

An introduction to the project related to a mobile detection of isocyanic acid produced as a by-product during the DeNO_x process in diesel vehicles.



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Introduction

Nitrogen oxides (NO_x) are amongst the primary pollutants. Nowadays, the NO_x emissions in cities are mainly originated from diesel vehicles. Controlling the emissions of NO_x from diesel vehicles has been a priority for the car manufactures. Different NO_x reduction techniques (DeNO_x technology) have been used to control the exhaust emissions of diesel vehicles. One of the most frequently used DeNO_x process is based on selective catalytic reduction (SCR). In this method urea is used to produce ammonia (NH₃) as a reduction catalyst for NO_x in the exhaust of a diesel vehicle (Figure 1). The DeNO_x process further leads to emission/leakage of considerable byproduct known as isocyanic acid (HNCO) along NH₃ (Heeb et al., 2011).

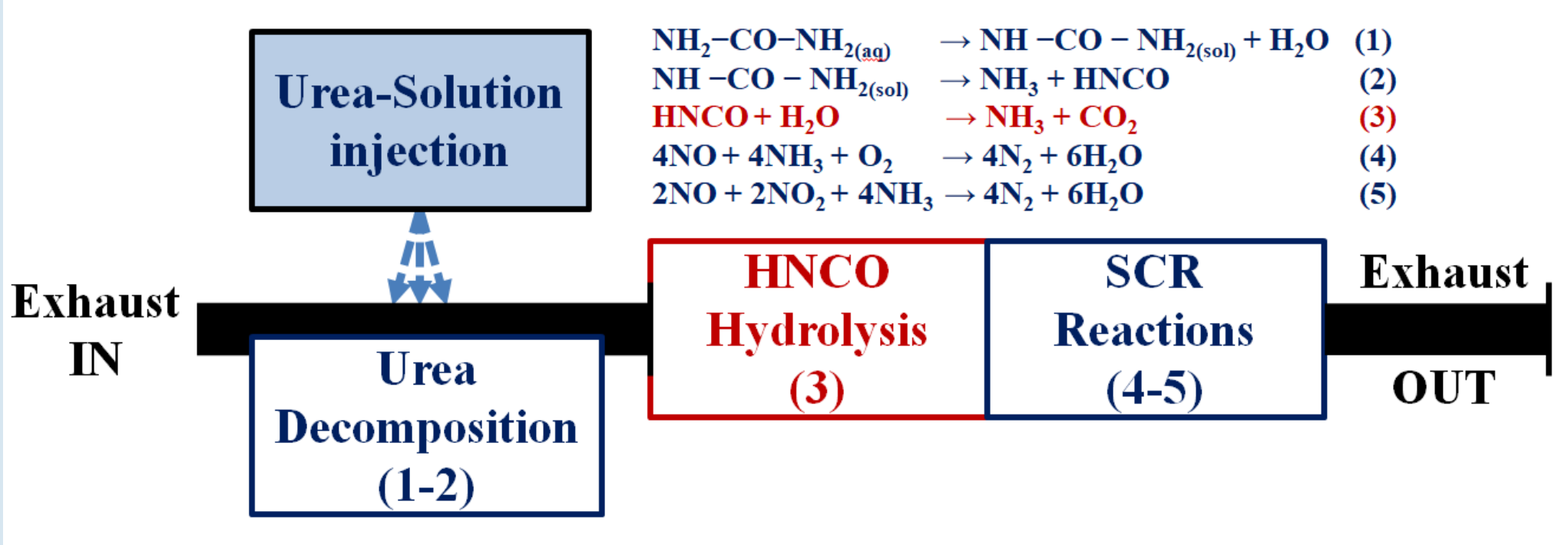


Figure 1: Schematic of the SCR process. Adapted from (Piazzesi, 2006)

Species	mg / m ³
HNCO	0.02
NO	30
NO ₂	6
HCN	2.1

Table 1: The MAK value of HNCO in comparison to some other species. The values are based on SUVA 2011.

