

Cavity ring-down spectroscopy for the investigation of high-temperature processes – sensitive detection of intermediates and further developments

The detailed understanding of chemical processes and reaction mechanisms requires the development of sensitive detection methods and sensors. Especially reactive intermediates and trace species may control such reactions to a large degree, and thus the detection of such species can lead to a better understanding of complex chemical processes. Spectroscopic techniques for the detection of these species are mostly employed due to their non-invasivity and non-destructive nature. One of the standard techniques for the detection of minor species is laser-induced fluorescence (LIF). However, for a quantitative LIF measurement energy transfer processes in the excited states (quenching, rotational and vibrational energy transfer, as well as polarization scrambling) must be taken into account, which are often unknown and difficult to quantify. Moreover, some molecules might not be fluorescent due to predissociation or strong quenching. As alternative, absorption spectroscopy can be employed, which is independent of these effects, but suffers from low detection limits of typically 10^{-4} cm^{-1} . In 1988, O’Keefe and Deacon introduced the cavity ring-down spectroscopy (CRDS), as a new, promising absorption technique for the detection of gaseous species down to the ppt-level. It is a multi-pass absorption technique whereby the sample is placed in a high-finesse cavity and the intensity decay of the laser beam is detected behind the output mirror as the beam traverses the cavity. The long residence time of the laser pulse in the optical cavity leads to an extremely long effective path length: mirror reflectivities up to 99.999 % yield absorption path lengths in the kilometer domain. Moreover, CRD measurements are made in the time domain, isolating the measurement from laser intensity noise. This combination gives the potential of extremely sensitive absorption measurements.

This thesis presents the application and characteristics of CRDS for the detection of intermediates and trace species in high-temperature environments. It provides an overview of CRDS theory, including a review of the so far detected species in high-temperature processes. Different CRDS experiments are assembled and adjusted for atmospheric as well as for the requirements of measurements in low-pressure flames. Additionally, a series of fundamental experiments are carried out which illustrate the power of pulsed laser CRDS, and modern variants of CRDS using continuous-wave lasers.

Fundamental aspects, such as the influence of laser bandwidth on the ring-down signal and the spatial resolution, are subject of investigation. In these experiments, a novel single-mode tunable laser (STL) is used for high resolution cavity ring-down measurements. This system operates by pulsed amplification of the output of a single-mode diode



laser in a modelless dye laser and provides widely tunable single-mode radiation with a bandwidth that is smaller than the spectral width of typical Doppler-broadened absorption lines. The high spectral purity of the source provides CRD curves that are well fitted by single-exponential decay functions, independent of detuning from line-centre of a spectral line and the intensity of the transitions. The high spectral resolution of the CRD spectra obtained using the STL allows accurate determination of the Gaussian and Lorentzian components of the Voigt profile used to describe the transition lineshape. Since the Gaussian contribution is due to Doppler broadening, the gas temperature, which has been derived from the measured width of this component, is found to be in good agreement with other techniques (CARS) or alternative strategies using CRDS. It is shown, that CRDS using a standard pulsed dye laser system may yield multi-exponential ring-down curves. This is due to the presence of spectral components within the laser linewidth that experience different absorption coefficients across the spectral profile of the transition. A bi-exponential function is found, in some cases, to be an adequate approximation to ring-down curves obtained from strongly absorbing transitions, but the corresponding results are difficult if not completely impossible to interpret. For a more consistent evaluation a mono-exponential fit to only the early part of the ring-down curve, which corresponds to the decay from 90 % to 50 % in intensity, has been found to be the best approximation.

A standard laser system may be still suitable for performing accurate CRDS measurements though, if the absorptivity in the cavity is weak, which can be achieved by careful choice of (weak) absorbance transitions under investigation. This is demonstrated by measurements in well-characterized hydrogen-air flames, where the results are in perfect agreement with simulations and data obtained by different spectroscopic techniques. Additionally, the influence of the laser bandwidth is studied theoretically. For this purpose, a simulation program has been developed and programmed, which allows to create realistic sets of CRDS-data. Using various hypothetical experimental situations, different evaluation strategies are developed and discussed.

A limitation of absorption techniques is the reduced spatial resolution which is due to the nature of line-of-sight measurements, i.e. local changes in concentration remain unresolved. However, by tomographic measurements that are analyzed by mathematic reconstruction algorithms, (centric) inhomogeneities of absorbing species could be resolved. Here, the results obtained in a Bunsen burner flame are found to be in excellent agreement with corresponding LIF measurements.

