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Comment

## ***Interactive comment on “Selective measurements of isoprene and 2-methyl-3-buten-2-ol based on NO<sup>+</sup> ionization mass spectrometry” by T. Karl et al.***

### **Anonymous Referee #2**

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This paper describes how NO<sup>+</sup> can be used to measure 232 MBO and isoprene in an ambient atmosphere that contains both of them, and represents a valuable advance in measurement capability. In general the paper is well written and informative. This paper should be published pending a few comments and editorial items to be dealt with.

General Comments Shouldn't this paper be in Atmospheric Measurement Techniques, since it is mainly a description of a measurement technique? Ambient data were shown briefly, only to make the point that the method works. In several places in the paper the authors make the point that the method is based on “PTR-MS technology”. This is

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very confusing since the ionization modes being examined in this paper are not PTR at all, perhaps the phrase “PTR-MS technology” was meant to allude to that but it doesn’t seem to go far enough, the method uses traditional PTR-MS instrumentation with alternate ion chemistry. Perhaps another phrase would work better.

### Specific Comments

Abstract- It seems from the body of the paper that the sensitivities quoted here are normalized. That should be stated clearly here.

Intro – Pg 19350, Line 24. There is an earlier paper by Rasmussen and Went (1965) that is usually attributed to this discovery.

Pg 19351, Line 22. What is a “biochemical stat”?

Method – Pg 19353, Lines 20-25. These reactions are not complete. Where do the  $N^+$  and  $NO$  come from? It would be nice to see all the relevant reactions in order understand how this ion source works. Also, why not number the reaction the same as the rate constants?

Pg 19354 – line 13 – what is the unit “Th” ? And doesn’t it require a decimal point? Later on it is used without a decimal point.

Results - Pg 19356 – lines 9-11, and Figures 1 A&B. The Figures do not make the stated point that ionization by reaction  $NO^+$  occurs without significant fragmentation, because the Figures only show the spectra at the main ion,  $\pm 0.3$  amu or so. In order to make this point the authors need to show us the whole spectrum, or at least 33 – 69 amu. It would also be nice to see what kinds of clusters there might be at higher masses.

Pg 19357. Line 5. Is there anyway to match the high resolution mass to an empirical formula? It seems like  $CF_3^+$  is very close. It would be nice to know more since many people have PTR-MS instruments that are not high resolution TOFs and might want to try this ion chemistry. Also if it is a fluorinated compound, that might indicate an inlet

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artefact from Teflon PFA. Perfluoro compounds are not always destroyed completely in oxidation catalysts that are typically used to zero these instruments.

Conclusions Pg 19359, Line16. Is the reaction that 232 MBO undergoes after the normal PTR really 'collisional dissociation', I have always thought of it as 'dehydration'. Perhaps you could think of dehydration as a special class of collisional dissociation, but the distinction may be important, as the NO+ ionization method might be useful for other alcohols for which dehydration is facile enough to be a problem.

Reference List – A number of references are out of alphabetical order.

Figures – The figure quality is poor (blurry labels) perhaps, this is a version problem.

References used in this review

Rasmussen, R., and F. Went, Volatile organic material of plant origin in the atmosphere, Proc. Nat. Acad. Sci., 53, 215-220, 1965.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 19349, 2012.

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