Health Impact

HNCO is a highly toxic species with a severe impact (in/direct) on the human health. It leads to atherosclerosis, cataracts, and rheumatoid arthritis via carbamylation reactions in humans. 1ppb of HNCO is about sufficient to start carbamylation reactions (Roberts et al., 2011) in the body.

HNCO in the troposphere

HNCO Sources other than SCR

1. Photo-oxidation of amines and amides (e.g., Lee and Wexler, 2013).
2. Pyrolysis of nitrogen-containing biomolecules (Hansson et al., 2004).
3. Biomass burning (direct correlation with nitriles, HCN) (Warneke et al., 2011).

HNCO Sinks

1. OH oxidation (lifetime≈decades)
2. Photolysis is unlikely (UV absorption @< 280 nm) (Zhao et al., 2014, Borduas et al., 2016 and references therein).
3. Lifetime, based on the heterogeneous removal is in the range of days to a few weeks (Young et al., 2012).

Expected HNCO levels

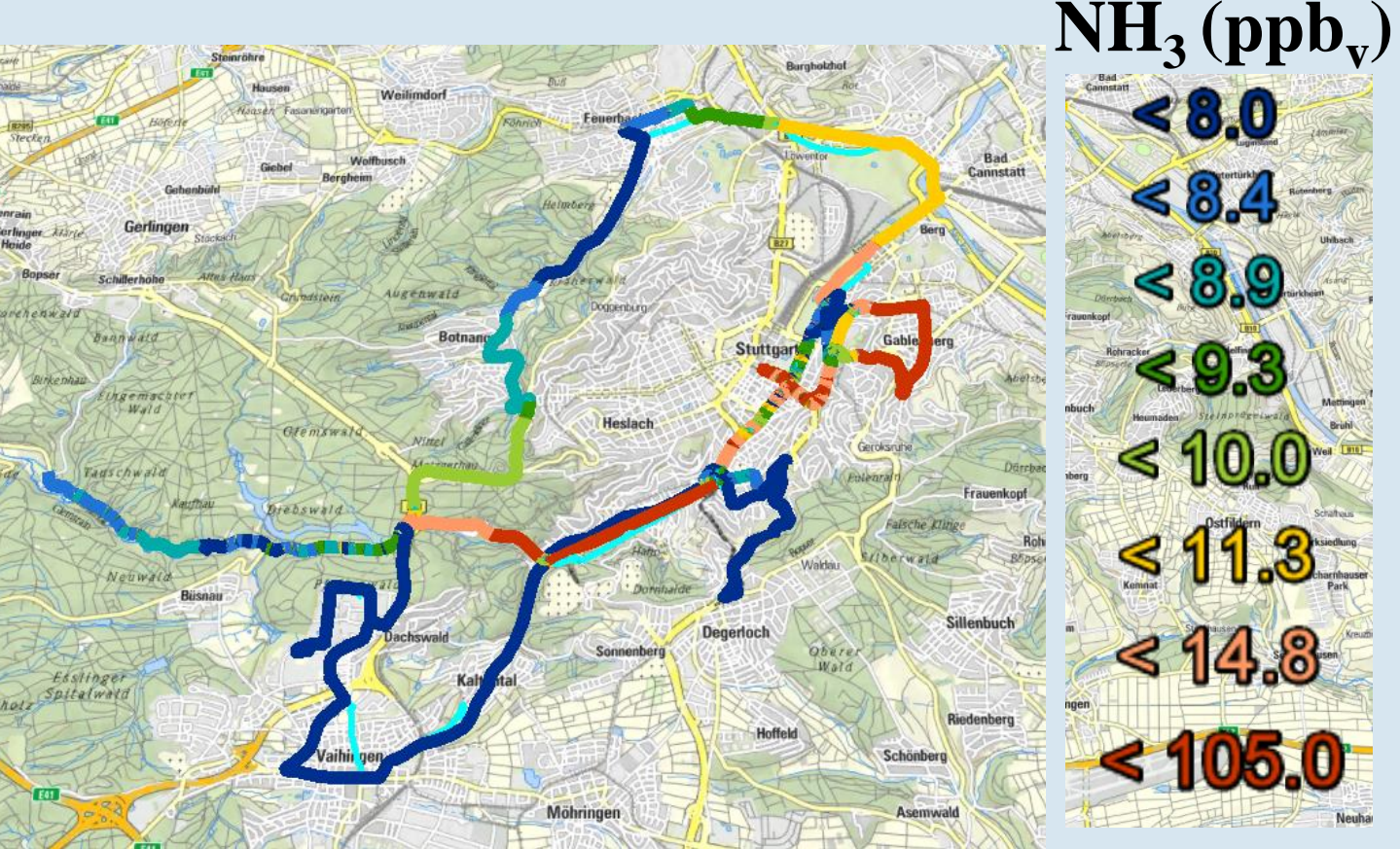


Figure 3: NH₃ was measured in Stuttgart during the winter of the year 2017. The levels of NH₃ based on MOBILAB measurements were upto 100ppbv in the urban region. Based on NH₃ levels, an expected HNCO level can be in the range of 1-16ppbv.

Outlook

- Integration of electronics/ DAQ system in the mobile vehicle (MOBILAB).
- Lab-testing and characterization need to be performed to assess the stability of optics.
- Detection limit expected to be about 100 ppt by using 2F lock-in amplifier technique.
- By only replacing the laser and cuvette, this instrument can be used as an independent method for HCHO, NO₂, and HONO.

