Kinetics of the OH + NO₂ reaction: Effect of water vapour and new parameterisation for global modelling.

Damien Amedro[1], Matias Berasategui[1], Arne J. C. Bunkan[1] Andrea Pozzer[1], Jos Lelieveld[1] and John N. Crowley[1]

[1]Division of Atmospheric Chemistry, Max-Planck-Institute for Chemistry, 55128 Mainz, Germany

Correspondence to: John N. Crowley (john.crowley@mpic.de)

Supplementary information

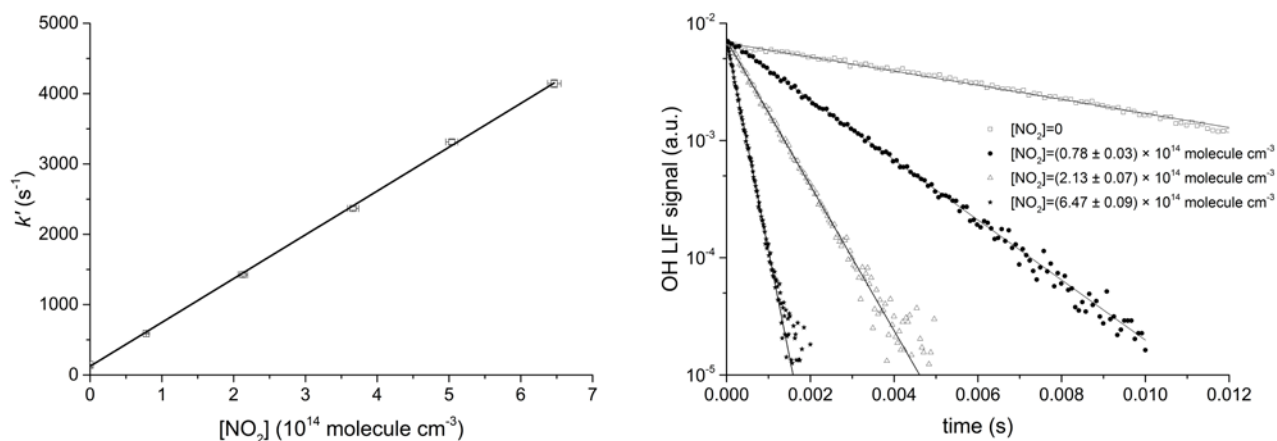
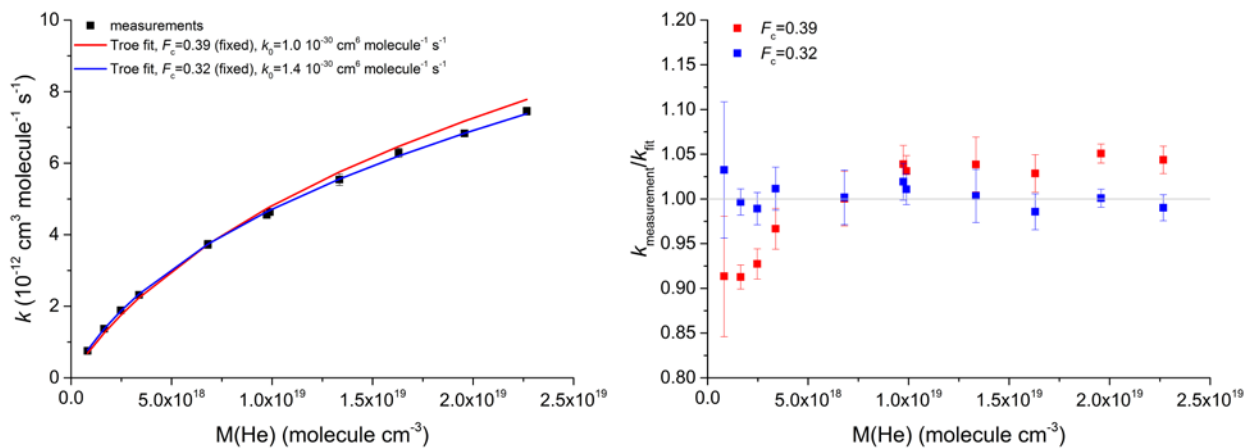



Figure S1. *Left panel*: Plots of k' versus [NO₂] at 500 Torr He and 292 K. The lines are least-squares fits to the data using Eq. (2) (see main text). Error bars are 2σ statistical only. *Right panel*: Exponential decay of the OH LIF signal in 500 Torr He, at 292 K, and at four different NO₂ concentrations. The solid lines are fits to the datasets using Eq. (1) (see main text).

