Characterisation of Two Photon Excited Fragment Spectroscopy (TPEFS) for HNO₃ detection in gas-phase kinetic experiments

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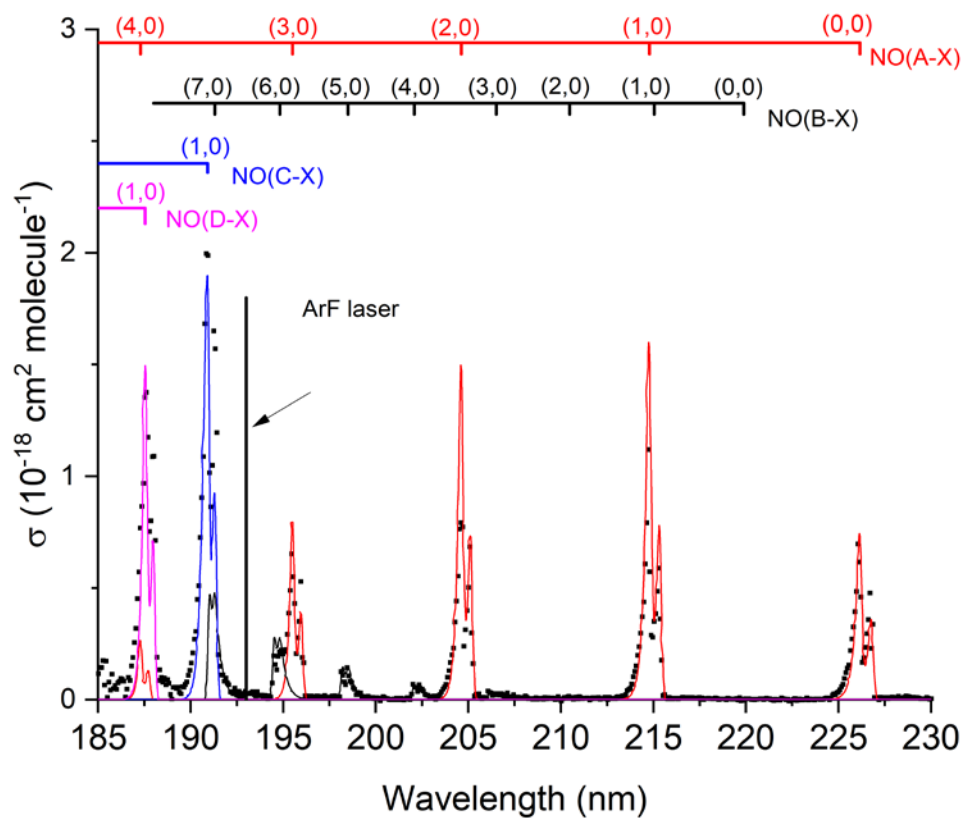*   Correspondence to: john.crowley@mpic.de