Important References

- Heeb, N. V., Zimmerli, Y., Czerwinski, J., Schmid, P., Zennegg, M., Haag, R., Seiler, C., Wichser, A., Ulrich, A., Honegger, P., Zeyer, K., Emmenegger, L., Mosimann, T., Kasper, M., and Mayer, Atmos Environ, 45, 3203-3209, 2011.
- Kofahl, C.: Bau und Kalibrierung einer HNCO-Quelle, Universität Rostock, Jülich, 61 p. pp., 2014.
- Piazzesi, G.: The Catalytic Hydrolysis of Isocyanic Acid (HNCO) in the Urea-SCR Process, PhD, Swiss Federal Institute of Technology-ETH Zurich, 2006.
- Roberts, J. M., Veres, P. R., Cochran, A. K., Warneke, C., Burling, I. R., Yokelson, R. J., Lerner, B., Gilman, J. B., Kuster, W. C., Fall, R., and de Gouw, J., P Natl Acad Sci USA, 108, 8966-8971, 2011.
- Young, P. J., Emmons, L. K., Roberts, J. M., Lamarque, J. F., Wiedinmyer, C., Veres, P., and VandenBoer, T. C., J Geophys Res-Atmos, 117, ArtD10308 10.1029/2011jd017393, 2012.

TDLAS instrument for HNCO

Different techniques have been used in the past for the detection of HNCO. These techniques, maily based on CIMS, and FTIR methods. However, these methods have some disadvantages. For example, the CIMS method is not entirely interference-free and the FTIR technique is not suitable for a mobile detection. To achieve sensitivity, selectivity, compactness, and a mobile detection capability, we have selected the tunable diode laser absorption spectroscopy (TDLAS). The working principle is based on (quantitatively) Beer-Lambert law.

