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Insights into the chemistry of iodine new particle formation: the role of iodine oxides and the source of iodic acid.

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Gómez Martin et al. (2022), Insights into the chemistry of iodine new particle formation: the role of iodine oxides and the source of iodic acid, Journal of the American Chemical Society, Accepted May 2022

Motivation

- Iodine chemistry is an important driver of new particle formation in the marine and polar boundary layer, but there is contradictory evidence about iodine gas-to-particle conversion.
- Laboratory studies indicate that the photooxidation of iodine produces iodine oxides (I_xO_y), which are well-known particle precursors (Gómez Martín et al., Nat. Commun., 2020)
- By contrast, nitrate anion chemical ionization mass spectrometry (CIMS) observations in field and environmental chamber studies have been interpreted as evidence of a dominant role of iodic acid (HIO_3) in iodine-driven particle formation (He et al., Science, 2021)
- Ab initio calculations indicate that the iodate core ions observed by CIMS can be generated from $I_xO_y + NO_3^-$ (Lewis et al., EGU21-13817).
- Ab initio calculations indicate that HIO_3 cannot form from $I_xO_y + H_2O$. But what about the water dimer? (Xia et al., Environ. Sci. Tech., 2020)
- Bromide CIMS observations indicate the existence of gas phase HIO_3 (Wang et al. AMT, 2021)
- The composition of dry particles is I_2O_5 (Saunders et al. ZPC., 2010). Particles formed under high RH are HIO_3 (Gómez Martín et al. Nat. Commun. 2020; He et al., Science, 2021)

Methodology

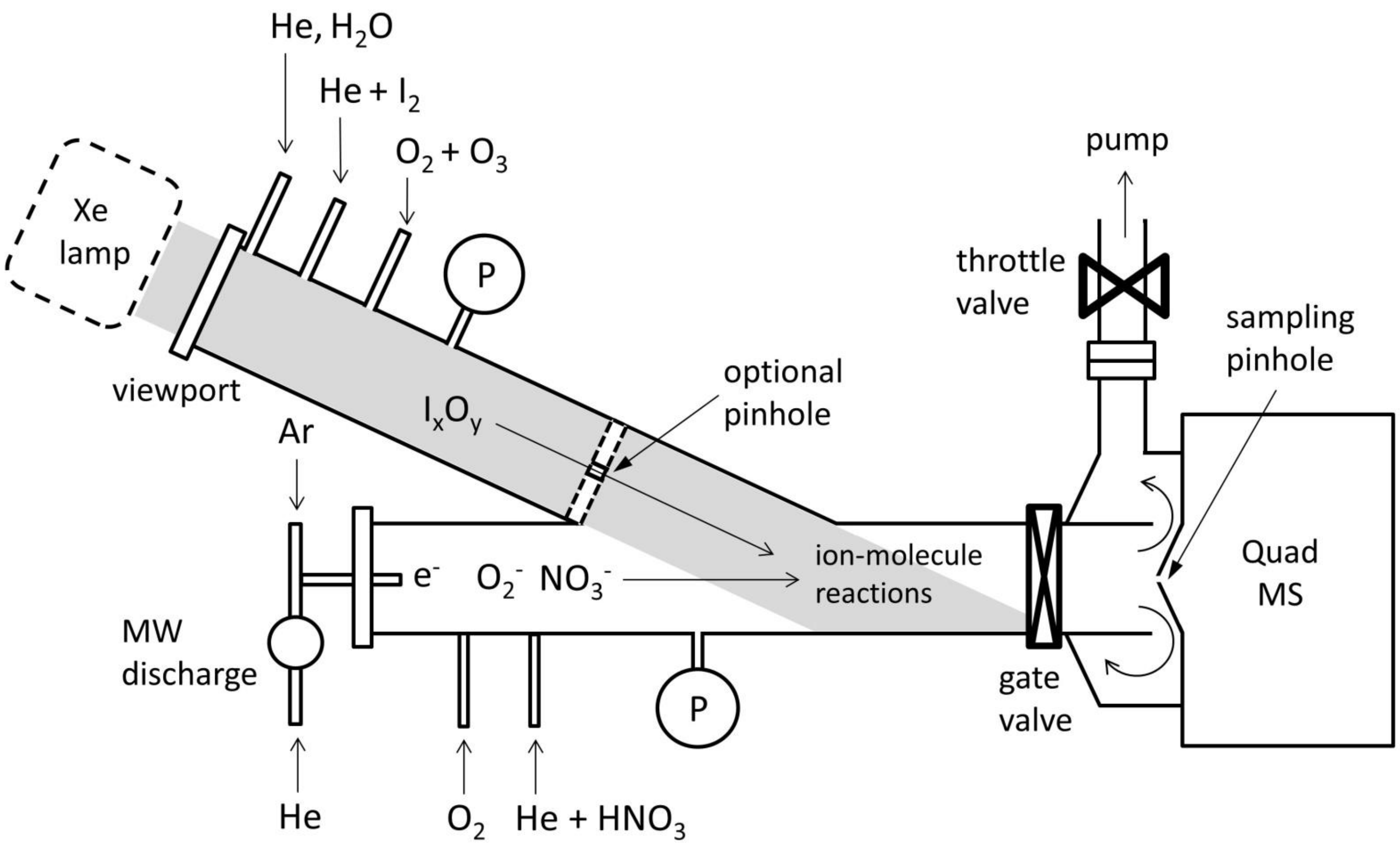
Ion-molecule reaction products study

Experiments

- Flowing afterglow-fast flow tube coupled to a I_xO_y flow tube with broad band continuous photolysis
- Mass spectrometric detection of ion-molecule reaction products.
- Different pressure and water vapor concentration regimes.

