

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

Reviewer #3:

Except for cases where secondary chemistry is an issue, the major source of uncertainty in rate constants from laser or flash photolysis experiments with fluorescence detection of OH arises from uncertainty in the concentration of the excess reagent, in this case NO₂. Since optical absorption is used to quantify [NO₂] in this study, and if there are no other systematic errors associated with the path length, etc., the main source of uncertainty depends on the NO₂ absorption cross sections that are used. The paper discusses the various sources of cross sections obtained from the literature, especially from the Belgian group and the work of Nizkorodov et al. (2004). The paper makes that statement (p. 7, lines 2-4), that the high pressure spectra from Nizkorodov lead to an overestimation of the NO₂ concentration (underestimation of the crosssections) by up to 20% when compared to the other studies.

I have read the Nizkorodov paper and believe that the present authors have misinterpreted the results. Nizkorodov acquired spectra from low pressure (0.5-5 Torr) to high pressure (300-760 Torr) and a range of temperatures (214-298 K) at high spectral resolution (0.06 cm⁻¹). My reading of their paper indicates that the primary purpose of this was to determine the pressure and temperature dependences of the broadening coefficients. They determined the broadening coefficients by finding the best agreement between their low-pressure spectrum convolved with a Lorentzian line shape, and the actual experimental spectra at (T,p). Having determined these broadening coefficients, they recommended using the convolved spectra for further applications (such as the one described in the Amedro et al. paper) rather than the actual spectra at (T,p). When comparing the low-pressure spectra from both the Vandaele (2002) and Nizkorodov (2004) papers, the cross sections are nearly identical (well within 10%).

If Mollner et al. (2010) used the procedure recommended by Nizkorodov et al. for the derivation of reference spectra at (T,p), then because Amedro et al. used the Vandaele NO₂ spectrum for their reference, it is unlikely that the differences in rate constants between the two studies is due to differences in reference spectra. Unfortunately Mollner et al. were not specific concerning the exact method used to derive their reference spectra from the combination of the Nizkorodov and Vandaele results, but it is very likely that they used the convolution method since there were authors in common between the two studies.

I believe that Amedro et al. should clarify their manuscript to reflect the above comments. The implication is that there are other possible sources of systematic error that affect the rate constant determinations although these are not particularly obvious.

These issues have been addressed in response to the comments of Frank Winiberg (SC1). We have modified the text regarding the Nizkorodov and Vandaele spectra and the impact on the rate coefficients derived. We write:

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 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 NO₂ spectra of Nizkorodov et al. (2004) which were recorded at pressures ≥ 75 Torr, resulted in an overestimation of the NO₂ 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.

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 .