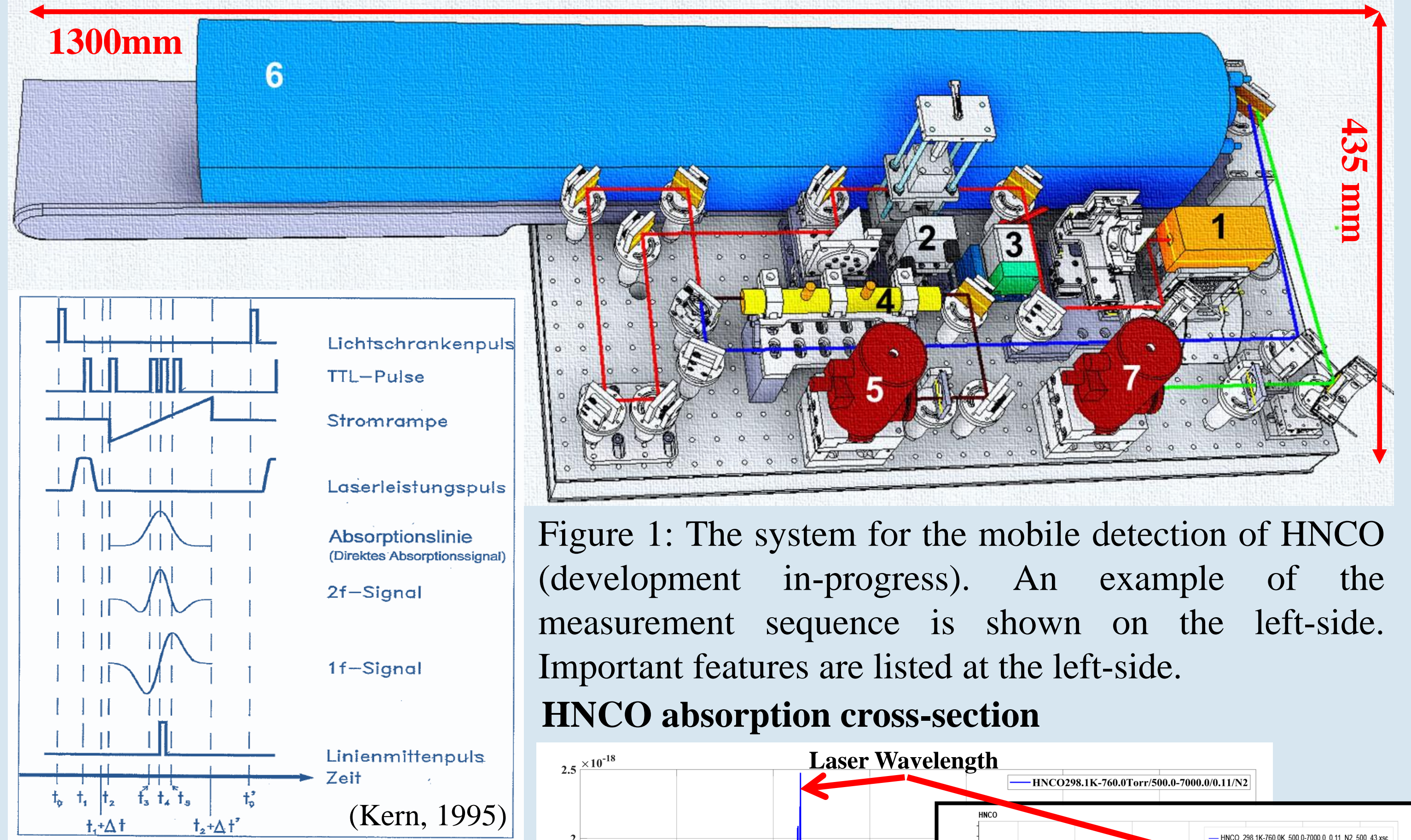


Figure 1: The system for the mobile detection of HNCO (development in-progress). An example of the measurement sequence is shown on the left-side. Important features are listed at the left-side.

