Co-Editor Decision: Reconsider after major revisions (23 Sep 2016) by Dr. Jens-Uwe Grooß

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

CEC:

Comments to the Author:

Dear authors,

In my impression, you should have considered more of the reviewers comments. So please consider the remaining points expressed by the two reviewers as well as the following technical points:

Title: "after dark" means to my knowledge something like "after it did get dark". It could be mis-understood as "after the dark period", which would be at morning. You also mention the peak at sunrise, so I also would prefer to be the title as suggested by reviewer #1 ("Nighttime Iodine chemistry" or so.)

AC:

We have changed the title to “Nighttime atmospheric chemistry of iodine”.

CEC:

"buildup of HOI"

In your figure 4 (HOI scenario 1) HOI is clearly decreasing during night and it is not building up, although the shown HOI emissions are increasing. You could likely visualize the nighttime values better, if the used colour label differences would not be linear, but e.g. logarithmic. But in the text should be clarified, that part of the emitted HOI has a faster or slower sink depending on scenario.

AC:

We have corrected that statement in the manuscript (page 13, lines from 6 to 9)

CEC:
"which is converted into I2/IBr/ICl through heterogeneous recycling" (2 times) What do you mean by that? According to your reaction list in the attachment there the HOI would react to IBr/ICl on the aerosols but not to I2.

AC:

Thanks!. You are right; we have corrected it and replaced "I_2/IBr/ICl" by "IBr/ICl".

CEC:

"Figures 4 and 5" please use "local time" a x-coordinate as suggested by the reviewer and mention the two-day spin-up elsewhere.

AC:

We have replaced "Time" by "Local time" in x-axis labels, and mentioned "after two days of simulation time" in the text (P13, L2 and P13, L18).

CEC:
"Figure 4 middle right" please do not truncate the colour labels of the contour plot.
AC:

Labels have been replaced by a color scale.

CEC:

"Figure 5": please use also IONO2 instead of INO3 in the bottom panels to be consistent with the text.

AC:

corrected

CEC:
"Figure 6": please explain in more detail which NO3 value is plotted (certain local time, average nighttime or what).

AC:

We now mention in the text (P14, L16) and in the caption of figure 6 that it refers to NO_3 peak nighttime concentration.

CEC:
"figure 7-9, colour bar label" use (greek) Delta HOI and Delta I2 as you show a difference.
AC:

Thank you for the suggestion. We have now included the Delta in the label of the three figures.

Non-public comments to the Author:

Dear authors,

thank you for submitting the revised version. Since I am not an expert in modelling at the molecular level, I asked Florent Louis and one other reviewer to look, whether their comments have been answered sufficiently. As you see, they still have some points, which I would ask you to consider.

regards, Jens-Uwe Grooß

Anonymous Referee #1

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

Suggestions for revision or reasons for rejection (will be published if the paper is accepted for final publication)

In my opinion, the scientific content of the revised version of the manuscript is sufficient to justify publication in ACP. Unfortunately, however, the authors ignored several suggestions from the reviewers to improve the presentation quality which is also important for a high-quality article. In particular, I would like to reiterate the following points:

RC:

Thank you for showing the iodine reaction mechanism in the supplement. You mention that the scheme is referenced in page 22 line 12 in the main text but I cannot find it there. Although the supplement now shows all iodine reactions, the non-iodine reactions in the model are still not listed. For example, IO + BrO is listed but BrO + BrO is not listed, even though this reaction will also have an indirect effect on reactive iodine concentrations.

AC:

You are correct, supplementary information is referenced in page 5 line 10. Now, we have also cited, in the same page and line, the work of Ordoñez et al., 2012, which includes all iodine and non-iodine reactions included in the model. We think that it would be redundant to include the same supplement that has already been included in Ordoñez et al., 2012.

RC:

I know that LT refers to local time. However, this may not be clear to all readers. I think that all acronyms should be explained in the text when they are used for the first time.

AC:

Acronym LT (Local Time) has now been defined in Page 15, line 1.

RC:

It may be customary to quote vibrational frequencies as wave numbers but it is incorrect. It is like saying "the frequency of green light is 500 nm".

AC:

Although it may be incorrect, this is the conventional units for vibrational frequency which is accepted by the community. So we respectfully prefer to keep table 2 in its current form.

RC:

Provided that enough significant digits are shown, it is fine to show the numbers in the plots of Figs. 4 and 5 instead of using a color scale. Nevertheless, I still find it confusing if two plots in the same row use slightly different color schemes. It makes a comparison unnecessarily complicated.

AC:

Thanks for the suggestion. We have now replaced figures 4 and 5 by new ones including the same colour scale.

RC:

The information that "nighttime" refers to the average between midnight and 01:00 local time is important and should be shown in the figure caption. If you want to avoid repetition, it could be removed from the text.

AC:

(from 0:00 to 1:00 LT) has been included in the figure captions.

RC:

The effect of the new chemistry on DMS is quite indirect. You mention that DMS changes because of NO3. In addition, the new iodine chemistry will most probably also affect bromine chemistry, and different BrO will also affect DMS concentrations. I think that either this should also be discussed, or figure 9 should be removed, as another reviewer had suggested.

AC:

The effect of this iodine chemistry on bromine is negligible, so we would expect a direct effect on DMS through NO_3. Therefore we respectfully prefer to keep figure 9 in the manuscript.

Referee #4: LOUIS, Florent

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:

I posted an interactive comment on "Iodine chemistry after dark" by Saiz-Lopez et al. on July 4th 2016. This paper represents a very important contribution dealing with atmospheric iodine chemistry. I made several comments. There is still one comment for which the authors do not take into account my recommendation.

It concerns the spin-orbit correction (SOC) for iodine-containing species involved in the studied reactions. I previously reported "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".

There are large differences between SOC values for I and IO (-17 and -5 kJ mol-1) in the manuscript and the literature data (-30 and -14 kJ mol-1). I would expect the authors will revise their energetics according to the most reliable data. Kinetic parameters should be also re-evaluated.

AC:

We have followed the reviewer’s suggestion and included these recent spin-orbit corrections in the calculated reaction energetics of the three reactions. For reaction 4, the estimated rate coefficient remains unchanged, although k_4 is possibly a lower limit because of the increasing spin-orbit correction across the potential surface from HOI to IO. This is now discussed in the following changes in Section 3 of the paper (page 6, line 11 to page 7, line 11):

"Spin-orbit corrections of -30.0 (Mečiarová et al., 2011), -14.4 (Khanniche et al., 2016), -5.9 (Šulková et al., 2013) and -4.8 (Kaltsoyannis and Plane, 2008) kJ mol^{-1} were applied to the energies of I , IO, HOI and $IONO_2$, respectively.