5   **Figure S2.** *Left panel*: Measurements of k_1 as a function of He density. The blue line corresponds to a fit using equation (2) whereby F_c was fixed to 0.32 leading to $k_0^{He} = 1.4 \times 10^{-30}$ cm^6 molecule^{-2} s^{-1}. The red line corresponds to a fit using equation (2) whereby F_c was fixed to 0.39 leading to $k_0^{He} = 1.0 \times 10^{-30}$ cm^6 molecule^{-2} s^{-1}. Other parameters were fixed to: $m = 3.1$, $k_\infty = 6.3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} and $n = 0$. *Right panel*: Ratio of the measured rate constant vs. the parametrisation using $F_c = 0.39$ and $F_c = 0.32$

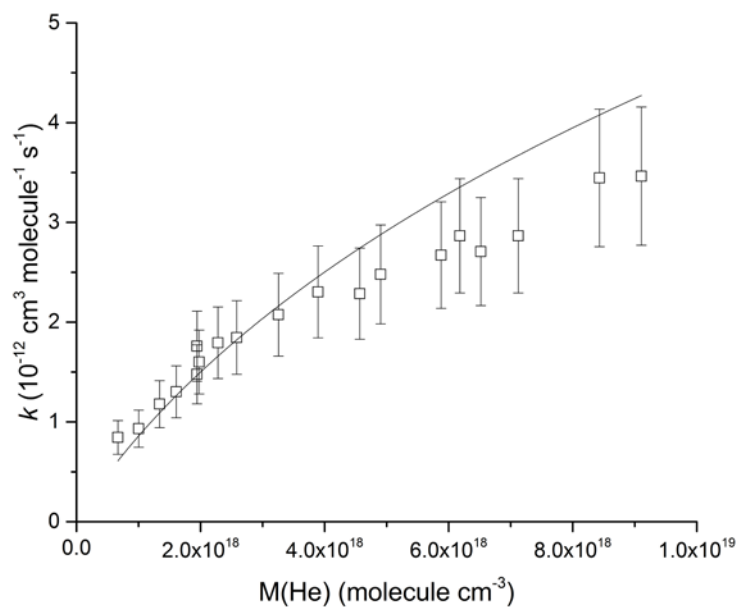



Figure S3. Comparison with previous experimental data. The data points are measurements by Morley and Smith (1972) at 300 K, the solid line represents our parametrisation.

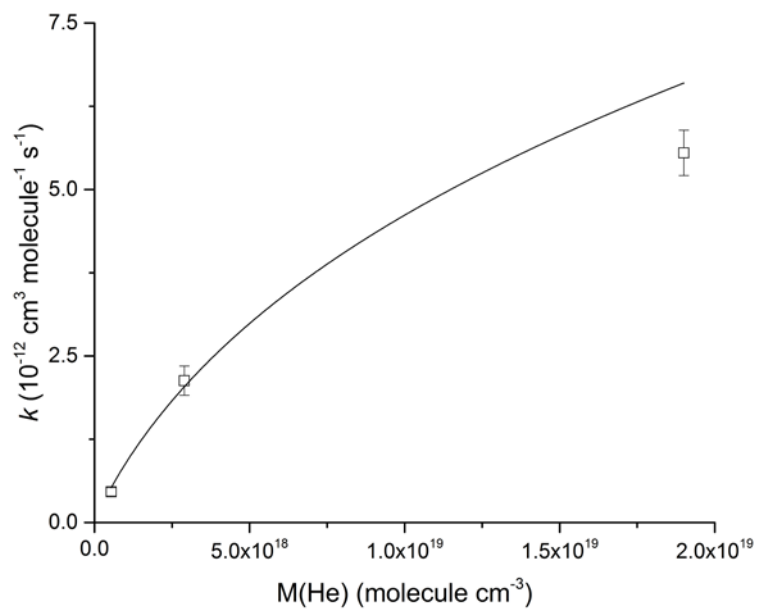



Figure S4. Comparison with previous experimental data. The data points are measurements by Wine et al. (1979) at 297 K, the solid line represents our parametrisation.