HNCO absorption cross-section

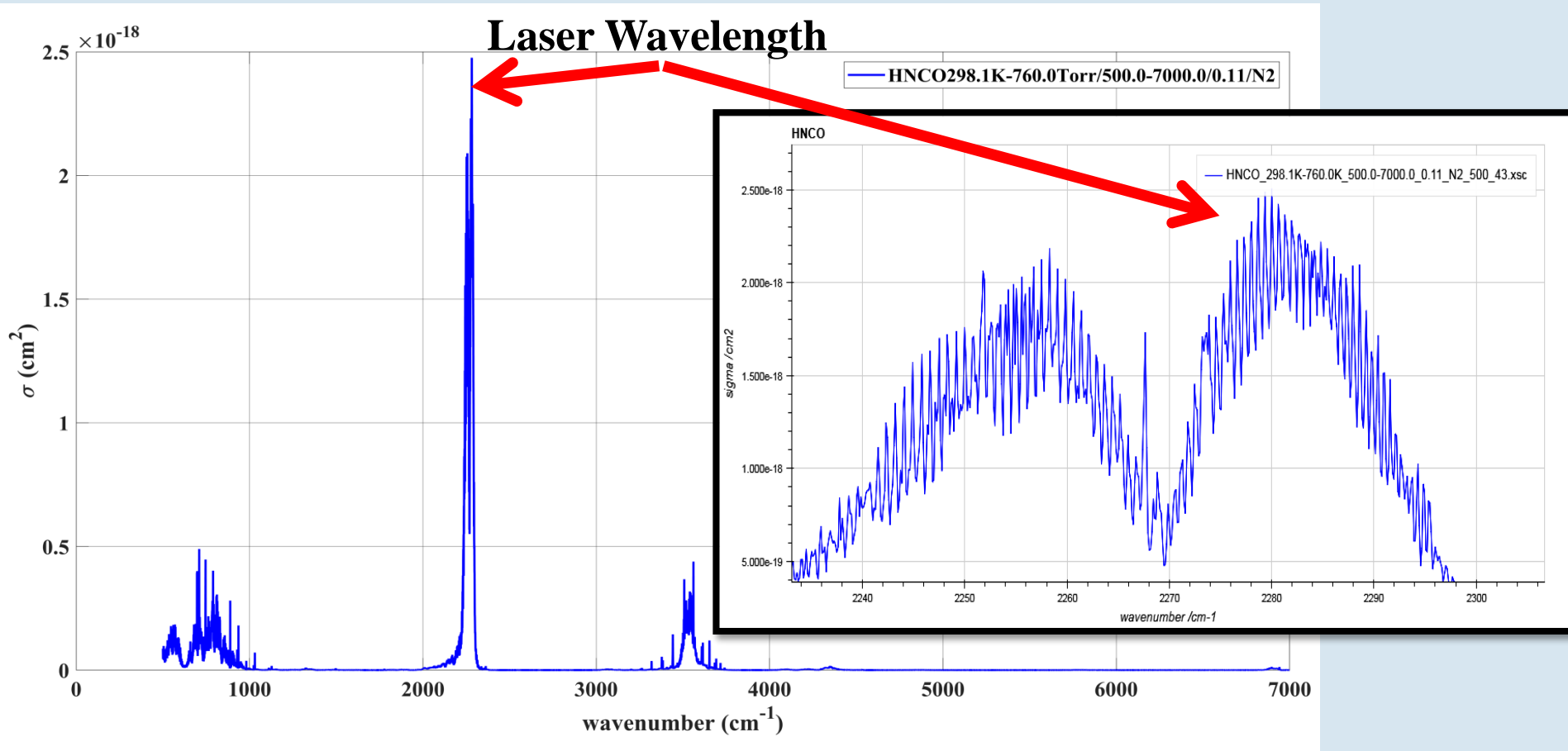


Figure 2: The absorption cross-section of HNCO as a function of wavelength number. (Sharpe et al., 2004).