Reaction 2 is endothermic by 2.6 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 19.8 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 re-arranges to the $IONO_2$ + 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 an IO--HNO_3 complex, which can then dissociate to the products IO + HNO_3. The vibrational frequencies, rotational energies and geometries (in Cartesian co-ordinates) of these intermediates are listed in Table 2. Overall, the reaction is exothermic by 14 kJ mol^{-1}. The energies of the HOI--NO_3 complex and the transition state are assigned the same spin-orbit correction as HOI (-5.9 kJ mol^{-1} (Šulková et al., 2013)), whereas the IO--HNO_3 complex is assigned the spin-orbit correction of IO (-14.4 kJ mol^{-1} (Khanniche et al., 2016)). This reflects the H-OI bond only increasing from 0.97 Å in HOI to 1.1 Å in the transition state, compared with 1.7 Å in the IO—HNO_3 complex. The spin-orbit correction for the transition state is therefore likely to be closer to that of HOI. Assigning the HOI spin-orbit correction therefore means that the barrier is highest with respect to the reactants, so that the estimated rate coefficient (see below) may be a lower limit."

page 8, line 23 to page 9, line 10:

"The uncertainty in k_4 arises principally from the estimated capture rate coefficient (see above), and the height of the barrier below the entrance channel. As discussed above, the spin-orbit correction of the transition state is likely to be larger than the value of -5.9 kJ mol^{-1} corresponding to HOI, so k_4 is possibly a lower limit. For instance, if the barrier height is decreased by 3 kJ mol^{-1}, k_4 increases by a factor of 1.9. If the barrier is lower by 8.5 kJ mol^{-1} (corresponding to the transition state having the same spin-orbit correction as IO), then k_4 would increase by a factor of 5.1. Nevertheless, noting that the capture rate coefficient could be lower – perhaps by a factor of 2 - than the estimate used here, we prefer to use the value for k_4 calculated with the potential surface in Figure 3. Of course, if k_4 is larger, then the atmospheric impacts of reaction 4 discussed in Section 4 will be even more pronounced."

RC:

For the second comment dealing with the treatment of low frequency modes in the intermediate species, I would suggest the authors to mention only in the

manuscript : "The rigid-rotor harmonic oscillator approximation has been used for all species". Hindered rotor treatment for low frequency modes could influence the entropy contribution. Of course, it will depend on the rotational barrier height, its periodicity and the model used. It is often used without any available experimental data.
AC:

We have adopted this suggestion (page 7, line 23).

RC:
Other comments have been properly answered by the authors.

Nighttime atmospheric chemistry of iodine ~~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 $k(T) = 2.7 \times 10^{-12} (300\ K / T)^{2.66}$ 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 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 (Hoffmann et al., 2001; O'Dowd et al., 2002; McFiggans et al., 2004; Gomez Martin et al., 2013; 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).

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),

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 of the MBL iodine loading (Jones et al., 2010; Mahajan et al., 2010a; Großmann et al., 2013; 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 the ~~a~~ global modelling studies~~y~~ by Saiz-Lopez et al. (2014) and (Ordóñez et al., 2012) (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:

$$HOI + NO_2 \rightarrow I + HNO_3 \quad \text{(R2)}$$

$$HOI + HNO_3 \rightarrow IONO_2 + H_2O \quad \text{(R3)}$$

$$HOI + NO_3 \rightarrow IO + HNO_3 \quad \text{(R4)}$$

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 of -30.0 (Mečiarová et al., 2011), -14.4~~17~~ (Khanniche et al., 2016),~~and~~ -5.9 (Šulková et al., 2013) and -4.8 (Kaltsoyannis and Plane, 2008) kJ mol^{-1} were applied to the energies of I , ~~and~~ IO, HOI and $IONO_2$, respectively.~~(Šulková et al., 2013); 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 2.6~~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 19.8~~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 re-arranges to the $IONO_2$ + 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 an IO--HNO_3 complex, which can then dissociate to the products IO + HNO_3. The vibrational frequencies, rotational energies and geometries (in Cartesian co-ordinates) of these intermediates are listed in Table 2. Overall, the reaction is exothermic by 141 kJ mol^{-1}. The energies of the HOI--NO_3 complex and the transition state are assigned the same spin-orbit correction as HOI (-5.9 kJ mol^{-1} (Šulková et al., 2013)), whereas the IO--HNO_3 complex is assigned the spin-orbit correction of IO (-14.4 kJ mol^{-1} (Khanniche et al., 2016)). This reflects the H-OI bond only increasing from 0.97 Å in HOI to 1.1 Å in the transition state, compared with 1.7 Å in the IO—HNO_3 complex. The spin-orbit correction for the transition state is therefore likely to be closer to that of HOI. ~~(Khanniche et al., 2016)~~Assigning the HOI spin-orbit correction therefore means that the barrier is highest with respect to the reactants, so that the estimated rate coefficient (see below) may be a lower limit. ~~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, using the rigid-rotor harmonic oscillator approximation for all species. 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} $(T/300\ K)^{1/6}$ 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 $\langle \Delta E \rangle_{down}$ = 300 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 K / T)$^{2.66}$ 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 R4 under atmospheric conditions are IO + HNO_3. The uncertainty in k_4 arises principally from the estimated capture rate coefficient (see above), and~~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~~ the height of the barrier below the entrance channel. As discussed above, the spin-orbit correction of the transition state is likely to be larger than the value of -5.9 kJ mol^{-1} corresponding to HOI, so k_4 is possibly a lower limit. For instance, if the barrier height is decreased by 3 kJ mol^{-1}, k_4 increases by a facto~~and so is likely to be no more than a factor~~ of 1.9~~2~~. If the barrier is lower by 8.5 kJ mol^{-1} (corresponding to the transition state having the same spin-orbit correction as IO), then k_4 would increase by a factor of 5.1. Nevertheless, noting that the capture rate coefficient could be lower – perhaps by a factor of 2 - than the estimate used here, we prefer to use the value for k_4 calculated with the potential surface in Figure 3. Of course, if k_4 is larger, then the atmospheric impacts of reaction 4 discussed in Section 4 will be even more pronounced.

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 (Read et al., 2008; Saiz-Lopez et al., 2008; Mahajan et al., 2009; Mahajan et al., 2010a; Mahajan et al., 2010b; Lawler et al., 2014). 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; Lee et al., 2009; Read 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 (von Glasow et al., 2002; Saiz-Lopez et al., 2008; Mahajan et al., 2009; Leigh et al., 2010; Mahajan et al., 2010a; Mahajan et al., 2010b; 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 $\gamma = 0.01$ 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 (Carpenter et al., 2013; MacDonald et al., 2014). Figure 4 shows the resulting diurnal evolution of the HOI and I_2 mixing ratios in the two scenarios, after two days of simulation time. 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. 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. On the other hand, HOI concentrations decrease during night until dawn, when they drop to zero. 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).

