. The bottom panel of Figure 7 shows the expected decrease of NO_3 levels associated with the inclusion of reactions R1 and R4, with decreases of up to ~4 pmol/mol (up to 60%) over marine polluted regions. We model global percentage reductions in the NO_3 concentrations of 7.1% (60S-60N), with nitrate removal of up to 80% in non-polluted remote oceanic regions with low NO_3 levels. This in turn can affect the modelled oxidation of DMS by NO_3. We estimate that the reduction in NO_3, due to the inclusion of R1 and R4, results in a model increase in DMS levels of up to 7 pmol/mol (about 20%) in marine regions affected by continental pollution outflow (Fig. 9). We therefore suggest that the inclusion of the new nighttime iodine chemistry can have a large, so far unrecognized, impact on the nocturnal oxidizing capacity of the marine atmosphere.

The hourly evolution of the main species involved in this study is shown in Figures 10 and 11, which include the levels of HOI, I_2, $IONO_2$ and NO_3 in the MBL over regions where nocturnal iodine is modelled to be particularly active. The first region is located within the Mediterranean

Sea, an area that shows large differences during the summer months when high ozone levels drive large emissions of HOI and I_2 from the sea, and the high levels of NO_3 at nighttime make this chemistry especially important. The hourly average in August is shown in Figure 10 for HOI, $IONO_2$ and I_2. HOI and $IONO_2$ (Fig 10) are the species whose concentration differ most between scenarios as HOI is removed and $IONO_2$ produced by R4 (and, to a lesser extent, R1). Over a Pacific Ocean region at the south of~~the coastal region of~~ the Baja California Peninsula, the modelled differences between the two scenarios are even higher than over the Mediterranean Sea (Figure 11). Large differences in MBL NO_3, up to 28%, are modelled during the night caused by pollution outflow from the west coast of Mexico and USA.

6. Summary and conclusions

The viability of the reaction of HOI with NO_2, HNO_3 and NO_3 has been studied by theoretical calculations. The results indicate that only the reaction of HOI with NO_3, to yield IO + HNO_3, is possible under tropospheric conditions. The inclusion of this reaction, along with that of I_2 + NO_3, has a number of significant implications: *i*) nocturnal iodine radical chemistry is activated; *ii*) this causes enhanced nighttime oceanic emissions of HOI and I_2; *iii*) nighttime iodine species are partitioned into high levels of $IONO_2$; *iv*) the IO spike, modelled by current iodine models but not shown by observations, is removed; and, *v*) a reduction of the levels of nitrate radical in the MBL, with the associated less efficient oxidation of DMS, which has important implications for our understanding of the nocturnal oxidizing capacity of the marine atmosphere.

Acknowledgments

This work was supported by the Spanish National Research Council (CSIC). The National Center for Atmospheric Research (NCAR) is funded by the National Science Foundation NSF. The Climate Simulation Laboratory at NCAR's Computational and Information Systems Laboratory (CISL) provided the computing resources (ark:/85065/d7wd3xhc). As part of the CESM project, CAM-Chem is supported by the NSF and the Office of Science (BER) of the US Department of Energy. This work was also sponsored by the NASA Atmospheric Composition Modeling and Analysis Program Activities (ACMAP, number NNX11AH90G).

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Tables

Table 1: Night time reactions of emitted inorganic iodine compounds considered in addition to the iodine chemistry scheme used by (Saiz-Lopez et al., 2014).

No.	Reaction	Notes
R1.	$I_2 + NO_3 \rightarrow I + IONO_2$	1.5×10^{-12} cm^3 $molecule^{-1}$ s^{-1} [*Chambers et al.*, 1992]
R2.	$HOI + NO_2 \rightarrow I + HNO_3$	Endothermic by 9 kJ mol^{-1} and the transition state is 73 kJ mol^{-1} above the reactants
R3.	$HOI + HNO_3 \rightarrow IONO_2 + H_2O$	Exothermic by 11 kJ mol^{-1}. The reaction first forms a complex 21 kJ mol^{-1} below the reactants but this rearranges to the products via a transition state that is 110 kJ mol^{-1} above the reactants.
R4.	$HOI + NO_3 \rightarrow IO + HNO_3$	Exothermic by 11 kJ mol^{-1} with all transition states below the reactants. $k(T) = 2.7 \times 10^{-12} (300\ K / T)^{2.66}$ cm^3 $molecule^{-1}$ s^{-1}

Table 2. Calculated vibrational frequencies, rotational constants and energies of the stationary points and asymptotes on the HOI + NO_3 doublet potential energy surface

Species	Geometry[a]	Vibrational frequencies[b]	Rotational constants [c]	Potential energy [d]
HOI + NO_3		603, 1084, 3803 & 261, 261, 805,1108, 1108, 1126	623.9, 8.182, 8.076 & 13.84, 13.84, 6.919	0.0
IOH-NO_3 complex	O 1.623,0.284,-0.331 H 1.484,-0.657,-0.043 I 0.009,1.205,0.286 N -0.456,-2.265,0.030 O -1.052, -3.321,-0.0473 O -1.147,-1.195,-0.228 O 0.742,-2.161,0.333	55, 84, 118, 161, 196, 615, 629, 667, 705, 803, 968, 1228, 1273,1491, 3268	5.610, 0.916, 0.806	-24.0
IO-H-NO_2 TS	O 0.309,1.515,0.247 H -0.834,1.314,-0.017 I 1.280,-0.089,-0.093 N -2.349,-0.133,0.019 O -3.518, ,-0.429,-0.035 O -1.444,-0.962,0.257 O -2.019,1.117,-0.187	1249*i*, 70, 97, 103, 225, 472, 676, 698, 797, 806, 1041, 1147, 1308, 1513, 1626	6.300, 0.864, 0.767	-16.4
IO-HNO_3 complex	O 0.571,1.350,0.348 H -1.111,1.098,-0.020 I 1.870,0.0645,-0.152 N -2.503,-0.202,0.0186 O -3.673,-0.396,-0.170 O -1.654,-0.986,0.401 O -2.081,1.090,-0.242	35, 43, 76, 126, 198, 623, 677, 703, 772, 798, 939, 1331, 1416, 1713, 3281	7.058, 0.605, 0.566	-34.8
IO + HNO_3		648 & 477, 585, 649, 782, 901, 1320, 1345, 1738, 3724	9.844 & 13.01, 12.05, 6.258	-10.6

[a] Cartesian co-ordinates in Å. [b] In cm^{-1}. [~~b~~c] In GHz. [~~c~~d] In kJ mol^{-1}, including zero-point energy and spin-orbit coupling of I and IO (see text).

