

Author response to anonymous referee #1 on “An intercomparison of HO₂ measurements by Fluorescence Assay by Gas Expansion and Cavity Ring–Down Spectroscopy within HIRAC (Highly Instrumented Reactor for Atmospheric Chemistry)” by L. Onel et al.

Note: The changes in the manuscript addressing the comments of the referee #1 are highlighted in yellow below. Question 6 was answered before Q4 to follow the order of changes in the text as the answers to Q6 and Q4 are inter-correlated.

Specific comments

Q1: In the abstract, you give the gradient (with a small error bar) of a 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.

The abstract has been changed according to the suggestion of the referee:

“At 1000 mbar total pressure the correlation plot of [HO₂]_{FAGE} versus [HO₂]_{CRDS} gave an average gradient of 0.84 ± 0.08 for HO₂ concentrations in the range $\sim 4\text{--}100 \times 10^9$ molecule cm⁻³ while at 150 mbar total pressure the corresponding gradient was 0.90 ± 0.12 on average for HO₂ concentrations in the range $\sim 6\text{--}750 \times 10^8$ molecule cm⁻³.”

Q2: 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.

The line on page 5 has been rephrased:

“The CRDS technique was chosen to confirm the HO₂ measurements by the FAGE method as CRDS is a direct absorption method that does not require the chemical conversion of HO₂ to

another species. Reported here are the first CRDS measurements of HO₂ carried out in an atmospheric simulation chamber.”

Q3: 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.

Formaldehyde has a small contribution to the change in the background absorption during the scans shown in Figure 3, page 12. The absorption cross section of CH₂O at the wavelength of interest, 1506.43 nm, $\sigma_{\text{CH}_2\text{O}}$, has been estimated at the two HIRAC operating pressures (150 mbar and 1000 mbar) by measuring the ring-down time at 1506.43 nm before and after delivering CH₂O in a few known concentrations, determined by using the chamber *in situ* FTIR system. At both pressures $\sigma_{\text{CH}_2\text{O}}(1506.43 \text{ nm}) \sim 3 \times 10^{-23} \text{ cm}^2 \text{ molecule}^{-1}$. A few times higher value is shown in Figure 1 reported by Ruth et al. (2015), i.e. cross sections between $\sim 0.5\text{--}1.5 \times 10^{-22} \text{ cm}^2 \text{ molecule}^{-1}$ at around 1506.43 nm at 2 mbar of pure CH₂O, which may be explained by a reduced pressure broadening.

The cross sections of CH₃OH at 1506.43 nm at the two operating pressures are: $\sigma_{\text{CH}_3\text{OH}, 150 \text{ mbar}} = (9.95 \pm 0.42) \times 10^{-23} \text{ cm}^2 \text{ molecule}^{-1}$ and $\sigma_{\text{CH}_3\text{OH}, 1000 \text{ mbar}} = (8.11 \pm 0.05) \times 10^{-23} \text{ cm}^2 \text{ molecule}^{-1}$ (supplementary information). Therefore, $\sigma_{\text{CH}_2\text{O}}$ was about 3 times lower than $\sigma_{\text{CH}_3\text{OH}}$ at both 150 mbar and 1000 mbar. In the HIRAC experiments, CH₂O is formed by the CH₃OH + Cl reaction in the presence of O₂ (in a stoichiometric ratio CH₂O:CH₃OH = 1:1), and can react further with Cl. However, during the several minutes required to obtain the laser scans shown in Figure 3, the CH₂O + Cl reaction was negligible and, hence the [CH₂O] produced was approximately equal to the decrease in [CH₃OH]. Therefore, the decrease in background absorption due to the CH₃OH consumption is $\sim 30\%$ counteracted by the formation of CH₂O. In light of this effect, the first paragraph on page 12 has been changed to:

“During the measurements, the background absorption decreased mainly due to the removal of CH₃OH by the CH₃OH + Cl reaction (Reaction (R17)). [CH₃OH] decreased by $\sim 15\%$ during the scan at 150 mbar and $\sim 10\%$ during the scan at 1000 mbar, as determined using FTIR measurements (supplementary information), to form CH₂O through Reaction (R17) followed by (R18). Section S7 in the supplementary information shows that $\sigma_{\text{CH}_3\text{OH}}$ is ~ 3 times higher

than $\sigma_{\text{CH}_2\text{O}}$ at both pressures, hence $\sim 30\%$ of the decrease in the absorption background due to the CH_3OH consumption was counteracted by the formation of CH_2O . The spectrum was measured from larger to smaller wavelengths (right to left), hence the decrease in background absorption with time (decreasing λ) during a scan.”