Figure 5 shows the diurnal evolution of IO, NO_3 and $IONO_2$ in both model scenarios after two days of simulation time. 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, 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 peak nighttime concentration is in fact highly coupled to k_4, with the expected uncertainty in k_4 of one order of magnitude (see above) giving rise to a factor of two change 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 averaged (from 00LT to 01LT (Local Time)) 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 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 coasts 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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1 **Tables**

2

3 Table 1: Night time reactions of emitted inorganic iodine compounds considered in addition to
4 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 x 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}

5
6

1 **Table 2.** Calculated vibrational frequencies, rotational constants and energies of the stationary
2 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

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

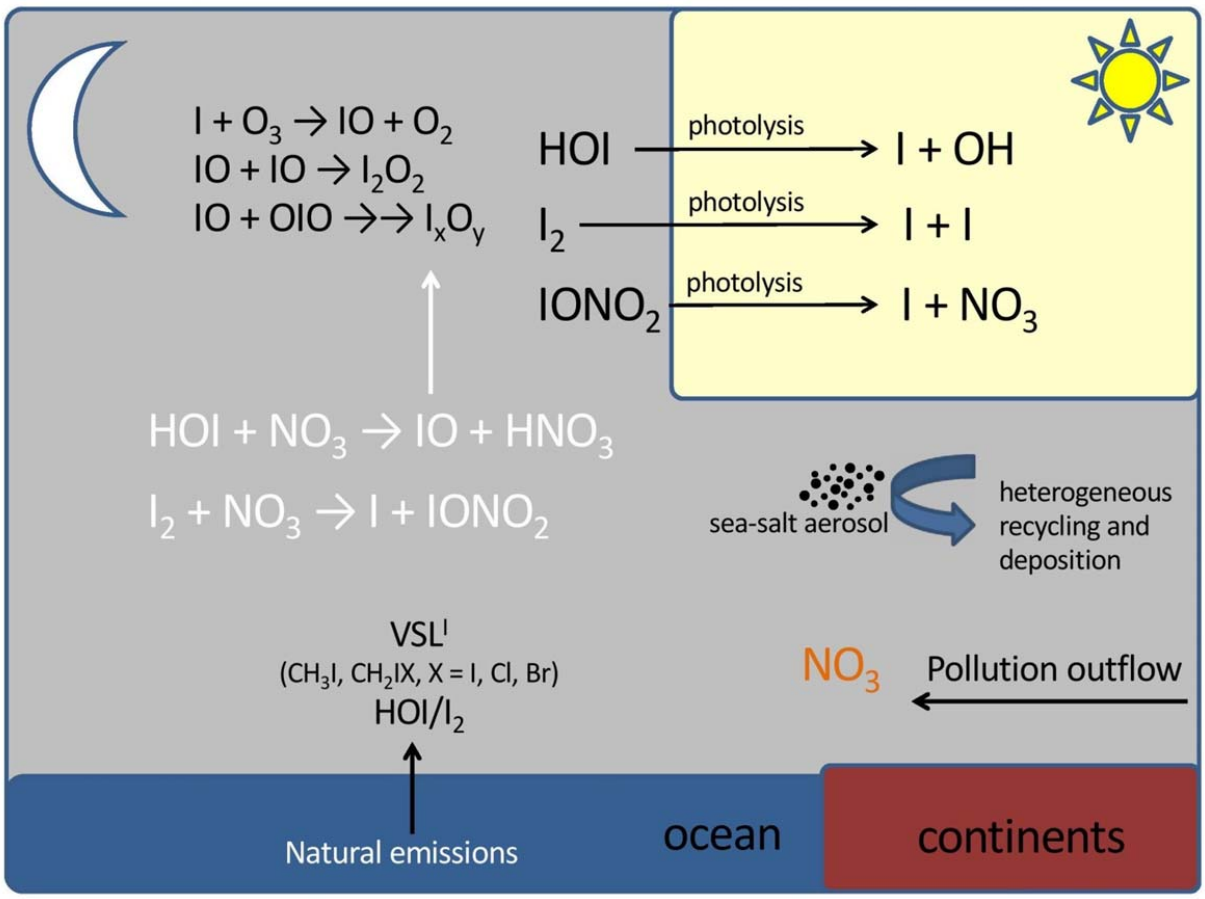


Figure 1. New nocturnal iodine chemistry (in white) implemented in the THAMO and CAM-Chem models.

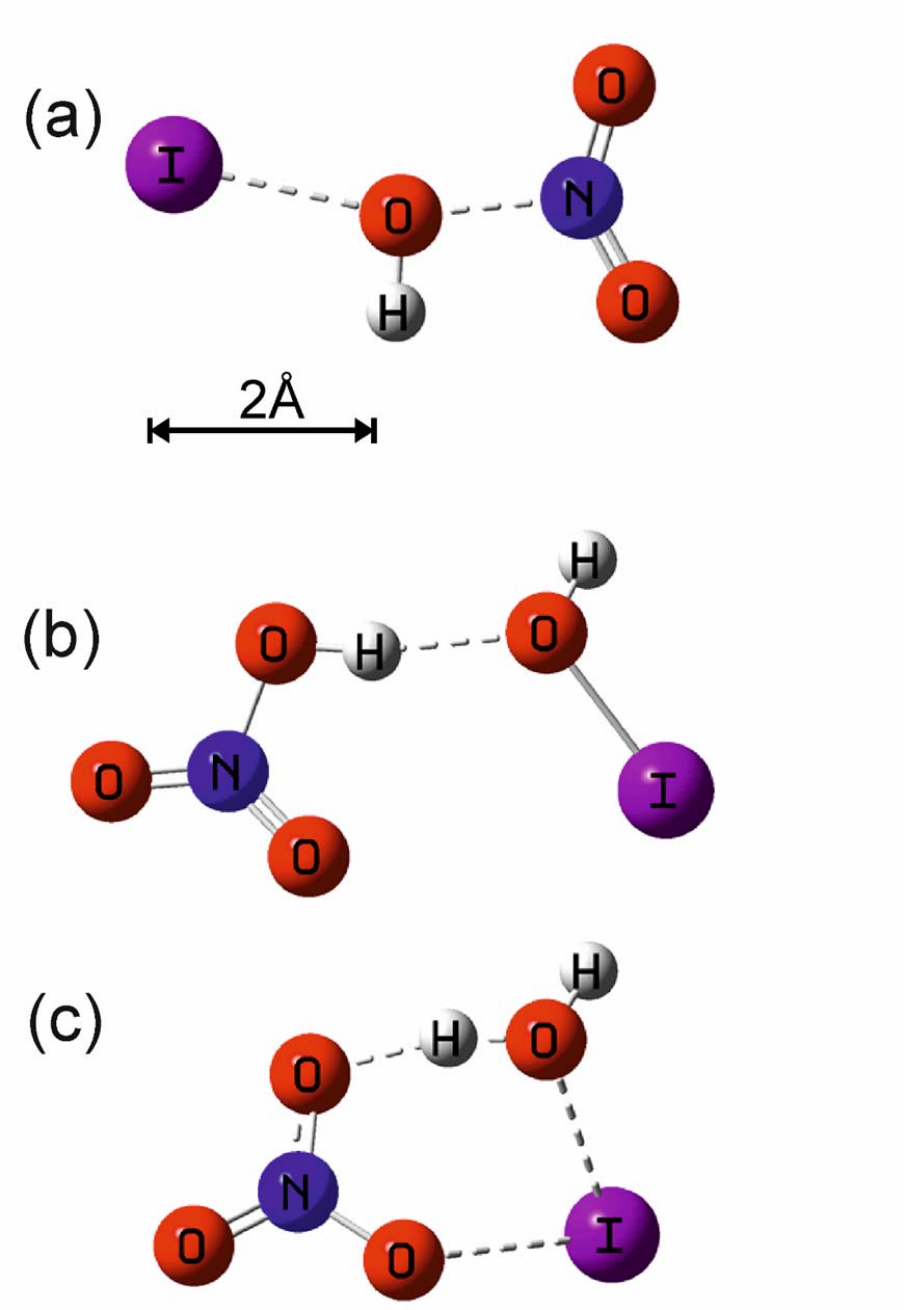


Figure 2: (a) Transition state for the reaction between HOI and NO_2 to form HNO_3 + I; (b) complex formed between HOI and HNO_3, which then reacts via transition state (c) to form IONO2 + H_2O.