Theory

- PES of relevant ion-molecule reactions at different levels of theory



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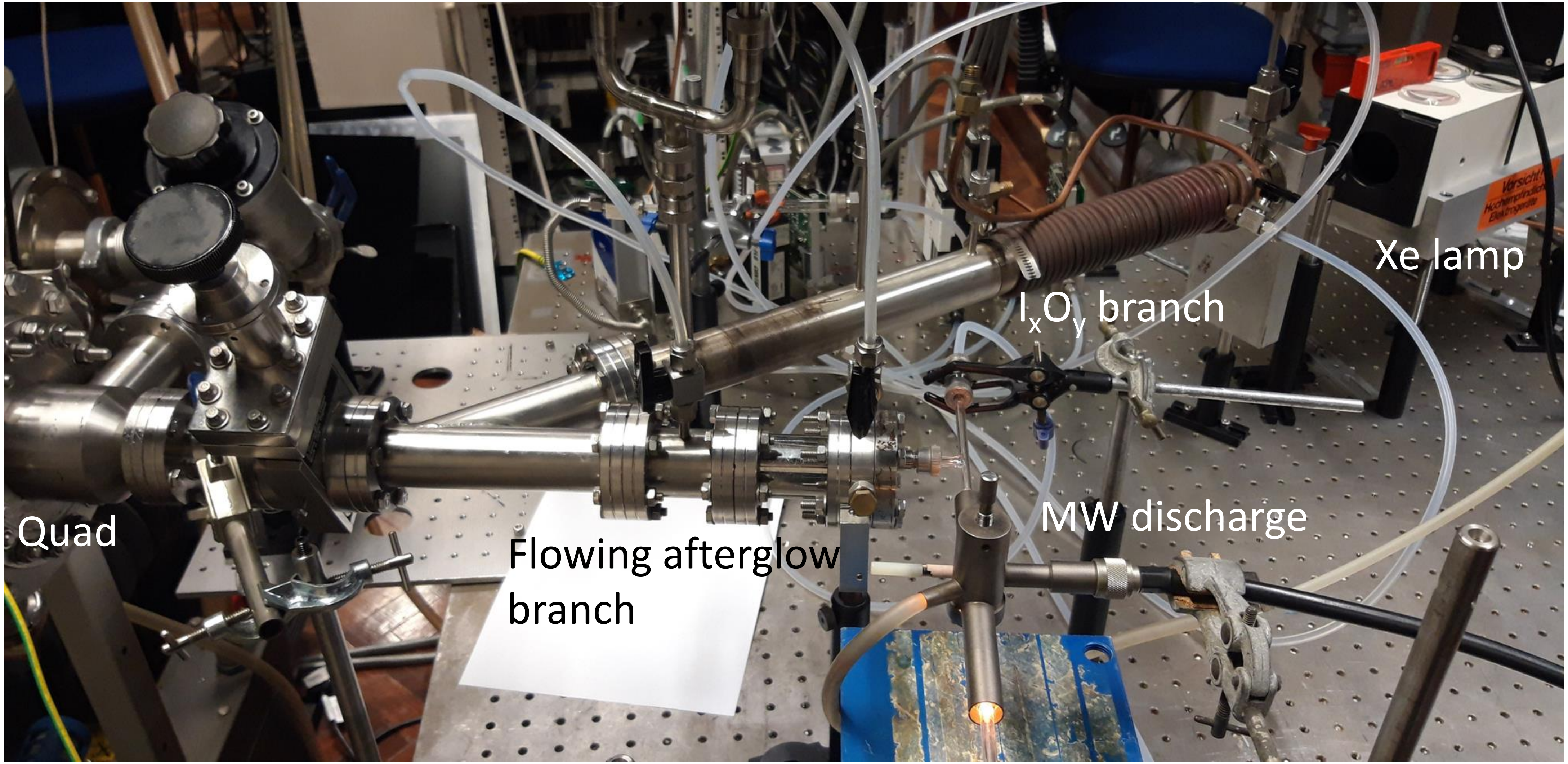
Methodology