TDLAS instrument Calibration

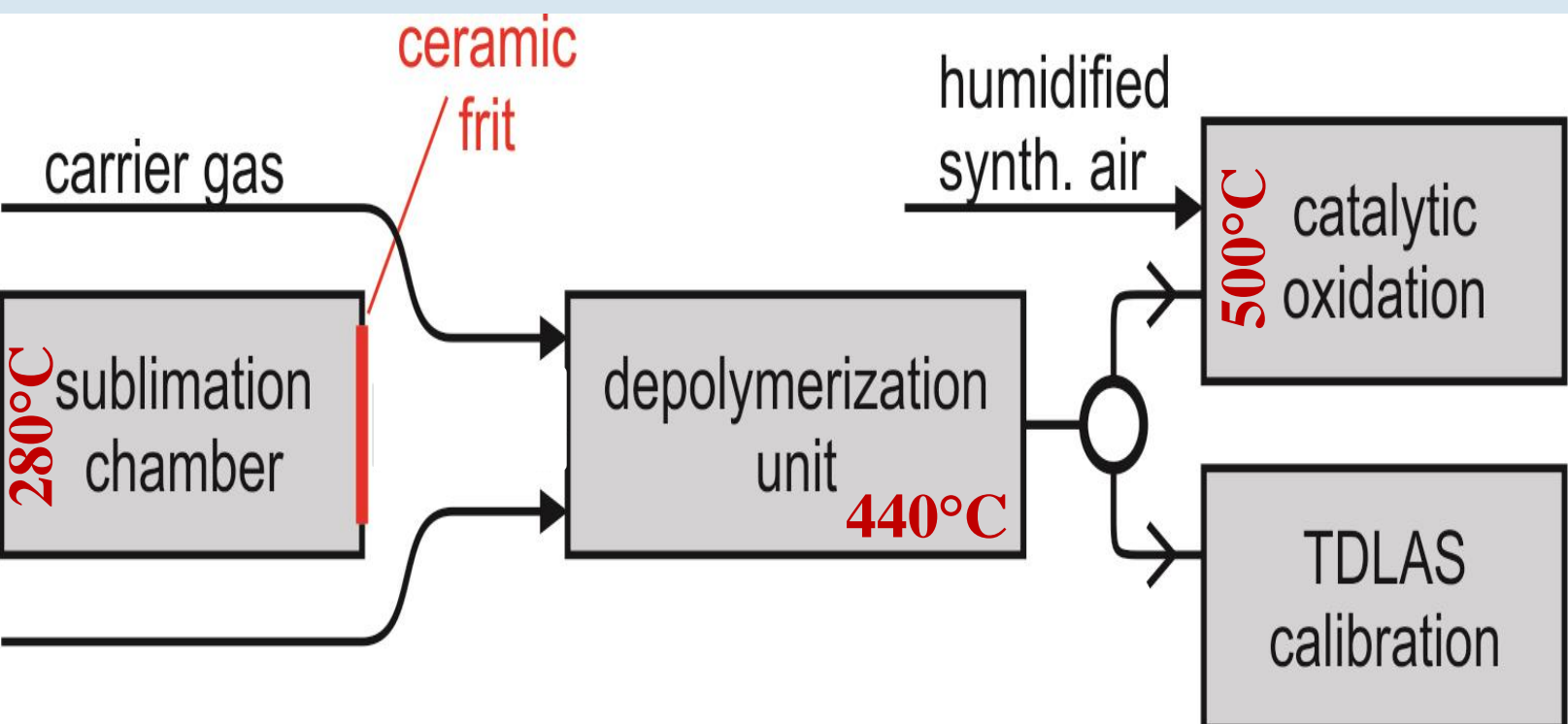


Figure 1: HNCO generator based on the decomposition of Cyanuric acid (CNOH)₃. In the sublimation chamber at 280°C, (CNOH)₃ is heated. HNCO is formed in the depolymerization unit (@440°C) via thermal depolymerization in the presence of a carrier gas (e.g. Helium in this case). The catalytic chamber is used to destroy HNCO at 500°C in the presence of humidified air. The figure is taken from Klemp et al., (will be submitted).

Calibration unit (Lab Characterization)

Figure 2: ¹³C-NMR spectrum of HNCO based on the sample (in CDCl₃) taken after the depolymerization unit. This test was done to confirm the formation of HNCO in the depolymerization unit.