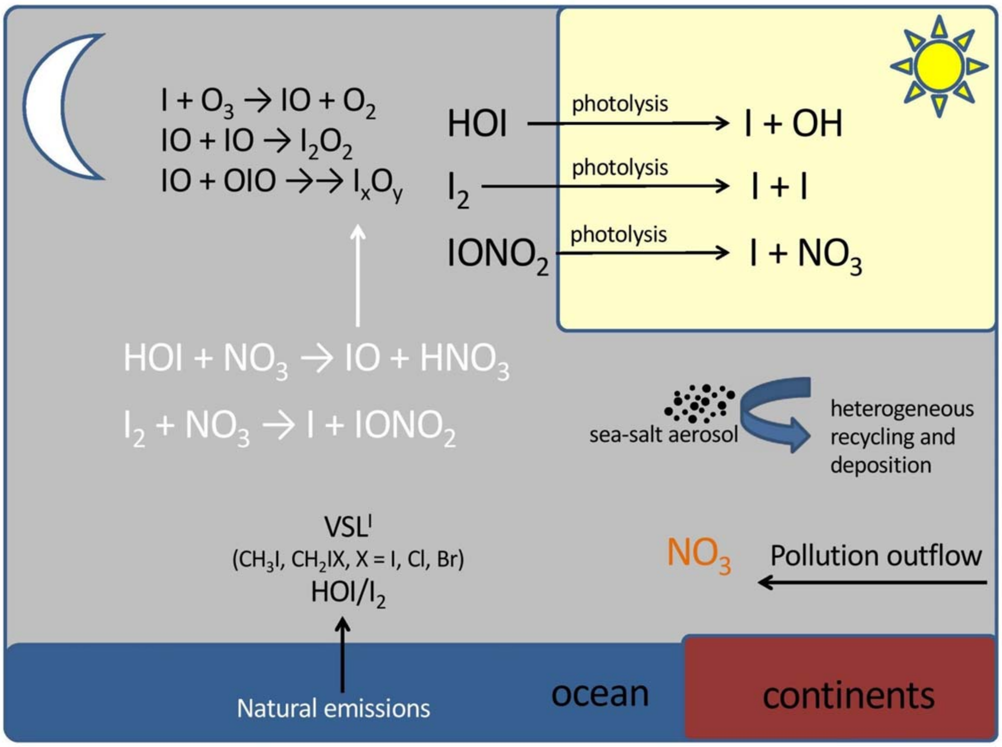

Figure 1. New nocturnal iodine chemistry (in white) implemented in the THAMO and CAM-Chem models.

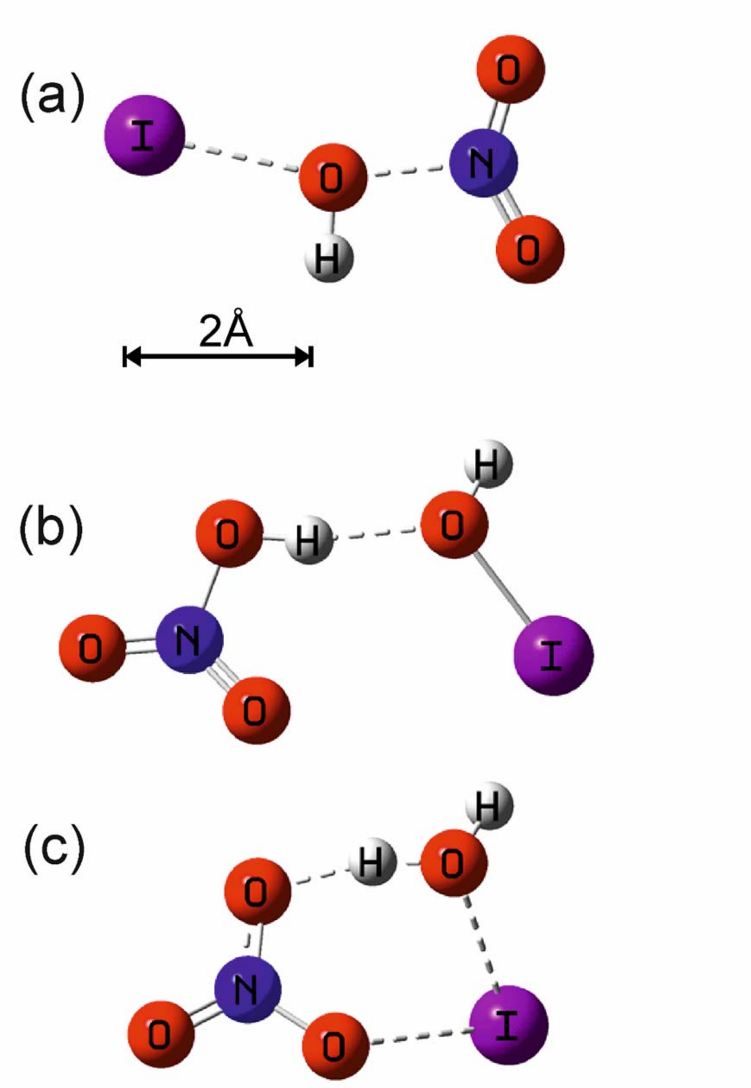

Figure 2: (a) Transition state for the reaction between HOI and NO_2 to form HNO_3 + I; (b) complex formed between HOI and HNO_3, which then reacts via transition state (c) to form IONO2 + H_2O.

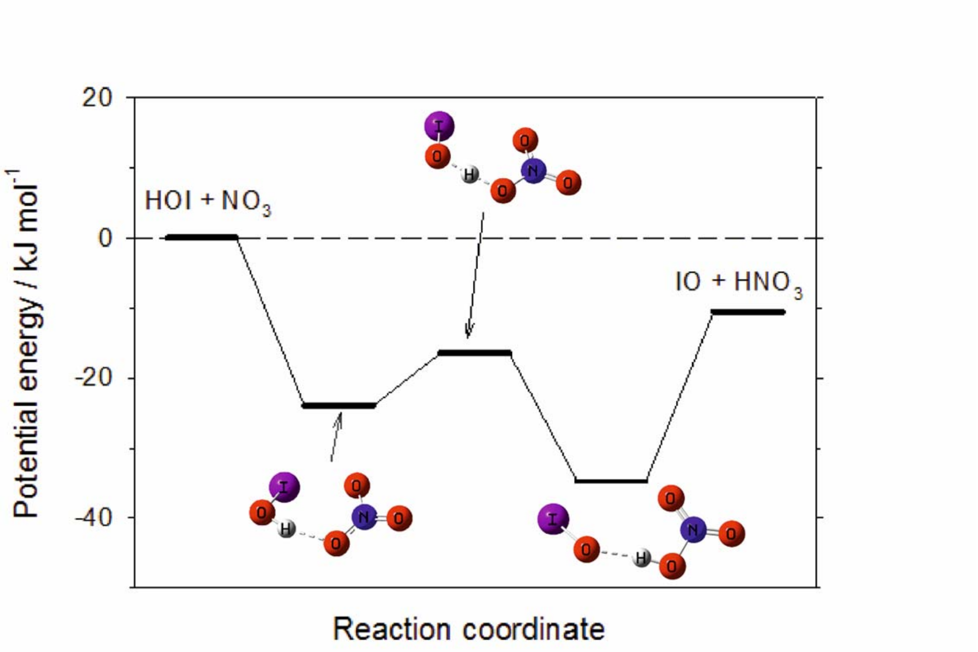

Figure 3. Potential energy surface for the reaction between HOI and NO$_3$, which contains two intermediate complexes separated by a submerged barrier.