Supplementary Information

Figure S1. NO absorption spectrum (black dots) at 298 K and 19 Torr N_2 bath-gas ([NO] = 3.1 × 10^{16} molecule cm^{-3}). The spectral resolution ($\delta\lambda$) was 0.16 nm. The grey line indicates the position of the ArF laser pulse at 193 nm. The black, blue, red and purple absorption lines were assigned using LIFBASE.[1]
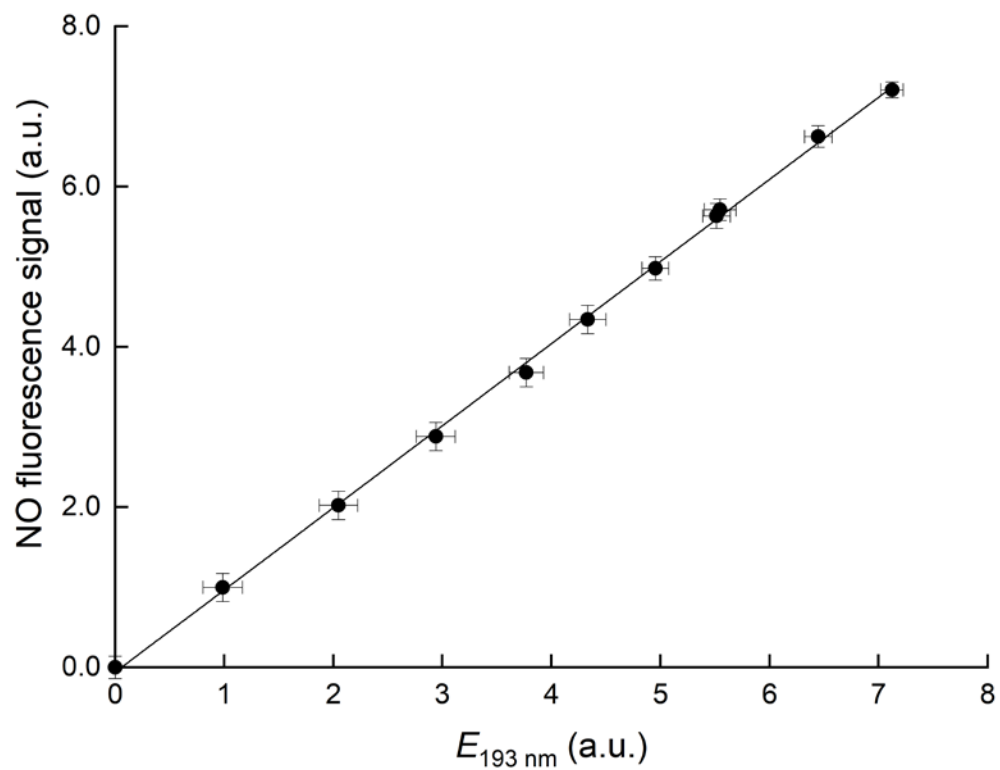
Figure S2. NO fluorescence signal as a function of 193 nm laser energy. The NO fluorescence signal was recorded with a PMT through a (310 ± 5) nm interference filter. Conditions: Room temperature, 60 Torr N_2, $[NO] = 4.1 \times 10^{15}$ molecule cm^{-3}.
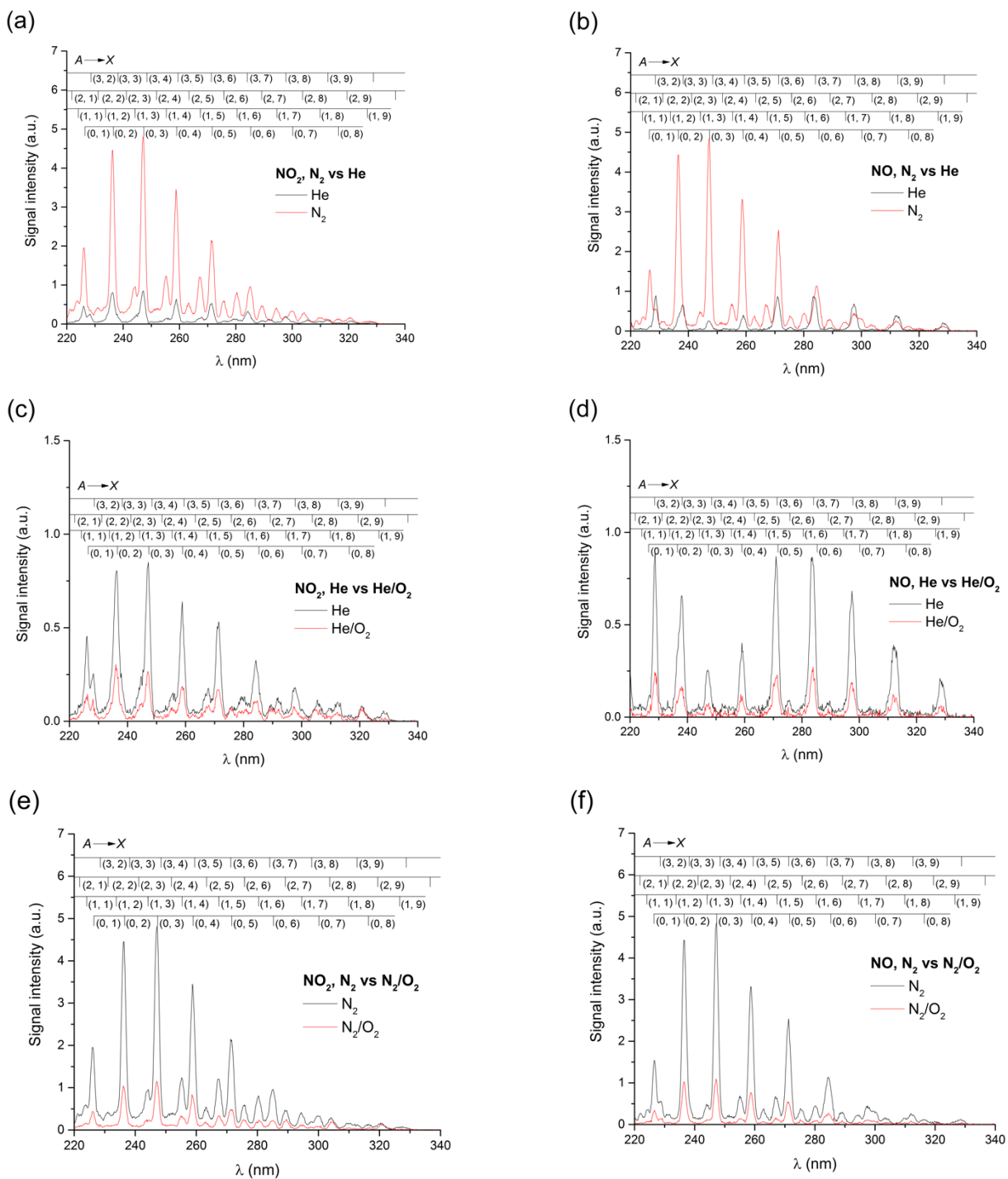
Figure S3. Emission following excitation of NO and NO₂ at 193 nm (65 Torr total pressure, [NO] = 2.6 × 10^{15} molecule cm^{-3}, [NO₂] = 2.1 × 10^{15} molecule cm^{-3}, [O₂] = 0 or 4.0 × 10^{16} molecule cm^{-3}.

