

Review of "Chemical ionization mass spectrometry utilizing benzene cations for measurements of volatile organic compounds and nitric oxide"

This manuscript describes very interesting work on developing benzene cations as a reagent ion for CIMS. The authors demonstrate the surprising and novel result that benzene CIMS can be used to make sensitive measurements of NO in polluted environments. The paper is well written and has several notable strengths. These include the novel ionization energy-based classification, which is a very nice contribution that provides predictive power for work on other compounds. In addition, the two field deployments demonstrate both capabilities (excellent NO measurements) and limitations (isoprene interferences in some urban areas) with a high level of transparency. I highly recommend the paper for publication and would ask the authors to consider the relatively minor points below.

Line 36 – GC methods are not inherently highly sensitive; it depends on the detector. For example, ECDs are sensitive and the GC provides separation (i.e., selectivity).

Line 41 – Missing space between "10" and "Hz".

Line 42 – Maybe instead of saying "ionizes them," replace with "reactions".

Line 59 – I am not sure a TOF-CIMS with a resolution of 9000 is not more complex than a GC-FID and a NO_x box. Certainly bigger and a lot more expensive. I think the time resolution and the ability to detect species without separation are the largest advantages.

Line 73 – Maybe say "relatively unexplored" instead of "less explored".

Line 90 – The krypton lamp is referred to as both UV and VUV. I would probably stick to VUV to avoid confusion.

Line 101 – Reaction R2 is written as an equilibrium reaction, and I think this is correct. So R5 should probably be as well. In fact, the temperature-dependent data show this is true for at least some of the adducts in the SI. I also think it would be reasonable to give an estimate of the thermal lifetime of the benzene cation dimer. This can be done using the equilibrium constant (already reported in the SI) along with an estimate of the forward rate constant for R2 (i.e., Su formulation) to derive a rate constant (and lifetime) for R-2. This could be compared to the residence time in the IMR. I think this would be informative. In addition, the residence time in the IMR is 10 ms; how is this determined? This is not obvious to me. You should also report the pressure in the IMR in the main body, not just in the SI.

Line 162 – It is a strong statement to say that charge transfer always dominates for low IE even when other channels are available. I would soften that a bit, as I am not sure it will transfer to all molecules and reagent ions.

Line 164 and other places – Statements such as "classified into into "mid IE class"" are always a little awkward. Maybe just say you have three classes: Low, Mid, and High IE, and refer to them as "mid IE," for example. Not a big deal, but I trip on these sentences.

Line 180 – I am not sure I buy the electric field-assisted charge transfer. If you keep it in, you should at least have a reference to this effect in this section.

Line 188 – The oxygen chemistry of isoprene-derived ions is very interesting (and frustrating for detection). Is there evidence for O_2^+ in the mass spectra? If so, that would support it as a driver of the effect but would not be a good sign and would indicate that the ion chemistry is not being controlled well in the ion source. Second, does this type of chemistry happen with other species such as 1,3-butadiene, etc.? These results also beg the question as to why nitrogen was used as the dilution gas when the results in air may be so different. **I think this needs to be addressed and is one of my largest concerns about the work, although I applaud the authors for their transparency.** At a minimum, you need to state what dilution gas is used for all the results (i.e., H_2O dependence, etc.).

Line 229 – How do you know the output of your NH_3 permeation device? The manufacturers only measure mass loss, which may be considerably larger than the emission of NH_3 (or other gases). You may be more sensitive than you think.

Line 235 – You could calculate a collisional rate constant and use your reaction time to estimate a maximum sensitivity.

Line 309 and later – **The humidity dependence is larger than I expected, and I am skeptical it can be fit out to obtain accurate sensitivities.** I appreciate the proposed explanation of the observations (Figure 3). However, I wonder why not run at lower pressures (I am not sure why 55 mbar is considered ideal when you have water effects this large). Perhaps if you halve the IMR pressure, you may see a large decrease in water impacts, as your mechanism indicates it is higher order in water. I would also consider sampling less ambient gas and using more ion source flow or a dilution flow as well. You might sacrifice sensitivity but gain a lot in stability with respect to both water and temperature. **This is my other large concern as to how well this method can be applied.**

Overall, there is an impressive amount of work and thought detailed in this publication.