

## Referee 1

We thank the referee for a positive assessment of our manuscript. The comments (in black), our response (in blue) and changes to the manuscript (in red) are listed below.

R. Dörich and co-workers have presented convincing laboratory evidence that iodide-CIMS instruments efficiently detect HNO<sub>3</sub> as NO<sub>3</sub><sup>-</sup> but ONLY in the presence of ozone (which converts I<sup>-</sup> into IO<sub>x</sub><sup>-</sup> ions, which in turn react with HNO<sub>3</sub>). This finding has substantial implications for field studies using such instruments, and suggests that some previous measurements have been incorrectly interpreted. This is one more example of how the powerful tool of chemical ionisation should be used very carefully, with due consideration of possible side reactions, including indirect pathways such as that discovered here. The study is definitely worth publishing in AMT. I have only very minor corrections and questions as described below.

-On line 135, reaction (R6) should presumably be reaction (R7), i.e. I<sup>-</sup> + HNO<sub>3</sub> not I<sup>-</sup> + H<sub>2</sub>O.

Correction made

-On line 153, the product should presumably be IO<sub>3</sub><sup>-</sup> not IO<sub>2</sub><sup>-</sup>.

Correction made

-Line 159: Maybe mention already here the the O<sub>2</sub> concentration in the quoted studies was MUCH less than that in the atmosphere (or in these measurements) - I had a hard time reconciling the dominance of IO<sub>3</sub><sup>-</sup> with the stated rate coefficients, since I kept assuming 0.2 atm O<sub>2</sub>. Also, is it the lack of an IO<sub>3</sub><sup>-</sup> + O<sub>2</sub> reaction that drives the equilibrium toward IO<sub>3</sub><sup>-</sup> ? We now mention that the O<sub>2</sub> concentrations were ~4x that of O<sub>3</sub>. The question of what changes the equilibrium concentrations of IO<sub>x</sub> in our system is addressed later in the manuscript.

With the O<sub>3</sub> (~1-5 × 10<sup>10</sup> molecule cm<sup>-3</sup>), O<sub>2</sub> concentrations (~4 × that of O<sub>3</sub>) and reaction times used in these studies...

Could the authors use e.g. gas-phase acidity / proton affinity data to estimate thermodynamic parameters (at least endo/exothermicity) for reactions R13-R15 (and also R19-R21)?

We have add some information regarding thermodynamic properties for the “new” reaction of IO<sub>x</sub><sup>-</sup> with HNO<sub>3</sub>:

Using heats of formation (in kJ mol<sup>-1</sup> at 298 K) of ΔH<sub>f</sub>(IO<sub>3</sub><sup>-</sup>) = -211 (Eger et al., 2019), ΔH<sub>f</sub>(HNO<sub>3</sub>) = -134 (Goos et al., 2005), ΔH<sub>f</sub>(HOIO<sub>2</sub>) = -95 (Khanniche et al., 2016) and ΔH<sub>f</sub>(NO<sub>3</sub><sup>-</sup>) = -312 (Goos et al., 2005) we calculate that reaction R15 is exothermic by ~62 kJ mol<sup>-1</sup>.

The reactions listed in R19-R21 are well known and documented as CIMS detection schemes; in this case the addition of thermodynamic properties is not necessary.

Could the authors speculate about the reasons for the differences in rate coefficients for reactions R13...R15? The ion size seems to play a role, but is that enough to explain a difference of a factor of 3 between IO<sup>-</sup> and IO<sub>3</sub><sup>-</sup>?

We state that “The results indicate qualitatively that IO<sub>3</sub><sup>-</sup> is the most reactive of the IO<sub>x</sub><sup>-</sup> anions towards HNO<sub>3</sub>, but that all three contribute to HNO<sub>3</sub> detection.” As the referee states, ion-size may play a role but there will be other factors. Given the assumptions made in deriving these “approximate” rate coefficients, and our lack of theoretical tools to examine ion-molecule reactions in detail, we feel that discussion of the apparent differences in rate coefficients is not appropriate.

-Line 221: “shut of” should be “shut off”

Correction made