(a) NO₂ excitation, N₂ and He bath-gases.

(b) NO excitation, N₂ and He bath-gases.

(c) NO₂ excitation, He and He/O₂ bath-gases

(d) NO excitation, He and He/O₂ bath-gases.

(e) NO₂ excitation, N₂ and N₂/O₂ bath-gases

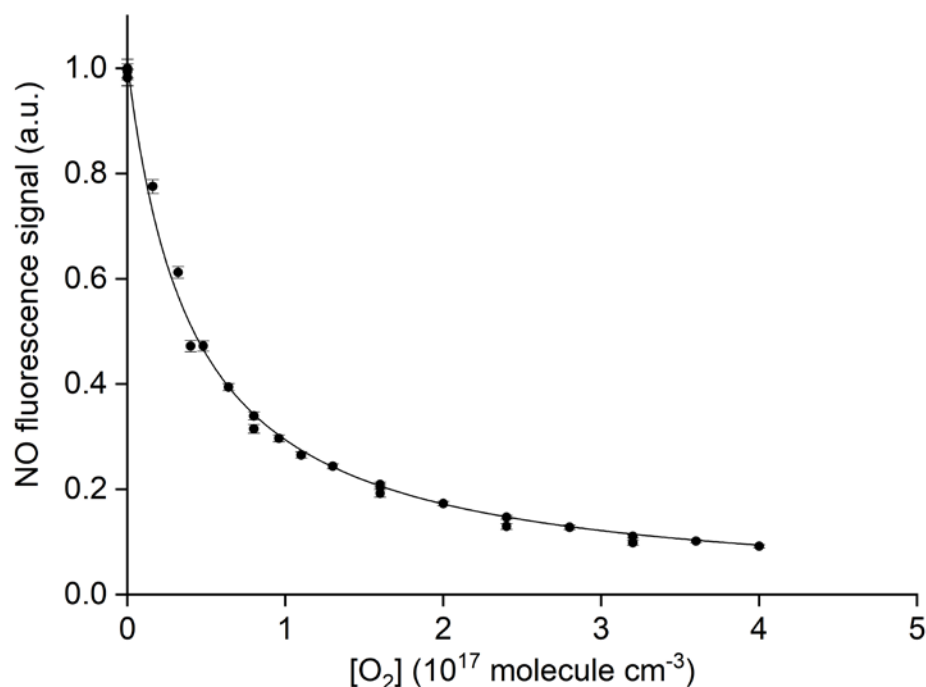(f) NO excitation, N₂ and N₂/O₂ bath-gases.