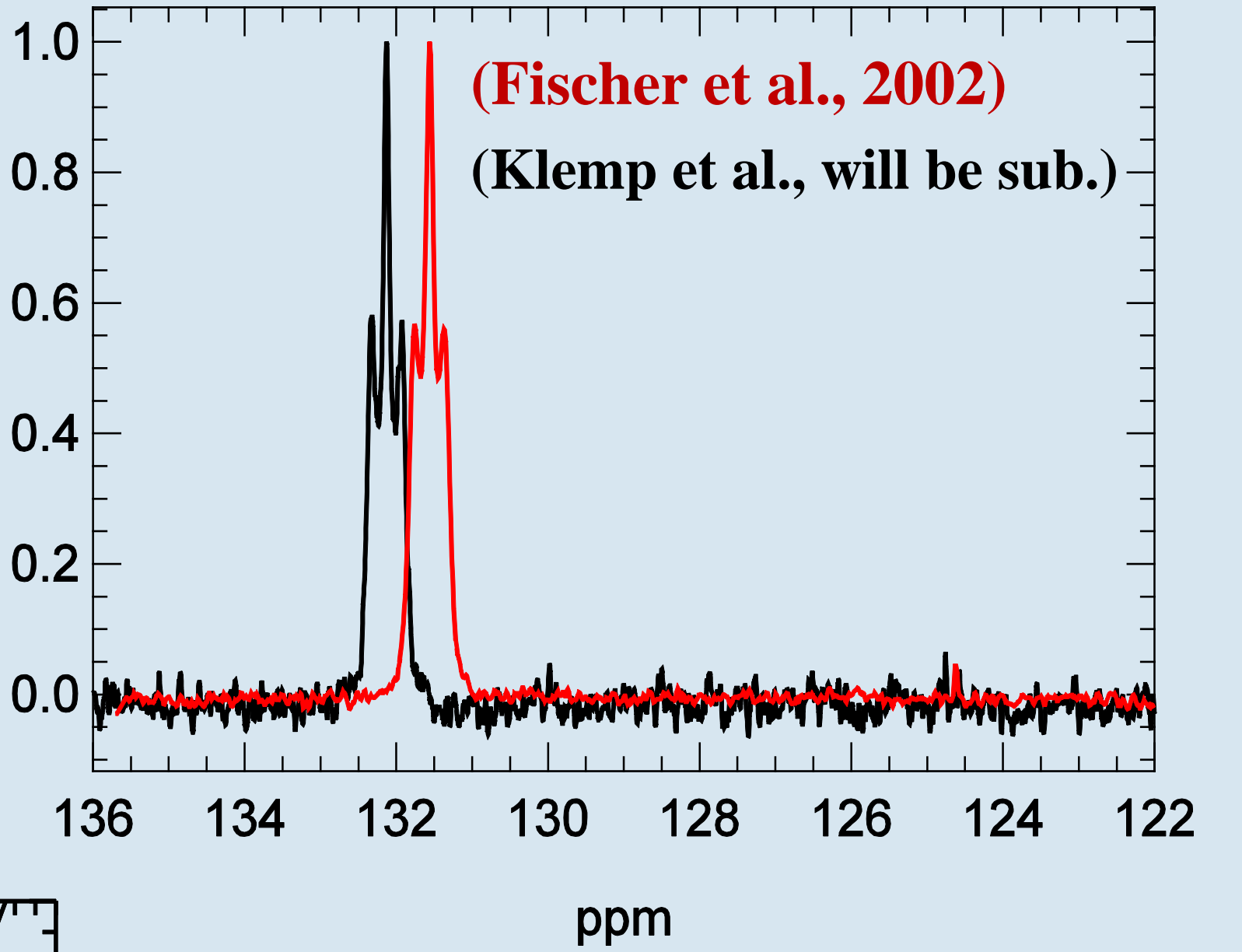
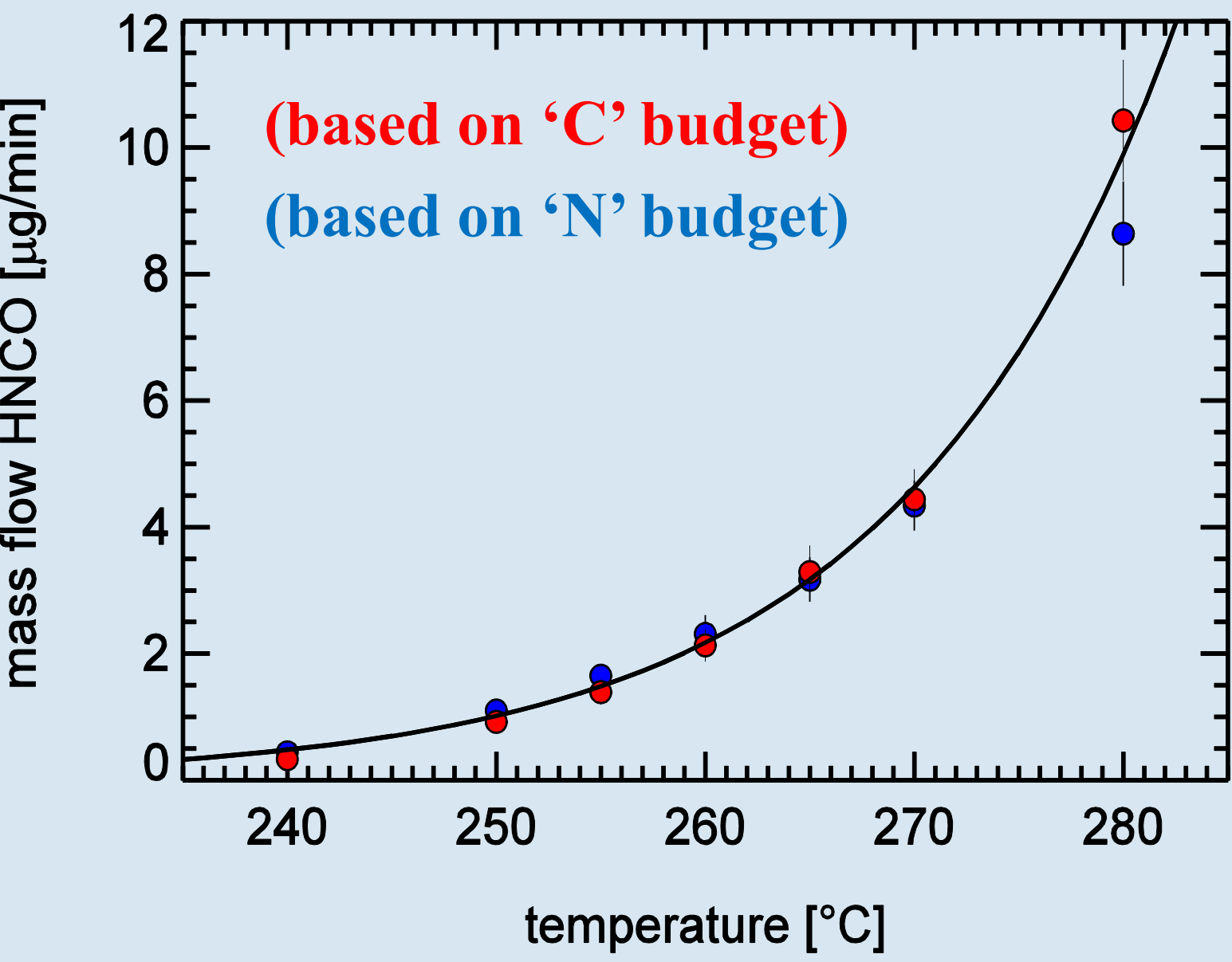


Figure 3: Quantified mass flow of HNCO as a function of the sublimation chamber temperature.



Budget analysis was done to quantify mass flow of HNCO from the calibration unit. For the analysis, carbon and nitrogen based species were measured before and after the catalytic oxidation unit (Figure 1).

Before
CO+CO₂+NH₃+N₂O+NO+NO₂+HNCO
After
CO+CO₂+NH₃+N₂O+NO+NO₂+H₂O