

Interactive comment on “Identification of Gas-phase Pyrolysis Products in a Prescribed Fire: Seminal Detections Using Infrared Spectroscopy for Naphthalene, Methyl Nitrite, Allene, Acrolein and Acetaldehyde” by Nicole K. Scharko et al.

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Referee Comments: I found the paper to be both interesting and insightful. The evidence for the presence of the five gases reported on is convincing and clearly presented. Not only will this paper be useful for those interested in emissions from wild-fire, but it will also be useful to those looking to model emissions from other sources utilizing infrared spectroscopy. Two matters that could be addressed that would add to

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the paper's usefulness are given below. One part of the discussion that was missing is related to the comparison of the field spectra with database spectra. The PNNL database spectra are typically recorded at 5, 25 and 50 degrees Celsius whereas the spectra collected here are at 70 degrees Celsius. I would assume that the 50 C PNNL spectra would be used for comparison, but this was not mentioned.

Author Comments: We thank the referee for the review and insightful comments. The referee is correct, the 50°C PNNL reference spectra were used for analysis, and that was not explicitly mentioned in the text. We have revised the text to include the following, "The PNNL database provides reference spectra measured at 5, 25 and 50° C, all of which have been normalized to a number density of 296 K and 1 atmosphere. While not perfectly optimal, the PNNL 50° C reference spectra were used for evaluation to best match the bandshapes of the 70° C experimental data."

Referee Comments: Also, do you have a metric of how the PNNL reference spectral profiles change from 5 to 25 to 50 C such that it could be said that using 50 C reference spectra to measure 70 C experimental spectra would result in an error less than 'give number'.

Author Comments: This is an excellent point, and we included the referee's suggestion in the revision. Section 2.3 has been revised to include the following,

"The fit of the 323 K (50 ° C) PNNL reference data to the 343 K experimental spectra is obviously less than ideal. To correctly fit to the experimental spectra, reference data at 70 ° C are needed, but short of this knowledge of the temperature, partition function and individual line assignments are needed, and this changes for each line or set of lines for each molecule used in the fit. While MALT correctly accounts for gas temperature in all cases and for intensities of the HITRAN line-by-line data, it cannot do so for the PNNL reference data. At the higher temperatures there can be significant increase in population/intensity of the high-J lines, with decreases for the lines originating in low J values. The effect is more pronounced for smaller, more rigid

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molecules (e.g. allene, acetaldehyde) than for the bands associated with larger, less rigid molecules of low symmetry. Preliminary estimates for the quality of fit estimate errors in the 2 to 5 percent range, though the value depends strongly on the species and which waveband is used for the fit.”

Referee Comments: This would also be important to mention for the path length calibration process since this parameter is used in the measurement of the mixing ratios of the five gases discussed

Author Comments: The path length calibration was conducted at room temperature, and we have included the following text in Section 2.2, “Measurements conducted at room temperature of pure isopropyl alcohol (IPA, Sigma-Aldrich, 99.5%) at ten different pressures were collected and a Beer-Lambert Law plot was created to determine the length.”

Referee Comments: -Also, the authors may be in a unique position to comment on whether the analysis techniques used here (i.e. MALT5) could be also used in active or passive remote infrared sensing for these gases.

Author Comments: We appreciate the referee’s comment, and we have updated the manuscript with the following text along with citations to demonstrate the versatility of MALT. Section 2.3 includes the following, “The MALT analysis technique has previously been used in both open-path and extractive FTIR systems with active sources. (Burling et al., 2010; Burling et al., 2011; Akagi et al., 2013; Akagi et al., 2014). Additionally, the program has been used for ground-based solar FTIR measurements (Griffith et al., 2003).”

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