Enhanced chlorine atom activation by hydrolysis of iodine nitrates from marine aerosols at polluted coastal areas

E. H. Hoffmann[1], A. Tilgner[1], R. Wolke[2], H. Herrmann[1]

1 Atmospheric Chemistry Department (ACD),
  Leibniz Institute for Tropospheric Research (TROPOS), Leipzig, Germany
2 Modeling of Atmospheric Processes Department (MAPD),
  Leibniz Institute for Tropospheric Research (TROPOS), Leipzig, Germany

contact: erik.hoffmann@tropos.de

Motivation

Reactions of reactive halogen compounds are linked to different key tropospheric chemical subsystems. Halogen atoms (chlorine (Cl), bromine (Br) and iodine (I) atoms) react with ozone, NO_x and volatile organic compounds (VOCs). In anthropogenic influenced coastal regions with high NO_x concentrations, halogen monoxides (ClO, BrO and IO) affect the NO_x ratio by reacting with NO forming NO_2 and with NO_2 forming halogen nitrates (XNO_3, X = Cl, Br, and I) (1).

The subsequent formation of XNO_3 at polluted coastal areas can be crucial to initialise the activation of Cl atoms by formation of XCl species. The XNO_3 can be taken up into marine aerosols, where it fast hydrolyse into nitrate and a hypohalogenous acid (HOX). The HOX reacts further with chloride leading to XCl. Hence, XNO_3 formation in polluted coastal areas can have high potential to initialize a cycle of Cl atom activation.

Model studies indicated, that at conditions with NO_2 concentrations above 100 ppt, the ICl photolysis dominates Cl atom release over $ClNO_2$ photolysis, due to INO_3 formation and subsequent hydrolysis in marine aerosols (2). Nevertheless, possible important effects of INO_3 hydrolysis have not yet been investigated under NO_x polluted conditions, i.e. with NO_2 concentrations above 1 ppb.

Therefore, in the current study (3), the effect of INO_3 formation on Cl atom activation is investigated for an anthropogenically polluted environment under maritime influences using the air parcel model SPACCIM (4).

Model description

Multiphase chemistry simulations in a polluted coastal environment are performed with the adiabatic air parcel model SPACCIM. The multiphase chemistry in SPACCIM is represented by following mechanisms:

- Gas-phase mechanism MCMv3.2 (5) together with aqueous-phase mechanism CAPRAM4.0 (6)

- The halogen module 2.1 (7), extended to treat XNO_3 hydrolysis (see Table 1)

- Air parcel travels from the marine coastal sea over an anthropogenically polluted environment (see Fig. 1)

- Additional sensitivity studies without considered hydrolysis of XNO_3

Table 1: Implemented reaction rate constants of XNO_3 hydrolysis. The star comments that the INO_3 hydrolysis is estimated to be at least as fast as the $ClNO_3$ hydrolysis.