A paragraph has also been added at the end of Section S7 in the supplementary information:

“In addition, a few measurements of the decrease in the ring-down time when CH_2O was delivered in known concentrations to the chamber have been performed to estimate that the absorption cross section of CH_2O at 1506.43 nm is $\sim 3 \times 10^{-23} \text{ cm}^2 \text{ molecule}^{-1}$ on average at both 150 mbar and 1000 mbar. This estimated $\sigma_{\text{CH}_2\text{O}}$ is a few times lower than the value reported by Ruth et al. (2015) using 2 mbar of pure CH_2O , and can be rationalised by the air-broadening in the present measurements.”

Q6: 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?

The investigations into any $[\text{HO}_2]$ gradient across the radius of HIRAC found an almost constant $[\text{HO}_2]$ at both operating pressures (Sect. 2.3.3), as expected as circulation fans were used to homogenize the gas mixture in the chamber. As the HIRAC diameter represented 86% of the cavity length, the approximation of a uniform k_{loss} has been employed in the analysis of the HO_2 temporal decays measured by the CRDS system.

A paragraph has been added in Sect. 3.3.1, above Figure 5, to clarify this point:

“The obtained σ_{HO_2} is in good agreement with $\sigma_{\text{HO}_2} = (1.25 \pm 0.19) \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1}$ generated by the analysis presented in Section 3.2. The wall-loss rate coefficient, $k_{\text{loss}}(\text{CRDS}) = (0.11 \pm 0.01) \text{ s}^{-1}$, is slightly higher than $k_{\text{loss}}(\text{FAGE}) = (0.09 \pm 0.02) \text{ s}^{-1}$, determined by fitting the kinetic decays to calibrate the FAGE instrument. This result was expected as the FAGE instrument was measuring $[\text{HO}_2]$ in the gas mixture sampled from one point at $\sim 230 \text{ mm}$ from the HIRAC wall, while CRDS measured across the total width of the chamber (1200 mm) and the two 100 mm long system of flanges coupling the cavity mirrors to the chamber (Fig. 2).

The investigations into the $[\text{HO}_2]$ gradient across the HIRAC diameter (86% of the distance between the two cavity mirrors, $L = 1400$ mm) found a practically constant $[\text{HO}_2]$ (Sect.2.3.3) due to the reactive mixture homogenized by the circulation fans. As the length of the systems of flanges coupling the mirrors, where the reactive mixture might not be homogenized, represented only 14% of L , k_{loss} was considered uniform over the entire cavity length.”

Q4: Page 14, line 7: do you use $l=1,4$ m in equation 9? Are you sure that the HO_2 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 HO_2 concentration over (at least) the last 10 cm before the mirrors due to many walls surrounding this area (looking at Figure 2). This of course makes only 20 cm out of a total of 140cm, but still, it might change the conclusions from the observed decay.

Equation 9 considers that HO_2 is present across the entire cavity length, $L = 1.4$ m.

The FAGE measurements of HO_2 across the HIRAC width described in Sect. 2.3.3 in the main manuscript showed that $[\text{HO}_2]$ is almost homogeneous across the chamber diameter. The mirrors were not protected with a flow of air. Since the mirrors are in a "recess", we can expect the $[\text{HO}_2]$ to be smaller in their proximity. Future experiments using a flow of clean air in front of the mirrors are planned to test the sensitivity of the results to a virtual zero $[\text{HO}_2]$ in front of the mirrors. In the ‘worst case scenario’ with the present system (no purge flow in front of the mirrors) $[\text{HO}_2] = 0$ over a distance of 10 cm in front of the mirrors and, then the absorption coefficient, α_{HO_2} , will be higher by a factor $R = L/L_{\text{HO}_2} = 1.4/1.2 = 1.17$, where L is the distance between the two cavity mirrors (1.4 m) and L_{HO_2} is the chamber diameter, where HO_2 is present (1.2 m).

