Atmospheric Measurement Techniques Discussions

Atmos. Meas. Tech. Discuss., referee comment RC1
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Comment on amt-2021-57

Anonymous Referee #1

Referee comment on "Iodide CIMS and *m/z* 62: the detection of HNO_3 as NO_3^- in the presence of PAN, peroxyacetic acid and ozone" by Raphael Dörich et al., Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2021-57-RC1, 2021

R. Dörich and co-workers have presented convincing laboratory evidence that iodide-CIMS instruments efficiently detect HNO3 as NO3- - but ONLY in the presence of ozone (which converts I- into IOx- ions, which in turn react with HNO3). 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- + HNO3 not I- + H2O.

-On line 153, the product should presumably be IO3- not IO2-.

-Line 159: Maybe mention already here the the O2 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 IO3- with the stated rate coefficients, since I kept assuming 0.2 atm O2… Also, is it the lack of an IO3- + O2 reaction that drives the equilibrium toward IO3-?

-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)?

-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- and IO3-?

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