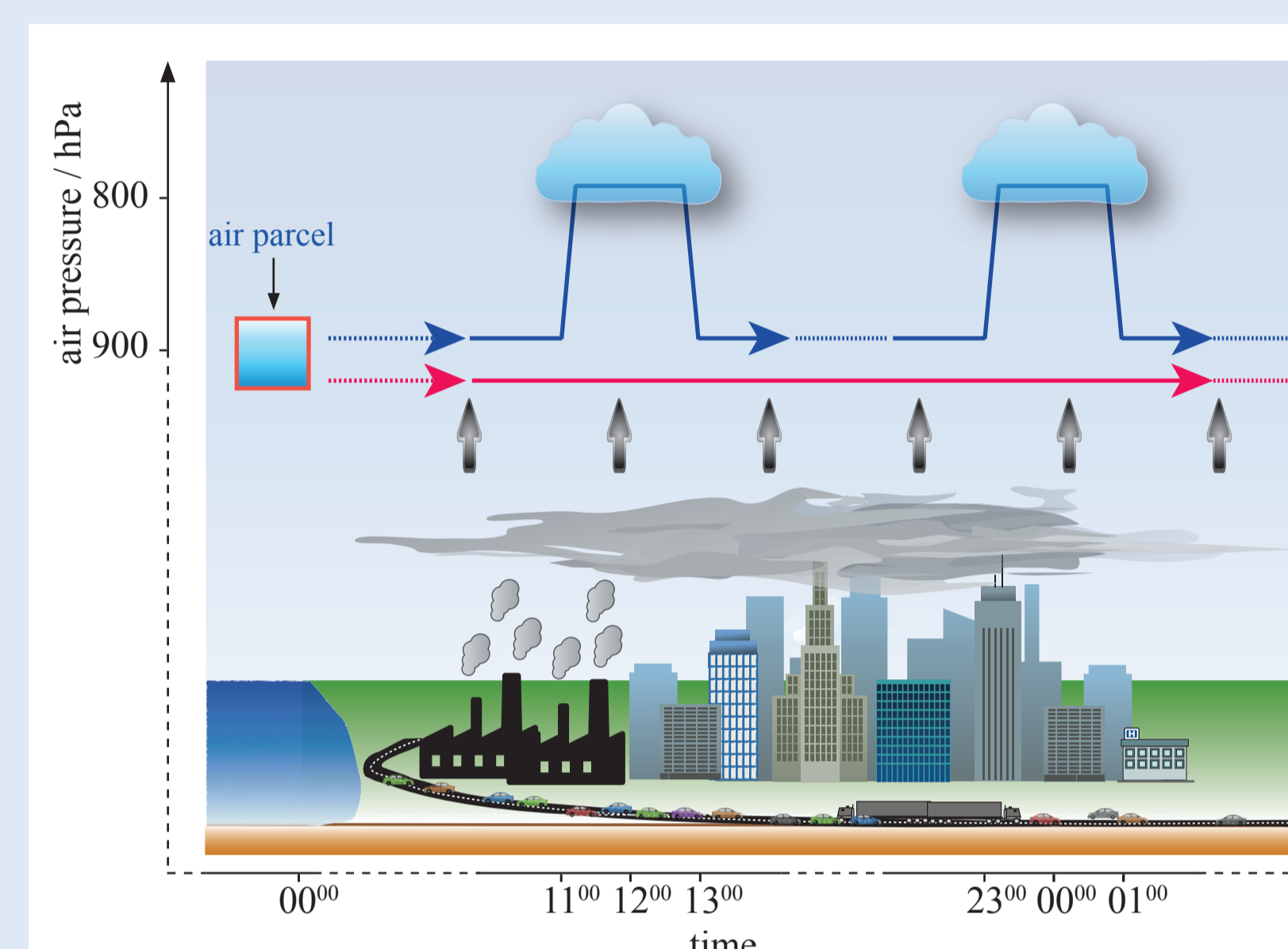|	k_{298} / l mol^{-1} s^{-1}	E_A/R / K	Reference
$ClNO_3$	2.8×10^4	2800	(8)
$BrNO_3$	1.0×10^9		(9)
INO_3^*	2.8×10^4	2800	

Fig. 1: Schematic of two meteorological scenarios, (1) with cloud occurrence (blue line) and (2) without cloud occurence (red line), used in the model simulations. The model runs 72 hours at 45°N. The grey arrows represent urban emissions, which interact with the air parcel of marine origin. (3)