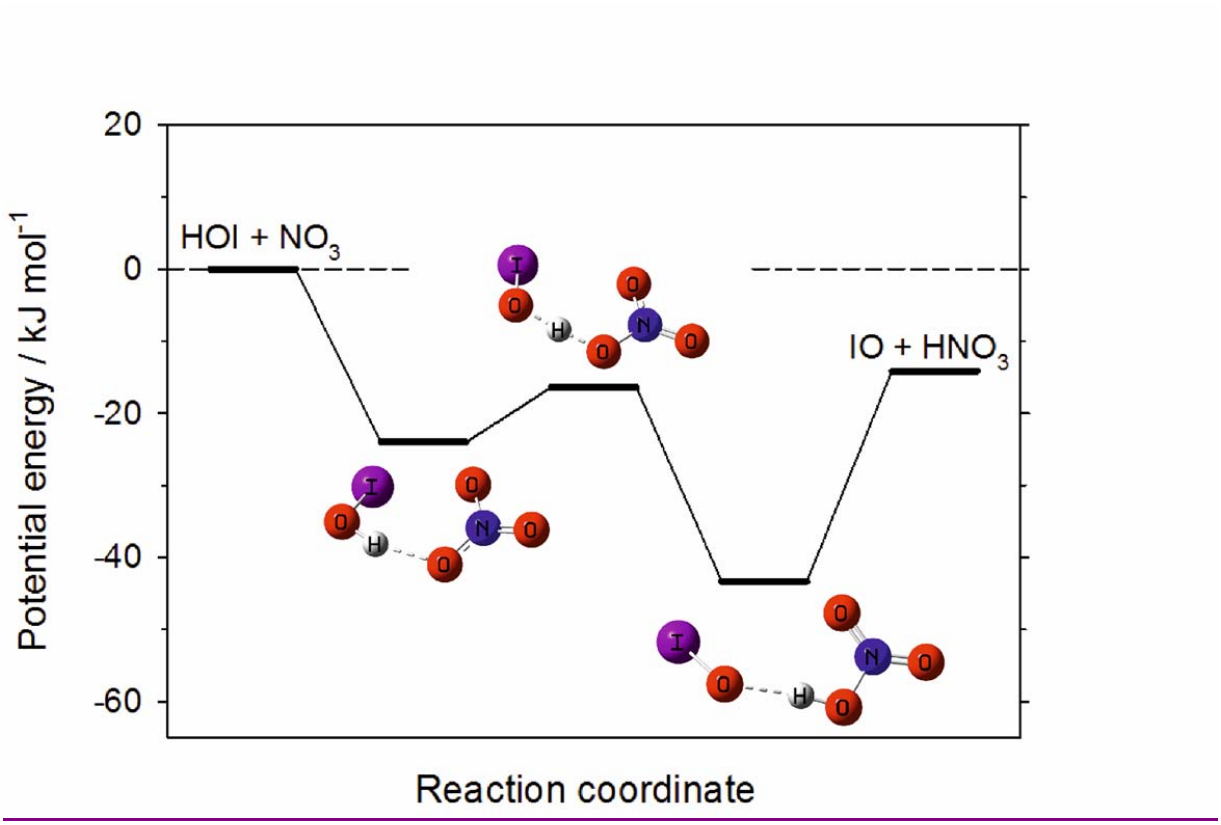


Figure 3. Potential energy surface for the reaction between HOI and NO_3, which contains two intermediate complexes separated by a submerged barrier.

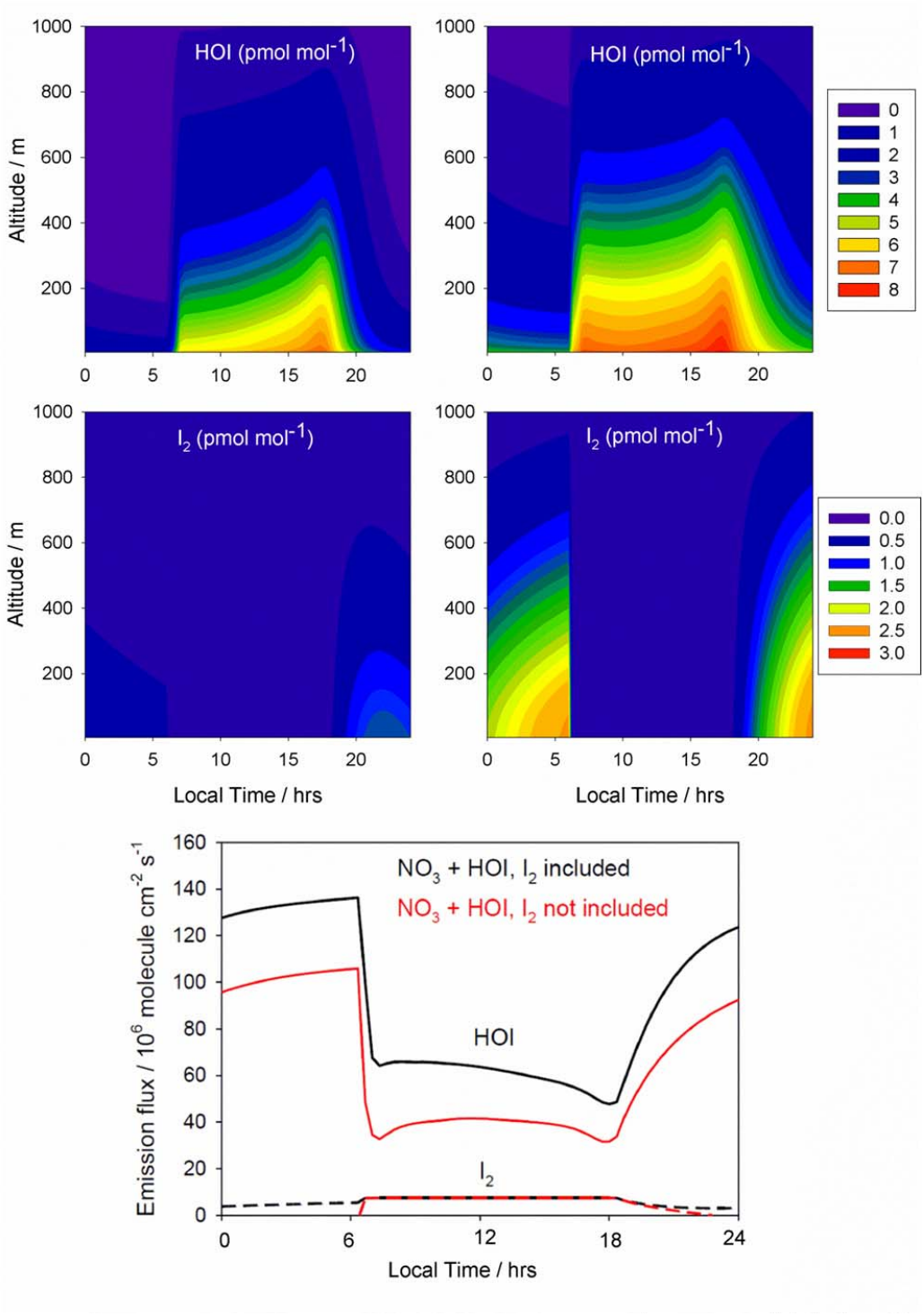


Figure 4. THAMO modeled diurnal variation of HOI, I_2 (upper panels) and the HOI/I_2 flux from the ocean surface (bottom panel). The right hand panels are from scenario 1, which do not include night time reactions of HOI and I_2 with NO_3, while the left hand panels include the reactions in scenario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

