

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

Comment from Frank Winiberg

This manuscript sets out the detailed and thorough study of the rate coefficients for the reaction of OH + NO₂, over a matrix of pressures and temperatures relevant to Earth's lower atmosphere. Great detail is applied to the accurate quantification of NO₂ in this study; indeed, this is where there is potential for significant systematic errors in these types of kinetic experiments, as NO₂ readily dimerizes to N₂O₄. Alongside four different methods for ensuring the accurate determination of [NO₂], the authors note some irregularities in the literature pertaining to the most recent measurements of the NO₂ absorption cross-section in the UV/Visible region reported by Vandaele et al. (2002) and Nizkorodov et al. (2004). In particular, the difference between reported low pressure (pure spectra) and those recorded at higher pressures (dilute NO₂). The authors state that the reason for these discrepancies remains unclear, especially for the work by Nizkorodov et al. (2004).

Before responding to the specific points raised below we first outline the importance of choosing the correct reference spectrum for the kinetic analysis.

As Frank Winiberg confirms (his Figures below), the use of the high-resolution Nizkorodov spectrum measured at high pressure to derive NO₂ cross sections will lead to (pressure dependent) differences of up to 15 % in the concentration of NO₂ derived (compared e.g. to Vandaele), thus in the rate coefficient calculated and in the shape of the fall-off curve.

As correctly stated by Fred Winiberg, The Mollner et al study used a combination of the Vandaele et al. (2002) and Nizkorodov et al. (2004) data to form their cross section. Exactly how the two spectra were combined is however unclear (we do not know if they were simply averaged) and it is not possible (for us) to know what rate coefficients would have been derived if Mollner et al would have used only the VanDaele data or only the Nizkorodov data. Additionally, the reasons for using two different spectra rather than using the Nizkorodov data set, which was obtained in the same laboratory, are not stated by Mollner et al.

We now write (3.1.2)

At ultra-high resolution, rovibrational lines in the NO₂ 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 γ (γ being the half width at half maximum of a Lorentzian) in air of 0.081 and 0.116 cm⁻¹ atm⁻¹ 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 low-resolution spectra at any pressure by convoluting a pressure dependent, Lorentzian line width to a NO₂ spectrum obtained at low pressure and then degrading it (using a Gaussian slit-function) to the resolution of our 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 NO₂ 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 simply 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 d Nizkorodov et al. (2004) that were obtained at pressures

of < 75 Torr. In contrast, using the NO_2 spectra of Nizkorodov et al. (2004) which were recorded at pressures ≥ 75 Torr, resulted in an overestimation of the NO_2 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 emphasize 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 impact ($< \sim 3\%$) on the cross-section we derived at 365 nm.

And (3.2.1)

The most recent dataset (Mollner et al., 2010) was also obtained using PLP-LIF and covered pressures up to 900 Torr N_2 at 298 K. Mollner et al. (2010) monitored NO_2 in-situ via UV-visible broadband absorption using reference spectra from Vandaele et al. (2002) and Nizkorodov et al. (2004), though it is not clear how these two spectra were used or combined.

In section 3.1.2, we indicated that using the spectra of Nizkorodov et al. (2004) that were obtained at pressures > 75 Torr could lead to an overestimation of the NO_2 concentration, which would result in an underestimation of k_5 . We are unable to assess the extent to which this may have influenced the Mollner et al. (2010) values of k_5 . On average, our parametrisation overestimates their measurement by $\approx 15\%$ (Fig. S8).

We have re-performed our convolution procedure and confirm all of the observations made by Frank Winiberg. We thank FW for pointing out this mistake.

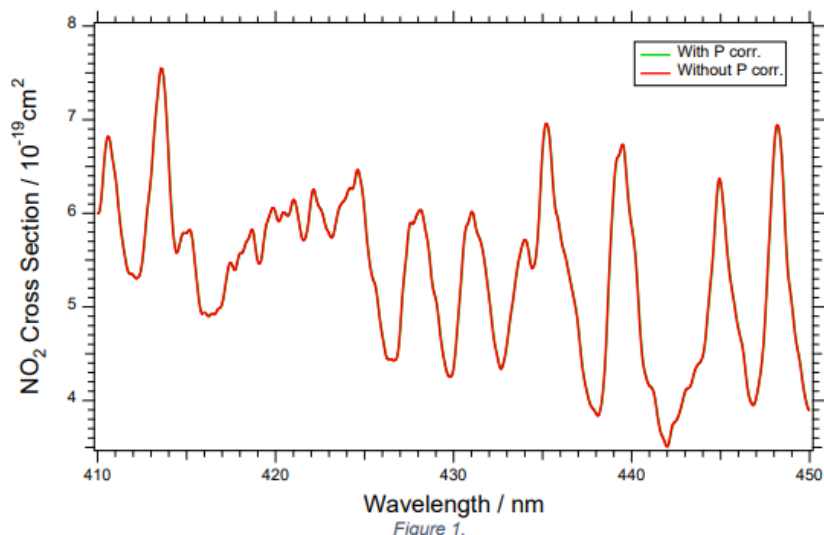
We would like however to re-emphasize that this has zero impact on the rate coefficients we report.

