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Supplement of

Kinetics of the OH + NO₂ reaction: rate coefficients (217–333 K, 16–1200 mbar) and fall-off parameters for N₂ and O₂ bath gases

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Supplementary Information

Calculation of uncertainty associated with determination of k_5

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The total uncertainty stems from:

- 1) The statistical error of the linear fit of the plot of k' versus $[\text{NO}_2]$ (σ_{meas})
- 15 2) The uncertainty associated with $[\text{NO}_2]$ measurements using optical absorption ($\sigma_{[\text{NO}_2]} = 3\%$). This value was obtained from the spread in cross-sections of the different reference spectra.
- 3) the NO_2 concentration correction due to the N_2O_4 formation at low temperatures ($\sigma_{\text{N}_2\text{O}_4 \text{ corr}}$) which is a function of the magnitude of the correction, and the error associated with K_{eq} (which we conservatively derive from the difference in values of K_{eq} preferred by the NASA and IUPAC panels).

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The formula used is:

$$\sigma_{k_5} = 2 \times k_5 \times \sqrt{\left(\frac{\sigma_{\text{meas}}}{k_5}\right)^2 + (\sigma_{[\text{NO}_2]})^2 + (\sigma_{\text{N}_2\text{O}_4 \text{ corr}})^2}$$

$$\text{where } \sigma_{\text{N}_2\text{O}_4 \text{ corr}} = \left(1 - \frac{[\text{NO}_2]_{\text{ave}}}{[\text{NO}_2]_0}\right) \times \sqrt{\left(\frac{\sigma_{[\text{NO}_2]_{\text{ave}}}}{[\text{NO}_2]_{\text{ave}}}\right)^2 + (\sigma_{K_{\text{eq}}})^2}$$

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where $[\text{NO}_2]_{\text{ave}}$ is the average of the corrected $[\text{NO}_2]$ using NASA and IUPAC equilibrium constant, $[\text{NO}_2]_0$ is the NO_2 concentration measured optically, $\sigma_{[\text{NO}_2]_{\text{ave}}}$ is the standard deviation of $[\text{NO}_2]_{\text{ave}}$ and $\sigma_{K_{\text{eq}}}$ is the uncertainty of the equilibrium constant which we set to 50%.

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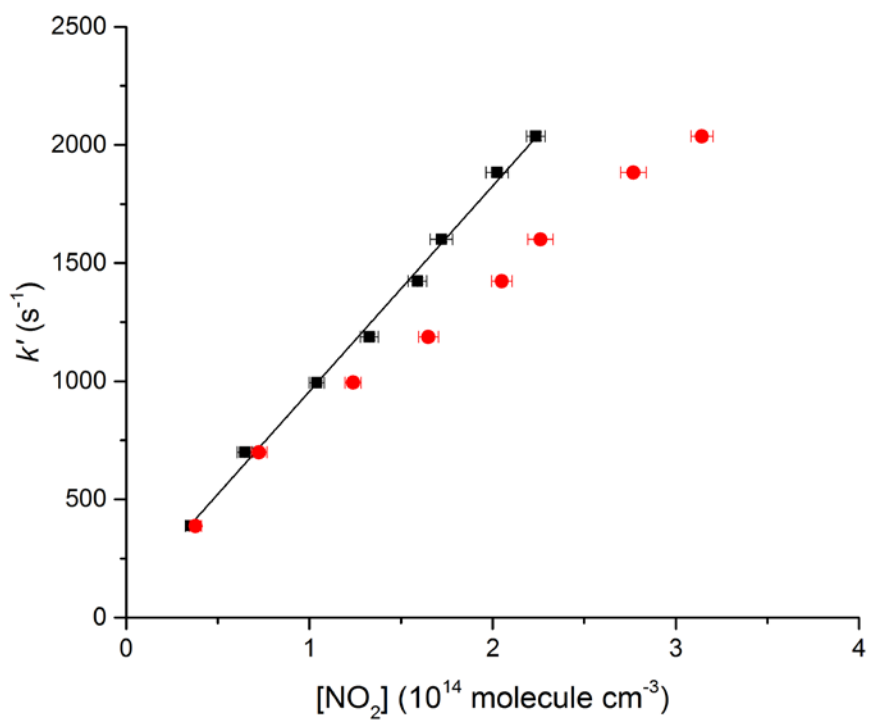


Figure S1. Red circles: Bimolecular plot of the OH reaction with NO_2 measured at 78.8 Torr N_2 and 217 K. The black squares were obtained by accounting for loss of NO_2 via N_2O_4 formation.