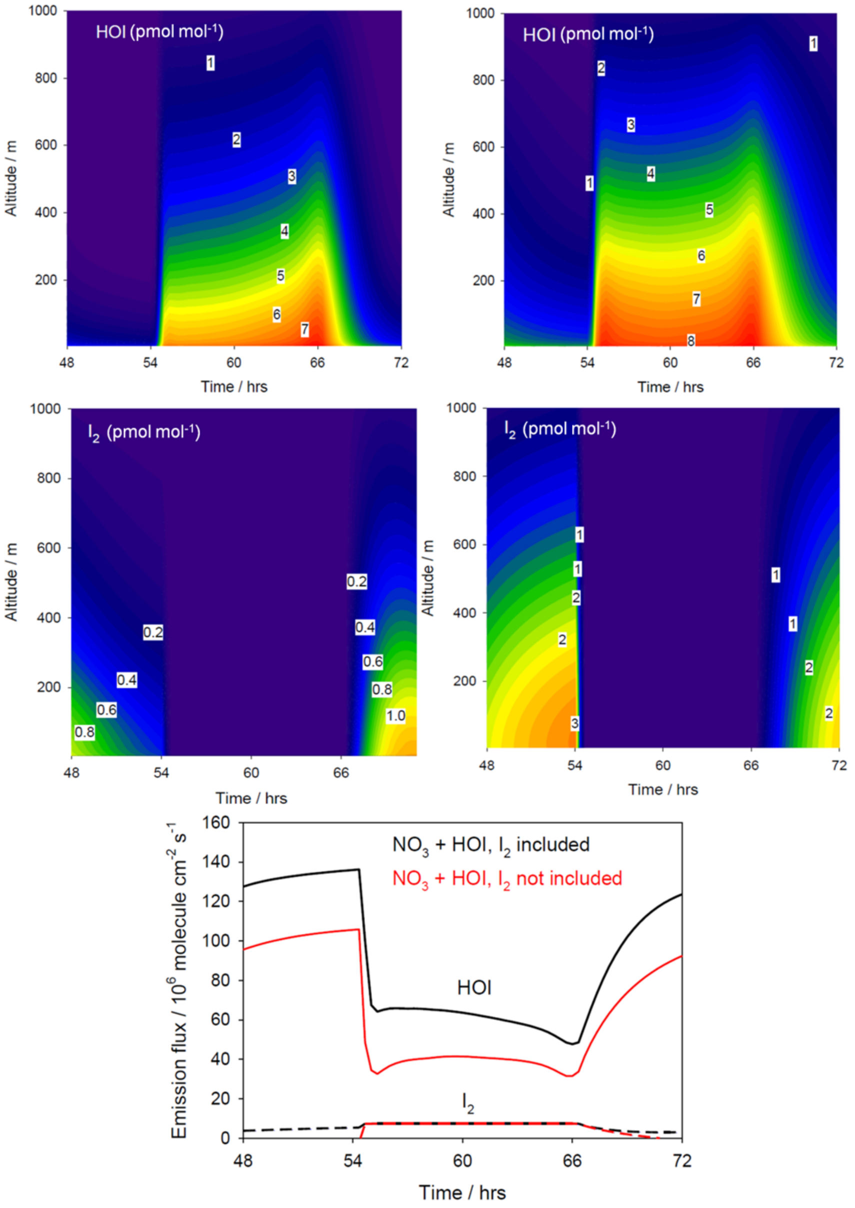

Figure 4. THAMO modeled diurnal variation of HOI, I_2 (upper panels) and the HOI/I_2 flux from the ocean surface (bottom panel). The right hand panels are from scenario 1, which do not include night time reactions of HOI and I_2 with NO_3, while the left hand panels include the reactions in scenario 2. In bottom panel red lines represent scenario 1, while black lines correcpond to scenario 2.

