

This manuscript sets out the detailed and thorough study of the rate coefficients for the reaction of OH + NO<sub>2</sub>, over a matrix of pressures and temperatures relevant to Earth's lower atmosphere. Great detail is applied to the accurate quantification of NO<sub>2</sub> in this study; indeed, this is where there is potential for significant systematic errors in these types of kinetic experiments, as NO<sub>2</sub> readily dimerizes to N<sub>2</sub>O<sub>4</sub>.

Alongside four different methods for ensuring the accurate determination of [NO<sub>2</sub>], the authors note some irregularities in the literature pertaining to the most recent measurements of the NO<sub>2</sub> 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 NO<sub>2</sub>). The authors state that the reason for these discrepancies remains unclear, especially for the work by Nizkorodov et al. (2004).

The paper from Nizkorodov et al. (2004) describes how a pure spectrum of ~1 Torr NO<sub>2</sub> 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<sub>2</sub> spectrum with a pressure dependent Lorentzian line shape function. As described by the authors here (P7 L11):

*"At ultra-high resolution (< 0.5 cm<sup>-1</sup>, ~0.008 nm at 405 nm), rovibrational lines in the NO<sub>2</sub> spectrum broaden at higher pressures. 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. 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<sub>2</sub> 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<sub>2</sub> 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 ( $\lambda_{\text{center}} = 420$  nm, Full Width Half Max (FWHM) ~0.002 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.

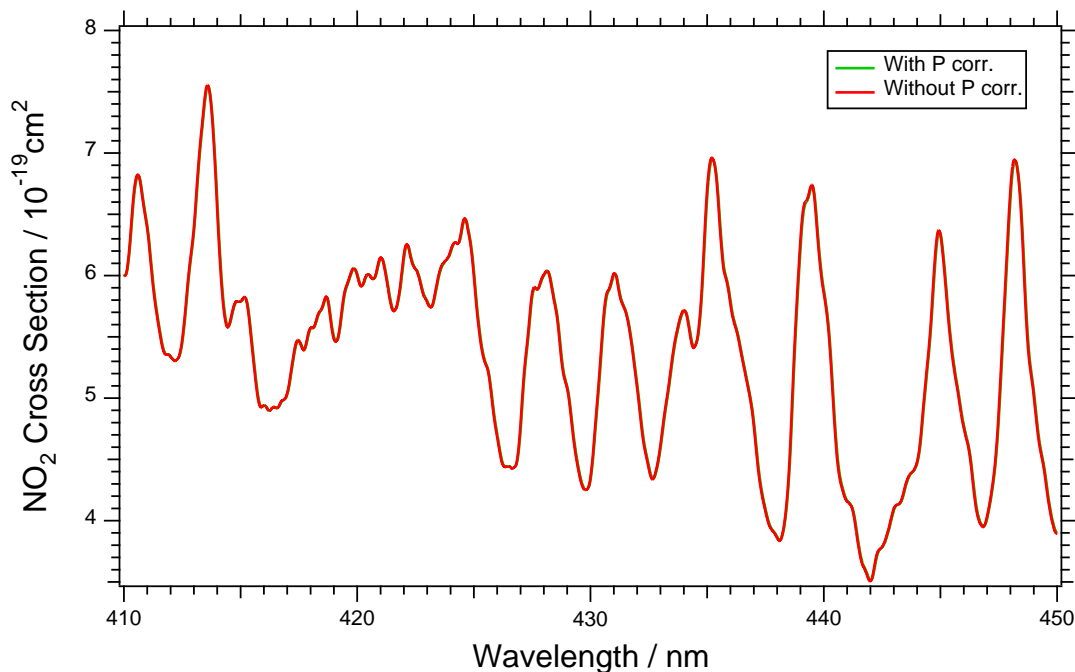


Figure 1.

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 NO<sub>2</sub> 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.