A paragraph has been added after Figure 5:

Equation (9) employs the approximation that $[\text{HO}_2]$ is constant along the entire length of the cavity, L . Future experiments using a flow of clean air in front of the both cavity mirrors are planned to protect them from (potential) contamination due to the reactive mixture and to test if the results of the analysis of the HO_2 temporal decays remain unchanged by a virtual zero concentration of HO_2 in front of the mirrors.

Analysis was performed considering the worse case scenario that no HO_2 radicals were present over the two 100 mm distances between the cavity mirrors and the main HIRAC chamber, i.e. $[\text{HO}_2] = 0$ over 14% of L . This analysis found the same wall-loss rate coefficient on average,

$k_{\text{loss}} = (0.11 \pm 0.01) \text{ s}^{-1}$, as the average value obtained assuming that $[\text{HO}_2]$ is constant across the entirety of L . The extracted σ_{HO_2} , $(1.18 \pm 0.22) \text{ cm}^2 \text{ molecule}^{-1}$ on average, has overlapping overall errors (at the 1σ level) with that found by the analysis where $[\text{HO}_2]$ was considered homogeneous along the entire L , $(1.02 \pm 0.18) \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1}$ (further details in Sect. S9.2 in supplementary information).

A paragraph and a table (Table S5) have also been added at the end of the Sect. S9.2 in the supplementary information:

“As the cavity mirrors are mounted 100 mm from the chamber internal wall, $[\text{HO}_2]$ is expected to be lower along the 100 mm distance before each mirror compared to $[\text{HO}_2]_{\text{HIRAC}}$. Investigations have been carried out to test the sensitivity of the results shown in Table S4 to the approximation that $[\text{HO}_2]$ is homogeneous across the entire cavity length (the distance between the mirrors), $L = 1400 \text{ mm}$. The absorption coefficient has been re-computed by considering that HO_2 is absent in the systems of flanges connecting the mirrors to the chamber (14% of L). In this worst case scenario, the absorption coefficient is higher by a factor equal to the ratio between L and the HIRAC diameter, where HO_2 is present, L_{HO_2} (1200 mm):

$$\alpha_{\text{HO}_2} = \frac{L/L_{\text{HO}_2}}{c} \left(\frac{1}{\tau} - \frac{1}{\tau_0} \right) = \frac{1.17}{c} \left(\frac{1}{\tau} - \frac{1}{\tau_0} \right), \quad (\text{S6})$$

The fit of Eq. (S5) to the experimental temporal decays of α_{HO_2} computed using Eq. (S6) yielded the results shown in Table S5. The averaged values of the parameters are: $\sigma_{\text{HO}_2} = (1.18 \pm 0.22) \text{ cm}^2 \text{ molecule}^{-1}$ and $k_{\text{loss}} = (0.11 \pm 0.01) \text{ s}^{-1}$. It can be concluded that the use of the factor of 1.17 results in a change in σ_{HO_2} within its overall 1σ error and does not change k_{loss} .”

Q5: Page 14, determination of sigma_HO2: You consider the wall loss for CRDS measurements to be the same for FAGE and for CRDS measurements.

We determined the value of k_{loss} by treating it as a floating parameter in the fits to the kinetic decays. At 150 mbar k_{loss} obtained for the CRDS measurements is slightly higher than the one found by the analysis of the FAGE data, as expected as FAGE sampled from a point close to

the middle of HIRAC, while CRDS measured across the chamber diameter: $k_{\text{loss}}(\text{CRDS}) = (0.11 \pm 0.01) \text{ s}^{-1}$ (Section 3.3.1, page 14) and $k_{\text{loss}}(\text{FAGE}) = (0.09 \pm 0.02) \text{ s}^{-1}$ (Section 2.3.2, page 9). There is an almost constant $[\text{HO}_2]$ across the HIRAC radius (using FAGE measurements of HO_2 ; Section 2.3.3) showing/indicating that the circulating fans have homogenized the concentration within the chamber. The small difference (20%) between $k_{\text{loss}}(\text{CRDS})$ and $k_{\text{loss}}(\text{FAGE})$ is due to the two cavity mirrors mounted on the outside of HIRAC, 100 mm apart from the chamber, where the gas mixture might not be homogenized. However, 200 mm represents only 14% from the entire cavity length (1400 mm), explaining why $k_{\text{loss}}(\text{CRDS})$ and $k_{\text{loss}}(\text{FAGE})$ are relatively similar to each other (overlapping error limit at 1σ level).