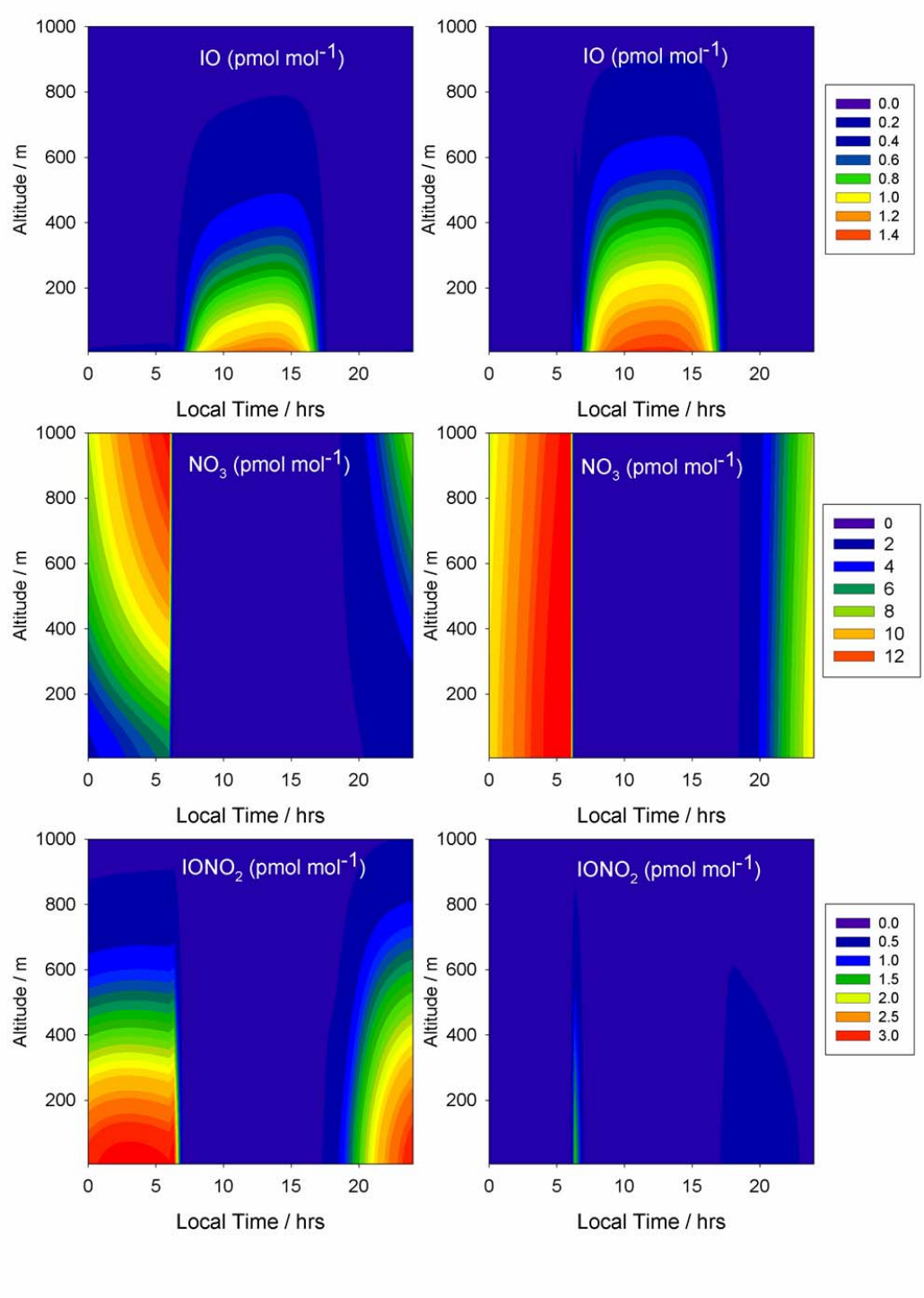


Figure 5. THAMO modeled diurnal variation of IO, NO_3 and the $IONO_2$. The right hand panels are from scenario 1, which do not include night time reactions of HOI and I_2 with NO_3, while the left hand panels include the reactions in scenario 2.

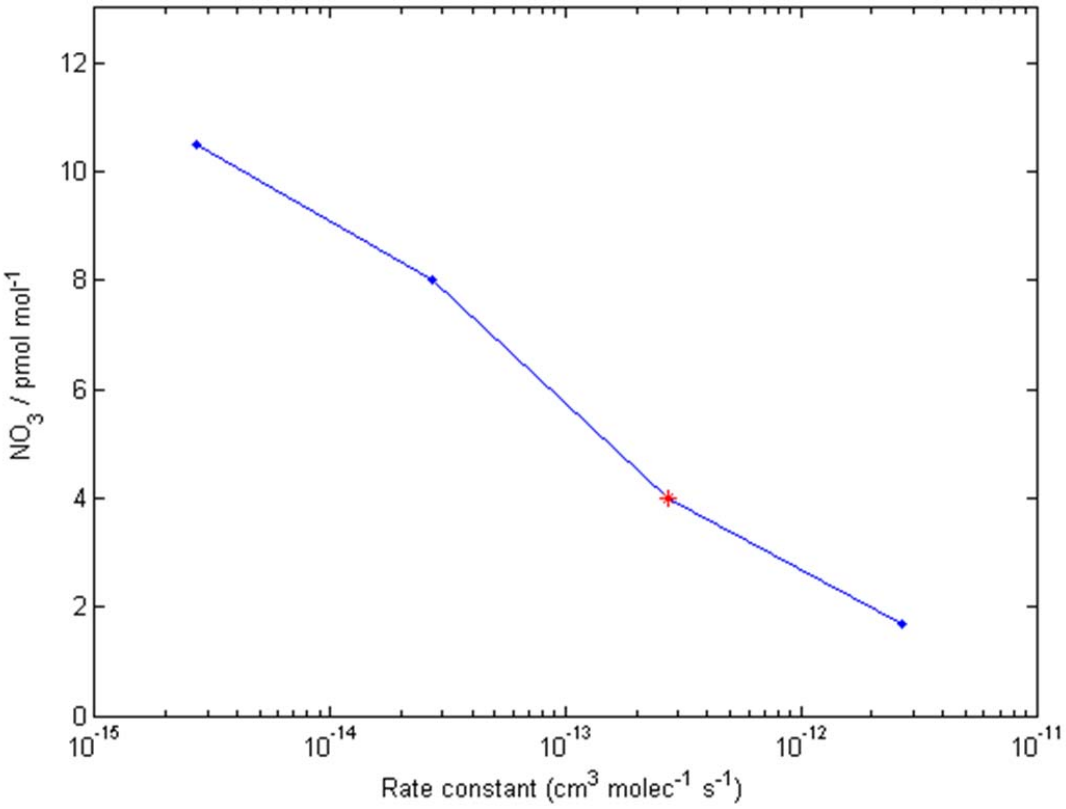


Figure 6. Sensitivity run showing the effect of the uncertainty in the rate constant estimation on the reduction of NO_3 peak nighttime concentration at the surface - the red point is the theoretical estimate.

