

The following contains the comments of the referee (black), our replies (blue) indicating changes that will be made to the revised document (red).

## **Reviewer #1**

This is a very carefully executed and analyzed kinetic study of a very important reaction in the atmosphere. The literature reports conflicting data, so this new study is welcome. I have only one significant technical issue for the authors to address, plus a number of requests for clarification or corrections of minor points.

We thank the reviewer for the careful review and the positive assessment of our manuscript.

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### **Significant technical issue:**

From the reported maximum flow rate of 9900 sccm and the 500 cm<sup>3</sup> reactor size, the residence time of the gas in the reactor would be as high as 3.6 seconds (at 1.2 bar and 298 K). This is inconsistent with the statement on page 3 (line 24) “A fresh gas sample was thus available for photolysis at each laser pulse (laser frequency =10 Hz).” Since the authors made an effort to keep the flow rate relatively constant, it would seem that the gas sample would typically have been subjected to at least ~15 laser pulses. Please address this issue, especially in light of the comments, further down, on the large extent of O atom production from NO<sub>2</sub> photolysis.

Related to this, the manuscript states “We additionally carried out some experiments at a lower repetition rate to ruleout any influence of product build-up on the measured rate coefficient.” I would like the authors to document these experiments (at least in the Supplementary Information).

The photolysis pulse enters the cell at right angles to the gas-flow. The linear-velocity of the gas flow at the center of the reactor is  $\approx 10 \text{ cm s}^{-1}$ . As the width of the excimer laser beam is 0.8 cm, the volume illuminated by the laser is replenished with a time constant of  $\sim 0.1 \text{ s}$ . We have modified the text to explain this:

For all experiments, the axial flow velocity in the reactor was kept roughly constant at  $\sim 10 \text{ cm s}^{-1}$  by adjusting the flow rate from 270 and 9900 cm<sup>3</sup> (STP) min<sup>-1</sup> (sccm). As the  $\sim 8 \text{ mm}$  wide laser beam was normal to the direction of flow, this ensured that a fresh gas sample was available for photolysis at each laser pulse (laser frequency = 10 Hz).

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### **Minor points**

Section 2.1 Please list - the energy of the photolysis laser pulse - the delay time between photolysis and probe pulses, and the gate width, if different than in Wollenhaupt et al., 2000.

The energy of the photolysis pulse is already given in section 2.1: We wrote: “...with laser fluences of 5-40 mJ cm<sup>-2</sup> per pulse...” (13, p3). The acquisition set up is identical to the one described in Wollenhaupt et al.

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Page 3, line 20. 500 cm<sup>-3</sup> should be 500 cm<sup>3</sup>.

Correction made

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Section 3.1.1 Please specify the temperature at which these experiments were carried out

The experiments related to the NO<sub>2</sub> cross sections were performed at room temperature. We now mention this:

We performed two experiments (at room temperature) that indicate that, from 20 to 800 Torr of N<sub>2</sub>, any pressure dependence in the NO<sub>2</sub> absorption cross-section at 365 nm can safely be neglected.

Section 3.1.2 The paragraph describing the pressure-dependence of the NO<sub>2</sub> absorption spectrum is confusing. I believe that part of this is because at least one of the citations of Vandaele et al., 2002 should be Vandaele et al., 1998. Possibly, too, contradiction noted between the two papers Vandaele may be resolved by noting that the 1998 paper could only detect a pressure dependence at 500-833 nm, whereas the discussion here is for 400-450 nm. Also, the manuscript seems to state (page 7, lines 11-15) that applying the broadening factor of Nizkorodov et al. (2004) to the data of Nizkorodov et al. (2004) does not agree with the spectra of Nizkorodov et al. (2004). Are you saying their reported broadening factor is inconsistent with their data? In any case, some clarification would be helpful.

We have re-written this section:

At ultra-high resolution, rovibrational lines in the NO<sub>2</sub> spectrum broaden at higher pressures and the two more recent studies by Vandaele et al. (2002) and Nizkorodov et al. (2004) reported pressure broadening factors  $\gamma$  ( $\gamma$  being the half width at half maximum of a Lorentzian) in air of 0.081 and 0.116 cm<sup>-1</sup> atm<sup>-1</sup> respectively, corresponding to ~0.0013 nm and ~0.0019 nm at 1 atm and 405 nm respectively. Using the broadening factors above, one can generate spectra at any pressure by convoluting a pressure dependent, Lorentzian line width to a NO<sub>2</sub> spectrum obtained at low pressure and then degrading it (using a Gaussian slit-function) to the resolution of the spectrometer. When applying these convolutions to the Vandaele et al. (2002) dataset we found no difference in cross-sections when using their spectra obtained at higher pressure or when using a calculated, pressure-broadened spectrum obtained at low pressure.