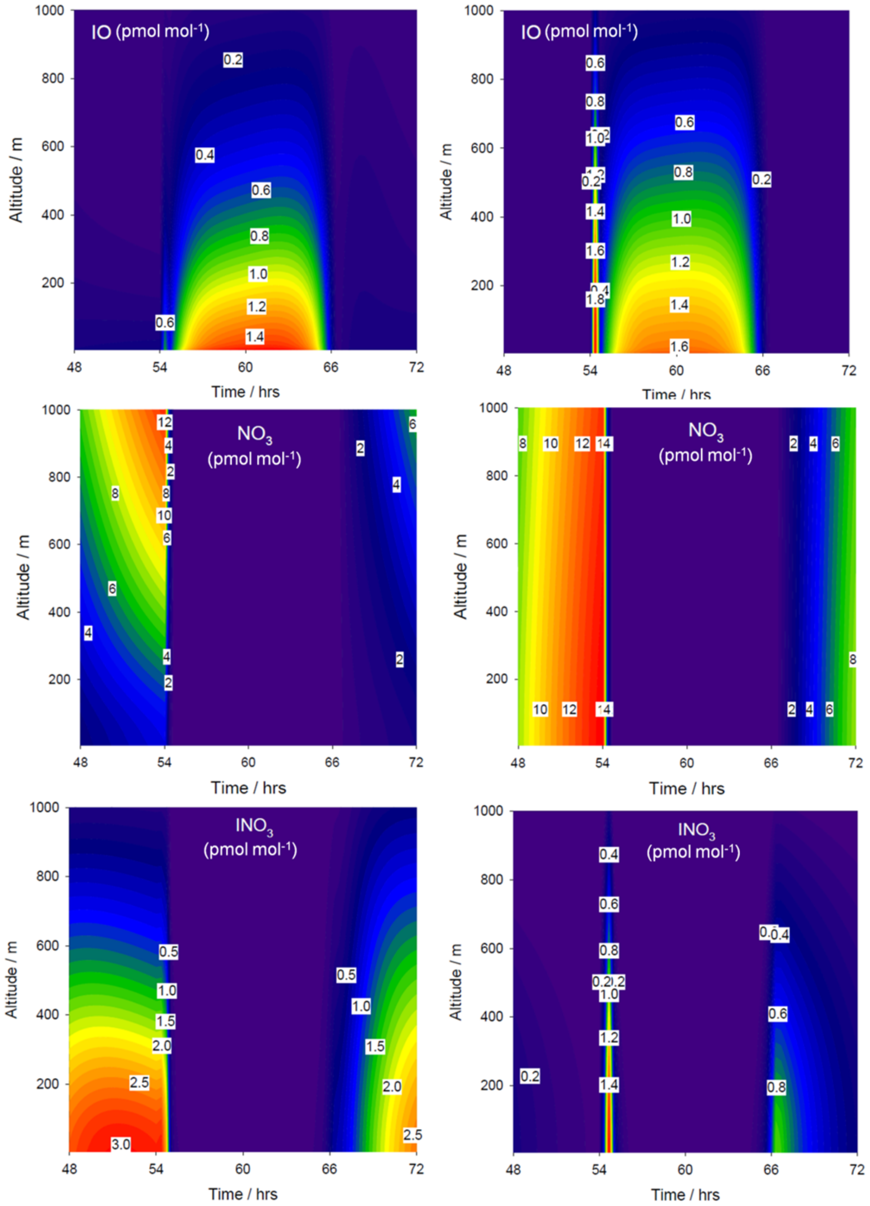

Figure 5. THAMO modeled diurnal variation of IO, NO_3 and the $IONO_2$. The right hand panels are from scenario 1, which do not include night time reactions of HOI and I_2 with NO_3, while the left hand panels include the reactions in scenario 2.

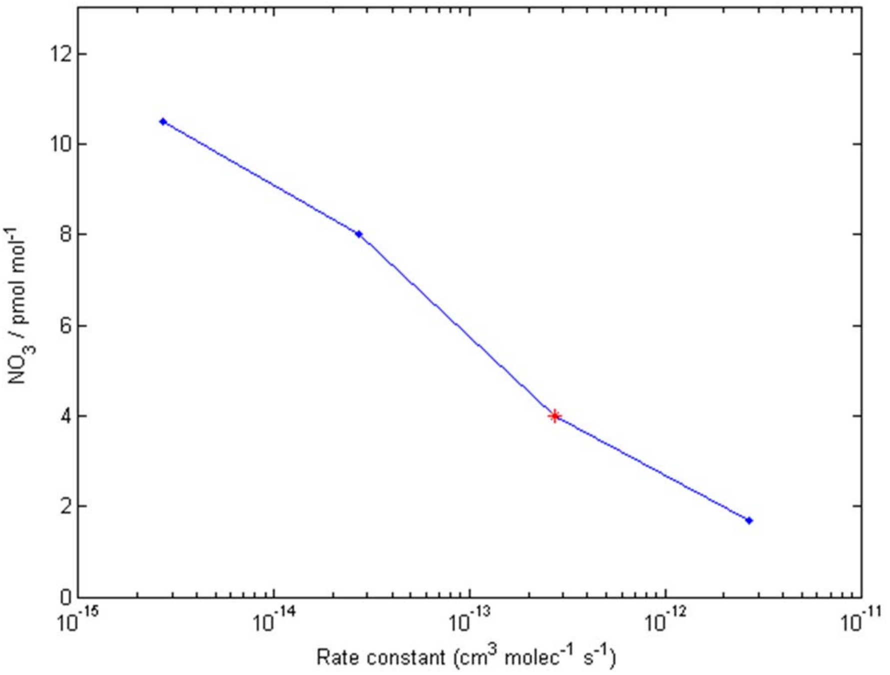

Figure 6. Sensitivity run showing the effect of the uncertainty in the rate constant estimation on the reduction of NO_3 at the surface - the red point is the theoretical estimate.

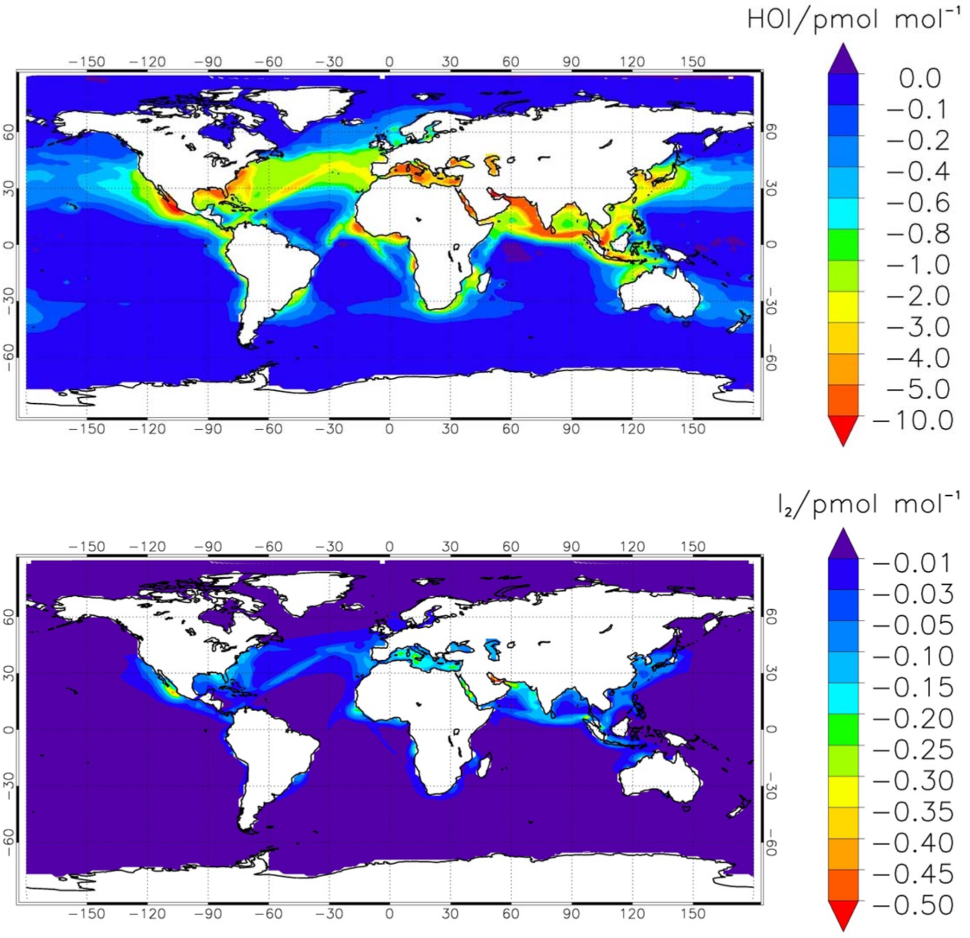

Figure 7. Modelled annual average of HOI (a) and I_2 (b) during night time at the surface level. The panels show the difference in volume~~vertical~~ mixing ratio between the simulations with and without reactions (1) and (4~~2~~).