Figure S4. NO fluorescence signal recorded with a PMT through a 310 nm interference filter as a function of O_2 concentration. The black line is a fit according to the equation below, from which we derive a quenching rate coefficient of $(1.5 \pm 0.1) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} for the NO(A) state.

$$\Gamma = \frac{kf(\mathrm{NO}\,(A))}{kf(\mathrm{NO}\,(A)) + kq_{O_2}(\mathrm{NO}\,(A)) \times [O_2] + kq_{\mathrm{NO}}(\mathrm{NO}\,(A)) \times [\mathrm{NO}] + kq_{N_2}(\mathrm{NO}\,(A)) \times [\mathrm{NO}]}$$

where k_f is the natural lifetime (4.9×10^6 s^{-1}) of the A(v'=0) state of NO,[2] $k_q(N_2) = 4.6 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1},[3] $k_q(\mathrm{NO}) = 2.7 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1},[3] and $k_q(O_2)$ are the quenching rate constants (in cm^3 molecule^{-1} s^{-1}) of the first electronic state of NO by N_2, NO and O_2.
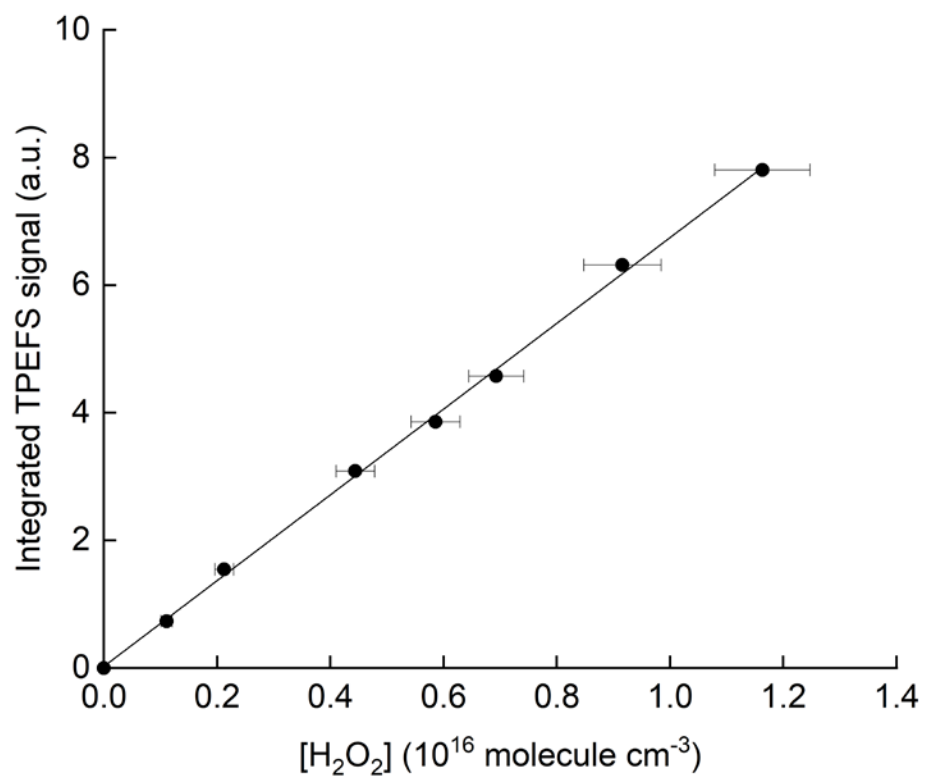
Figure S5. Integrated TPEFS signal as a function of [H_2O_2]. The experimental conditions were 50 Torr N_2 and ~298 K. Error bars are overall uncertainty at 2σ.
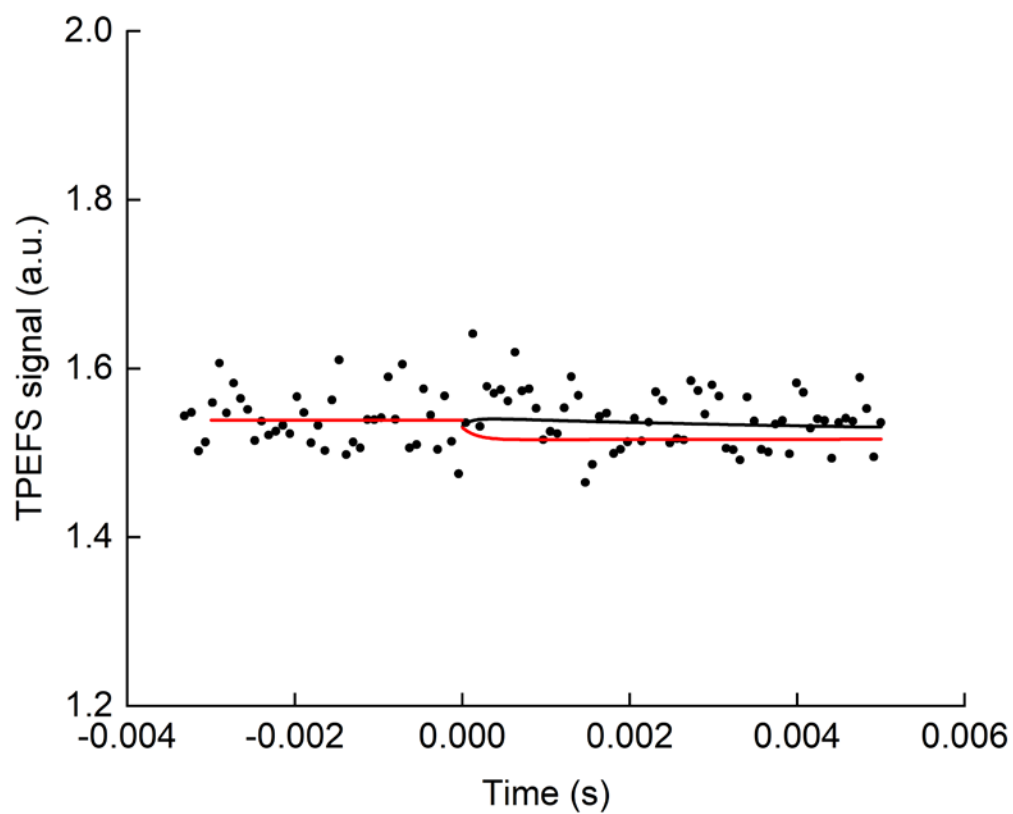
Figure S6. Experiment to detect HO_2 using TPEFS. At time t = 0, H_2O_2 was photolyzed using a 248 nm laser to form OH and thus HO_2. The red line corresponds to a simulation of the expected reduction in signal caused by depletion H_2O_2. The difference between the black and red lines at t > 0 was used to set an upper limit to the signal from HO_2. Conditions: p = 60 Torr N_2, $[H_2O_2]$ = 2.4 × 10^{15} molecule cm^{-3}, laser-fluence (248 nm) = 6.8 10^{16} photon cm^{-2}.