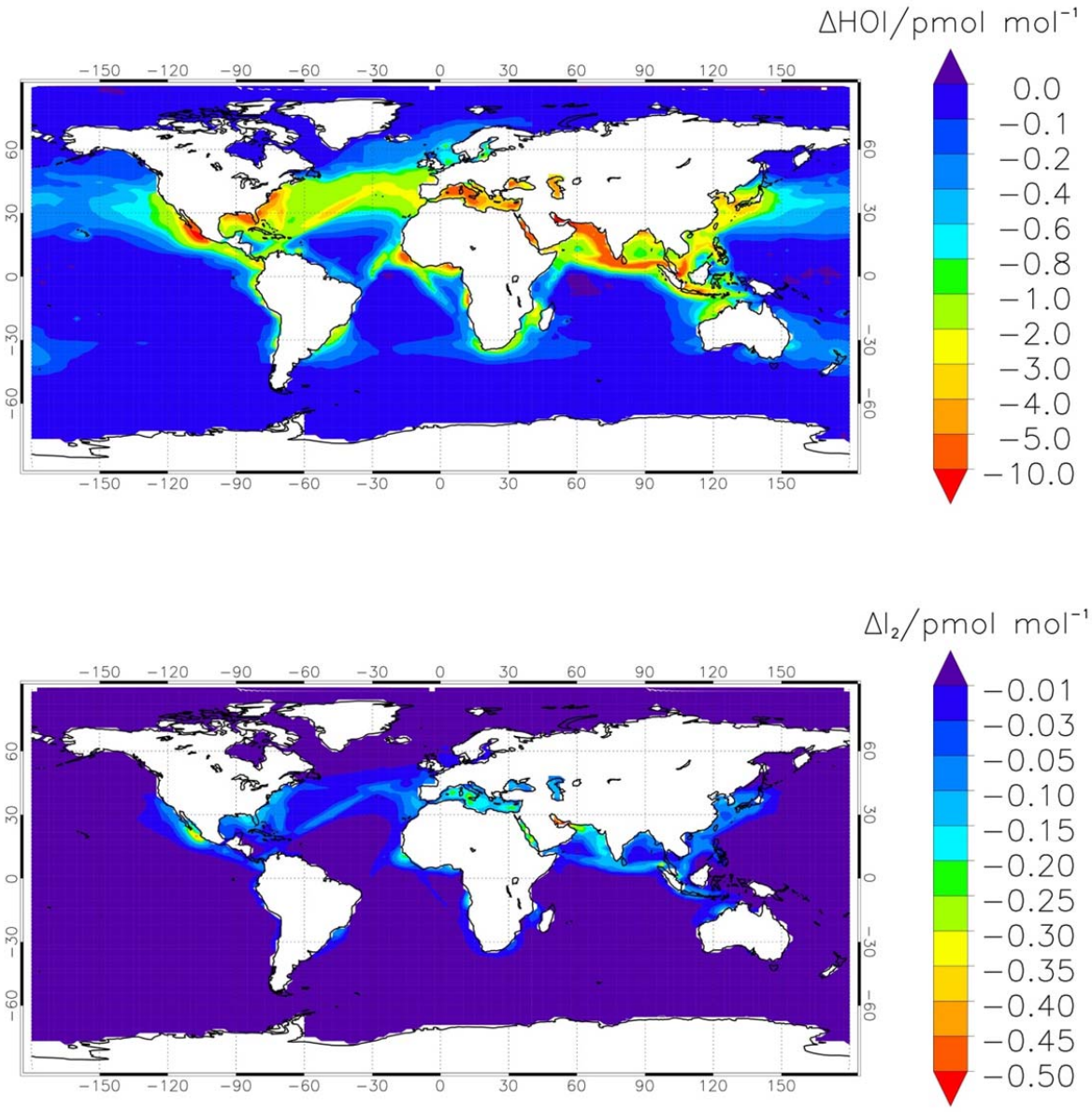
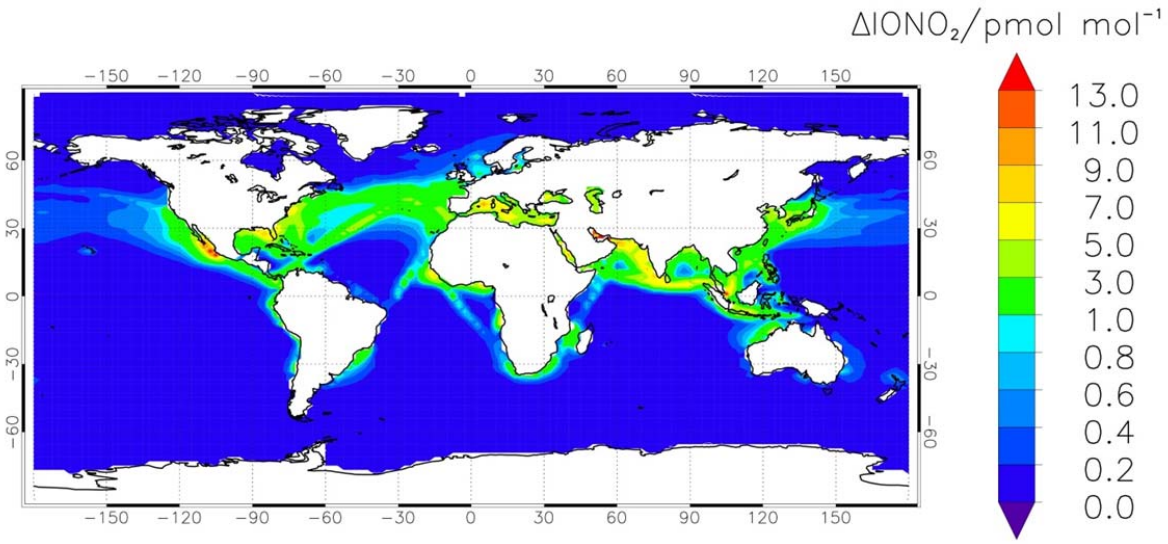


Figure 7. Modelled annual average of HOI (a) and I_2 (b) during night time (from 0:00 to 1:00 LT) at the surface level. The panels show the difference in volume mixing ratio between the simulations with and without reactions (1) and (4).