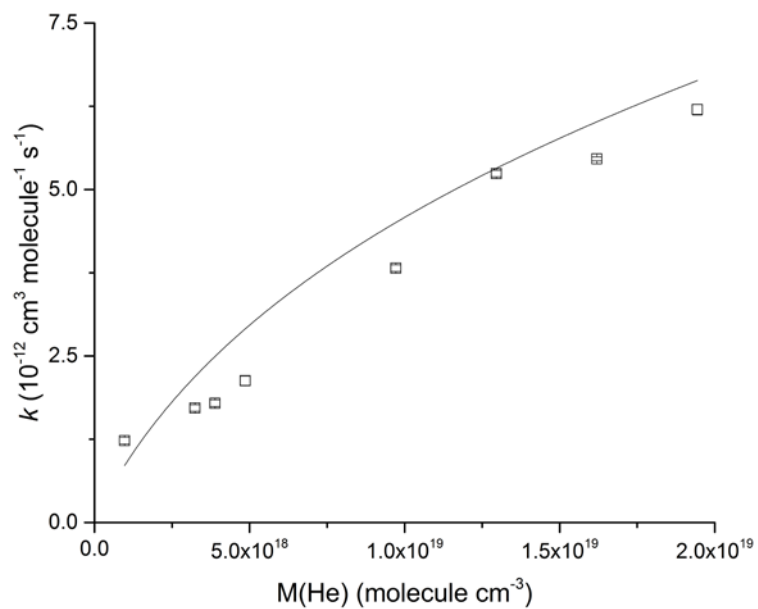



Figure S5. Comparison with previous experimental data. The data points are measurements by D'Ottone et al. (2001) at 298 K, the solid line represents our parametrisation.

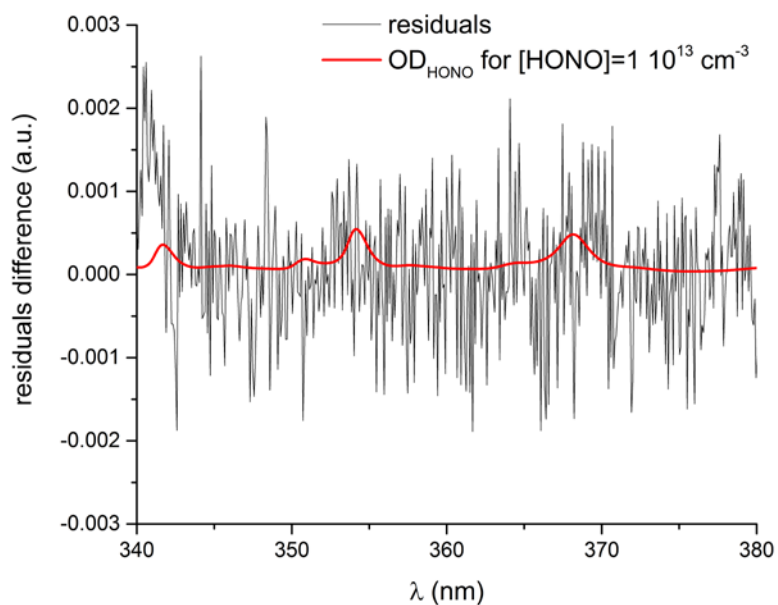
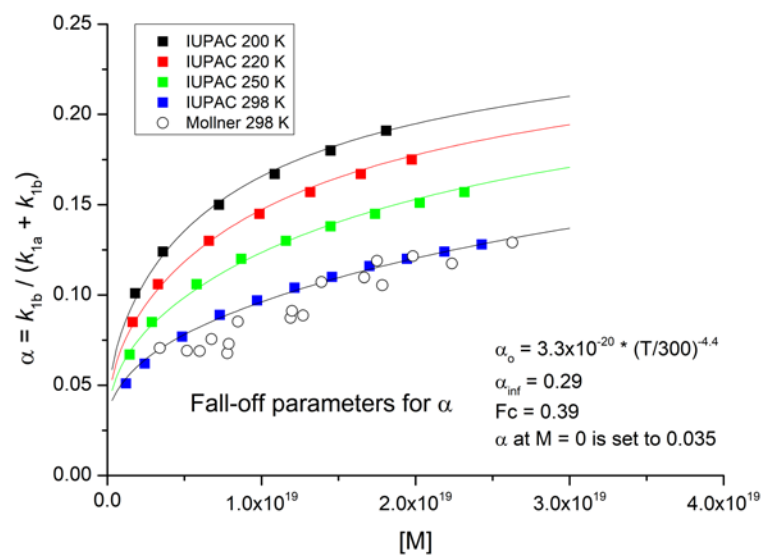