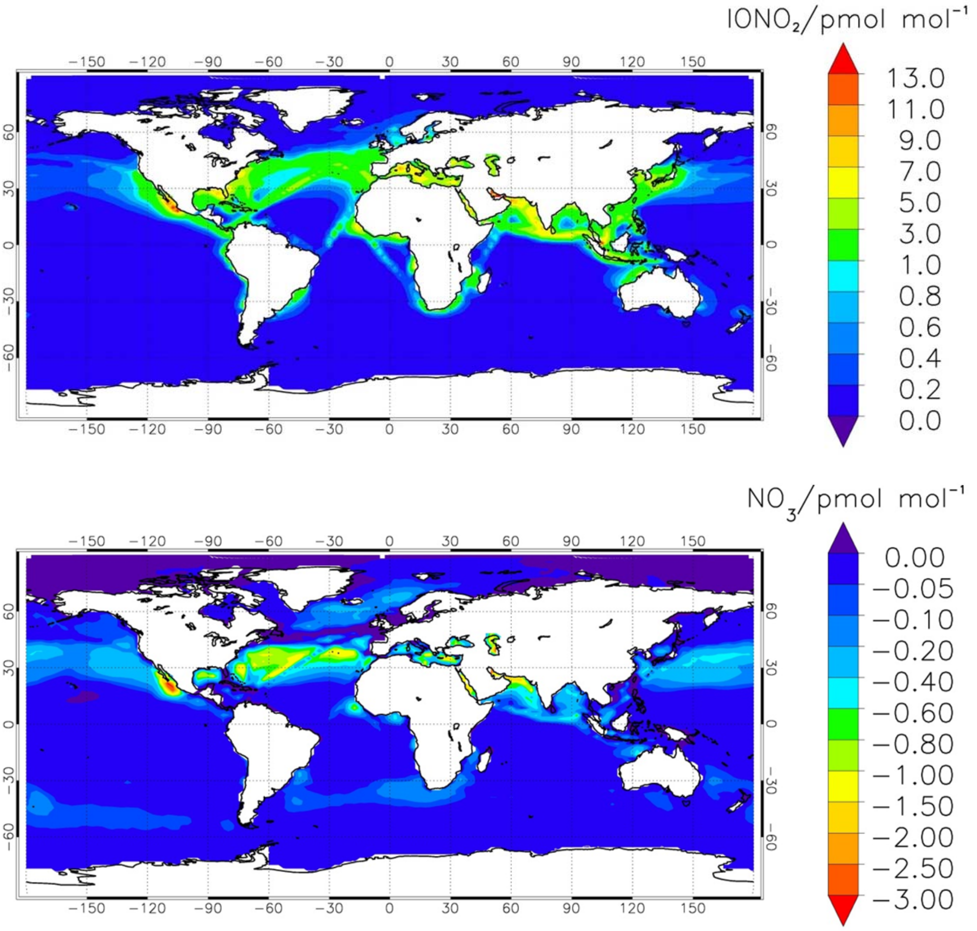

Figure 8. Modelled annual average of $IONO_2$ (a) and NO_3 (b) during night time at the surface level~~over the ocean surface~~, as the difference in volume mixing ratio between the simulations with and without reactions (1) and (4~~2~~).

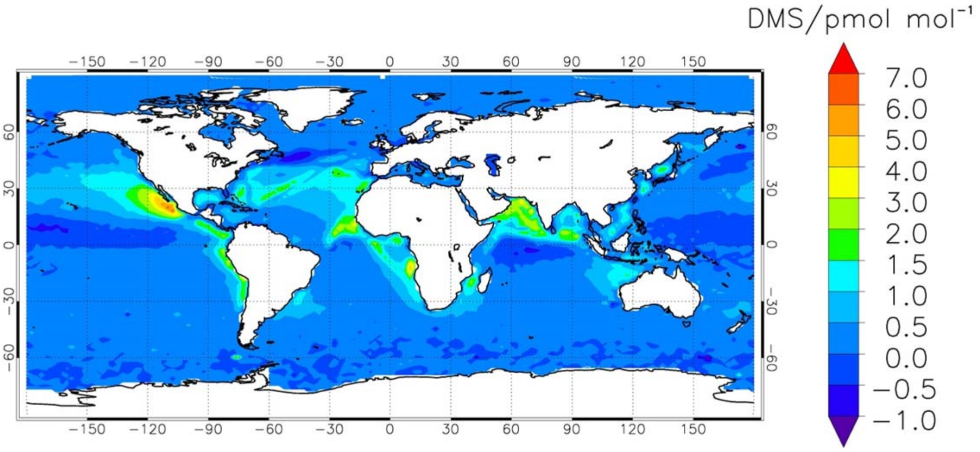

Figure 9. Increase in the DMS levels during~~at~~ night time at the surface level~~over the ocean surface~~ due to the inclusion of the reactions R1 and R4~~2~~ in CAM-Chem.

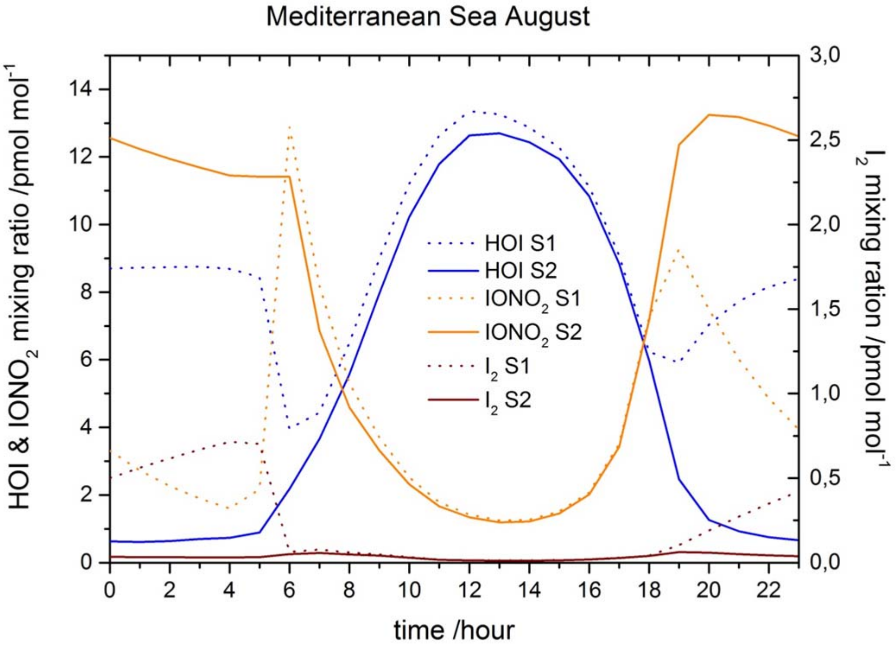

Figure 10. Hourly averaged concentration of HOI, IONO$_2$ and I_2 in the Mediterranean Sea at the surface level (lon:10º→20ºE, lat:33º→40ºN)