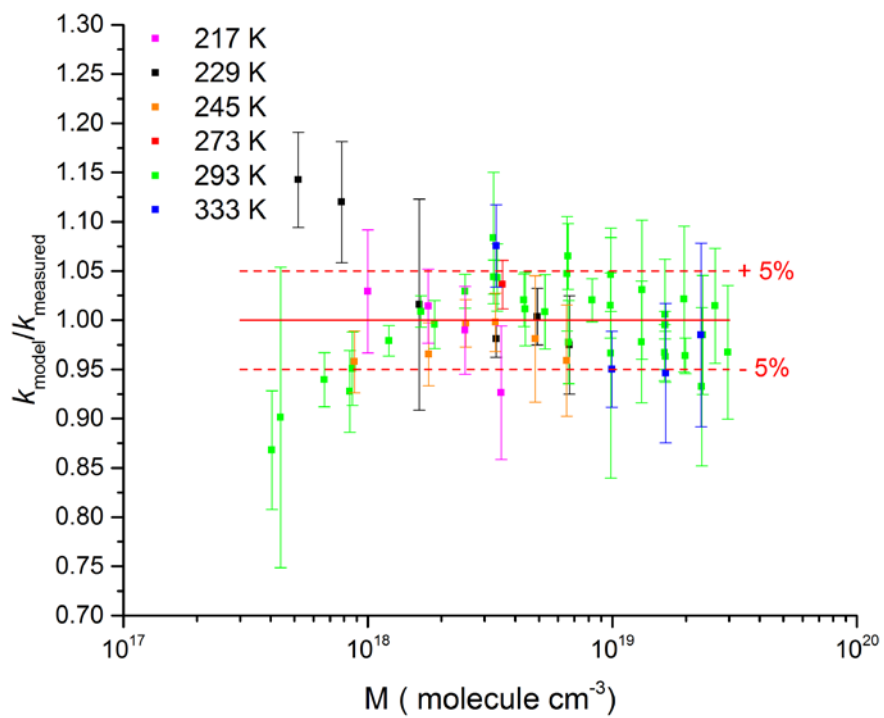


Figure S2. Ratio of the parametrised rate coefficient (k_{param}) to measurements (k_{meas}) as a function of the molecular density (M) for 6 different temperatures.