The paper from Nizkorodov et al. (2004) describes how a pure spectrum of ~ 1 Torr NO_2 recorded at a given temperature can be corrected for pressure and temperature effects. The method used for the pressure correction involves the convolution of the pure NO_2 spectrum with a pressure dependent Lorentzian line shape function. As described by the authors here (P7 L11):

“At ultra-high resolution ($< 0.5 \text{ cm}^{-1}$, $\sim 0.008 \text{ nm}$ at 405 nm), rovibrational lines in the NO_2 spectrum broaden at higher pressures. The two more recent studies by Vandaele et al. (2002) and Nizkorodov et al. (2004) reported pressure broadening factors γ (γ being the half width at half maximum of a Lorentzian) in air of 0.081 and 0.116 $\text{cm}^{-1} \text{ atm}^{-1}$ respectively, corresponding to $\sim 0.0013 \text{ nm}$ and $\sim 0.0019 \text{ nm}$ at 1 atm and 405 nm respectively. At our much lower resolution, we are insensitive to effects of pressure broadening. However, using the broadening factor above, one can generate pressure dependent spectra by convoluting a pressure dependent, Lorentzian line width to a low-pressure pure NO_2 spectrum and then degrading it to the resolution of the spectrometer. We applied this method to the Vandaele et al. (2002) and Nizkorodov et al. (2004) datasets and found that, for both datasets, the 298 K absorption cross sections in the 400 to 450 nm range decreased by up to 7% at a pressure close to one atmosphere when comparing generated and measured reference spectra.”

When repeating this analysis using the method in as much detail provided by the authors, I was unable to recreate this 7% difference. Figure 1 shows the NO_2 absorption spectra reported by Nizkorodov et al. recorded at 0.99 Torr, convolved with (green trace), and without (red trace), the pressure dependent Lorentzian function ($\lambda_{\text{center}} = 420 \text{ nm}$, Full Width Half Max (FWHM) $\sim 0.002 \text{ nm}$). Both spectra have been convolved with an instrument lineshape (ILS) function, defined by a Gaussian with a FWHM = 0.2

nm (similar to the instrument resolution reported in Mollner et al. (2010)). Integrated areas for the Gaussian and Lorentzian function were normalized to a total of 1 before convolution.



Both datasets are visually indistinguishable and a linear regression comparing the two datasets in this spectral window yields a slope of 1.00.

Care has to be taken during the convolution process. For example, truncating the Lorentzian function after normalizing can cause integrated area to be lost, and would therefore reduce the final NO₂ cross section. Examining three different convolution methods (Linear, Circular and Acausal), no difference was found in calculated cross section in this spectral window (some phase shift was observed in the Acausal case, but easily accounted for). Additionally, when performing this treatment to a window of a spectrum, the Lorentzian can cause observable absorption to be removed from the window of interest as the lines become broadened at higher pressures. When comparing the convolution method applied to the entire literature spectrum and a windowed spectrum (410 – 450 nm), negligible difference was observed.

More detail from the authors on the convolution process and results therein would be of importance to reinforce the statement on P7 L16:

“...(ii) use of a spectrum generated from reported pressure broadening factors introduced an additional error and uncertainty to the absolute cross sections, especially at high pressures.”

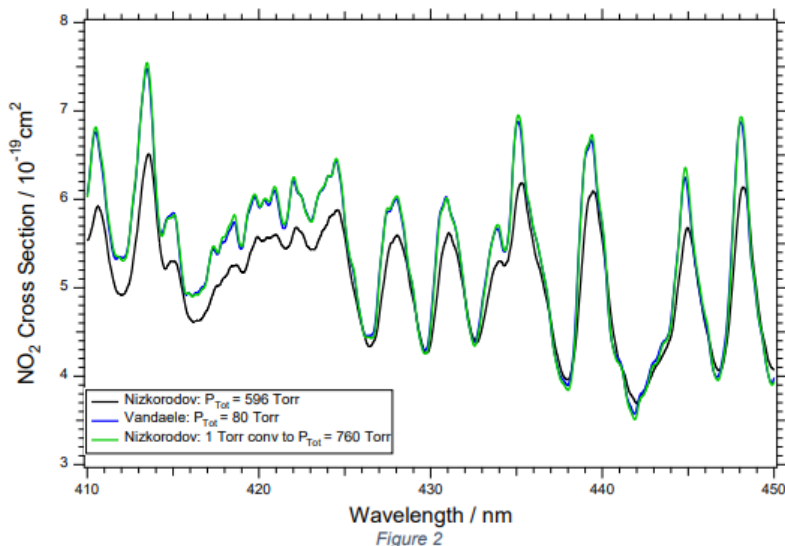
- Could the authors comment more on their convolution process?