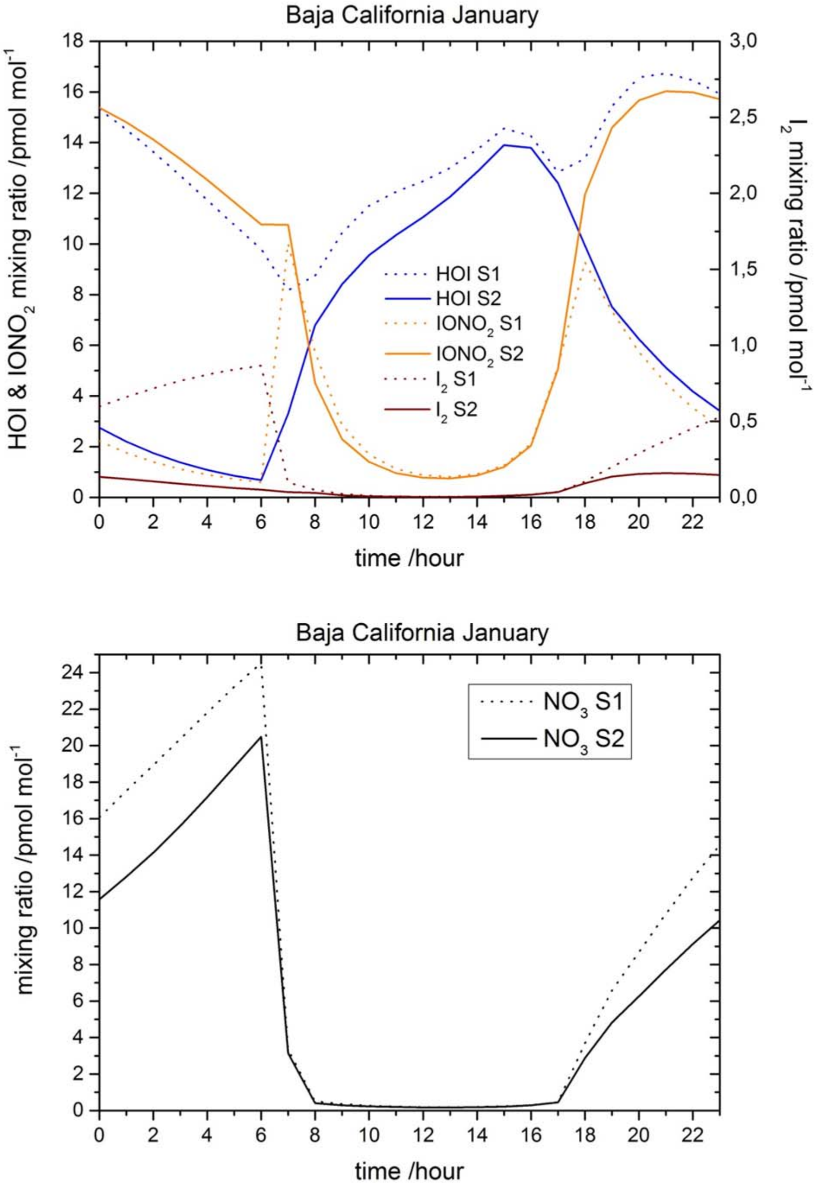

Figure 11. Hourly averaged concentration of HOI, IONO$_2$ and I_2 (upper panel) and NO$_3$ (bottom panel) in the Pacific Ocean at the south of ~~close to~~ Baja California peninsula at the surface level (lon:-110º→-106ºE, lat:16º→23ºN)

Supplementary information for

Iodine chemistry after dark

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Table 1. Iodine chemistry scheme in CAM-Chem: Bimolecular, thermal decomposition and termolecular reactions.

Reaction	**k / cm^3 molecule^{-1} s^{-1}**	**Notes**
$I + O_3 \rightarrow IO + O_2$	2.1×10^{-11} $e^{(-830 / T)}$	1
$IO + O_3 \rightarrow OIO + O_2$	3.6×10^{-16}	2
$I + HO_2 \rightarrow HI + O_2$	1.5×10^{-11} $e^{(-1090 / T)}$	3
$IO + NO \rightarrow I + NO_2$	7.15×10^{-12} $e^{(300 / T)}$	1
$IO + HO_2 \rightarrow HOI + O_2$	1.4×10^{-11} $e^{(540 / T)}$	1
$IO + IO \rightarrow OIO + I$	2.13×10^{-11} $e^{(180/ T)} \times$ $[1 + e^{(-p / 191.42)}]$	1, 4
$IO + IO \rightarrow I_2O_2$	3.27×10^{-11} $e^{(180 / T)} \times$ $[1 - 0.65\ e^{(- p / 191.42)}]$	1, 4
$IO + OIO \rightarrow I_2O_3$	$w_1 \cdot \exp(w_2 \cdot T)$ [a]	4, 5, 6 [g]
$OIO + OIO \rightarrow I_2O_4$	$w_1 \cdot \exp(w_2 \cdot T)$ [b]	4, 5, 6 [g]
$I_2 + O \rightarrow IO + I$	1.25×10^{-10}	1
$IO + O \rightarrow I + O_2$	1.4×10^{-10}	1
$IO + OH \rightarrow HO_2 + I$	1.0×10^{-10}	7
$I_2O_2 \rightarrow OIO + I$	$w_1 \cdot \exp(w_2 / T)$ [c]	5, 6 , 8 [g]
$I_2O_2 \rightarrow IO + IO$	$w_1 \cdot \exp(w_2 / T)$ [d]	5, 6 , 8 [g]
$I_2O_4 \rightarrow 2\ OIO$	$w_1 \cdot \exp(w_2 / T)$ [e]	5, 8 [g]
$I_2 + OH \rightarrow HOI + I$	$1.8 \text{ x } 10^{-10}$	3
$I_2 + NO_3 \rightarrow I + IONO_2$	1.5×10^{-12}	9
$I + NO_3 \rightarrow IO + NO_2$	1.0×10^{-10}	1
$OH + HI \rightarrow I + H_2O$	1.6×10^{-11} $e^{(440 / T)}$	1
$I + IONO_2 \rightarrow I_2 + NO_3$	9.1×10^{-11} $e^{(-146 / T)}$	5
$HOI + OH \rightarrow IO + H_2O$	2.0×10^{-13}	10
$IO + DMS \rightarrow DMSO + I$	3.2×10^{-13} $e^{(-925 / T)}$	11
$INO_2 \rightarrow I + NO_2$	1008×10^{15} $e^{(-13670 / T)}$	12, 13, 14
$IONO_2 \rightarrow IO + NO_2$	$w_1 \cdot \exp(w_2 / T)$ [f]	5, 15
$INO + INO \rightarrow I_2 + 2NO$	8.4×10^{-11} $e^{(-2620/T)}$	3
$INO_2 + INO_2 \rightarrow I_2 + 2NO_2$	4.7×10^{-13} $e^{(-1670 / T)}$	1
$OIO + NO \rightarrow IO + NO_2$	1.1×10^{-12} $e^{(542 / T)}$	14
$HI + NO_3 \rightarrow I + HNO_3$	1.3×10^{-12} $e^{(-1830 / T)}$	16
$IO + BrO \rightarrow Br + I + O_2$	0.30×10^{-11} $e^{(510/T)}$	1
$IO + BrO \rightarrow Br + OIO$	1.20×10^{-11} $e^{(510/T)}$	1
$I + BrO \rightarrow IO + Br$	1.44×10^{-11}	17, 18, 19