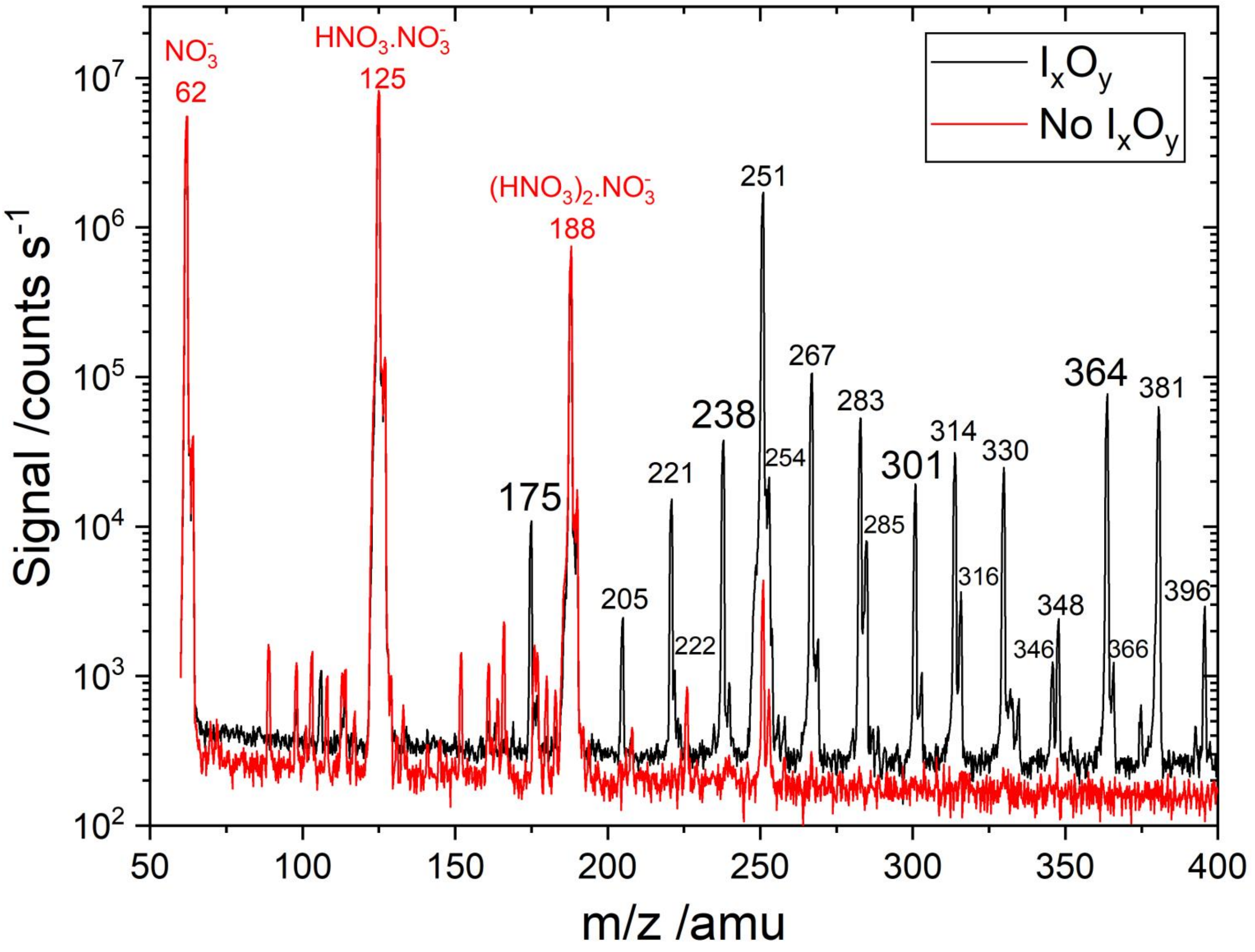
Picture of the experimental set-up



Results: dry experiments

No water added, 3 Torr

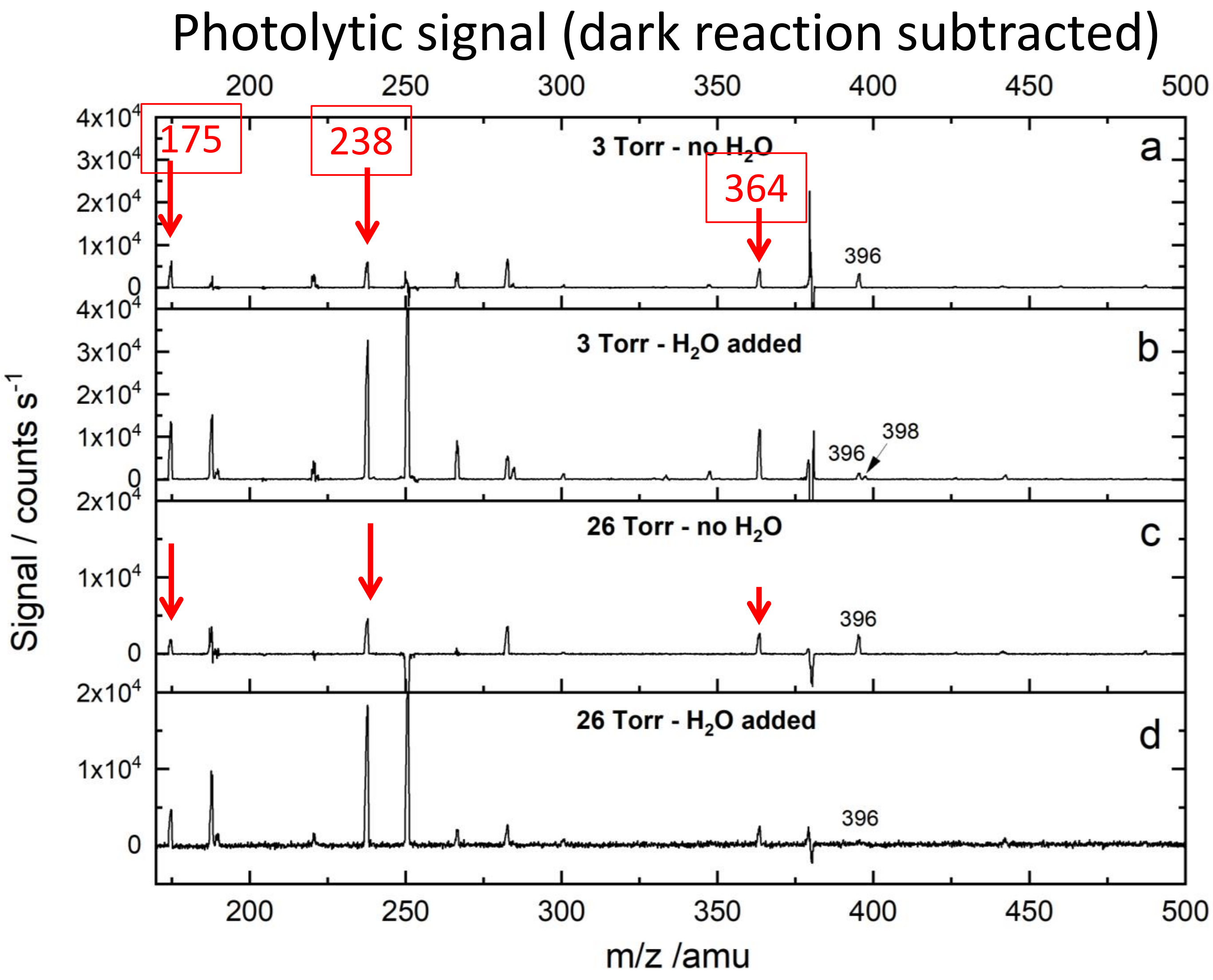
- $[H_2O] < 2\times10^{13}$ molecule cm^{-3} (4 orders of magnitude lower than ambient).
- Dark reaction generates products. Light enhances signal.
- Iodine oxide - nitrate ion clusters $I_xO_y.NO_3^-$ are observed (m/z = 348, 364, 396). $I_2O_5.NO_3^-$ only observed with light.
- Iodate core ions $(HNO_3)_n.IO_3^-$ are observed (m/z = 175, 238, 301).
- $IO_nNO_2.NO_3^-$ (n=1-3) clusters are observed (m/z=251, 267, 283).



