

Comment on amt-2021-421

Anonymous Referee #2

Referee comment on "Identification, monitoring, and reaction kinetics of reactive trace species using time-resolved mid-infrared quantum cascade laser absorption spectroscopy: development, characterisation, and initial results for the CH₂OO Criegee intermediate" by Zara S. Mir et al., Atmos. Meas. Tech. Discuss.,
<https://doi.org/10.5194/amt-2021-421-RC1>, 2022

The paper describes a new set-up combining laser-photolysis with time-resolved absorption spectroscopy using cw-QCL lasers. For validation, a part of the spectrum of the simplest Criegee intermediate, CH₂OO, has been measured as well as the rate constant of the reaction between CH₂OO and SO₂. The paper shows the future potential of the experimental set-up, without showing any new data. I have a few minor remarks that could improve the paper.

Figure 3: it would be interesting to see the signal on a longer time scale to have an idea about the influence of diffusion.

Figure 4: I guess CH₂I₂ does not absorb in this wavelength range, because otherwise it would influence the measured spectrum? Even though possible to calculate by everybody, it would be good to indicate the time it took to measure the spectrum to give an idea to the reader. I calculated that it has taken more than 60 hours to measure the spectrum, which is rather long given the quality of the obtained spectrum compared to the spectrum available in the literature. Why is the quality so low? Given the S/N ratio of the kinetic decay in Figure 5, which has been obtained also from averaging over 1000 laser pulses and with even lower concentration of CH₂I₂, I would have expected a much better S/N ratio in the spectrum.

Line 274: I don't understand the sentence: "The pre-photolysis region was defined as -4000 µs to -500 µs, owing to detection of some radiofrequency noise associated with the Q-switch delay of the photolysis laser which was set to 280 µs, and the post-photolysis region as 500 µs to 6000 µs, where t = 0 is the time at which the photolysis laser is fired." Is the Q-switch at -280 µs, and does the noise still influence even after the laser pulse, or

why is there such a long post-photolysis delay? The signal in Figure 5 looks perfect from the first μs on. Maybe show an example of a typical signal with pre-trigger to clarify?

Why do the data in Figure 5 show that the diode does not drift? Because Figure 5 is the average of 1000 photolysis shots, the average could still be a good quality decay, even if the wavelength changed during the measurement, no?

It would make it easier for the reader if Table 1 would also contain the corresponding reaction numbers.

The difference in pathlength is somewhat strange: would it not have been possible to measure both kinetics with the same alignment to verify if this is the reason for the change? Also I'm wondering if the k_{phys} has changed a lot between both experiments: with CH_2OO it is 500 s^{-1} , which should leave to a visible increase of the CH_3I kinetic in Figure 3, but Figure 3 looks like a k_{phys} well below 100 s^{-1} .

The error bars in Figure 6 are very small: I guess they are statistical from the exponential fitting? Please show a few examples of decays at the highest pseudo-first order rates, it would be interesting to see the quality of the data, especially with respect to the noise from the photolysis laser described above. Maybe this could be done as supplementary material.

Because you can know the initial CH_2OO concentration as well as the formed SO_3 , you should be able to measure the yield of SO_3 . Did you try?