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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Measuring atmospheric naphthalene with laser-induced fluorescence" *by* M. Martinez et al.

Anonymous Referee #1

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General comments. This is a high quality paper showing some very interesting measurements.

In this short paper naphthalene concentrations are measured, probably unintentionally (at least when the raw data were taken), using an instrument designed to measure OH concentrations using UV laser-induced fluorescence. In order to subtract laser scattered light from the OH signal, the laser wavelength is tuned off resonance from an OH transition, and the signal monitored. Fortuitously, the laser wavelength is alternatively tuned to the red and then to the blue of the OH transition, and it was noticed that the two offline signals were not the same, but one had a component from naphthalene fluorescence excited by the laser. The difference in the two off-line points was used to measure naphthalene, with signals calibrated in the laboratory. Concentrations were measured in an urban campaigns in New York City, Nashville and Houston, and also

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for the aircraft instrument whilst sampling exhaust from another aircraft. The detection limit of 20 ppt is very impressive (1 min), and was as low as 6 ppt (10 mins), but even for this decection limit naphthalene was only measurable on some occasions for some campaigns, making it difficult to correlate with other VOCs. As the naphthalene concentrations were obtained as an added extra (during OH offline points only), the sampling conditions were not designed for naphthalene measurements, and so the datasets obtained, although comprehensive, are probably not optimum.

The only other measurements of gaseous naphthalene are using methods with long averaging times, and so having a time resolution of tens of seconds to minutes is highly novel. There have very few measurements of naphthalene. The present apparatus though is large, complex and expensive, and although high quality naphthalene measurements are demonstrated with good time resolution, it is doubtful if it would be used purely for measurements of naphthalene when OH is not being measured. However, the paper demonstrates that measurements of naphthalene are possible using LIF, and paves the way for further development, perhaps of a smaller, less expensive instrument, that still offers excellent time response. If this could be done, and naphthalene monitored routinely, perhaps as a maker for PAH species, then this would a significant advance.

More specific comments.

(1) I was very surprised that H2O did not quench naphthalene, but quenching is significant for O2 and N2. Normally (e.g. OH(A), H2O quenches very rapidly, but apparently not in the case of naphthalene. One argument is that naphthalene is a non-polar molecule, whereas OH is, and so one would not expect any significant interaction between them.

(2) Does the presence of naphthalene on one side of an OH transition affect the concentration of OH that is obtained following the data analysis? Was the identification of naphthalene recognised from the beginning, or at some later date after OH concentra-

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tions had been published? If the data reduction analysis computer software took the average of the two off line points in order to subtract scattered light, then an error in the OH concentrations could result.

(3) A temperature of 294 K is assumed in the fluorescence chamber. Some cooling in the expansion is expected, and so the temperature may be lower?

(4) Correlations with NOx and CO are given, that are also measured with good time resolution. Was there any correlation with other VOCs, e.g. NMHC, or oxy-VOCs, that may have similar emission sources, and hence some source apportionment could be carried out? A correlation is given for total NMHC in NY City. The problem is probably that these species were measured with poor temporal resolution.

Technical corrections (there were very few errors)

(1) The 3 kHz refers to the pulse repetition frequency, and this should be stated

(2) ŞofflinesŤ replace with Şoffline pointsŤ

(3) pollutants ŞlikeŤ NOx and CO , replace ŞlikeŤ with Şsuch asŤ

(4) Insert ŞtheŤ before Şsame sourcesŤ on page 8.

(5) Table 1. first column, ŞMissionŤ

(6) Figure 1. Label the largest of the OH peaks. Also, there is a P line in there as well as Q1(2) and Q1(3)?

(7) Figure 3. Should say ŞOHŤ and not ŞairŤ in line 4 of the caption? Also make clear that the bottom two panels are for naphthalene fluorescence (rather than for OH).

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 343, 2004.