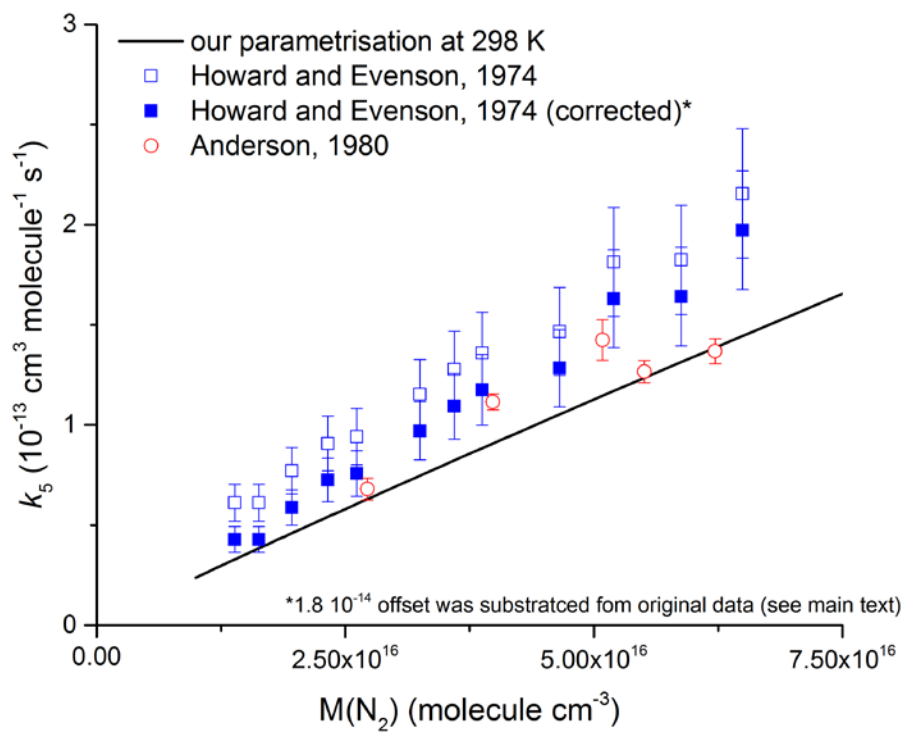


Figure S3. Comparison of the present parametrisation with low-pressure measurements by Howard and Evenson (1974) (open and closed blue squares) and Anderson (Anderson, 1980) (open red circles).

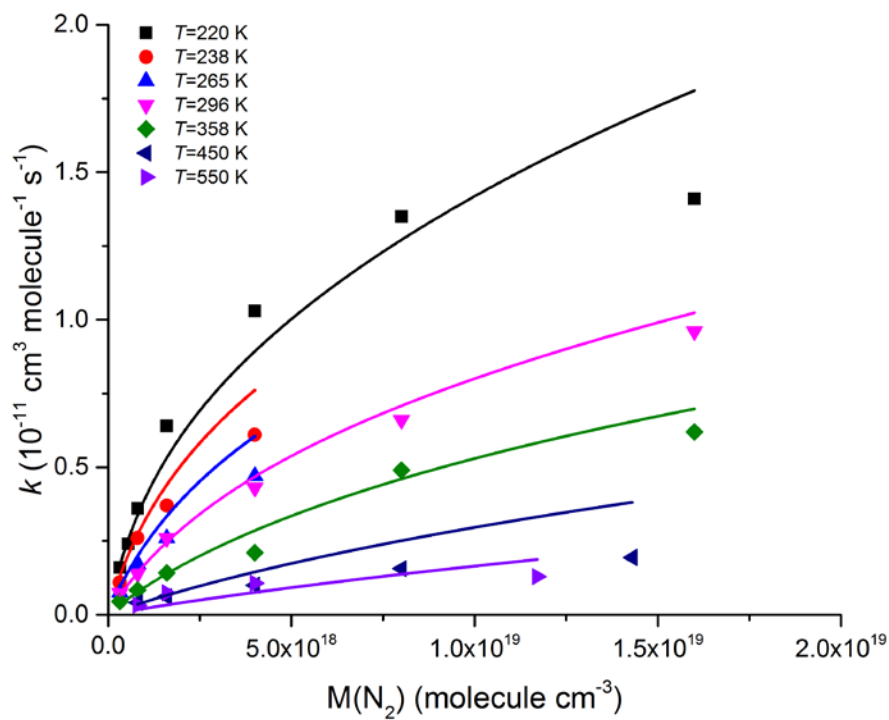


Figure S4. Comparison of the present parametrization with values of k_5 reported by Anastasi and Smith (1976), who report 36% overall uncertainty in k_5 (2σ)

