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Atmospheric Chemistry and Physics Discussions

Supplement of

Nighttime measurements of HO_x during the RONOCO project and analysis of the sources of HO_2

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Supplementary Information

1 Leeds Aircraft FAGE instrument characterisation

1.1 Instrument calibration

The results from the February 2011 calibration, following the winter RONOCO fieldwork, are shown in Fig. S1.

1.2 Factors affecting sensitivity

The theoretical sensitivity, as a function of the detection cell pressure, is given by:

$$C(P_{\text{cell}}) = D \cdot T_{\text{OH}} \cdot \phi_{\text{f}} \cdot f_{\text{gate}} \cdot [\text{OH}]_{\text{cell}} \quad (1)$$

where P_{cell} is the pressure inside the detection cell, D is a collective term for pressure-independent variables (laser power, OH absorption cross-section, laser linewidth, physical overlap of laser and gas beams, solid angle of fluorescence collection, transmission of collection optics, quantum yield of the channel photomultiplier tube), T_{OH} is the transmission of OH through the inlet and pre-detection assembly, ϕ_{f} is the OH fluorescence quantum yield, f_{gate} is the fraction of the total OH fluorescence detected within the photon counter gate, and $[\text{OH}]_{\text{cell}}$ is the number density of OH in the detection cell (Creasey et al., 1997; Faloona et al., 2004; Heard, 2006; Dusanter et al., 2009). Apart from the laser power, the terms contributing to *D* remain constant throughout a measurement period, and are accounted for by regular calibrations. Laser power is measured by photodiodes positioned in the OH and HO_2 detection cells, and the recorded OH and HO_2 signals are normalised to the measured laser power.

1.2.1 Effects of water vapour concentration on sensitivity

The fluorescence quantum yield, ϕ_{f}, is given by the ratio of the rate of radiative decay to the total rate of decay:

$$\phi_{\text{f}} = \frac{\tau^{-1}}{\Gamma} = \frac{k_{\text{rad}}}{k_{\text{rad}} + \sum_i k_{\text{q}i}[\text{q}_i]} \quad (2)$$

where τ is the fluorescence lifetime of the OH in the absence of quenchers (= 688 ns) (German, 1975), Γ is the total rate of decay of excited OH, $k_{\mathrm{rad}} = \frac{1}{\tau_{\mathrm{rad}}}$ is the rate constant for radiative decay, $k_{\mathrm{q}i}$ is the rate constant for quenching of the OH fluorescence by ambient molecule *i*, and $[\mathrm{q}_i]$ is the number density of the quenching species *i*. N_2, O_2, and H_2O are the most important atmospheric quenchers of OH fluorescence. The ambient mixing ratios of N_2 and O_2 are constant. The ambient concentration of water vapour, however, varies sufficiently (0–4 %) that its effect on instrument sensitivity must be taken into account during field measurements (Stevens et al., 1994). The fraction of OH fluorescence collected within the photon counting gate, f_{gate}, is dependent on the OH fluorescence lifetime, and therefore on the rate of quenching by water vapour.

Given a measured sensitivity at a known water vapour concentration, the theoretical reduction or increase in sensitivity at other water vapour concentrations can be calculated. The fraction of OH fluorescence collected in the photon counting gate, f_{gate}, and the fluorescence quantum yield, ϕ_{f}, are given by:

$$f_{\mathrm{gate}} = e^{-\Gamma t_1} - e^{-\Gamma t_2} \tag{3}$$

$$\phi_{\mathrm{f}} = \frac{\tau^{-1}}{k_{\mathrm{rad}} + k_{\mathrm{q,N_2}}[\mathrm{N_2}]_{\mathrm{cell}} + k_{\mathrm{q,O_2}}[\mathrm{O_2}]_{\mathrm{cell}} + k_{\mathrm{q,H_2O}}[\mathrm{H_2O}]_{\mathrm{cell}}} \tag{4}$$

where t_1 = 110 ns and t_2 = 1110 ns are the start and end times of the photon-counting gate, respectively, and $[\mathrm{N_2}]_{\mathrm{cell}}$, $[\mathrm{O_2}]_{\mathrm{cell}}$, and $[\mathrm{H_2O}]_{\mathrm{cell}}$ are the concentrations inside the detection cell. Knowledge of the ambient pressure and the detection cell pressure enables calculation of $[\mathrm{N_2}]_{\mathrm{cell}}$, $[\mathrm{O_2}]_{\mathrm{cell}}$, and $[\mathrm{H_2O}]_{\mathrm{cell}}$, and therefore f_{gate} and ϕ_{f}, for any ambient water vapour concentration which was measured on the aircraft. Since C_{OH} is directly proportional to the product of f_{gate} and ϕ_{f}, a correction factor can be applied to C_{OH} as follows:

$$C_{\mathrm{OH}}(\mathrm{H_2O}) = C_{\mathrm{OH,meas}} \cdot \frac{f_{\mathrm{gate}} \cdot \phi_{\mathrm{f}}}{f'_{\mathrm{gate}} \cdot \phi'_{\mathrm{f}}} \tag{5}$$

where f_{gate} and ϕ_{f} are the values calculated for a calibration at a known water vapour concentration, and f'_{gate} and ϕ'_{f} are the values calculated for other water vapour concentrations.

A summary of ambient and detection cell water vapour concentrations and the instrument sensitivity to OH and HO_2 during the RONOCO and SeptEx field measurement campaigns is given in Table S1. The range of ambient water vapour concentrations exceeds the range that can be reliably achieved during a calibration. For this reason, theoretical water-dependent sensitivities were calculated for the RONOCO and SeptEx data, using the ambient water vapour concentration, the ambient pressure, and the detection cell pressure measured during the flights, to adjust the sensitivities measured during the calibrations that followed each measurement campaign.

1.2.2 Effects of pressure on sensitivity

The pressure inside the detection cell, P_{cell}, changes with external pressure during aircraft FAGE measurements. The internal pressure affects a number of parameters in Eq. (6), namely the number density of OH inside the detection cell, $[OH]_{cell}$, OH transmission, T, OH fluorescence quantum yield, ϕ_f, and therefore the fraction of OH fluorescence detected in the photon counting gate, f_{gate}.

The experimental pressure dependence of C_{OH} and C_{HO2} has been investigated by Commane (2009; see also Commane et al., 2010) following the method of Faloona *et al*. (2004) and Martinez *et al*. (2010). The pressure inside the detection cell can be varied between 1.6 and 2.7 Torr by varying the diameter of the inlet pinhole between 0.50 and 0.85 mm, to mimic a change in external pressure. Calibrations can therefore be conducted over a range of cell pressures applicable to aircraft-based measurements. During the RONOCO aircraft campaign, P_{cell} ranged between a maximum of 1.9 Torr at ground level to 1.2 Torr at 6 km. C_{OH} and C_{HO2} were found to be independent of pressure over the range of pressures experienced during typical aircraft-based measurements, and within the reproducibility of calibration results, in agreement with the theoretical calculations.

The pressure-dependent calibration method using different sized pinholes relies on the assumptions that losses of OH and HO_2 to the inside of the pinhole does not change significantly with pinhole diameter, and that the flow regime remains similar for pinholes of different diameter. The method has been validated by calibration of the aircraft FAGE instrument for sensitivity to HO_2 at different external pressures inside the atmospheric simulation chamber HIRAC at the University of Leeds using the photolysis of formaldehyde followed by time-dependent measurements of HO_2 (Winiberg et al., 2014). The FAGE inlet was positioned inside the chamber, with the detection cells located outside the chamber. The

pressure inside the detection cells ranged between 1.1 and 1.9 Torr. Little variation in C_{HO2} was found over the range of pressures studied, in agreement with the results of Commane (2009). At 1.1 Torr, C_{HO2} was 8.0 ± 1.6 × 10^{-8} count s^{-1} mW^{-1} $molecule^{-1}$ cm^3, and at 1.9 Torr C_{HO2} was 1.2 ± 0.24 × 10^{-7} count s^{-1} mW^{-1} $molecule^{-1}$ cm^3, the two values being the same within their combined uncertainties.

Table S1. Ambient and detection cell water vapour concentrations, C_{OH}, and C_{HO2} during RONOCO and SeptEx. Mean values are given in parentheses.

