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Atmospheric Measurement Techniques
Discussions

Interactive comment on "An intercomparison of HO_2 measurements by Fluorescence Assay by Gas Expansion and Cavity Ring–Down Spectroscopy within HIRAC (Highly Instrumented Reactor for Atmospheric Chemistry)" *by* Lavinia Onel et al.

Anonymous Referee #1

Received and published: 5 September 2017

General comments: The paper describes the measurement of HO2 radical concentration in the HIRAC chamber at two different pressures (150 and 1000 mbar) using two different methods: FAGE and cw-CRDS in the near IR. This is an interesting paper, as it shows for the first time the comparison between these two techniques. The absorption cross sections of HO2 at both pressures are obtained using two different methods, and both methods agree reasonably well. I recommend this paper for publication once the following comments have been considered.

Specific comments: In the abstract, you give the gradient (with a small error bar) of a

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correlation plot between FAGE and cw-CRDS measurements for both pressures. This gradient depends on the absorption cross sections used for converting the cw-CRDS measurements into absolute concentrations. Further down in the abstract, you precise that you find 2 different absorption cross sections in rather good agreement using two different methods. The reader can get confused about this, and maybe you should precise that the gradient given in the abstract is the average of both values (at least this is what I guess you did). The error bar should also be larger in this case.

Page 5, line 17: the sentence “CRDS was chosen for validation of FAGE because it requires no calibration” seems a bit inappropriate to me because as long as the absorption cross section at a given pressure is not well known (which is difficult for radicals), CRDS is not absolute. I could conceive this idea if you do experiments at one given pressure in different chemical environments, and then you use CRDS to validate FAGE against possible interferences, but I think it might be too simplified to say for the moment that you can use CRDS to validate FAGE.

Page 12: Did you check if the absorption of the product CH2O does contribute to the background? Absorption cross sections for CH3OH and CH2O are in the same range (Ruth et al., Z Phys Chem 229 (10-12), 1609 (2015)), so I guess that even if yes it would not change your conclusions, as it only counteracts on the decreased background due to CH3OH. However, a small discussion on the possible absorption of CH2O could be given.

Page 14, line 7: do you use l=1,4m in equation 9? Are you sure that the HO2 concentration is homogeneous from the center of the chamber down to the last cm in front of the mirrors? You do not protect your mirrors with a small flow of clean air? I would suspect a strong decrease of HO2 concentration over (at least) the last 10cm before the mirrors due to many walls surrounding this area (looking at Figure 2). This of course makes only 20cm out of a total of 140cm, but still, it might change the conclusions from the observed decay. This is linked to my next point:

Page 14, determination of sigma_HO2: You consider the wall loss for CRDS measurements to be the same for FAGE and for CRDS measurements. However, I would expect that the wall loss constant is a function of the distance to the wall, i.e. close to zero in the center and very high close to the walls. So if for FAGE measurements equation 10 might be right, a uniform k_loss over the entire absorption path might not be applicable for CRDS measurements. Can you comment on that?

Looking at the absorption cross sections, I see that your measured value at 150 mbar (1.02e-19) is around 20% below the calculated one (1.25e-19), while at 1000 mbar the measured value (3.87e-20) is around 10% above the calculated one (3.44e-20). Why you say broad agreement for the 1000mbar and good agreement for the 150mbar, I would say the other way around, but maybe my English is not perfect... Even though the error bars are overlapping for both pressures, I'm still wondering why the measured value is above at 1000mbar and below at 150 mbar, compared to the calculated one. Pressure broadening has a very strong impact on the 1000mbar value, so comparing it with the measured one I conclude that the broadening coefficients have been slightly overestimated in the calculations. So fine-tuning the broadening coefficient to the measured sigma_1000 mbar, and then re-calculating the value at 150mbar, should lead to a $\approx$10% higher value at 150 mbar. Now the error bars start to not agreeing anymore. Could the diffusion be linked to this?

I have plotted your data from tables S4 and S5, i.e. k_loss as a function of the absorption cross section. For both pressures there is a tendency of increased loss rate with increased sigma (same trend is visible for the FAGE calibration factors). It would be interesting to see if there is also a correlation with the initial radical concentration. I see that you have varied the initial Cl2 concentration by a factor of 3 to 4, but unfortunately these values are not given in the tables. Can you comment on that?

Technical corrections: Page 3, line 26: you describe general CRDS, but the switching off the laser beam above threshold is specific to cw-CRDS. Maybe this detail is not needed in the introduction; it might be confusing to the reader not familiar with CRDS.

Page 3, line 35: for completeness you might also want to cite a recent paper on the measurement of the spectrum and absorption cross sections of the electronic transition of HO2 (and DO2) around 1420 nm: E. Assaf et al. JQSRT 201, 161-170 (2017)

Page 4, line 5: long time averaging times

Page 4, line 31: HO2

Page 11, line 30 : in in

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