The precision in the CRDS measurement was poorer at 1000 mbar than at 150 mbar. Therefore, at 1000 mbar the FAGE signal decays recorded simultaneously with the α_{HO_2} temporal decays were scaled to overlap α_{HO_2} vs. time and then analysed to obtain σ_{HO_2} (Sect. 3.3.2, page 15). This assumption has been made as the scaled FAGE measurements were in a very good agreement with the CRDS measurements (Figure 6 in the main manuscript), suggesting that a possible small difference between $k_{\text{loss}}(\text{CRDS})$ and $k_{\text{loss}}(\text{FAGE})$, similar to the difference found at 150 mbar, is ‘unobservable’. In addition, even though the analysis of the CRDS data resulted in significantly higher statistical errors in σ_{HO_2} , the average value agrees very well with the average σ_{HO_2} obtained by the analysis of the scaled fluorescence signal: $\sigma_{\text{HO}_2}(\text{CRDS}) = (3.68 \pm 0.69) \times 10^{-20} \text{ cm}^2 \text{ molecule}^{-1}$ and $\sigma_{\text{HO}_2}(\text{FAGE}) = (3.87 \pm 0.11) \times 10^{-20} \text{ cm}^2 \text{ molecule}^{-1}$. The value of $k_{\text{loss}}(\text{CRDS})$, $(0.076 \pm 0.028) \text{ s}^{-1}$ is higher but has overlapping error limits with $k_{\text{loss}}(\text{FAGE}) = (0.045 \pm 0.004) \text{ s}^{-1}$.

In light of these comments, section 3.3.2 of the main manuscript has been changed as follows:

“...Therefore, the statistical uncertainties in the kinetic analysis of the α_{HO_2} temporal decays were relatively high at 1000 mbar, having values of 19% in σ_{HO_2} and 37% in k_{loss} at the 1σ level on average. By comparison, the precision of the kinetic method at 1σ level at 150 mbar was 3% in $\sigma_{\text{HO}_2, 150 \text{ mbar}}$ and 10% in $k_{\text{loss}, 150 \text{ mbar}}$. In order to reduce the CRDS statistical uncertainties at 1000 mbar, the FAGE signal decays monitored at the same time with the α_{HO_2} decays were used to determine $\sigma_{\text{HO}_2}(1000 \text{ mbar})$. In this approach the fluorescence signal

decays were scaled to overlap α_{HO_2} vs. time by multiplying the FAGE signal by $f = \frac{(\bar{\alpha}_{\text{HO}_2})_0}{(\bar{S}_{\text{HO}_2})_0}$, where $(\bar{\alpha}_{\text{HO}_2})_0$ and $(\bar{S}_{\text{HO}_2})_0$ are the mean absorption coefficient and the mean FAGE signal before the UV lamps are turned off. Equation (10), where $k_{\text{self-r.}}$ was fixed to $2.85 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2004), was fitted to the scaled signal decays (Fig. 6 shows an example) to obtain an average $\sigma_{\text{HO}_2}(\text{FAGE}) = (3.87 \pm 0.74) \times 10^{-20} \text{ cm}^2 \text{ molecule}^{-1}$ (further details in supplementary information), where the error limits are overall errors (19%) quoted at the 1σ level. The value of $\sigma_{\text{HO}_2}(\text{FAGE})$ agrees very well with the average absorption cross section obtained by fitting Eq. (10) to the temporal decays recorded by the CRDS system, $\sigma_{\text{HO}_2}(\text{CRDS}) = (3.68 \pm 0.99) \times 10^{-20} \text{ cm}^2 \text{ molecule}^{-1}$ (Sect. 9.3 in supplementary information), where the overall 1σ uncertainty is 27%. Both values are in good agreement with $\sigma_{\text{HO}_2} = (3.44 \pm 0.37) \times 10^{-20} \text{ cm}^2 \text{ molecule}^{-1}$ computed by the model described in Section 3.2, which considered the contribution of the air-broadened HO_2 absorption lines (Thiebaud et al., 2007) to the overall cross section at 1506.43 nm. As the precision in $\sigma_{\text{HO}_2}(\text{FAGE})$ (3%) is much higher than the precision in $\sigma_{\text{HO}_2}(\text{CRDS})$ (19%), $\sigma_{\text{HO}_2}(\text{FAGE})$ was used in the intercomparison of the CRDS and FAGE measurements (Sect. 3.5.2).’’