We also fitted our experimental measurement of NO<sub>2</sub> optical density (405 to 440 nm) using the lower resolution spectra reported by Merienne et al. (1995) and Yoshino et al. (1997). Use of these reference spectra resulted in excellent agreement with those from Vandaele et al. (2002). This reflects the fact that although lines widths increase at increasing pressure, once degraded to our spectral resolution, there is no discernible change in the cross-sections in the 410-440 nm range. The same conclusion can be drawn when working with the spectra of Nizkorodov et al. (2004) that were obtained at pressures of < 75 Torr. In contrast, using the NO<sub>2</sub> spectra of Nizkorodov et al. (2004) which were recorded at pressures  $\geq$  75 Torr, resulted in an overestimation of the NO<sub>2</sub> concentration by up to 20 % (at 596 Torr) when compared to those listed above. For these reasons, we use the spectrum reported by Vandaele et al. (2002) measured at 80 Torr as a reference spectrum throughout this work. We emphasise that use of any other spectrum (including the Nizkorodov spectrum obtained at low pressure and subsequently broadened (using their parameters) to any other pressure would have no significant (< ~3%) on the cross-section we derived at 365 nm.

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On page 9, lines 23-27, discussing the correction for N<sub>2</sub>O<sub>4</sub> formation. I suggest the authors note here that the size of these corrections is listed in Table 1 for each (P,T) set of conditions.

We have followed this suggestion:

At temperatures above 273 K, no correction to [NO<sub>2</sub>] was necessary, but amounted to 0.5 to 3.5 % at 245 K, 4 to 26% at 229 K and 6 to 29 % at 217 K, the largest corrections being associated with the highest NO<sub>2</sub> concentrations (see Table 1).

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On page 9, line 32, “respectively resulting in a factor ten change in [OH]”.

- There should be a comma after “respectively”

Correction made

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- “[OH]” presumably refers to “[OH]0”

Yes, see reply below.

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- the factor of “ten” is only a factor of three at 500 Torr (according to the data in Table 1)

The text has been modified to indicate that the factor 10 refers to 200 Torr data:

In two sets of experiments, at total pressures of either 200 or 500 Torr N<sub>2</sub>, the 248 nm laser fluence was varied by a factor 7 (from ~ 5 to 35 mJ cm<sup>-2</sup>) and the H<sub>2</sub>O<sub>2</sub> and HNO<sub>3</sub> concentrations by 4 and 6 respectively, resulting (at 200 Torr) in a factor ten change in [OH]<sub>0</sub> (from ~10<sup>11</sup> to 10<sup>12</sup> molecule cm<sup>-3</sup> (see Table 1).

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Page 10, lines 5-9. While NO<sub>2</sub> has a very low cross section at 248 nm, the cross-section of HONO<sub>2</sub> is only twice as large. Given that [NO<sub>2</sub>] is typically much larger than [HONO<sub>2</sub>], we may expect [O]<sub>0</sub> to be 2-4 × [OH]<sub>0</sub>. I agree with the authors that this would not be a problem if “A fresh gas sample was thus available for photolysis at each laser pulse,” but I am not clear on that point. In any case, I would like to see the manuscript acknowledge that [O]<sub>0</sub> ≈ 2-4 × [OH]<sub>0</sub>.

We have clarified the question of the fresh gas sample at each pulse above.

The relative OH to O(<sup>3</sup>P) concentration varies with [NO<sub>2</sub>]. The maximum O(<sup>3</sup>P) / OH ratio occurs when [HNO<sub>3</sub>] or [H<sub>2</sub>O<sub>2</sub>] are low and [NO<sub>2</sub>] is high. In fact, NO<sub>2</sub> (generally less than 1 × 10<sup>15</sup> molecule cm<sup>-3</sup>) is not much larger than HNO<sub>3</sub> (5 – 10 × 10<sup>14</sup> molecule cm<sup>-3</sup>) so typically the largest (initial) O(<sup>3</sup>P) / OH ratio would be about 1. We now mention this in the manuscript:

Photolysis of NO<sub>2</sub> is inefficient as the cross-section of NO<sub>2</sub> is low at 248 nm (1 × 10<sup>-20</sup> cm<sup>2</sup> molecule<sup>-1</sup> IUPAC (2019)) but can result in approximately equivalent initial O(<sup>3</sup>P) and OH concentrations. However, the presence of O(<sup>3</sup>P) has negligible impact on chemistry as its fate is mainly reaction with NO<sub>2</sub> to form NO, which also reacts only slowly with OH.