Model results
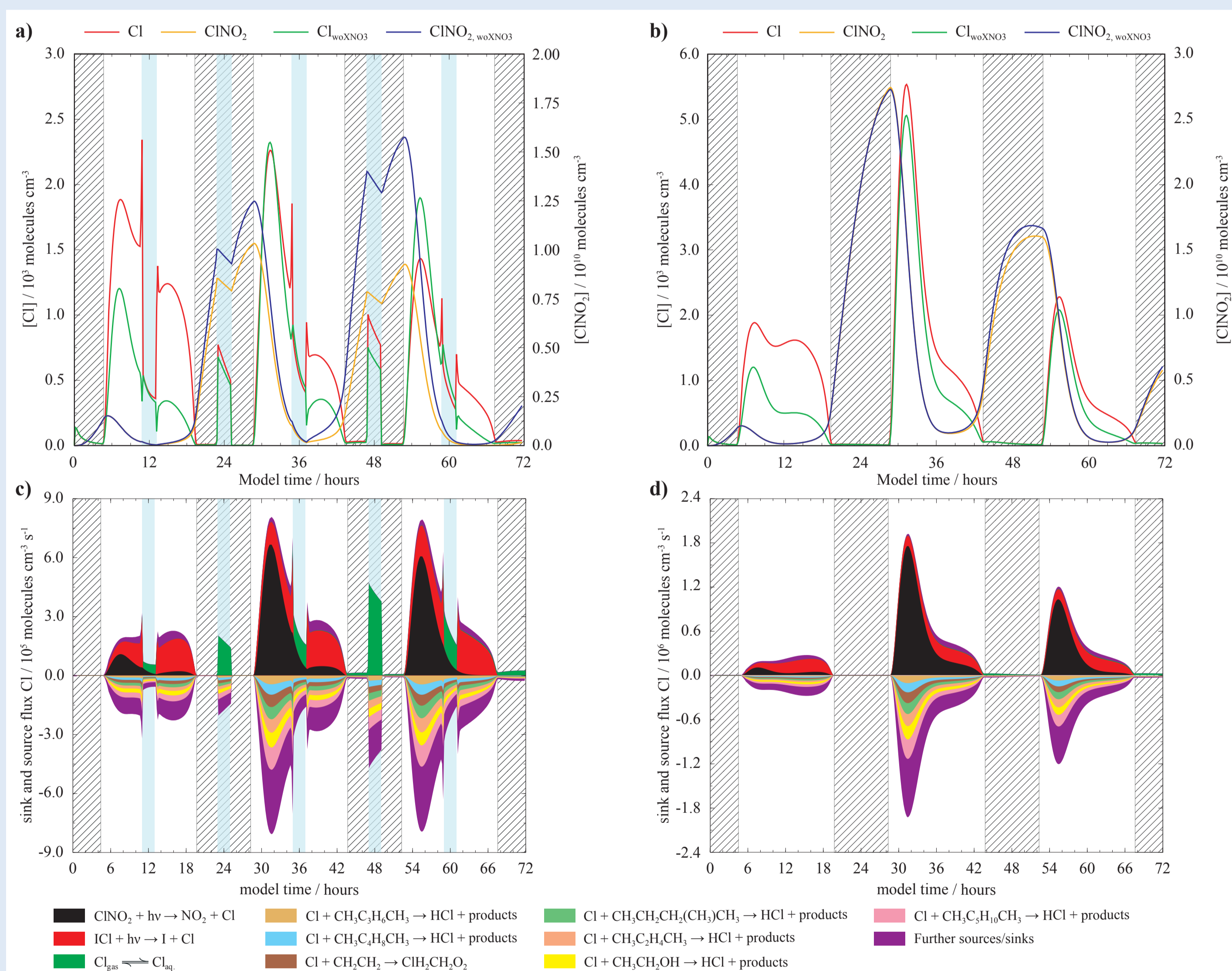
Chlorine atom activation

Fig. 2: Modelled concentration profiles of Cl atoms (left y-axis) and $ClNO_2$ (right y-axis) in the gas phase for model scenarios with and without XNO_3 hydrolysis under cloud (a) and cloud-free (b) conditions. Corresponding modelled time-resolved sink and source fluxes of Cl atoms under cloud (c) and the cloud-free (d) conditions are presented below. (3)

- Strong morning peak of Cl atoms from $ClNO_2$ photolysis and stronger second shoulder in Cl atom concentration at afternoon from ICl photolysis

- $ClNO_2$ photolysis dominates forenoon and ICl photolysis afternoon Cl atom activation.

- Higher importance of ICl photolysis within the scenario with cloud occurrence, because of effective INO_3 uptake during formation and evaporation of the cloud

- Nighttime clouds act as Cl atom source due to ETR of NO_3 with chloride.

- 15% of overall mean flux of Cl atom activation results from this reaction sequence.

Chemistry of reactive iodine

- Main reaction pathway of IO in the gas phase is reation with NO_2 into INO_3

- Around 25% and 38% of INO_3 is taken up into particles/cloud droplets, residual one is photolysed.

- Hydrolysis of INO_3 and subsequent reaction with chloride results into ICl

- One third of formed ICl interacts with bromide yielding IBr

- Evaportaion of ICl/IBr into the gas phase and further photolysis.

- Effective I atom recycling enables important Cl atom activation flux.