Results: wet experiments

Water added, 3 Torr and 26 Torr

- 3 Torr: $[H_2O] = 8\times10^{15}$ molecule cm^{-3} and $[(H_2O)_2]\sim 2\times10^{12}$ molecule cm^{-3}.
- 26 Torr: $[H_2O] = 2.5\times10^{17}$ molecule cm^{-3} (close to ambient levels) and $[(H_2O)_2]\sim 4\times10^{14}$ molecule cm^{-3}.
- At the highest pressure almost all signal is photolytic (diffusion to walls reduced).
- All signals increase with water, except $I_2O_5.NO_3^-$, which is removed.
- Some new minor peaks appear with water, e.g. m/z = 334, 351, 398. These are potentially linked to HIO_3.

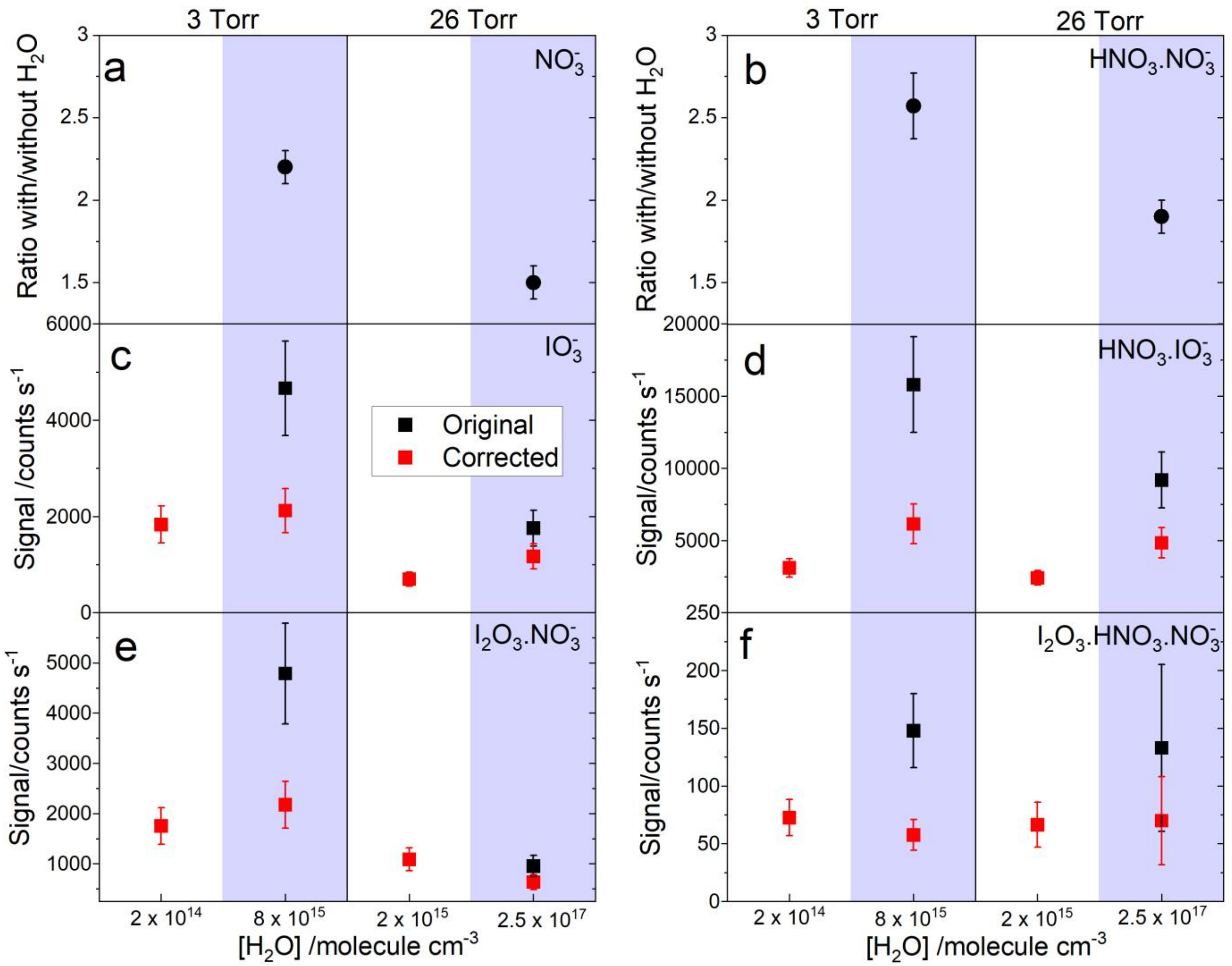


- The nitrate reagent ion signals increase with water: a correction of product signals is needed.

Results: wet experiments

After correction for increase reagent ion signal in the presence of water:

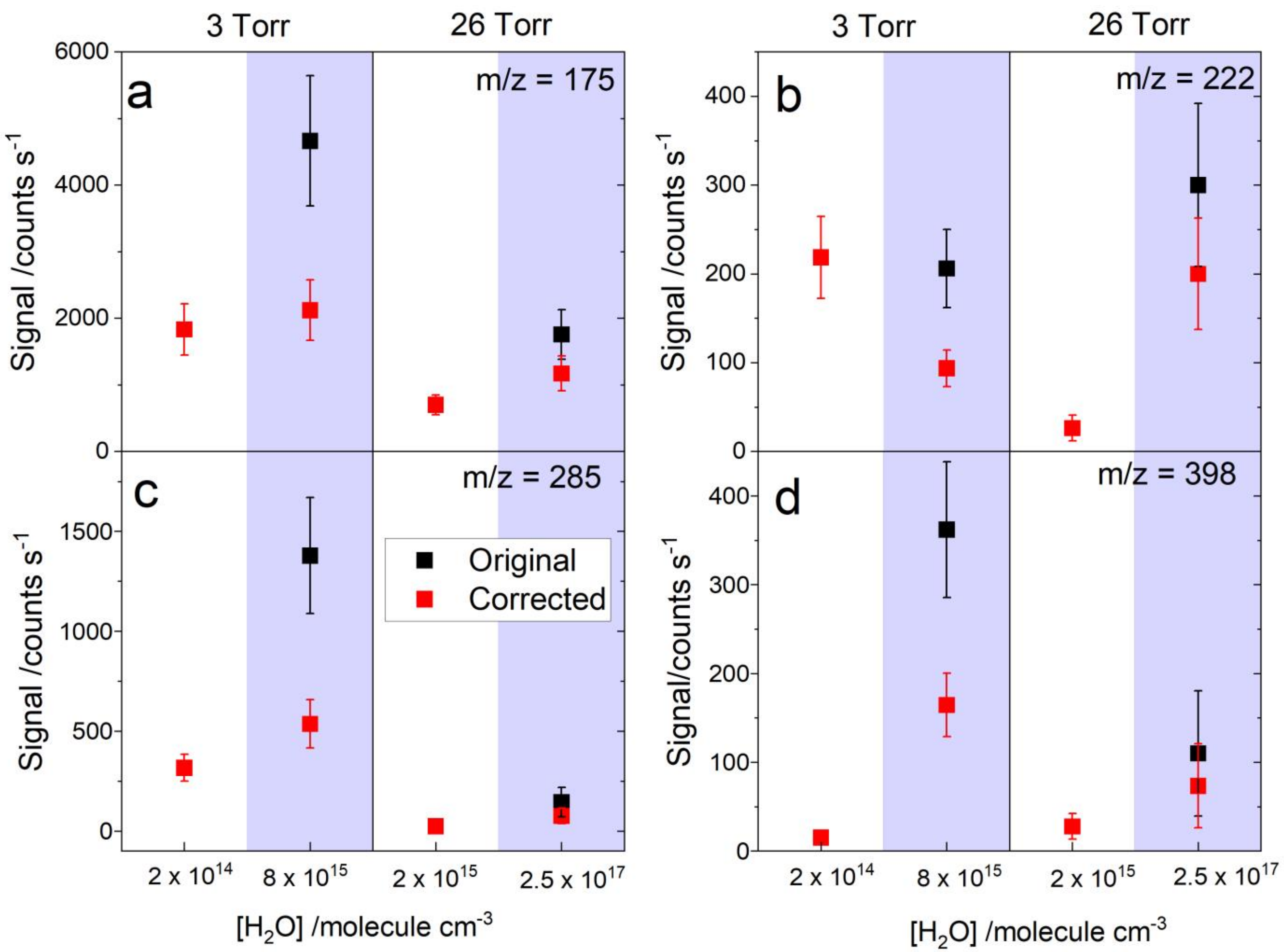
- Factor of ~ 2 enhancement of m/z = 175 and m/z = 238 ⇒ Possible contribution of HIO_3 to these signals in the form of $HIO_3.(HNO_3)_n.NO_3^-$ (n=0,1,2).
- The I_xO_y, y=2-4 clusters signals do not change with water ⇒ Not a source of HIO_3.



Corrected photolytic signal in red

Results: wet experiments

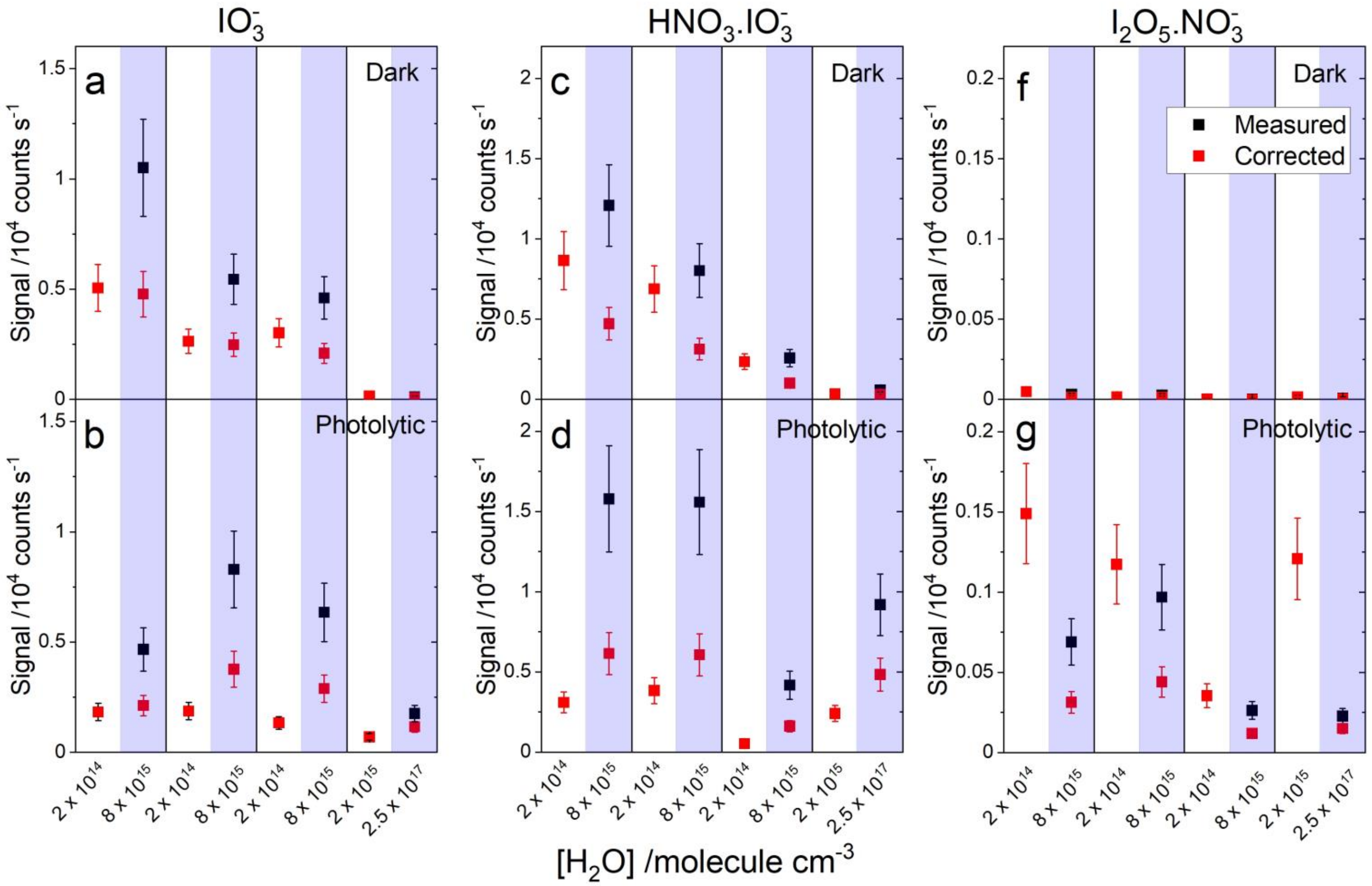
- m/z = 222 (previously attributed to $HIO_2.NO_3^-$) and m/z = 285 (previously attributed to $HIO_2.HNO_3.NO_3^-$) do not behave consistently when water is added.
- m/z = 398 increases with water (it has been attributed to $HIO_2.HIO_3.NO_3^-$, but it can also be attributed to $H_2O.I_2O_4.NO_3^-$ or $H_2I_2O_5.NO_3^-$).
- The m/z = 398 signal is very small in the dark.