[We have re-performed our convolution procedure and can confirm the observations of Frank Winiberg. We have not identified the source of the 7% difference we found previously.](#)

- Was the 7% difference observed in the pure convoluted spectrum with respect to the pure spectrum or the measured spectrum at 750 Torr?

- Was the 7% difference observed with respect to the respective high pressure Nizkorodov et al. (2004) and Vandaele et al. (2002) spectra?
- Was the 7% decrease observed uniformly across the entire spectrum?
- Additionally, if there is indeed a 7% difference, could the authors comment on the quoted 7% uncertainty (2σ) in the Nizkorodov et al. (2004) study, which would encompass this deviation?

The authors decide on the 80 Torr measurement of Vandaele et al. (2002) to be used as their reference cross section in their kinetic study. Figure 2 shows the comparison the NO₂ cross sections measured by Vandaele et al. (2002) at 80 Torr, and Nizkorodov et al. (2004) at 1 and 596 Torr.



Again, all three spectra here have been convolved with a Gaussian ILS with FWHM = 0.2 nm, and the 1 Torr Nizkorodov et al. (2004) data has been convolved with the pressure broadening Lorentzian term. Clearly, the Vandaele et al. (2002) and Nizkorodov et al. (2004) spectra are within a few percent, and well within their respective quoted uncertainties (3.6 and 7% respectively (2σ)). I agree with the authors that there is a clear discrepancy on the order of $\sim 15\%$ in the measured cross sections when comparing these datasets to the Nizkorodov et al. (2004) measurements at 596 Torr (a linear regression comparing these two datasets yields a slope of ~ 0.85). I concur that it is unclear, when reading through Nizkorodov et al. (2004), as to the source of this discrepancy.

[We agree. This is the reason why we avoid using the cross-sections of Nizkorodov at high-pressure.](#)

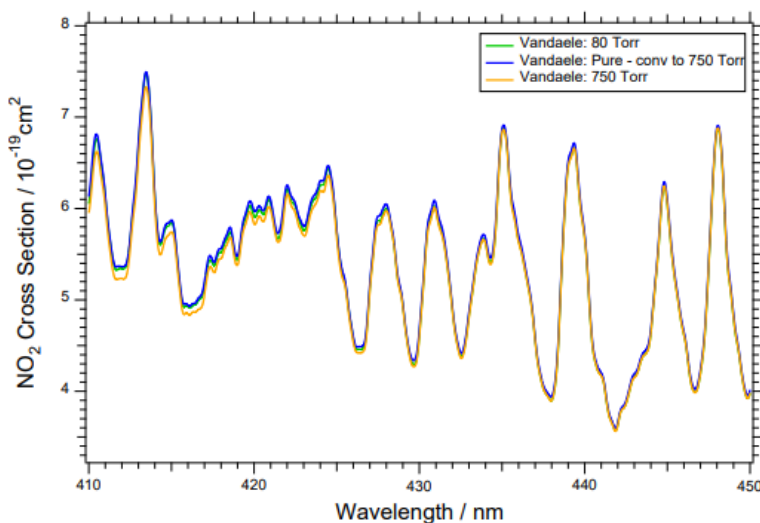
The authors postulate that the kinetic study of Mollner et al. (2010) could have been effected by the discrepancy in the Nizkorodov et al. (2004) cross section data. However, Mollner et al. (2010) state that they used a combination of the Vandaele et al. (2002) and Nizkorodov et al. (2004) data to form their cross section used in their kinetic study. Therefore, taking the mean of the two literature cross sections recorded at higher pressures would reduce the discrepancy of $\sim 15\%$ shown in Figure 2. This, in turn, would reduce the, possibly coincidental, $\sim 15\%$ discrepancy observed by the authors when comparing their rate coefficients to the Mollner et al. (2010) study.

[As this is not stated, we do not know if Mollner et al took a mean value at higher pressures and prefer not to speculate on how this would influence the uncertainty of measurement of \[NO₂\]. We also do not know why Mollner et al. chose not to rely on their own laboratory's \(Nizkorodov\) measurement of the](#)

NO₂ spectrum. Also, simply taking the mean of two cross-sections, one (or both) of which are influenced by systematic error, does not necessarily result in a value that is closer to the true one.