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Is it possible to harmonize the presentation of the IUPAC and JPL versions of the Troe expression? They are different, but the way the equations are formatted here makes it harder to see how they are similar.

Both expressions are based on the original work of Troe however the NASA panel make the approximation that the fall-off curve is symmetric which explains the different formula in the exponent of the broadening factor F. The Lindeman Hinshelwood part of the expression is identical for both panels. To keep the expressions recognizable, we prefer to write them as given by the panels.

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Page 11, line 29. “In low-pressure flow-tube studies, correction is rarely made for the surface-reaction induced heterogeneous loss of OH”. It would be good to append “...in reaction with NO<sub>2</sub>” to this sentence, to clarify that you are not referring to kw.

We have modified the sentence accordingly:

In low-pressure flow-tube studies, correction is rarely made for the surface-reaction induced heterogeneous loss of OH, in this case  $k_s[\text{NO}_2]_s$ , the manifestation of which is often a positive intercept in plots of  $k_{bi}$  as a function of molecular density (Anderson et al., 1974; Howard and Evenson, 1974).

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According to the JPL recommendations for R5b, dissociation of HOONO will have, at most, a rate constant of 20 sec<sup>-1</sup> under the conditions of this experiment. This means that HOONO dissociation is unimportant on the time scale of the experiment, so the present work determines the sum of the rate constants for R5a and R5b: formation of HONO<sub>2</sub> and HOONO; the manuscript should at least note this fact prominently. But in comparing the experimental data to the JPL and

IUPAC recommendations, it appears that comparison is made to the expressions for R5a, alone. While R5b is a modest fraction of the overall reaction, it is not entirely negligible (up to 17% of the reaction, using the JPL recommendation). This should be made explicit. The manuscript could also compare the present data to the sum of the recommendations to R5a and R5b.

Throughout the manuscript compare our measured rate constant with the sum of R5a + R5b given by IUPAC and JPL. WE now emphasize this at the end of section 1:

We note that the rate coefficients we obtain represent the total loss rate coefficient ( $k_5$ ) for OH loss (i.e. the sum of  $k_{5a}$  and  $k_{5b}$ )

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Caption to Figure 2: The text describes Figures 2a and 2b, while the caption incorrectly lists Figure 2b as an inset. The caption should specify the temperature of these experiments.

We have replaced the caption by:

Pressure dependence of the relative NO<sub>2</sub> absorption cross-section,  $\sigma_{365\text{ nm}}/\sigma_{185\text{ nm}}$ , at 185 and 365 nm. The solid line is a linear regression for all 3 datasets giving a slope of  $0.281 \pm 0.002$  (uncertainty is  $2\sigma$ , statistical only). The lower panel shows the slopes obtained at 20, 255 and 610 Torr plotted versus pressure. The measurements were performed at room temperature.

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Caption to Figure 4: Please specify the excitation wavelength. Also, the description of the lines is clearer in the text of the manuscript than here. The lines correspond to the values expected after correcting for NO<sub>2</sub> dimerization.

The excitation wavelength is now mentioned in the caption.

NO<sub>2</sub> LIF signal (following excitation at 564 nm) as a function of NO<sub>2</sub> concentration at 6 different temperatures from 218 to 320 K.

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Thoughts on formation of HOONO vs. HONO<sub>2</sub>

This work cannot address the competition between formation of HOONO and HONO<sub>2</sub>, and this fact should certainly not hinder publication. I want the authors to be aware of the fact that the difference in the values of  $\beta$  for O<sub>2</sub> and N<sub>2</sub> may not be the same for HOONO and HONO<sub>2</sub>, although discussion of this point may not be necessary here. The most recent paper I am aware of on the issue of bath gas mixtures and multichannel reactions is from M. P. Burke of Columbia (not this reviewer!): <https://pubs.acs.org/doi/pdf/10.1021/acs.jpca.8b10581>.

This is an interesting comment, though measurement of channel and bath-gas specific values of  $\beta$  is definitely beyond our experimental capability. As the effect on  $k$  when going from air to pure N<sub>2</sub> bath gas is small (< 4%), it is not likely that use of a different  $\beta$  for O<sub>2</sub> and N<sub>2</sub> for HOONO and HNO<sub>3</sub> would significantly impact on  $k$ .

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