$IO + ClO \rightarrow I + OClO$	$2.585 \times 10^{-12} e^{(280/T)}$	1
$IO + ClO \rightarrow I + Cl + O_2$	$1.175 \times 10^{-12} e^{(280/T)}$	1
$IO + ClO \rightarrow ICl + O_2$	$0.940 \times 10^{-12} e^{(280/T)}$	1
$IO + Br \rightarrow I + BrO$	2.49×10^{-11}	18, 19
$IO + NO_3 \rightarrow OIO + NO_2$	9.0×10^{-12}	20
$IO + CH_3O_2 \rightarrow CH_2O + I + HO_2$	2.0×10^{-12}	2[h]
$CH_3I + OH \rightarrow I + H_2O + HO_2$	$2.90 \times 10^{-12} e^{(-1100/T)}$	3
$I + NO_2 (+ M) \rightarrow INO_2 (+ M)$	$k_0 = 3 \times 10^{-31} \times (T / 300)^{-1}$ $k_\infty = 6.6 \times 10^{-11}$	3[i]
$IO + NO_2 (+ M) \rightarrow IONO_2 (+ M)$	$k_0 = 6.5 \times 10^{-31} \times (T / 300)^{-3.5}$ $k_\infty = 7.6 \times 10^{-12} \times (T / 300)^{-1.5}$	3[i]
$I + NO (+ M) \rightarrow INO (+ M)$	$k_0 = 1.8 \times 10^{-32} \times (T / 300)^{-1}$ $k_\infty = 1.7 \times 10^{-11}$	3[i]
$OIO + OH (+ M) \rightarrow HOIO_2 (+ M)$	$k_0 = 1.5 \times 10^{-27} \times (T / 300)^{-3.93}$ $k_\infty = 7.76 \times 10^{-10} \times (T / 300)^{-0.8}$	14[j]
$HOI + NO_3 \rightarrow IO + HNO_3$	$2.7 \times 10^{-12} (300/T)^{2.66}$	21

[1] IUPAC-2008 (Atkinson et al., 2007) ; [2](Dillon et al., 2006b); [3] JPL-2010 (Sander et al., 2011); [4](Gómez Martín et al., 2007); [5](Kaltsoyannis and Plane, 2008); [6](Galvez et al., 2013); [7](Bösch et al., 2003); [8] (Gómez Martín and Plane, 2009); [9](Chambers et al., 1992); [10](Chameides and Davis, 1980); [11](Dillon et al., 2006a); [12](McFiggans et al., 2000); [13](Jenkin et al., 1985); [14](Plane et al., 2006); [15](Allan and Plane, 2002); [16] (Lancar et al., 1991); [17](Laszlo et al., 1997); [18](Bedjanian et al., 1997); [19](Gilles et al., 1997); [20](Dillon et al., 2008); [21]This work.

[a] $w1= 4.687 \text{ x } 10^{-10} - 1.3855 \text{ x } 10^{-5} \text{ x } e^{(- 0.75 p / 1.62265)} + 5.51868 \text{ x } 10^{-10} \text{ x } e^{(-0.75 p / 199.328)}$

$w2 = -0.00331 - 0.00514 \text{ x } e^{(- 0.75 p / 325.68711)} - 0.00444 \text{ x } e^{(- 0.75 p / 40.81609)}$

[b] $w1 = 1.1659 \text{ x } 10^{-9} - 7.79644 \text{ x } 10^{-10} e^{(-0.75 p/22.09281)} + 1.03779 \text{ x } 10^{-9} \text{ x } e^{(-0.75 p / 568.15381)}$

$w2 = -0.00813 - 0.00382 \text{ x } e^{(- 0.75 p / 45.57591)} - 0.00643 \text{ x } e^{(-0.75 p / 417.95061)}$

[c] $w1 = 3.54288 \text{ x } 10^{10} + 1.8523 \text{ x } 10^{11} \text{ x } 0.75 p -1.45435 \text{ x } 10^{8} \text{ x } (0.75p)^{2} + 60799.4344 \text{ x } (0.75p)^{3}$

$w2 = -9681.65989 + 346.95538 \text{ x } e^{(-0.75 p / 343.25322)} + 251.78032 \text{ x } e^{(-0.75 p / 44.1466)}$

[d] $w1 = 255335000000 - 4418880000 \text{ x } 0.75 p + 85618600 \text{ x } (0.75 p)^{2} + 14218.81 \text{ x } (0.75 p)^{3}$

$w2 = -11466.82304 + 597.01334 \text{ x } e^{(-0.75 p / 1382.62325)} - 167.3391 \text{ x } e^{(-0.75 p / 43.75089)}$

[e] $w1= -1.92626 \text{ x } 10^{14} + 4.67414 \text{ x } 10^{13} \text{ x } 0.75 p - 3.68651 \text{ x } 10^{8} \text{ x } (0.75 p)^{2} - 3.09109 \text{ x } 10^{6} \text{ x } (0.75 p)^{3}$

$w2 = -12302.15294 + 252.78367 \text{ x } e^{(-0.75 p / 46.12733)} + 437.62868 \text{ x } e^{(-0.75 p / 428.4413)}$

[f] $w1 = -2.63544 \times 10^{13} + 4.32845 \times 10^{12} \times (0.75\ p) + 3.73758 \times 10^{8} \times (0.75\ p)^{2} - 628468.76313 \times (0.75\ p)^{3}$