The conclusions and results described above are the basis for further studies in fuel-rich flames close to the soot formation limit at low-pressure conditions. Propene (C_3H_6) is chosen as a fuel because of the importance of C_3 -intermediates and their potential to form benzene – a soot precursor – in a single step. For investigation of these flames, an adequate burner chamber is constructed, which is suitable for optical diagnostics at low

pressure. The burner is placed on a stage that allows for two-dimensional translation perpendicular to the detection axis. Tomographic measurements of the stabilized propene flames show that the inhomogeneous zone is negligible small.

In the next step, temperature profiles of individual flames are measured, which are essential for quantitative detection of intermediates. Standard techniques, like laser-induced fluorescence using OH-radicals, are not easily applicable for fuel-rich flames due to the low concentration of OH at temperatures lower than 1600 K. Thus, seeding of additional molecules, e.g. of the NO-radical, has been necessary in the past, but such molecules may affect the flame chemistry significantly. In this work it is demonstrated that seeding can be avoided when CRDS is employed. With CRDS, the OH-radical is detectable even at low concentrations, i.e. it can be used as a natural temperature probe.

Besides the hydroxyl radical (OH), methylene and formyl radicals ($^1\text{CH}_2$, HCO) are detected for the first time in fuel-rich propene flames. Concentration profiles of these radicals are measured at different fuel/oxidizer ratios between $\Phi = 1.5$ and $\Phi = 2.7$ (C/O 0.5 – 0.9). These concentration profiles obtained are discussed in the context of other species concentrations determined by LIF and are each compared to numerical simulations using the CHEMKIN package and a special mechanism for high-molecular fuels (Deutsches Luft- und Raumfahrtzentrum, Stuttgart). For OH and $^1\text{CH}_2$, the comparison shows a good agreement with respect to the concentration profile and only slight differences in the absolute values. In contrast HCO shows the inverse correlation. Thus an improvement of the reaction mechanism for low-pressure conditions with special focus on HCO is desired.

The measurements presented here extend the experimental data of fuel-rich propene flames, which so far contains concentration profiles for large molecules from REMPI- and EI-TOF-mass spectrometry, by addition of some important small radical intermediates. Additionally, resonances of the water molecule in the visible range at 650 nm have been detected by CRDS for the first time. Investigations of different fuels and spectral simulations show, that the spectral window at 650 nm is free of interference by other intermediates. This gives the opportunity to detect this combustion product at very low concentrations and furthermore suggests the usage of water resonances to determine the flame temperature. Besides, at wavelength around 430 nm CH- and C_2 -radical are detected qualitatively, which are two further intermediates with importance in the combustion chemistry.

Nitrogen dioxide (NO_2) is a further species of importance in combustion and atmospheric chemistry. For detection of NO_2 , a sensor based on continuous-wave CRDS – a modification of CRDS – has been developed and characterized. The use of continuous-wave lasers in cavity ring-down spectroscopy offers great potential for development of trace gas sensors because of the combination of compact lasers and low power consumption. The detection of NO_2 is demonstrated by absorption measurements of different NO_2/N_2



gas mixtures yielding a detection limit of 890 ppb for this sensor.

Not only the sensitive detection of trace species and reactive intermediates becomes feasible with CRDS. This thesis also presents the development and application of a new method to characterize the quality of laser radiation, i.e. to determine the amplified spontaneous emission (ASE)-content of narrow-band lasers with CRDS quantitatively. ASE is an undesired broadband signal of the laser output which reduces the quality of the laser beam. Tuning the laser wavelength with a strong absorption line, a bi-exponential ring-down curve could be observed containing both, a short ring-down time of the absorption feature and a long ring-down time from the empty cavity. The ASE-content could be determined easily and accurately by the ratio of these two components. Using two different laser systems quantitative measurements of ASE-contents down to 0.7 % could be demonstrated. In principle, this method even has the potential to detect ASE-contents one or two magnitudes lower and allows for real-time measurements on single-pulse level. Moreover, the low laser energy required for the measurements enables easy and fast optimization of the experimental setup.

In summary, CRDS is an excellent technique for the sensitive detection of gaseous species. Many substances that are difficult to quantify with other methods are easily accessible with CRDS. By introducing small modifications, it can be adapted to nearly any reaction system. Employing compact laser systems and detectors even opens the fascinating gate for stand-alone, transportable sensors.