- During cloud periods high importance of HOI for S(IV) to S(VI) oxidation
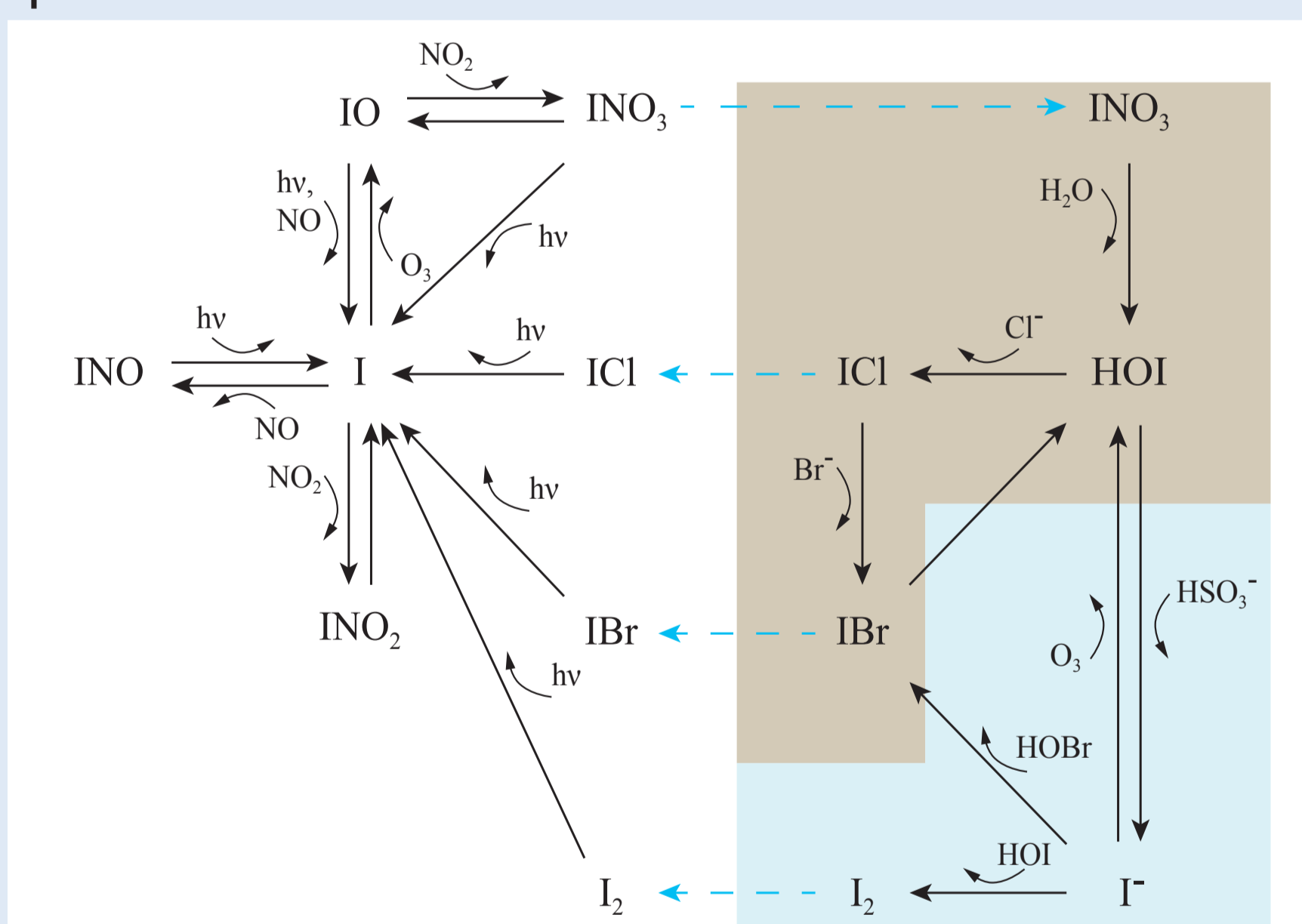
- Formed iodide reacts with HOI yielding I_2.

Fig. 3: Schematic representation of most important iodine cycles under non-cloud and in-cloud conditions within the cloud scenario. (3)

Conclusion

The numerical simulations reveal that iodine nitrate hydrolysis on sea salt aerosol particles effectively enhances the formation of Cl atoms. Consequently, INO_3 hydrolysis affects the atmospheric oxidation capacity, VOC oxidation, and ozone formation potential in polluted coastal areas. The simulations imply that an advanced treatment of halogen–NO_x chemistry in both the gas and the aqueous phase is necessary to improve the accuracy of present chemical transport models dealing air quality in polluted coastal areas.

References

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