	RONOCO summer, 2010	SeptEx, 2010	RONOCO winter, 2011
Ambient $[H_2O]$ / 10^{17} molecule cm^{-3}	1.03–3.55 (2.64)	0.318–3.63 (2.34)	0.016–4.37 (1.49)
Detection cell $[H_2O]$ / 10^{14} molecule cm^{-3}	2.64–9.18 (6.67)	0.648–8.86 (5.60)	0.004–10.6 (3.43)
C_{OH} / count s^{-1} mW^{-1} $molecule^{-1}$ cm^3	3.0×10^{-8}	3.0×10^{-8}	3.8×10^{-8}
C_{OH} corrected for mean $[H_2O]$ / count s^{-1} mW^{-1} $molecule^{-1}$ cm^3	2.9×10^{-8}	3.1×10^{-8}	4.3×10^{-8}
C_{HO2} / count s^{-1} mW^{-1} $molecule^{-1}$ cm^3	9.3×10^{-8}	9.3×10^{-8}	1.1×10^{-7}
C_{HO2} corrected for mean $[H_2O]$ / count s^{-1} mW^{-1} $molecule^{-1}$ cm^3	9.5×10^{-8}	9.6×10^{-8}	1.2×10^{-7}

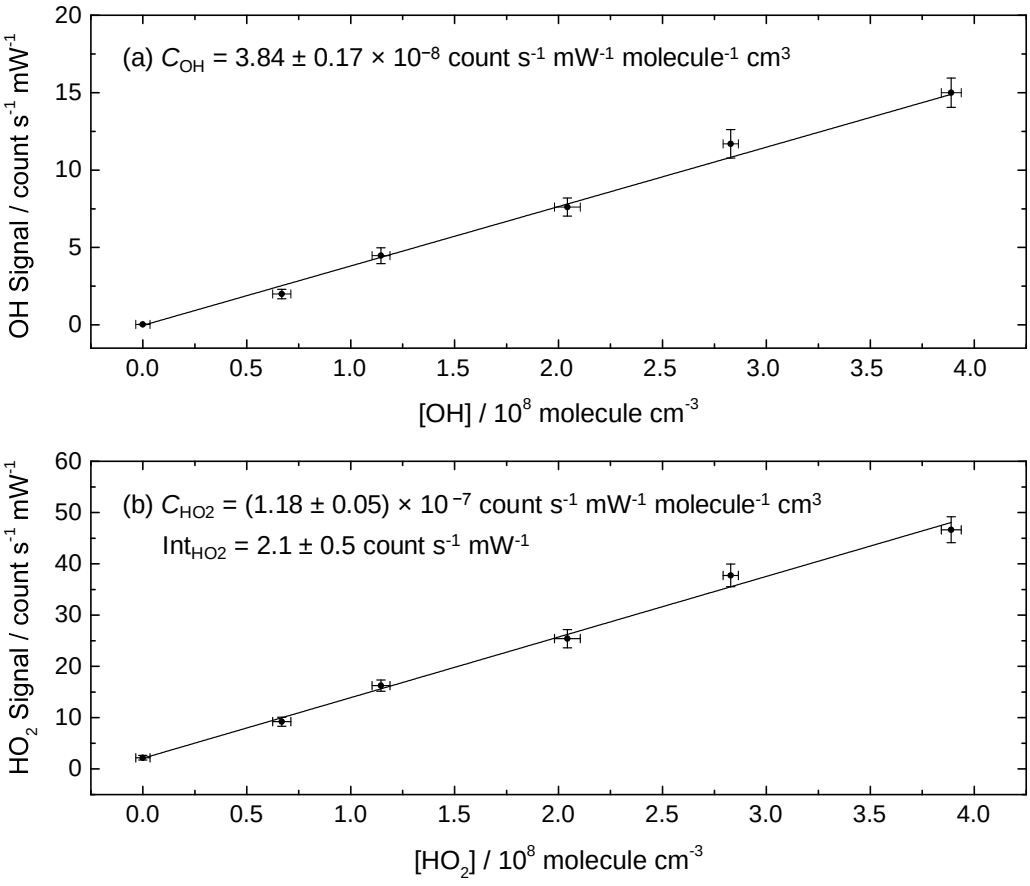

Figure S1. Results from a calibration of the aircraft FAGE instrument in February 2011, following the winter RONOCO fieldwork, at $[H_2O] = 9 \times 10^{16}$ molecule cm^{-3} (0.4 %). Data points represent average values for one minute of online data. *x* and *y* error bars represent the standard deviations of [OH] and [HO_2], and the normalised FAGE signals, respectively. The instrument sensitivity to OH, C_{OH}, is equal to (3.84 ± 0.17) × 10^{-8} count s^{-1} mW^{-1} $molecule^{-1}$ cm^{-3}. The instrument sensitivity to HO_2, C_{HO2}, is equal to (1.18 ± 0.05) × 10^{-7} count s^{-1} mW^{-1} $molecule^{-1}$ cm^{-3}. The intercept of the HO_2 calibration plot, an artefact caused by the addition of NO, is equal to 2.1 ± 0.5 count s^{-1} mW^{-1} molecule cm^{-3}.