A new paragraph also been added at the end of the section S9.3 in the supplementary information:

“The scaled FAGE signal decays were employed to determine σ_{HO_2} as the scaled S_{HO_2} decays overlapped very well with the $\alpha_{\text{HO}_2}(1000 \text{ mbar})$ vs. time measurements (Figure 6 in the main manuscript shows an example). In addition, the analysis of $\alpha_{\text{HO}_2}(1000 \text{ mbar})$ vs. time using Eq. (S5) provided an average $\sigma_{\text{HO}_2}(\text{CRDS}) = (3.68 \pm 0.69) \times 10^{-20} \text{ cm}^2 \text{ molecule}^{-1}$ (Table S6) in very good agreement with $\sigma_{\text{HO}_2}(\text{FAGE})$. The average rate coefficient of the wall-loss was $k_{\text{loss}}(\text{CRDS}) = (0.076 \pm 0.028) \text{ s}^{-1}$ and, hence $k_{\text{loss}}(\text{CRDS})$ and $k_{\text{loss}}(\text{FAGE})$ have overlapping error limits. The standard errors in the fit to the CRDS data were much higher than the standard errors in the fit to the scaled FAGE data: 19% associated with $\sigma_{\text{HO}_2}(\text{CRDS})$, compared to the only 3% fit precision in $\sigma_{\text{HO}_2}(\text{FAGE})$ and 37% associated with $k_{\text{loss}}(\text{CRDS})$ compared to the ~4 times lower fit precision in $k_{\text{loss}}(\text{FAGE})$ (10%).

Table S6. $\sigma_{\text{HO}_2}(1506.43 \text{ nm})$ and the wall-loss rate coefficient within HIRAC, k_{loss} , at 1000 mbar obtained by fitting Eq. (S5) to: (i) the temporal decays obtained by multiplying the FAGE signal, $(S_{\text{HO}_2})_t$, with $f = \frac{(\bar{\alpha}_{\text{HO}_2})_0}{(\bar{S}_{\text{HO}_2})_0}$, where $(\bar{\alpha}_{\text{HO}_2})_0$ and $(\bar{S}_{\text{HO}_2})_0$ are the average absorption coefficient and the mean FAGE signal before the UV lamps are extinguished, and (ii) $\alpha_{\text{HO}_2}(150 \text{ mbar})$ vs. time.

$10^{20} \times \sigma_{\text{HO}_2, \text{FAGE}}^a$ / $\text{cm}^2 \text{ molecule}^{-1}$	$k_{\text{loss, FAGE}}^a / \text{s}^{-1}$	$10^{20} \times \sigma_{\text{HO}_2, \text{CRDS}}^a$ / $\text{cm}^2 \text{ molecule}^{-1}$	$k_{\text{loss, CRDS}}^a / \text{s}^{-1}$
3.65 ± 0.04^b	0.046 ± 0.004	3.89 ± 0.52^b	0.08 ± 0.01
3.54 ± 0.06^b	0.029 ± 0.008	3.47 ± 0.47^b	0.07 ± 0.02
3.29 ± 0.05^b	0.028 ± 0.002	4.30 ± 0.26^b	0.07 ± 0.02
4.08 ± 0.06^b	0.034 ± 0.005	3.27 ± 0.68^b	0.08 ± 0.03
4.30 ± 0.30^c	0.070 ± 0.011	3.69 ± 0.63^c	0.01 ± 0.01
4.36 ± 0.13^c	0.062 ± 0.004	3.49 ± 1.56^c	0.14 ± 0.07

^a uncertainties quoted to 1σ

^b $[\text{HO}_2]_0 \sim 1 \times 10^{10} \text{ molecule cm}^{-3}$ (obtained by using: $[\text{HO}_2]_0 = (\alpha_{\text{HO}_2})_0 / \sigma_{\text{HO}_2}$)