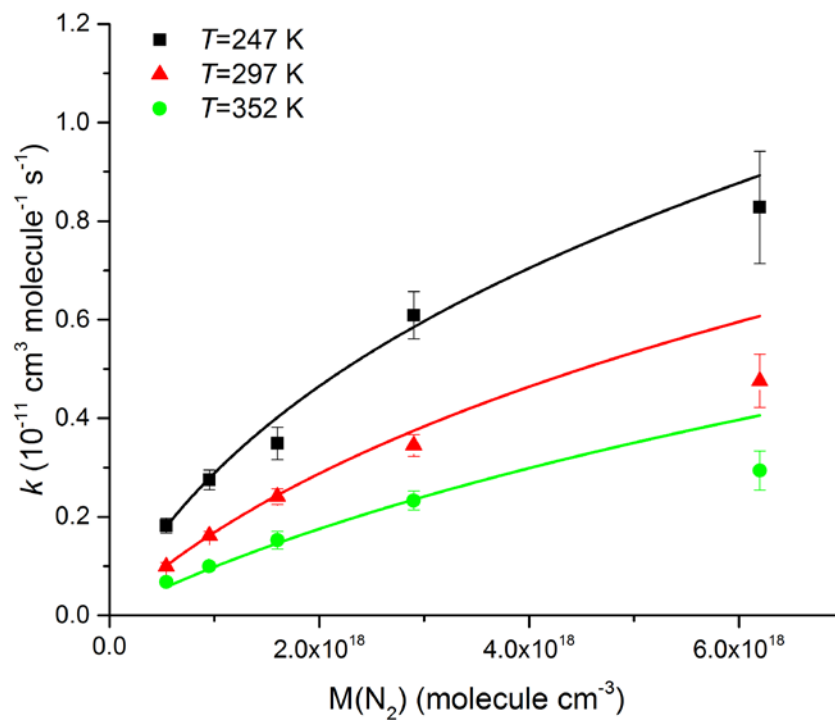


Figure S5. Comparison of the present parametrization with values of k_5 reported by Wine et al. (1979) where the error bars (2σ) represent total overall uncertainty.

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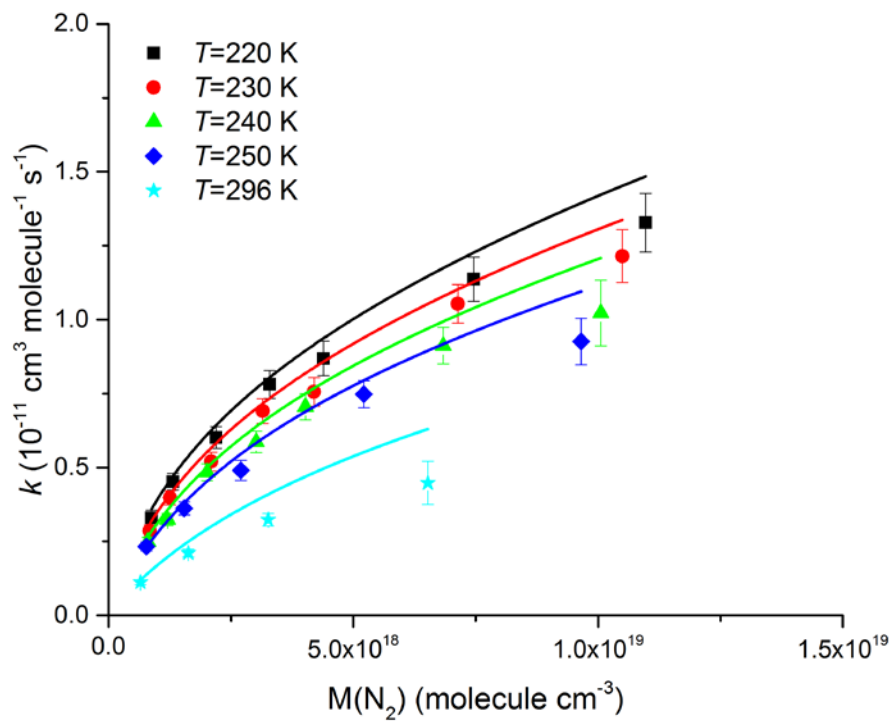


Figure S6. Comparison of the present parametrization with values of k_5 reported by Brown et al. (1999) where the error bars (2σ) represent total overall uncertainty.

