

Interactive comment on “A flow-tube based laser-induced fluorescence instrument to measure OH reactivity in the troposphere” by T. Ingham et al.

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Received and published: 15 June 2009

Responses to Referees

We thank both referees for their careful reading of the manuscript and comments.

Referee #1

1) In the present work, the flow regime was selected which gave a compromise between the time taken to mix the injector flow into the main flow, and OH signal stability after mixing such that the measured decays were very well described by a single exponential in laboratory studies. Laminar flow conditions were attempted but the reduced

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flow velocity required for the same diameter flow tube resulted in excessive mixing times such that a significant fraction of OH was removed by reaction prior to starting to pull the injector back to measure a decay. The lower k_{physical} observed in this work compared to Kovacs and Brune (2001) is indeed likely due to the “more turbulent” flow conditions, but it is beyond the scope of this paper to provide a detailed discussion of the two flow regimes. In both cases k_{physical} is an empirical, reproducible quantity. The manuscript will be modified to reflect some discussion of this.

2) The rate constants for the reactions of OH+O₃ and HO₂+O₃ are approximately 7×10^{-14} and 2×10^{-15} cm³ molecule⁻¹ s⁻¹, respectively. This ensures that the levels of O₃ generated in the injector when zero air is used, and following dilution into the main flow (typically < 100 ppbv), do not cause any significant loss of OH or HO₂ radicals. Measurements of k_{physical} with N₂ and zero air as injector gas confirm that there is no observable additional loss of OH when zero air is used within the uncertainty of the measurement.

3) The conditions of low [NO] for both cases are less than 1 ppbv. The manuscript will be modified accordingly.

4) The manuscript will be modified accordingly by increasing the uncertainty to 10% (1 sigma) to reflect the overall uncertainty in our measurements of the OH + CO and OH + n-hexane rate constants with the flow tube system. No additional calibration of the anemometer was undertaken.

5) The overall uncertainty in the simple treatment used for NO corrections comes from the uncertainty in [NO] measurement (ca. 5%), the uncertainty in the [HO₂]/[OH] ratio (1.75 ± 0.2) and the uncertainty in the rate constant for reaction R5 (HO₂ + NO) 15% (NASA/JPL 2006). These uncertainties propagate in a linear fashion, but the overall uncertainty does increase with increasing NO. The increased uncertainties for 1, 5, and 10 ppbv of NO are 1.2%, 4.9%, and 8.1%, respectively. The manuscript will be modified accordingly.

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Referee #2

1) The manuscript will be modified accordingly by the insertion of a table. 2) page 625, line 16-18. The manuscript will be modified accordingly. 3) page 625, line 18-21. The manuscript will be modified accordingly. 4) page 625, line 25-26. The manuscript will be modified by deletion of the sentence. 5) page 627, line 10. The manuscript will be modified by deletion of the sentence and reference. 6) page 629, line 12. The manuscript will be modified by replacement of “physical” with “wall”. 7) page 638. Please see response to Referee #1 point 4 above. 8) page 643. With $[\text{NO}] < 1\text{ppb}$ there is effectively no loss of HO_2 during a decay. If OH is observed to decay through an order of magnitude, the $[\text{HO}_2]/[\text{OH}]$ ratio at the end of the decay will be an order of magnitude greater than at the start of the decay. 9) page 643. Please see response to Referee #1 point 5 above. 10) page 644, section 4.1. The manuscript will be modified by deletion of the section. Response to technical comments: 11) page 623, line 24. The manuscript will be modified by deletion of “aldehyde”. 12) page 624, line 28. The manuscript will be modified accordingly. 13) page 634, line 3. The manuscript will be modified accordingly. 14) page 642, line 15. The manuscript will be modified accordingly. 15) Fig 5. The manuscript will be modified accordingly. 16) References. The manuscript will be modified accordingly.

V. Sinha

We thank V. Sinha for his helpful comments, and recognising that this is “a welcome addition and significant contribution”. A response is given below to each of the four points made.

1) We used the peak value rather than the average value. The manuscript will be modified to reflect these comments. 2) We agree it would be more difficult to dilute the NO in the same way as in the CRM method, given the higher flow rates. The instrument was calibrated the instrument under relevant ambient conditions of humidity. Where applicable directly the manuscript will be modified to reflect these comments. 3) The

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manuscript was not intended to cover a detailed description of other methods, nor a comparison with the LIF flow-tube method with the CRM method, rather just cover these points briefly. We agree with the comments made about the two methods, and where applicable directly the manuscript will be modified to reflect these comments. 4) In more polluted areas the flow velocity in the main tube can be increased (and the step size reduced) to reduce the reaction time and thus extend the dynamic range of the LIF instrument, but there is a limit to the overall flow rate that can be achieved, and this technique is not suited to measuring loss rates in excess of 100 s^{-1} . The accuracy is discussed in section 2.6, and the wall loss and its uncertainty is given in section 3.4, but we will modify the manuscript to reflect these comments where applicable.

Interactive comment on Atmos. Meas. Tech. Discuss., 2, 621, 2009.

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