Answer to Anonymous Referee #2

Thank you for your positive evaluation of our preprint and the helpful comments. Below we address your individual comments and describe the corresponding changes to the revised manuscript version. For the sake of clarity our answers are given in bold.

Main comments:

(1) The authors mention on page 10 that "A correction factor of 1.3 is applied in Fig. 4 for the 405 nm measurements", how did the authors calculate this correction factor?

As mentioned in the preprint (page 10, lines 243-245) the photolysis of NO_2 at wavelengths below about 420 nm affects the photoacoustic signal generation, which must be corrected when using the 405 nm laser in the calibration of the photoacoustic (PA) system. Two processes need to be considered here:

1.) Photolysis refers to the process in which high-energy photons cause the dissociation of NO_2 molecules into NO and O. In the wavelength region between the dissociation limit of NO_2 (λ=398 nm) and ~420 nm the quantum yield for the NO_2 photolysis rapidly decreases from unity to near zero. The wavelength dependence of the quantum yield has been measured by Roehl et al., 1994, resulting in a value of 0.41 for λ=405 nm. The actual emission peak was found around λ=404.8 nm for the PAAS unit PAAS-3L-01-003 used in this calibration (Fig. S5), so we estimated the yield from the adjacent yields for 404 nm and 405 nm given in Roehl et al. (1994). This means that 41% of the absorbed photons are used in the dissociation process and, therefore, are lost for the PA signal. Hence, the PA signal is reduced by a factor of 0.59, which can be accounted for in the calibration procedure by multiplying the 405 nm PA signal with a correction factor of 1/0.59=1.69.

2.) One key reaction that can occur after the dissociation of NO_2 is the formation of ozone (O_3), where the oxygen atom that is released by the NO_2 dissociation reacts with an oxygen molecule to form an ozone molecule ($O+O_2->O_3$). This reaction is exothermic, meaning that it releases 143 kJ/mol (=1.48 eV) of heat to the surrounding gas, which in turn contributes to the generation of the PA signal.

Consequently, about 20% of the initial 405 nm (3.06 eV) photon energy is gained back by the ozone formation:

1.48 eV * 0.41 = 0.61 eV -> 0.61 eV/3.06 eV = 0.20.

This reduces the loss of absorbed photon energy that is not available for generating the PA signal due to NO2 photolysis to a net loss of 21% (41% - 20%). As a result, a correction factor of approximately 1.3 must be applied to the 405 nm PA signal.

It is important to note that the contribution of the ozone formation to the PA signal has not been sufficiently investigated. Correction factors between 1.29 (Tien, Moosmüller, Arnott, 2013) and 1.56 (Nakayama et al., 2015) were reported for the 405 nm wavelength using the b_{abs} vs. b_{ext} method where the PA cell is filled with a very high concentration of NO_2 (typically several 100 ppm). These authors attribute the correction factors to the photodissociation yield only. However, a detailed analysis of the NO_2 photolysis requires the knowledge of the actual laser emission spectrum, which – to our knowledge – has not been measured in those studies.

After correcting the 405 nm calibration, the cell constants derived separately for the 405, 515, and 660 nm wavelengths agreed with the total constant by 0.2%, 6%, and 0.04%, respectively.

We added the following paragraph to the revised manuscript to explain our calculations more detailed:

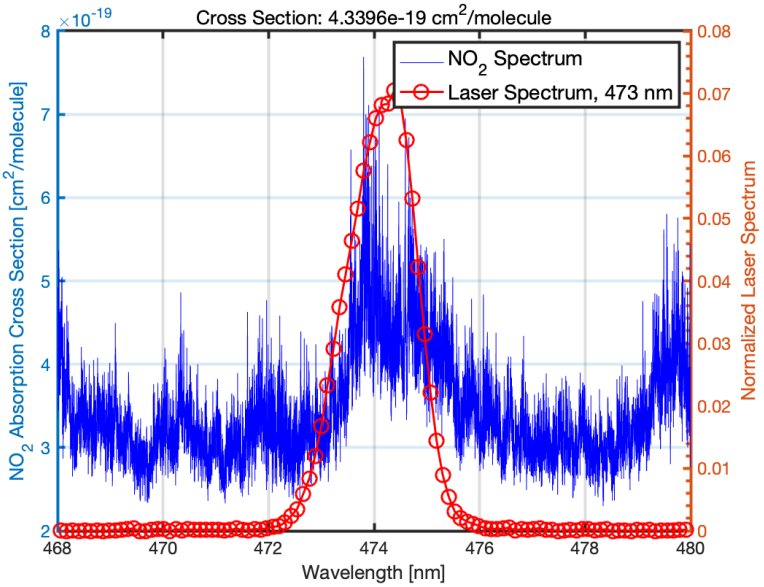
"According to the data presented in Roehl et al. (1994), the NO_2 photolysis quantum yield is 0.41 for the peak emission wavelength of 404.8 nm, as deduced for the PAAS-4λ unit used in this calibration (PAAS-3L-01-003, Fig. S5). This means that only 59% of the absorbed photon energy is transferred into the PA signal. However, after the dissociation of NO_2, the released oxygen atoms can react with oxygen molecules to form ozone. This reaction is exothermic and therefore has the potential to contribute to the generation of the PA signal. The released heat of 143 kJ/mol accounts for about 20% of the initially absorbed photon energy, increasing the energy fraction available for the generation of the PA signal to 79%. Based on this calculation a correction factor of 1.3 is applied in Fig. 4 for the 405 nm measurements, which is within the range of correction factors between 1.29 to 1.56 reported elsewhere for the same laser wavelength (Tian et al., 2013; Nakayama et al., 2015)."

(2) Why is there no calibration result for the 473 nm band in Figure 4?

As detailed in Section 2.1.1 on the "Laser System," the PAAS-4λ instrument family utilize a laser beam combiner capable of accommodating up to four lasers with user-defined wavelengths. For the very detailed calibration study presented in the manuscript, a unit (S/N PAAS-3L-01-003) was used that contained only three lasers with 405, 515, and 660 nm nominal emission wavelengths. That is why there is no 473 nm calibration shown in Fig. 4. We included the S/N of this unit into the caption of Fig. 4 to make this clearer.

(3) Why is the laser emission spectra information in the 473 nm band not shown in Figure S5? The same problem appears in Figure S6, Figure S7, Figure S8.

This has the same reason as detailed in the previous answer. The unit with S/N PAAS-3L-01-003 that was used for the laboratory calibration study shown in the manuscript hosts only three lasers with 405, 515, and 660 nm nominal emission wavelengths. That is why there is no 473 nm data shown in Fig. S5 (bottom), S6 and S7. The unit PAAS-4L-02-005 shown in Fig. S5 (top) hosts a 473 nm laser, which has been characterized in the same way as the other lasers (see figure below). We have excluded this graph from Fig. S5 since its primary objective is to illustrate how lasers emitting at the same nominal wavelength may have spectral shifts, resulting in a noteworthy modification of the laser emission's specific NO_2 absorption cross section that directly translates into the calibration constant.



The unit with S/N PAAS-3L-01-002 that was used in the intercomparison in Fig. S8 hosts four lasers emitting at 405, 515, 660, and 785 nm. However, the prototype instrument KITPAAS, which was used in the intercomparison shown in Fig. S8, hosts only three lasers with emission wavelengths of 445, 520, and 658 nm. We changed the captions of Fig. S6, S7, and S8 accordingly.