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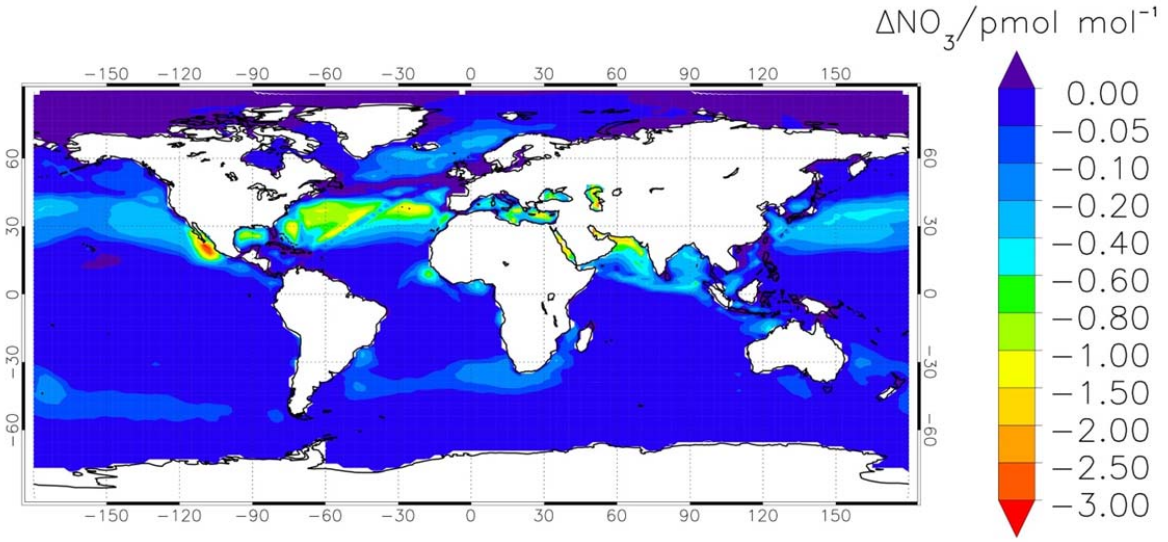

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3 **Figure 8.** Modelled annual average of $IONO_2$ (a) and NO_3 (b) during night time (from 0:00 to
4 1:00 LT) at the surface level, as the difference in volume mixing ratio between the simulations
5 with and without reactions (1) and (4).

6

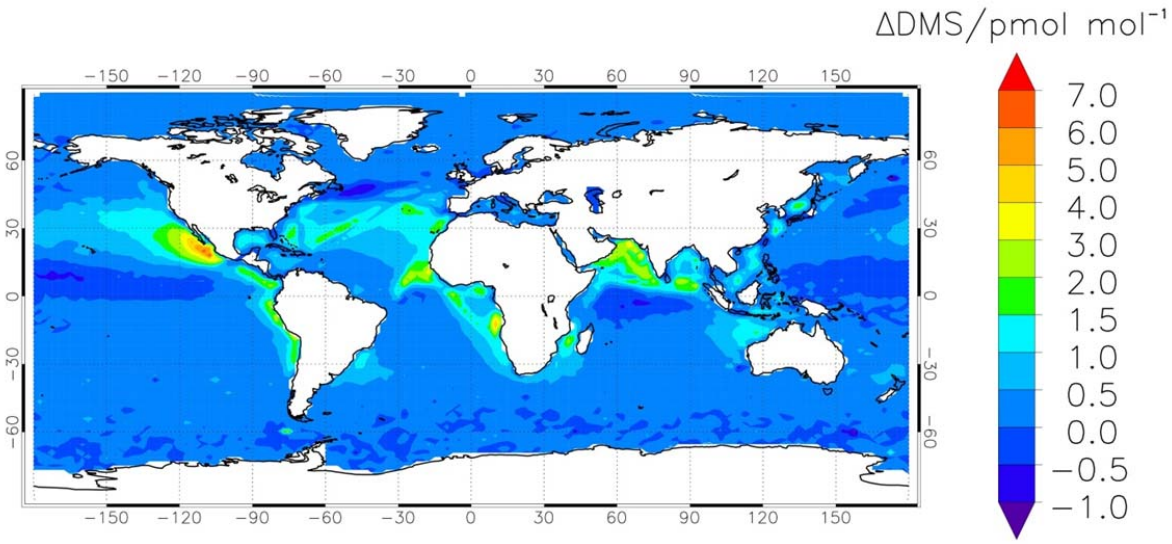

Figure 9. Increase in the DMS levels during night time (from 0:00 to 1:00 LT) at the surface level due to the inclusion of the reactions R1 and R4 in CAM-Chem.

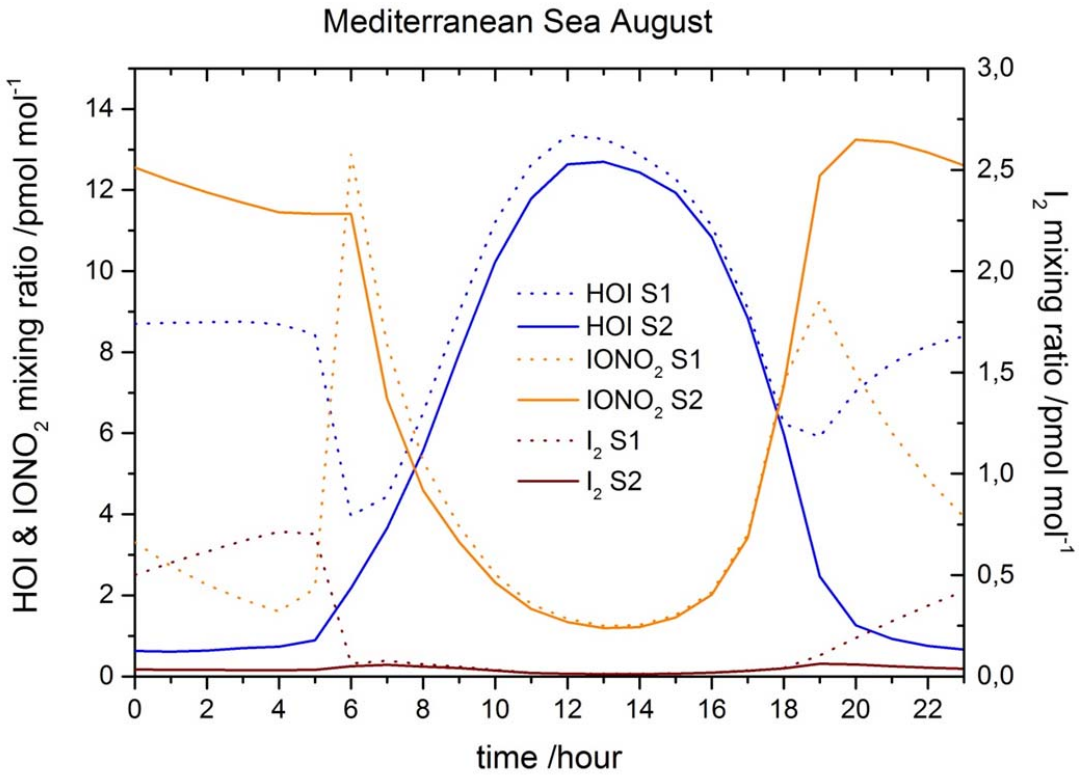

Figure 10. Hourly averaged concentration of HOI, $IONO_2$ and I_2 in the Mediterranean Sea at the surface level (lon:10º→20ºE, lat:33º→40ºN)