Additionally, Nizkorodov et al. (2004) note that measurements towards the edge of their measured spectral window are more uncertain (which this is). Additionally, deviations from the pure sample were measured by using integrated cross sections in the 415 – 525 nm region, which may have masked this area of larger discrepancy; indeed, there is better agreement between the Nizkorodov et al. (2004) spectra at wavelengths between 450 and 500 nm. Again, the reason for the 7% difference between the pure spectrum, convolved with a pressure dependent line shape, and the measured dataset is unclear; the discrepancy here is much greater.

Finally, the convolution method can be applied to the data from Vandaele et al. (2002). Figure 3 shows the Vandaele et al. (2002) reported NO₂ cross section data at 80 and 750 Torr, as well as a dataset recorded at 1 Torr, which was convolved with the Nizkorodov et al. (2004) pressure broadening factor representative of 750 Torr. Whilst the Nizkorodov et al. (2004) paper saw a much greater pressure dependence, applying this larger pressure dependent Lorentzian function to the data serves as an example to show the apparent non-effect of the convolution.



There is an observable, small difference between the three compared spectra. A linear regression, comparing the data recorded at 1 Torr and 750 Torr in the 400 – 450 nm spectral window, gives a slope of ~ 0.96 , within the quoted 4 – 5% uncertainty in Vandaele et al. (2002).

Exactly, and this is the reason why we used the cross-sections of Vandaele.

Again, it was difficult to ascertain where the 7% difference between these datasets comes from, as presented in the text.

- Could the authors clarify their choice of the 80 Torr Vandaele et al. (2002) spectra when the datasets in Figure 3 appear to be in such good agreement (within the 3.6% reported uncertainty)? Was the selection purely because of the relative difference in the spectra (i.e. was the 80 Torr data in the middle of the spread of values)?

The choice of the 80 Torr Vandaele spectrum was to some extent arbitrary. We have added the following text to clarify this:

We emphasize 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.

- Would the authors comment on whether a combination of literature spectra might be more appropriate as in Mollner et al. (2010)?

We have indicated that various spectra (with the exception of those obtained at high pressure by Nizkorodov) agree to within a few percent. There is therefore little to be gained by averaging.

If the authors feel that this discrepancy in the NO₂ absorption cross sections could play a role in the discrepancy between their rate coefficients and those of Mollner et al. (2010), it is essential to provide more information on the spectral analysis process for their work.

We indicate that this cannot be ruled out and Figure 2 above suggests that caution must be exercised when using the spectra of Nizkorodov (obtained at $p > 75$ Torr) to derive NO₂ cross sections. We emphasize that we found no pressure dependence in the cross-section of NO₂ at 365 nm and used this in deriving NO₂ concentrations and the rate coefficient, k_5 . The value of the cross section we used agrees to within 2% with previous values measured using an Hg-line but via measurement of NO₂ partial pressures.

Whether the difference in rate constant between our work and that of Mollner et al. has its origin in the use of the Nizkorodov et al. spectrum can only be fully resolved by reanalysis (by Mollner et al) of their dataset using either only Vandaele et al or only Nizkorodov et al.

We now write:

The most recent dataset (Mollner et al., 2010) was also obtained using PLP-LIF and covered pressures up to 900 Torr N₂ at 298 K. Mollner et al. (2010) monitored NO₂ in-situ via UV-visible broadband absorption using reference spectra from Vandaele et al. (2002) and Nizkorodov et al. (2004), though it is not clear how these two spectra were used or combined.

In section 3.1.2, we indicated that using the spectra of Nizkorodov et al. (2004) that were obtained at pressures > 75 Torr could lead to an overestimation of the NO₂ concentration, which would result in an underestimation of k_5 . We are unable to assess the extent to which this may have influenced the Mollner et al. (2010) values of k_5 . On average, our parametrisation overestimates their measurement by $\approx 15\%$ (Fig. S8).

References

Mollner, A. K., Valluvadasan, S., Feng, L., Sprague, M. K., Okumura, M., Milligan, D. B., Bloss, W. J., Sander, S. P., Martien, P. T., Harley, R. A., McCoy, A. B., and Carter, W. P. L.: Rate of gas phase association of hydroxyl radical and nitrogen dioxide, *Science*, 330, 646-649, doi:10.1126/science.1193030, 2010. Nizkorodov, S. A., Sander, S. P., and Brown, L. R.: Temperature and pressure dependence of high-resolution air-broadened absorption cross sections of NO₂ (415-525 nm) *J. Phys. Chem. A*, 108, 4864-4872, doi:10.1021/jp049461n, 2004. Vandaele, A. C., Hermans, C., Fally, S., Carleer, M., Colin, R., Merienne, M. F., Jenouvrier, A., and Coquart, B.: High-resolution Fourier transform measurement of the NO₂ visible and nearinfrared absorption cross sections: Temperature and pressure effects, *J Geophys Res-Atmos*, 107, 13, 10.1029/2001jd000971, 2002.
