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Interactive comment on “Kinetics of the OH + NO_2 reaction: Rate coefficients (217–333 K, 16–1200 mbar) and fall-off parameters for N_2 and O_2 bath-gases” *by* Damien Amedro et al.

Anonymous Referee #3

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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 cross

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sections) 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.

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