^c $[\text{HO}_2]_0 \sim 6 \times 10^{10} \text{ molecule cm}^{-3}$ (computed by using: $[\text{HO}_2]_0 = (\alpha_{\text{HO}_2})_0 / \sigma_{\text{HO}_2}$)”

Author’s note: As circulation fans were used during all the experiments, the “movement” of HO_2 within the chamber is only in part molecular diffusion, the rest is convection. Therefore, the below sentence was removed from the main text in Sect. 2.3.2 before Figure 1:

“Note that the parameter k_{loss} is dependent on the chamber conditions during the experiment and decreases with increasing pressure as expected for diffusive loss being the rate determining step in the wall-loss process; a value of $k_{\text{loss}} = (0.04 \pm 0.01) \text{ s}^{-1}$, has been obtained by the kinetic analysis of the FAGE signal decays measured at 1000 mbar in HIRAC in this work.”

Q7. Looking at the absorption cross sections, I see that your measured value at 150 mbar ($1.02\text{e-}19$) is around 20% below the calculated one ($1.25\text{e-}19$), while at 1000 mbar the measured value ($3.87\text{e-}20$) is around 10% above the calculated one ($3.44\text{e-}20$). 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...

The reviewer is right. Now ‘broad’ and ‘good’ are the other way round.

8. *Even though the error bars are overlapping for both pressures, I'm still wondering why the measured value is above at 1000 mbar and below at 150 mbar, compared to the calculated one. Pressure broadening has a very strong impact on the 1000 mbar 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 σ_{HO_2} at 1000 mbar, and then re-calculating the value at 150 mbar, should lead to a ~10% higher value at 150 mbar. Now the error bars start to not agreeing anymore. Could the diffusion be linked to this?*

A value of $(3.44 \pm 0.37) \times 10^{-20} \text{ cm}^2 \text{ molecule}^{-1}$ was computed for $\sigma_{\text{HO}_2}(1506.43 \text{ nm})$ at 1000 mbar assuming that the air-broadening coefficients for the absorption line centred at 1506.43 nm and the nearby lines are all the same and equal to the value reported by Ibrahim et al., (2007). However, no study has been performed to test if the broadening coefficients are (nearly) identical for all the absorption lines overlapping at 1000 mbar. Therefore, tuning the value for the “global” broadening coefficient to best fit $\sigma_{\text{HO}_2}(1000 \text{ mbar})$ obtained by the analysis of the HO_2 kinetic decays $((3.87 \pm 0.74) \times 10^{-20} \text{ cm}^2 \text{ molecule}^{-1})$ is not necessarily correct. For example, if the values of the broadening coefficients, γ_i , for the spectral lines in the vicinity of 1506.43 nm are higher than the broadening coefficient for the line centred at 1506.43 nm, $\gamma(1506.43 \text{ nm})$, then a slightly higher $\sigma_{\text{HO}_2}(1000 \text{ mbar})$ would be obtained than $\sigma_{\text{HO}_2}(1000 \text{ mbar})$ calculated here assuming $\gamma_i = \gamma(1506.43 \text{ nm})$. The value of $\sigma_{\text{HO}_2}(1000 \text{ mbar})$ obtained using $\gamma_i = \gamma(1506.43 \text{ nm})$ is 10% smaller than $\sigma_{\text{HO}_2}(1000 \text{ mbar})$ determined by the kinetic method, suggesting that indeed $\gamma_i > \gamma(1506.43 \text{ nm})$. However, if $\gamma_i > \gamma(1506.43 \text{ nm})$ a 10% higher σ_{HO_2} at 1000 mbar does not extrapolate into 10% higher σ_{HO_2} at 150 mbar, as the overlapping of the spectral lines at 150 mbar is less significant than the line overlapping at 1000 mbar. In addition, $\sigma_{\text{HO}_2}(150 \text{ mbar}) = (1.25 \pm 0.19) \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1}$ computed by using the reported spectral data agrees very well with the value found by Tang et al. (2010), $\sigma_{\text{HO}_2, 150 \text{ mbar}} = (1.29 \pm 0.23) \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1}$. We have therefore chosen not to make this (suggested) correction but simply make sure that we state the assumptions inherent in our modelling of the spectra.