Parameterisation of the rate coefficient (k_2) for reaction between OH and NO_2

$$k_2(P,T) = \frac{\left(x_{N2}k_0^{N2}\left(\frac{T}{300}\right)^{-m} + x_{O2}k_0^{O2}\left(\frac{T}{300}\right)^{-q} + x_{H2O}k_0^{H2O}\left(\frac{T}{300}\right)^{-o}\right)Mk_\infty\left(\frac{T}{300}\right)^{-n}}{\left(x_{N2}k_0^{N2}\left(\frac{T}{300}\right)^{-m} + x_{O2}k_0^{O2}\left(\frac{T}{300}\right)^{-q} + x_{H2O}k_0^{H2O}\left(\frac{T}{300}\right)^{-o}\right)M + k_\infty\left(\frac{T}{300}\right)^{-n}}F$$

where

$$\log F = \frac{\log F_c}{1 + \left[\log\left(\frac{\left(x_{N2}k_0^{N2}\left(\frac{T}{300}\right)^{-m} + x_{O2}k_0^{O2}\left(\frac{T}{300}\right)^{-q} + x_{H2O}k_0^{H2O}\left(\frac{T}{300}\right)^{-o}\right)M}{k_\infty\left(\frac{T}{300}\right)^{-n}}\right)/[0.75 - 1.27\log Fc]\right]^2}$$

The parameters used to generate the solid lines in Figure 10 were: $k_0(N_2) = 2.6 \times 10^{-30}$ cm^6 $molecule^{-2}$ s^{-1}, $k_0(O_2) = 2.0 \times 10^{-30}$ cm^6 $molecule^{-2}$ s^{-1}, $k_0(H_2O) = 2.6 \times 10^{-30}$ cm^6 $molecule^{-2}$ s^{-1}, $k_\infty = 6.3 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, $F_c = 0.39$ and the T-dependent parameters $m = 3.6$, $n = 0$, $o = 3.4$, $q = 3.6$ as reported by Amedro et al.[4, 5]

References.

1. J. Luque and D. R. Crosley, *LIFBASE (version 1.5)* http://www.sri.com/cem/lifbase, 1999.
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3. T. B. Settersten, B. D. Patterson and C. D. Carter, *J. Chem. Phys.*, 2009, **130**, 204302.
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