Corrected photolytic signal in red

Results: dry/dark vs wet/light

- m/z = 175 and m/z = 238 do not increase when water is present and the lights are off $\Rightarrow$ HIO_3 formation requires photolysis of an I_xO_y molecule.
- Other signals potentially linked to HIO_3 (m/z = 334, 351, 493) do not form in the dark.
- $I_2O_5.NO_3^-$ only appears with light and is removed by water $\Rightarrow$ I_2O_5 + water is a potential source of HIO_3.



Corrected signal in red

Discussion: attribution of signals and source of HIO_3

- The anion signals previously attributed to HIO_3 (m/z=175, 238, 301) appear without adding water alongside the $I_xO_y.NO_3^-$ signals.
- $IO_nNO_2.NO_3^-$ clusters (m/z=251, 267, 301) are linked to IO_nNO_2 molecules, which are coproducts of $I_xO_y + NO_3^-$ reactions (e.g. $I_xO_y + NO_3^- \rightarrow NO_3^- + IONO_2$, exothermic, no barrier).
- Addition of water causes an increase of m/z = 175, 238, 301 signals, without concurrent decrease of I_2O_y (y=2,3,4).

$\Rightarrow$ Signals m/z=175, 238, 301 are contributed both by I_xO_y and HIO_3.

- The m/z=175, 238, 301 signals in the dark do not increase by increasing H_2O.
- The m/z=334 ($IO_2.IO_3^-$) and 251 ($HIO_3.IO_3^-$) only appear when both light and water are present.
- The $I_2O_5.NO_3$ signal is not present in the dark and decreases with H_2O when the lights are on.

$\Rightarrow$ Signals m/z=175, 238, 301 are enhanced by a product of I_2O_5 + water, possibly HIO_3, which is also linked to the appearance of $IO_2.IO_3^-$ ($OIO.HIO_3$) and $HIO_3.IO_3^-$ (HIO_3 dimer).

BUT…

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Discussion: attribution of signals and source of HIO_3

- **Ab initio calculations at B3LYP/aug-cc-pVQZ indicate that $I_xO_y + H_2O$ reactions have barriers. This has been confirmed at CCSD(T) level for $I_2O_y + H_2O$ y=3,4,5.**
- Recent CCSD(T) level calculations (Xia et al., Environ. Sci. Tech. 2020) indicate that I_2O_5 + **$(H_2O)_2$** $\rightarrow$ HIO_3 is exothermic and barrierless.
- I_xO_y photolysis experiments show that I_3O_y have large absorption cross sections in the visible (Lewis et al., 2020), so they are a potential source of I_2O_5. Cluster anions $I_3O_y.NO_3^-$ (m/z=523, 539, 555) have been observed by nitrate CIMS (Sipilä et al., Nature, 2016) and $I_3O_y^+$ cations by PIMS (Gómez Martín et al., Nat. Commun. 2020).

$\Rightarrow$ HIO_3 may form from the sequence:

$$I_3O_y + h\nu \rightarrow I_2O_5$$

$$I_2O_5 + (H_2O)_2 \rightarrow H_2O.HIO_3 + HIO_3 \; ; \; k > 10^{-12} \text{ molecule cm}^{-3}\text{s}^{-1}$$

- Our ab initio calculations indicate that I_2O_3+$H_2O.Br^-$ $\rightarrow$ $HIO_3.Br^-$+ HOI is exothermic but has a barrier of 20 kJ mol^{-1}. Therefore $HIO_3.Br^-$ seen by Bromide CIMS appears to track only HIO_3.

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Discussion: attribution of other signals

- Our B3LYP/aug-cc-pVQZ calculations indicate that I_2O_3+ $(H_2O)_2 \rightarrow HIO_3$ has a 16 kJ mol^{-1} barrier.
- Our B3LYP calculations indicate that $I_2O_4 + (H_2O)_2 \rightarrow H_2I_2O_5 + H_2O$ (-75 kJ mol^{-1}) and $I_2O_4 + (H_2O)_2 \rightarrow H_2O.HIO_3 + HIO_2$ (-9 kJ mol^{-1}) are barrierless, so these are potential sources of parent molecules of the ions with m/z = 222 ($HIO_2.NO_3^-$), m/z =285 ($HIO_2.HNO_3.NO_3^-$) and m/z = 398 ($H_2I_2O_5.NO_3^-$).
- I_2O_2 is also a posible parent molecule of the m/z = 285 (ionization via $I_2O_2 + (HNO_3)_2.NO_3^- \rightarrow (HNO_3)_2.IO_2^- + IONO_2$ (-51 kJ mol^{-1}).
- However, the m/z = 398 signal is mainly photolytic, which suggest that it maybe linked to HIO_3 and HIO_2 as previously suggested ($HIO_2.HIO_3.NO_3^-$).
- The m/z = 493 signal ($I_2O_4.IO_3^-$) is photolytic and derives from the oxide-oxoacid cluster $I_2O_4.HIO_3$.