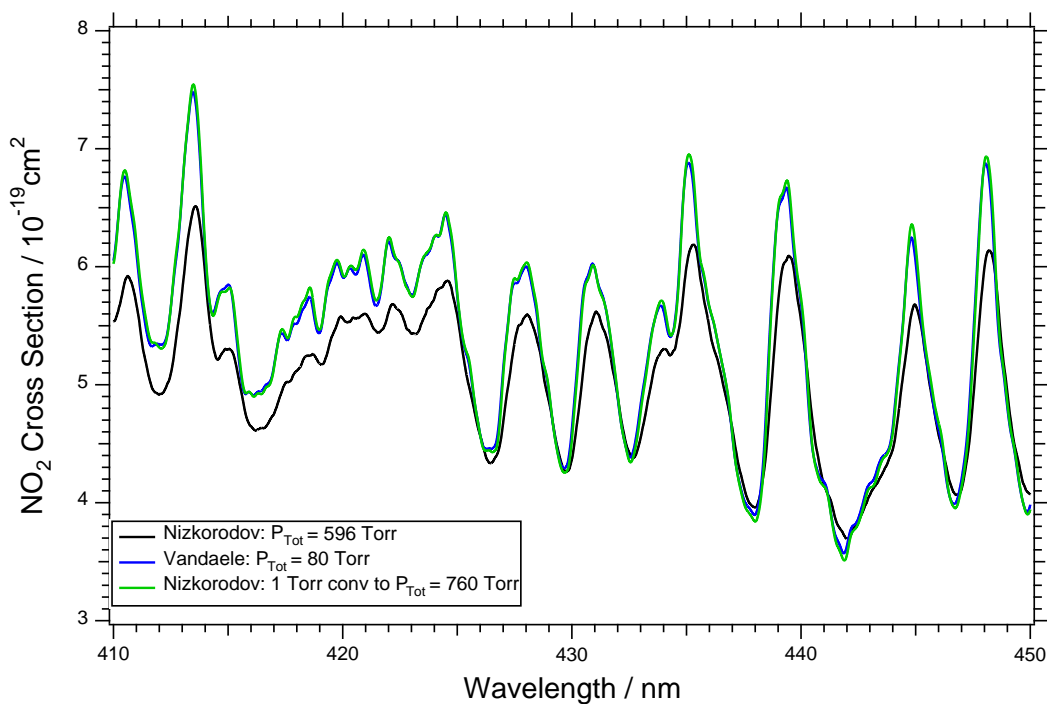
More detail from the authors on the convolution process and results therein would be of importance to reinforce the statement on P7 L16:

*“... (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?
- 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 ( $2\sigma$ ) 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  $\text{NO}_2$  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 ( $2\sigma$ )).

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  $\sim 0.85$ ). I concur that it is unclear, when reading through Nizkorodov et al. (2004), as to the source of this discrepancy. 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 ~15% shown in Figure 2. This, in turn, would reduce the, possibly coincidental, ~15% discrepancy observed by the authors when comparing their rate coefficients to the Mollner et al. (2010) study.

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 NO<sub>2</sub> 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.

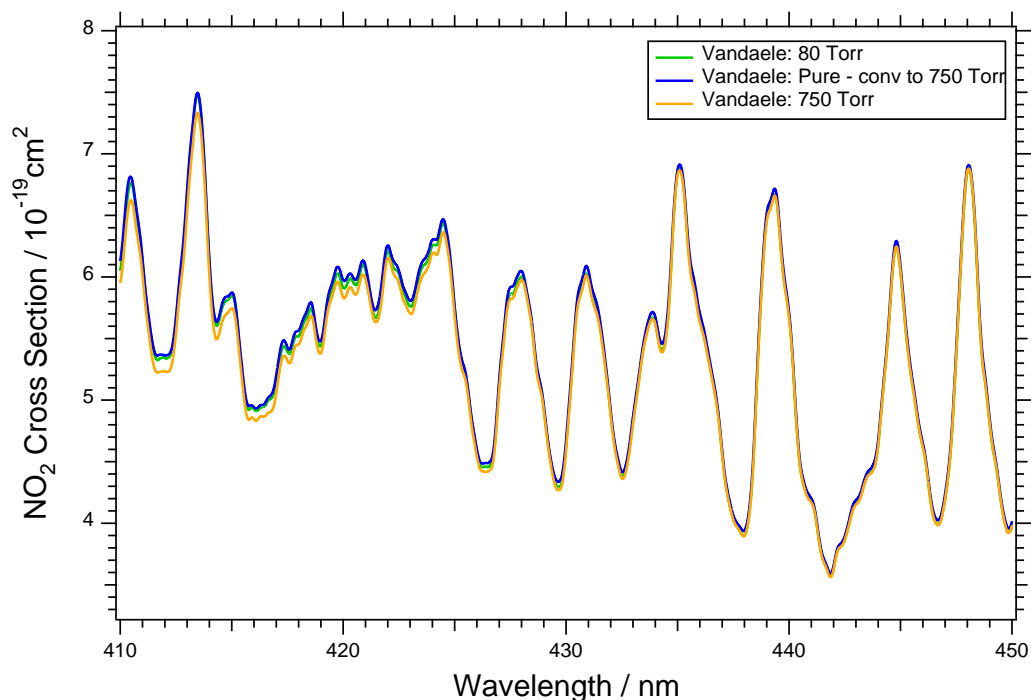


Figure 3

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).

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

If the authors feel that this discrepancy in the NO<sub>2</sub> 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.

## References

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