Q9. (A) *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 σ (same trend is visible for the FAGE calibration factors).*

(B) *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 Cl_2 concentration by a factor of 3 to 4, but unfortunately these values are not given in the tables. Can you comment on that?*

Answer to Q 9(A):

Analysis has been performed to investigate whether the weak correlation between k_{loss} and σ_{HO_2} had an effect on the fitting of the results using Eq. (10) (corresponding to Eq. (S5) in Sect. 9.2 in the supplementary information). The parameter $\sigma_{\text{HO}_2, 150 \text{ mbar}}$ was fixed to the value obtained by using the reported spectral data, $1.25 \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1}$ while k_{loss} was floated. The best fit returned a k_{loss} value ca. 30% higher than that obtained by floating both k_{loss} and σ_{HO_2} . However, the goodness of the fit was poorer, as shown by the values of the reduced chi-squared: (i) 0.9×10^{-21} when both k_{loss} and σ_{HO_2} were floated and (ii) 1.5×10^{-20} when σ_{HO_2} was fixed to $1.25 \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1}$ and only k_{loss} floated.

In addition, the analysis of the FAGE signal decays at 1000 mbar generated a FAGE calibration factor ($C_{\text{HO}_2} = (2.4 \pm 0.5) \times 10^{-7} \text{ counts cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ mW}^{-1}$) in very good agreement with the calibration factor at atmospheric pressure obtained by the conventional method of calibration using the flow tube ($C_{\text{HO}_2} = (2.6 \pm 0.4) \times 10^{-7} \text{ counts cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ mW}^{-1}$). This very good level of agreement shows that the kinetic analysis of the FAGE and CRDS data, respectively, provides a reliable method of determination of C_{HO_2} and σ_{HO_2} . Therefore, we think that no modification of the text is necessary.

Answer to Q 9(B) *(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?):*

The initial values for $[\text{HO}_2]$ are given in the text below the tables S4 – S6, which show σ_{HO_2} and k_{loss} obtained by the analysis of the absorption coefficient temporal decays at the two pressures. At 150 mbar all the values of σ_{HO_2} agree within $\sim 3\%$ even if the initial concentration of HO_2 was changed by a factor of two (Table S4). At 1000 mbar an increase in $[\text{HO}_2]_0$ by a factor of ~ 2 corresponds to $\sim 20\%$ increase in $\sigma_{\text{HO}_2}(\text{FAGE})$ and practically same $\sigma_{\text{HO}_2}(\text{CRDS})$ (agreement within $\sim 3\%$). Therefore, it can be concluded that the analysis results are independent of $[\text{HO}_2]_0$.

The main text above Fig. 5 has been changed to:

“Eq. (10) was fitted to eight temporal traces (Fig. 5 shows an example) where the $(\alpha_{\text{HO}_2})_0$ was varied by a factor of two to obtain an average $\sigma_{\text{HO}_2} = (1.02 \pm 0.18) \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1}$

(Table S4 in the supplementary information), where the error is a combination of systematic and statistical uncertainties at the 1σ level. The statistical error was only 3% showing that the analysis results are independent of $[\text{HO}_2]_0$.”

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.

Line 26 on page 3 has been changed as suggested by the referee:

“If the laser frequency matches one of the cavity resonance frequencies, optical power within the resonator quickly builds up, and a fraction of the circulating power leaks out through one mirror. A photodetector located at the back of this mirror measures the exponential decay in the light intensity (‘ring-down’) with a time constant that is a measure of the cavity losses.”

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)

The recent paper mentioned by the referee is now cited for completeness:

“Fittschen and co-workers have used the CRDS technique to perform time-resolved measurements of the HO₂ radicals, generated by pulsed laser photolysis in a flow cell, to extract spectroscopic (Thiebaud et al., 2007; Thiebaud and Fittschen, 2006; Ibrahim et al., 2007; Parker et al., 2011; Assaf et al., 2017) and kinetic (Thiebaud and Fittschen, 2006; Morajkar et al., 2014) information.”

The text has been also corrected according to the following suggestions of the referee:

Page 4, line 5: long time averaging times

Now it reads: “long averaging times”

Page 4, line 31: HO2

Now: HO₂

Page 11, line 30 : in in

One of them has been deleted.