Figure S6. Spectrum of the difference between the residuals of NO_2 spectra with and without H_2O ($[H_2O] = 4.5 \times 10^{17}$ molecule cm^{-3}, $[NO_2] = 1.7 \times 10^{15}$ molecule cm^{-3}) recorded at 50 Torr He, at room temperature. The red line corresponds to absorption by HONO at a concentration of 1×10^{13} molecule cm^{-3}.

5   **Figure S7.** Parameterisation of the temperature and pressure dependent yield of HOONO in the reaction between OH and NO$_2$.

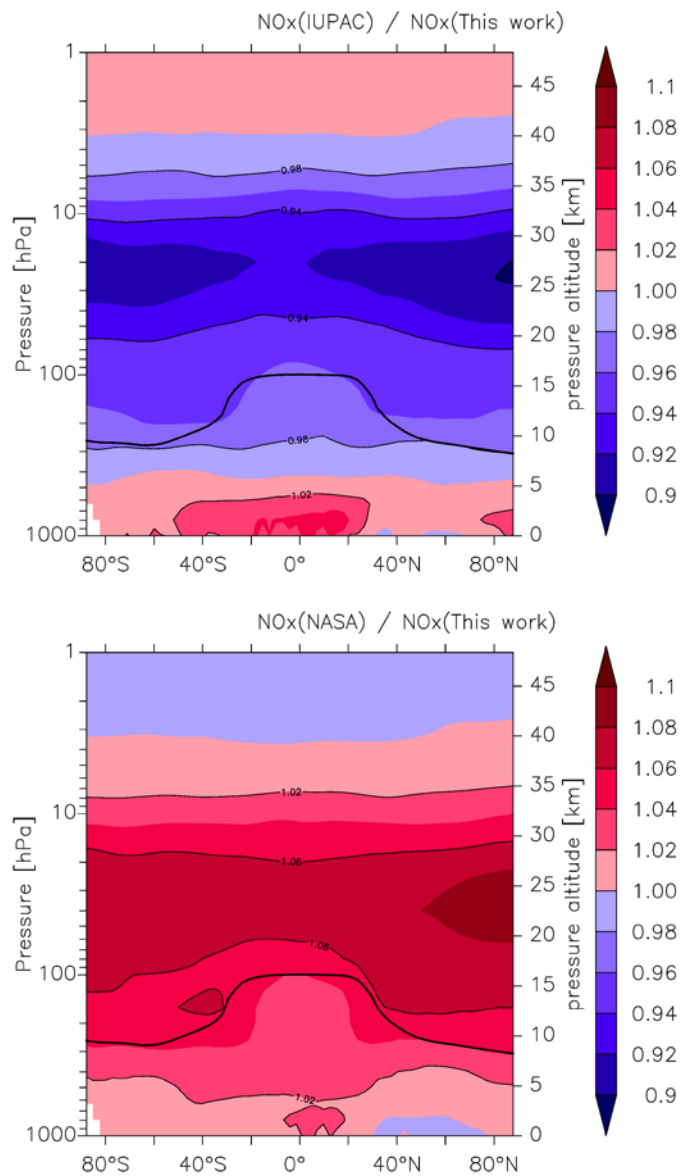



Figure S8. Effect of different parameterisations of k_1 on the global (zonal and yearly averaged) concentration of NO_X. The upper panel plots $[NO_X]_{IUPAC} / [NO_X]_{this\ work}$, the lower panel plots $[NO_X]_{NASA} / [NO_X]_{this\ work}$. The black line represents the model tropopause.