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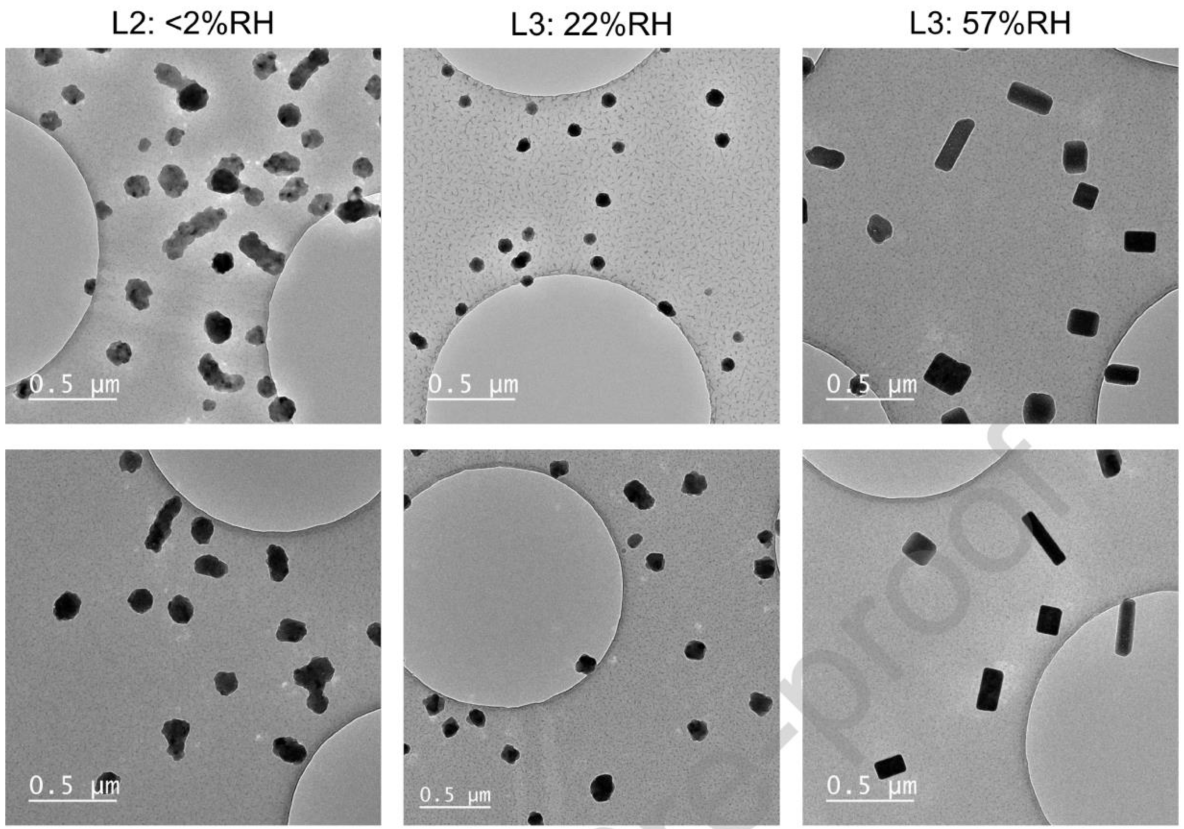
Discussion: nucleation mechanism

- Two nucleation mechanism appear to operate depending on the concentration of water vapor.
- At low humidity, I_xO_y form clusters which evolve towards particles with I_2O_5 composition.
- At high humidity, iodine oxides and oxoacids form mixed clusters that evolve towards a HIO_3 particle composition. Under these conditions pure I_xO_y clusters still form, but clustering with water transform them into particulate HIO_3.



R'Mili et al., Journal of Hazardous Materials, (2021)
https://doi.org/10.1016/j.jhazmat.2022.128729

- Recent experimental work shows that the morphology of IOPs is extremely dependent on the RH conditions. The threshold appears to be at 20% RH.

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Discussion: a dual nucleation mechanism

Photochemistry	References and Notes
$I_2 + hv \rightarrow I + O$ $HOI + hv \rightarrow I + OH$ $IO + hv \rightarrow I + O$ $OIO + hv \rightarrow I + O_2$	Evaluated kinetic and photochemical data for modelling of tropospheric iodine chemistry (Saiz-Lopez et al., 2014)
$I_2O_2 + hv \rightarrow IO + IO$ $I_2O_3 + hv \rightarrow IO + OIO$ $I_2O_4 + hv \rightarrow OIO + OIO$	Absorption cross sections have been determined from experimental data and quantum calculations (Lewis et al. 2020). The photolysis products have not been determined.
$I_2O_5 + hv \rightarrow IO_3 + OIO$	The absorption cross sections of I_2O_5 was not been determined in our previous experiments with PIMS, because I_2O_5 was not detected.
$I_3O_6 + hv \rightarrow I_2O_5 + IO$ $I_3O_7 + hv \rightarrow I_2O_5 + OIO$ $I_5O_{12} + hv \rightarrow I_3O_7 + I_2O_5$	Absorption cross sections have been determined from experimental data and quantum calculations (Lewis et al. 2020). The photolysis products have not been determined. Our new results indicate that I_2O_5 is a major photoproduct of I_xO_y with $x \geq 3$.