$w2 = -13847.85015 + 240.34465 \times e^{(-0.75\ p / 49.27141)} + 451.35864 \times e^{(-0.75\ p / 436.87605)}$

[g] The empirical expressions of the form $w_1 \cdot \exp(w_2 \cdot T)$ were obtained by non-linear least squares fitting of *Rice–Ramsperger–Kassel–Marcus* (RRKM) theoretical results for the indicated reaction rate constants and thermal dissociation rates in the (27 – 1013) hPa pressure range. RRKM calculations were carried out using the MESMER algorithm (Glowacki et al., 2012) as indicated in the corresponding references (e.g. (Galvez et al., 2013). Expression [a] produces negative values outside the range of modelled rate constants ($p < 20$ hPa), and therefore a fixed rate constant of 3×10^{-11} cm^3 molecule^{-1} s^{-1} was assumed. Expressions [e] and [f] generate negligible dissociation rates below ~500 hPa which become negative at ~8 hPa – in this case they are set to zero below that pressure.

[h] Updated heats of formation for IO, OIO, and CH_3O_2 (Dooley et al., 2008; Gómez Martín and Plane, 2009; Knyazev and Slagle, 1998) show that the only accessible exothermic product channel of CH_3O_2 + IO (Drougas and Kosmas, 2007) is $CH_2O + I + O_2$ ($\Delta H_r = -5 \pm 6$ kJ mol^{-1}), consistent with the high yield of I and low yield of OIO found experimentally (Bale et al., 2005; Enami et al., 2006). Sensitivity studies have been carried out (Saiz-Lopez et al., 2014) using the preferred rate constant for this reaction of 2×10^{-12} cm^3 molecule^{-1} s^{-1} (Dillon et al., 2006b), resulting in an enhancement of the ozone loss of 0.5% in the MBL and of less than 0.1% integrated throughout the troposphere in the J_{IxOy} scenario, and similarly negligible enhancements in the Base scenario. Impacts in the I_y partitioning are also very minor.

[i] The temperature and pressure dependent rate constant (k) is computed based on the low pressure (k_0) and the high-pressure (k_∞) rate coefficients following JPL-2010 (Sander et al., 2011).

[j] The Fast rate constants and a thermally stable product $HOIO_2$ have been predicted theoretically (Plane et al., 2006), but no experimental studies reporting observation of $HOIO_2$ and its photochemical properties in the gas phase are available. Since the level of uncertainty is even larger than for the I_xO_y, it has not been included in the mechanism.

Table 2. Iodine chemistry scheme in CAM-Chem: Photochemical reactions.

Reaction
$CH_3I + h\nu \rightarrow CH_3O_2 + I$
$CH_2I_2 + h\nu \rightarrow 2I$ [a]
$CH_2IBr + h\nu \rightarrow Br + I$ [a]
$CH_2ICl + h\nu \rightarrow Cl + I$ [a]
$I_2 + h\nu \rightarrow 2I$
$IO + h\nu \rightarrow I + O$
$OIO + h\nu \rightarrow I + O_2$
$INO + h\nu \rightarrow I + NO$
$INO_2 + h\nu \rightarrow I + NO_2$ [b]
$IONO_2 + h\nu \rightarrow I + NO_3$
$HOI + h\nu \rightarrow I + OH$
$IBr + h\nu \rightarrow I + Br$
$ICl + h\nu \rightarrow I + Cl$
$I_2O_2 + h\nu \rightarrow I + OIO$ [c]
$I_2O_3 + h\nu \rightarrow IO + OIO$ [c]
$I_2O_4 + h\nu \rightarrow OIO + OIO$ [c]

Photolysis rates are computed online considering the actinic flux calculation in CAM-Chem. The absorption cross-sections and quantum yields for all species besides the I_xO_y have been taken from IUPAC-2008 (Atkinson et al., 2007; Atkinson et al., 2008) and JPL-2010 (Sander et al., 2011).

[a] radical organic products are not considered.
[b] only the reaction channel reported in JPL 06-02 (Sander et al., 2006) is considered.
[c] photolysis reactions only considered in the J_{IxOy} scheme (Saiz-Lopez et al., 2014).

Table 3. Iodine chemistry scheme in CAM-Chem: Heterogeneous reactions.

Sea-salt aerosol reactions	**Reactive uptake**
$IONO_2 \rightarrow 0.5\ IBr + 0.5\ ICl$	$\gamma = 0.01$
$INO_2 \rightarrow 0.5\ IBr + 0.5\ ICl$	$\gamma = 0.02$
$HOI \rightarrow 0.5\ IBr + 0.5\ ICl$	$\gamma = 0.06$
$I_2O_2 \rightarrow$	$\gamma = 0.01^{\S}$
$I_2O_3 \rightarrow$	$\gamma = 0.01^{\S}$
$I_2O_4 \rightarrow$	$\gamma = 0.01^{\S}$

Values based on the THAMO model (Saiz-Lopez et al., 2008) and implemented in CAM-Chem following (Ordóñez et al., 2012).

[§] Deposition of I_xO_y species on sea-salt aerosols has been included following the free regime approximation.

Table 4. Iodine chemistry scheme in CAM-Chem: Henry's Law constants and dry deposition velocities.

Species	**k_0 (M atm^{-1})**	**Deposition velocity§ (cm s^{-1})**	**Reference**
IBr ^{ice}	2.4×10^{1}	–	1
ICl ^{ice}	1.1×10^{2}	–	1
HI	7.8×10^{-1}	1.0	1 [a]
HOI – (J_{IxOy} / *Base*)	1.9×10^{3} / 4.5×10^{3}	0.75	1 [b]
$IONO_2$ ^{ice}	1.0×10^{6}	0.75	2 [c]
INO_2 ^{ice}	3.0×10^{-1}	0.75	1 [d]
IO	4.5×10^{2}	–	2
OIO	1.0×10^{4}	–	2
I_2O_2	1.0×10^{4}	1.0	2
I_2O_3	1.0×10^{4}	1.0	2
I_2O_4	1.0×10^{4}	1.0	2

[§] Dry deposition velocities are based on the THAMO model (Saiz-Lopez et al., 2008).

[1] Values reported in (Sander, 1999).

[2] Values based on the THAMO model (Saiz-Lopez et al., 2008).

[a] Considering a dissociation constant $K_a = 3.2 \times 10^{9}$ and a temperature dependent coefficient c = 9800 K

[b] Within the range of values given in the corresponding reference.

[c] Virtually infinite solubility is represented by using a very large arbitrary number.

[d] Value assumed to be equal to those of $BrNO_2$.

[ice] Species for which ice-uptake is considered following (Neu and Prather, 2012).

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