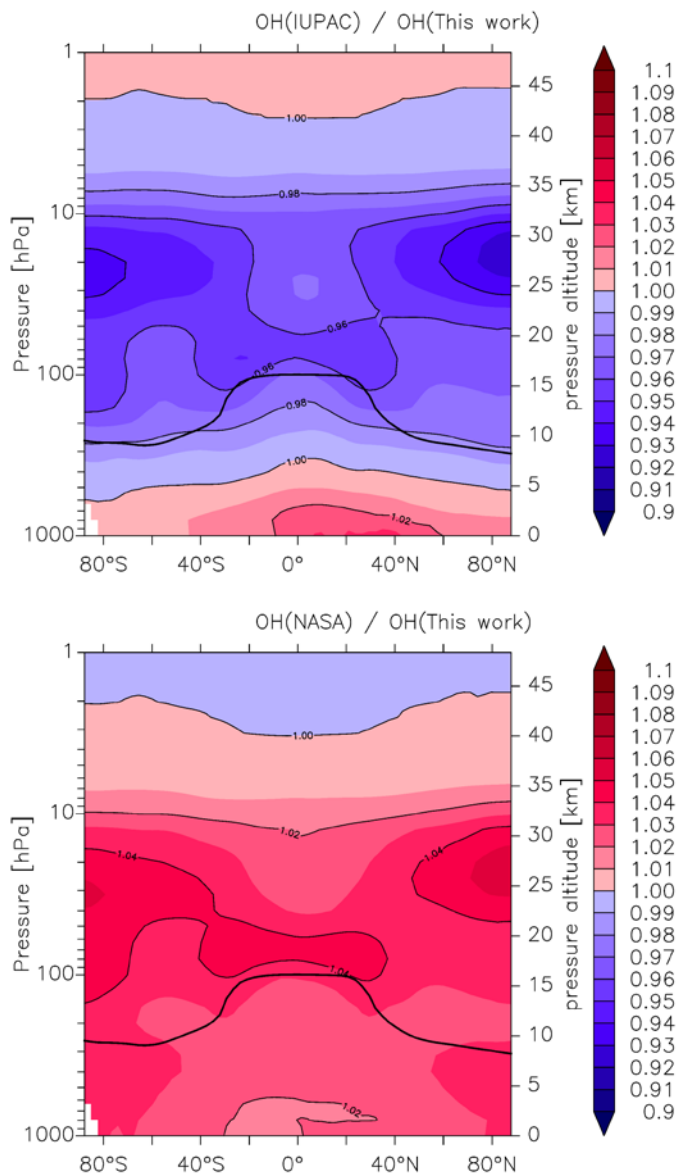



Figure S9. Effect of different parameterisations of k_1 on the global (zonal and yearly averaged) concentration of the hydroxyl radical, [OH]. The upper panel plots [OH]$_{\text{IUPAC}}$ / [OH]$_{\text{this work}}$, the lower panel plots [OH]$_{\text{NASA}}$ / [OH]$_{\text{this work}}$. The black line represents the model tropopause.

References

D'Ottone, L., Campuzano-Jost, P., Bauer, D., and Hynes, A. J.: A pulsed laser photolysis-pulsed laser induced fluorescence study of the kinetics of the gas-phase reaction of OH with NO_2, J. Phys. Chem. A, 105, 10538-10543, 2001.

5   Morley, C., and Smith, I. W. M.: Rate measurements of reactions of OH by resonance absorption. 1. Reactions of OH with NO_2 and NO, Journal of the Chemical Society-Faraday Transactions Ii, 68, 1016-&, 10.1039/f29726801016, 1972.

Wine, P. H., Kreutter, N. M., and Ravishankara, A. R.: Flash photolysis-resonance fluorescence kinetics study of the reaction $OH + NO_2 + M \rightarrow HNO_3 + M$, J. Phys. Chem., 83, 3191-3195, 1979.