

Interactive comment on “An ion-neutral model to investigate chemical ionization mass spectrometry analysis of atmospheric molecules – application to a mixed reagent ion system for hydroperoxides and organic acids” by Brian G. Heikes et al.

Anonymous Referee #1

Received and published: 22 September 2017

Heikes et al. have developed a model including some hundreds of ion - molecule reactions, and fit key parameters to match observed pressure and humidity dependencies of the sensitivities for four analyte molecules (formic acid, acetic acid, H₂O₂ and CH₃OOH) measured with a mixed reagent ion (mainly O₂⁻ and I⁻) - CIMS instrument. As a specific application, the authors show how the model can be used to monitor (and presumably correct for) interferences caused by isobaric cluster ion species. The work is interesting and valuable to the atmospheric science community, and I would encourage the authors to upload their model online in a user-friendly format in addition

C1

to reporting it in this article. (I strongly suspect that many more applications will be found for such a model in addition to the ones presented in the article). The authors have gone to great lengths in collecting and “homogenizing” a large amount of data from different sources, some of which are not easily rendered into compatible format. For example, ab initio calculations are typically good at computing relative energetics (e.g. reaction energies), but often fail at reproducing absolute energies (e.g. standard formation free energies, particularly for radical systems, and especially for complex radical clusters). Similarly (as the authors note), experiments performed for example with different carrier gases may yield quite different termolecular rate coefficients. The discrepancies discussed in the supplemental information are thus not particularly surprising. However, the authors seem well aware of these issues, and as far as I can tell have made reasonable and justified choices in how to assemble their model from the fragmented and sometimes contradictory source data they had available.

I warmly recommend that this manuscript be published in AMTD. I have a few minor questions, comments and further suggestions, which I hope the authors will consider when writing the final version of the manuscript.

-As a general comment, could the authors use their model (and/or the chemical understanding they have gained while constructing it) to qualitatively explain to a non-expert reader the reason for the “parabolic” behaviour exhibited by the sensitivity of so many analyte/ion combinations with respect to humidity? (E.g. figures 5,6,7 in their manuscript, and many cases of such behaviour reported elsewhere). Why does the sensitivity in these cases first increase, and then decrease, with increasing humidity? I have always assumed the initial increase is due to energy (non)accommodation effects, i.e. water stabilizing the ion-molecule clusters - I guess this is included in the model by reactions of the type R2 being termolecular, while R3 is bimolecular. Is this the explanation more subtle, or is the explanation more subtle? And is the subsequent decrease then related mainly to competition by polyhydrates, or what is going on? Also, why does I-(HFO) go up with H₂O while I-(HAc) goes down? The

C2

model should presumably provide some insight into this. A separate section explaining the reasons for the observed trends (in the SI if the authors feel the manuscript is too long) would be very useful to readers trying to understand the chemistry behind the CIMS measurements.

-Line 79: the word “expected” is a bit confusing: why did the authors “expect” to see these signals if the reactions forming the hydrates in question have too positive enthalpies/free energies? Am I missing something here? (The whole sentence is actually a bit hard to parse, I would suggest reformulating it.)

-The resolution of the figures are quite poor, making the figures hard to read - could you please make higher-quality figures? (Perhaps the poor resolution is due to some format conversion issue?) Also some of the figures could be made larger (e.g. Fig 1 & 2).

-I found the concept that the acidity of XH (or alternatively basicity of X-) can be used to quantitatively predict the (relative) binding of X- to different analytes quite interesting (R5 and surrounding discussion). Could this correlation be used more generally?

-Line 220-221, please specify that the pictures are plotted for the case A=H₂O₂ (this is sort of implicit from the discussion above, but specifying it would help the reader).

-Line 375, “too peaked” is a bit ambiguous, please reformulate

-Line 394: “preoxide” => “peroxide”

-Line 98 of the Supplemental Information: the number 10⁻² J / mol K seems too small (comparing e.g. to entropies given in the tables), perhaps the authors meant kJ / mol K, or alternatively 10⁺²?

Interactive comment on Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2017-286, 2017.