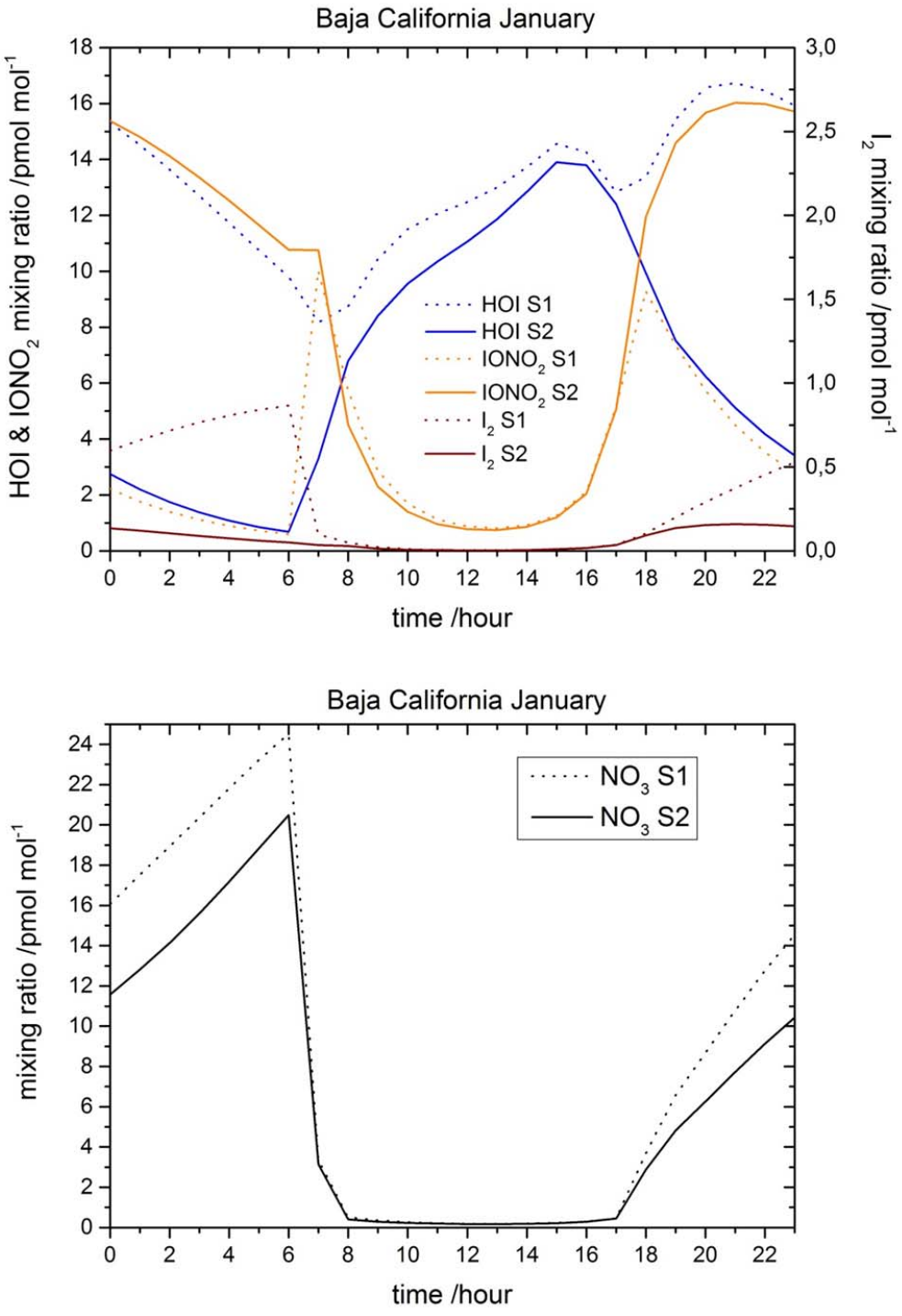

Figure 11. Hourly averaged concentration of HOI, $IONO_2$ and I_2 (upper panel) and NO_3 (bottom panel) in the Pacific Ocean at the south of Baja California peninsula at the surface level (lon: -110º→-106ºE, lat:16º→23ºN)

Supplementary information for

Nighttime atmospheric chemistry of iodine

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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**
$I + O_3 \rightarrow IO + O_2$	$2.1 \times 10^{-11}\ e^{(-830\ /\ T)}$	1
$IO + O_3 \rightarrow OIO + O_2$	3.6×10^{-16}	2
$I + HO_2 \rightarrow HI + O_2$	$1.5 \times 10^{-11}\ e^{(-1090\ /\ T)}$	3
$IO + NO \rightarrow I + NO_2$	$7.15 \times 10^{-12}\ e^{(300\ /\ T)}$	1
$IO + HO_2 \rightarrow HOI + O_2$	$1.4 \times 10^{-11}\ e^{(540\ /\ T)}$	1
$IO + IO \rightarrow OIO + I$	$2.13 \times 10^{-11}\ e^{(180/\ T)} \times [1 + e^{(-p\ /\ 191.42)}]$	1, 4
$IO + IO \rightarrow I_2O_2$	$3.27 \times 10^{-11}\ e^{(180\ /\ T)} \times [1 - 0.65\ e^{(-\ p\ /\ 191.42)}]$	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]
$I_2 + OH \rightarrow HOI + I$	1.8×10^{-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
$OH + HI \rightarrow I + H_2O$	$1.6 \times 10^{-11}\ e^{(440\ /\ T)}$	1
$I + IONO_2 \rightarrow I_2 + NO_3$	$9.1 \times 10^{-11}\ e^{(-146\ /\ T)}$	5
$HOI + OH \rightarrow IO + H_2O$	2.0×10^{-13}	10
$IO + DMS \rightarrow DMSO + I$	$3.2 \times 10^{-13}\ e^{(-925\ /\ T)}$	11
$INO_2 \rightarrow I + NO_2$	$1008 \times 10^{15}\ e^{(-13670\ /\ T)}$	12, 13, 14
$IONO_2 \rightarrow IO + NO_2$	$w_1 \cdot \exp(w_2\ /\ T)$ [f]	5, 15
$INO + INO \rightarrow I_2 + 2NO$	$8.4 \times 10^{-11}\ e^{(-2620/T)}$	3
$INO_2 + INO_2 \rightarrow I_2 + 2NO_2$	$4.7 \times 10^{-13}\ e^{(-1670\ /\ T)}$	1
$OIO + NO \rightarrow IO + NO_2$	$1.1 \times 10^{-12}\ e^{(542\ /\ T)}$	14
$HI + NO_3 \rightarrow I + HNO_3$	$1.3 \times 10^{-12}\ e^{(-1830\ /\ T)}$	16
$IO + BrO \rightarrow Br + I + O_2$	$0.30 \times 10^{-11}\ e^{(510/T)}$	1
$IO + BrO \rightarrow Br + OIO$	$1.20 \times 10^{-11}\ e^{(510/T)}$	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 $w1 = 4.687 \times 10^{-10} - 1.3855 \times 10^{-5} \times e^{(-0.75\,p / 1.62265)} + 5.51868 \times 10^{-10} \times e^{(-0.75\,p / 199.328)}$

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

b $w1 = 1.1659 \times 10^{-9} - 7.79644 \times 10^{-10} e^{(-0.75\,p/22.09281)} + 1.03779 \times 10^{-9} \times e^{(-0.75\,p / 568.15381)}$

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

c $w1 = 3.54288 \times 10^{10} + 1.8523 \times 10^{11} \times 0.75\,p - 1.45435 \times 10^{8} \times (0.75p)^2 + 60799.4344 \times (0.75p)^3$

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

d $w1 = 255335000000 - 4418880000 \times 0.75\,p + 85618600 \times (0.75\,p)^2 + 14218.81 \times (0.75\,p)^3$

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

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

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

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	$\gamma = 0.06$
$I_2O_2 \rightarrow$	$\gamma = 0.01$[§]
$I_2O_3 \rightarrow$	$\gamma = 0.01$[§]
$I_2O_4 \rightarrow$	$\gamma = 0.01$[§]

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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