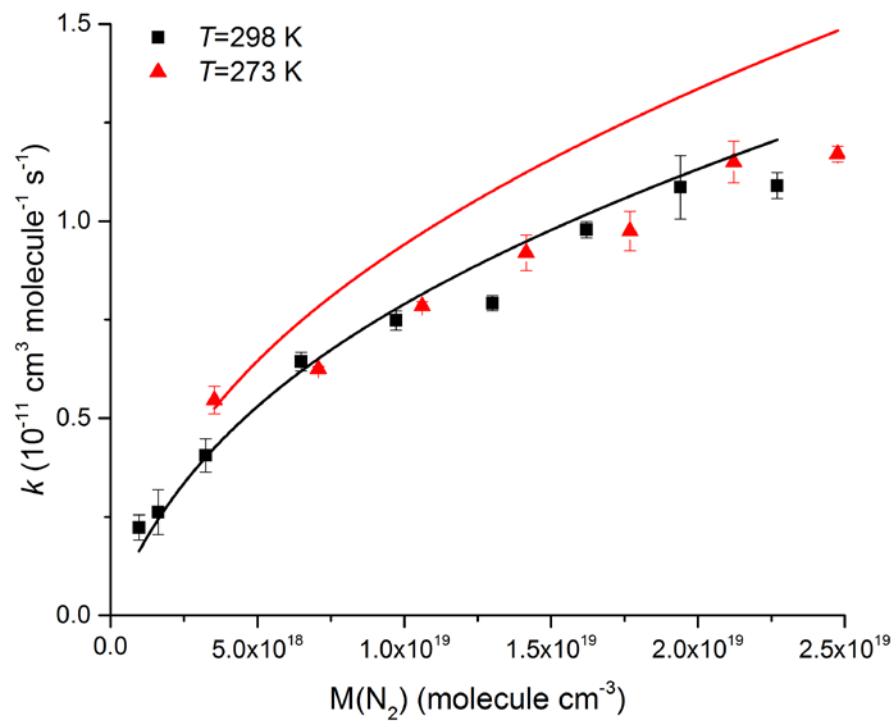


Figure S7. Comparison of the present parametrization with values of k_5 reported by D'Ottone et al. (2001) where the error bars (2σ) represent total overall uncertainty.

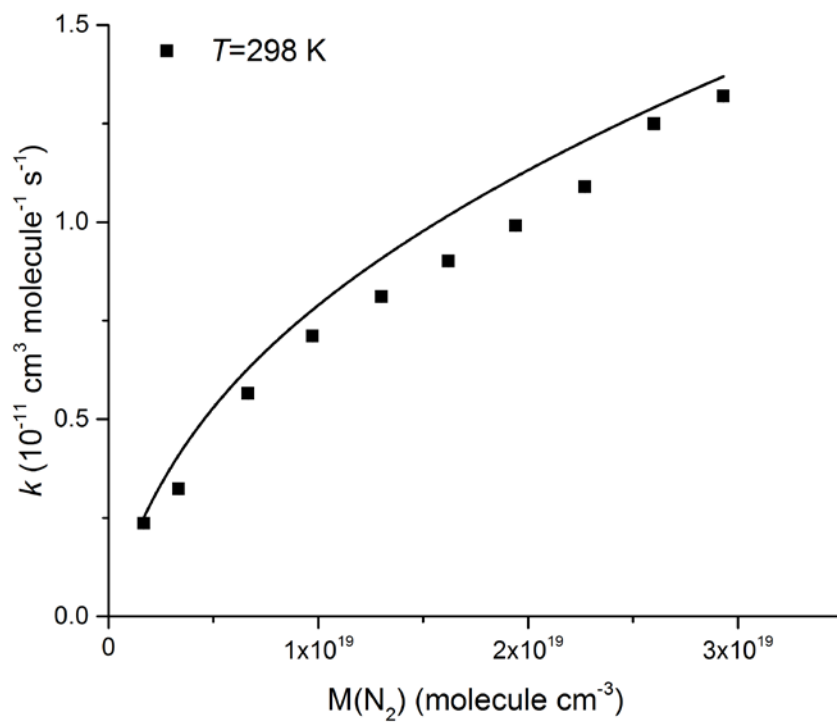


Figure S8. Comparison of the present parametrization with values of k_5 reported by Mollner et al. (2010). The reported 2σ (statistical) uncertainty is $< 2\%$ is within the symbol size.