Chemistry	References and Notes
$I + O_3 \rightarrow IO + O_2$ $IO + IO \rightarrow I + OIO$ $\rightarrow I_2O_2$ $IO + OIO \leftrightarrow I_2O_3$ $OIO + OIO \leftrightarrow I_2O_4$	Evaluated kinetic and photochemical data for modelling of tropospheric iodine chemistry (Saiz-Lopez et al., 2014)
$I_2O_2 + OIO \rightarrow I_2O_3 + IO$ $I_2O_2 + I_2O_2 \rightarrow I_2O_3 + I_2O$ $I_2O_4 + OIO \rightarrow I_3O_6$ $I_2O_4 + I_2O_4 \rightarrow I_3O_6 + OIO$ $\rightarrow I_3O_7 + IO$ $I_2O_4 + I_2O_5 \rightarrow I_3O_7 + OIO$ $I_3O_6 + I_2O_3 \leftrightarrow I_5O_9$ $I_3O_6 + I_2O_4 \leftrightarrow I_5O_{10}$ $I_3O_6 + I_2O_5 \leftrightarrow I_5O_{11}$ $I_3O_7 + I_2O_3 \leftrightarrow I_5O_{10}$ $I_3O_7 + I_2O_4 \leftrightarrow I_5O_{11}$ $I_3O_7 + I_2O_5 \leftrightarrow I_5O_{12}$ $I_3O_7 + I_3O_7 \rightarrow I_5O_{12} + OIO$	The aggregation and dissociation rate constants of $I_2O_y + I_2O_z$ reactions were calculated with the master equation solver MESMER using CCSD(T)//MP2/aug-cc-pVTZ energies, but the complete PES of these reactions was not explored (Galvez et al. 2013). PIMS observations indicate that I_3O_y (y = 4-7) molecules form, rather than adducts with 4 iodine atoms (Gómez Martín, 2013, 2020). I_2O_3 was found to be very strongly bound and chemically stable and to form weakly bound aggregates -hence its fate remains unclear. The rate constants of some reactions involving I_2O_y (y = 2-4) generating I_3O_y (y = 4-7) where estimated by numerical modelling of I_xO_y time traces obtained in flow tube experiments with PIMS detection (Gómez Martín, 2020). These semiquantitative estimates obtained from a tentative mechanism show that the rate constants of I_xO_y aggregation reactions are close to the collision number. Analogous reactions of I_2O_5, not considered in previous work because this molecule was not detected, are now included in this table.
$I_2O_4 + (H_2O)_2 \rightarrow H_2I_2O_5 + H_2O$ $\rightarrow HIO_2 + H_2O.HIO_3$	$H_2I_5O_2$ has been observed in previous work using nitrate CIMS and it is also observed in the present work. Possible source of HIO_2
$I_2O_5 + (H_2O)_2 \rightarrow HIO_3 + HIO_3.H_2O$	Source of HIO_3. The PES of this reaction has been reported(Xia et al., 2020; Khanniche et al, 2016)
$HIO_2 + HIO_3 \leftrightarrow H_2I_2O_5$ $HIO_3 + HIO_3 \leftrightarrow (HIO_3)_2$ $HIO_3 + OIO \leftrightarrow OIO.HIO_3$ $HIO_3 + I_2O_2 \leftrightarrow I_2O_2.HIO_3$ $HIO_3 + I_2O_3 \leftrightarrow I_2O_3.HIO_3$ $HIO_3 + I_2O_4 \leftrightarrow I_2O_4.HIO_3$ $HIO_3 + I_2O_5 \leftrightarrow I_2O_5.HIO_3$	Theoretical estimates of the forward and reverse rate constants of the $HIO_3 + HIO_3$ and of $HIO_3 + I_2O_4$ aggregation reactions have been reported (Gómez Martín, 2020). The $I_2O_y.HIO_3$ adducts have been observed in the CLOUD chamber experiments using nitrate CIMS (He et al., 2021). They are also observed in the present work (m/z < 500 amu)
$I_2O_4 + H_2O.HIO_3 \leftrightarrow I_2O_4.H_2O.HIO_3$ $H_2I_2O_5 + HIO_3 \leftrightarrow H_2I_2O_5.HIO_3$ $H_2I_2O_5 + I_2O_4 \leftrightarrow H_2I_2O_5.I_2O_4$ $H_2I_2O_5 + H_2I_2O_5 \leftrightarrow (H_2I_2O_5)_2$ $I_2O_4 + I_2O_4 \leftrightarrow (I_2O_4)_2$ $I_2O_4.HIO_3 + I_2O_4 \leftrightarrow (I_2O_4)_2.HIO_3$ $H_2I_2O_5.I_2O_4 + HIO_3 \leftrightarrow H_2I_2O_5.I_2O_4.HIO_3$ $H_2I_2O_5.HIO_3 + I_2O_4 \leftrightarrow H_2I_2O_5.I_2O_4.HIO_3$ $H_2I_2O_5.HIO_3 + HIO_3 \leftrightarrow H_2I_2O_5.(HIO_3)_2$	The $(I_2O_4)_n.H_2O.(HIO_3)_m$ adducts have been observed in the CLOUD chamber experiments using nitrate CIMS (He et al., 2021) as anions with m/z > 500 amu (outside the mass range in the present work). The nucleation mechanism proceeds by addition of HIO_3 and I_2O_4 to pre-existing molecular clusters.

Conclusions

- Nitrate CIMS signals are contributed both by oxides and oxoacids (we estimate that by 50% under MBL conditions).
- By contrast, bromide CIMS provides a clean HIO_3 signal.
- Nitrate CIMS can detect $IONO_2$ as $IONO_2.NO_3^-$. Hence, nitrate CIMS is potentially capable of detecting this key iodine reservoir in the atmosphere.
- Two iodine particle formation regimes exist depending on the concentration of water vapour.
- Under dry conditions I_xO_y drive particle formation, while under humid conditions both oxides and oxoacids contribute.
- The threshold appears to be at intermediate RH, which means that different mechanisms may operate in different atmospheric environments (e.g. Polar regions vs coastal MBL).
- For high water concentrations nucleation is slower, which may explain why iodine particle formation is so eficient in Polar regions, where iodine emisions are less intense compared to coastal particle formation events.