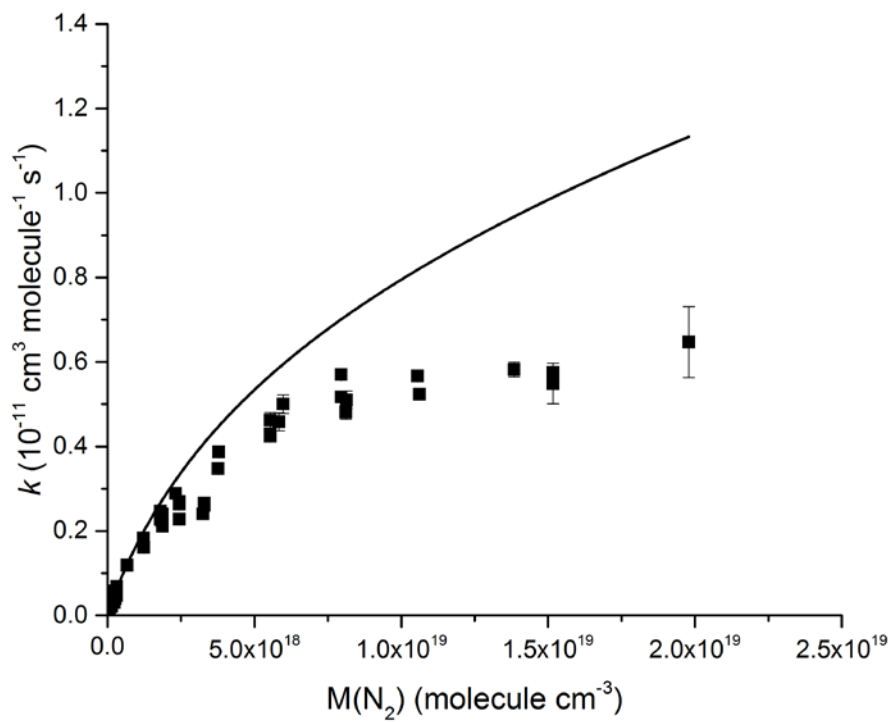


Figure S9. Comparison of the present parametrization with values of k_5 reported by Donahue et al. (1997) where the error bars (2σ) represent total overall uncertainty.

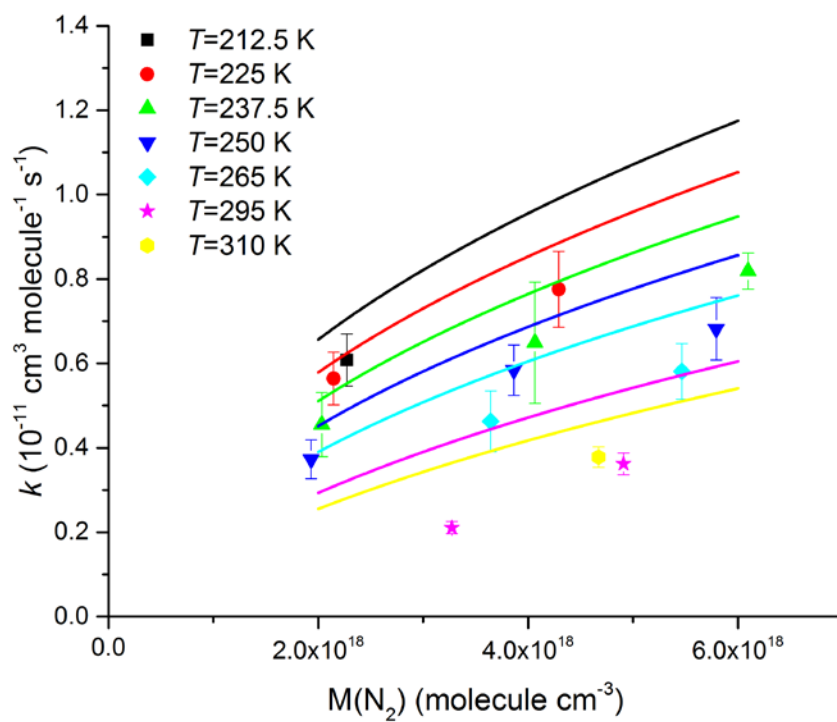


Figure S10. Comparison of the present parametrization with values of k_5 reported by Dransfield et al. (1999).

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