TRIPLE Q: A three channel quantum cascade laser absorption spectrometer for fast multiple species concentration measurements

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A compact and transportable three channel quantum cascade laser system (TRIPLE Q) based on mid-infrared absorption spectroscopy has been developed for time-resolved plasma diagnostics. The TRIPLE Q spectrometer encompasses three independently controlled quantum cascade lasers (QCLs), which can be used for chemical sensing, particularly for gas phase analysis of plasmas. All three QCLs are operated in the intra-pulse mode with typical pulse lengths of the order of 150 ns. Using a multiplexed detection, a time resolution shorter than 1 μs can be achieved. Hence, the spectrometer is well suited to study kinetic processes of multiple infrared active compounds in reactive plasmas. A special data processing and analysis technique has been established to account for time jitter effects of the infrared emission of the QCLs. The performance of the TRIPLE Q system has been validated in pulsed direct current plasmas containing N₂O/air and NO₂/air. © 2011 American Institute of Physics. [doi:10.1063/1.3633952]

I. INTRODUCTION

Over the last two decades chemical sensing using laser absorption spectroscopy (LAS) in the molecular fingerprint region from 3 to 20 μm has been established as a powerful in situ diagnostic tool for molecular plasmas. The non-intrusive, selective, and time-resolved detection and quantification of transient and stable molecular species provide important information on the gas phase composition and chemistry of complex gas mixtures in electric discharges. Molecular plasmas are increasingly being used not only for basic research, but also due to their favourable properties, for material’s processing technology. These fields of application have stimulated the development of infrared (IR) spectroscopic techniques for industrial requirements. In order to exploit the capabilities of mid-infrared tunable diode laser absorption spectroscopy (TDLAS) for effective and reliable on-line plasma diagnostics and process control in research and industry, transportable tunable infrared multi-component acquisition systems (IRMA, TOBI) have been developed.

An infrared multi-component acquisition system (IRMA) may be equipped with up to four different diode lasers, which are operated simultaneously. In this way, a time resolution as short as 10 ms has been achieved. Further progress in fast multi-species detection was reported for the two laser beam infrared (TOBI) system using two multiplexed tunable diode lasers at the same time. In comparison to the IRMA system, the TOBI spectrometer was especially designed for higher detection speed. Rapid scan software enables transient plasma conditions to be investigated on time scales of tens of microseconds. The control software combines direct absorption with sweep integration to measure the absolute concentrations of several molecular species and provides continuous digital output, which might be used for process control. The optical system thereby supports both in situ measurements in a plasma reactor and ex situ diagnostics of gas phase samples extracted into a multi-pass cell.

The essential cryogenic cooling of lead salt diode lasers (and also of the detectors), that are typically operated at temperatures below 100 K, remains the main drawback of mid-IR TDLAS. Hence, systems based on lead salt diode lasers are large in size since they require complementary equipment such as closed cycle refrigerators and/or cryogens such as liquid nitrogen. The recent development and commercial availability of quantum cascade lasers (QCLs) for wavelengths longer than 3.4 μm and inter-band cascade lasers (ICLs) for shorter wavelength offer an attractive new option for mid-IR LAS. In conjunction with integrated distributed feedback (DFB) gratings, the emission wavelength of this new class of thermoelectrically cooled semiconductor lasers can be custom tailored over a wide range throughout the molecular fingerprint region. The DFB-QCLs provide continuous mode-hop free wavelength tuning. Their total emission range is typically limited to less than 7 cm⁻¹ (for a heat sink temperature between ± 30 °C). Compared with a (incomplete) coverage of hundreds of wavenumbers in the case of temperature tuned multi-mode lead salt TDLs, it is clear that the application of DFB-QCLs requires a relatively precise selection of the laser. Recently tunability over much broader spectral ranges than with a typical DFB-QCL has been achieved using external cavity (EC) configurations. Nowadays, EC-QCL, which are available in pulsed or continuous wave working mode, can be tuned over more than 100 cm⁻¹ and provide mode-hop free tuning ranges in the order of 60 cm⁻¹. Meanwhile the variety of QCLs and ICLs are considered as substitutes for lead salt TDLs, which has led to a rapid development of IR-LAS from a niche position to a standard diagnostic technique.

For a better understanding of molecular processes in non-equilibrium plasmas, mid-IR LAS is a valuable tool since
it directly provides number densities of molecular species. Particularly under non-stationary excitation conditions, time-resolved techniques combining both high sensitivity and high-speed data acquisition are essential. In this respect, the fast frequency chirp of pulsed QCLs, which is in the range of about tens of MHz per ns (i.e., $\sim 0.001$ cm$^{-1}$/ns), known as intra-pulse mode, offers advantages for chemical sensing: entire absorption spectra of up to $\sim 1$ cm$^{-1}$ (30 GHz) are recorded during a few hundred nanoseconds pulse width which fits very well to highly time-resolved measurements of rapidly changing chemical processes. Studies under turbulent gas phase conditions have become feasible because the data acquisition time is shorter than random fluctuations in the sub-millisecond range.

An ideal spectrometer that facilitates the investigation of transient phenomena in molecular plasmas should, therefore, combine high time-resolution with high sensitivity to detect key species in the gas phase and the potential of (simultaneous) multi-species monitoring. Although in situ experiments tackling all these three criteria are still challenging, a significant improvement of existing spectrometers has become feasible due to the aforementioned progress in mid-IR laser technology. Therefore, this article concerns a compact and transportable three channel QCL system (TRIPLE Q) developed for highly time-resolved plasma diagnostics. The TRIPLE Q spectrometer encompasses three different QCLs, which can be used for gas phase chemical sensing in general or, particularly, for plasma diagnostics of molecular species. All three QCLs are operated in the intra-pulse mode with typical pulse lengths of the order of 100–200 ns. Using a multiplexed detection regime, a (total) time resolution below 1 $\mu$s can be achieved to study kinetic processes of multiple infrared active compounds in plasmas. A special data processing and analysis technique considers time jitter effects of the infrared emission of the QCLs. The article gives a survey of the optical subsystem, the data processing, and the data analysis technique. The performance of the TRIPLE Q system has been assessed in pulsed direct current (dc) plasmas in N$_2$O-air and NO$_2$-air gas mixtures. The accuracy and sensitivity limits of the system are discussed based on the identification of main noise sources and uncertainties.

II. OPTICAL SUBSYSTEM

In Fig. 1, the schematic diagram of the TRIPLE Q spectrometer connected to a pulsed dc discharge tube is shown. Figure 2 provides details of the optical subsystem. The three QCLs are separately housed in temperature-stabilised laser heads and are individually operated by its corresponding pulsed laser driver (Q-MACS Basic, neoplas control). The divergent radiation of each QCL is collimated using an off-axis parabolic (OAP) mirror, $d = 25.4$ mm, $f = 40$ mm) and guided to a shared OAP of bigger diameter ($d = 50.8$ mm, $f = 125$ mm). Each laser illuminates a part of the shared OAP, which re-focuses the individual beams on an IR transparent lens ($d = 8$ mm, $f = 0.4$ cm) to create a single collimated (multi-wavelength) laser beam that covers the three different QCL centre wavelengths. Strictly speaking, the shared OAP and the lens form an optical telescope to reduce the beam diameter to about 4 mm. This multi-wavelength beam is directed through the dc discharge tube and finally focused onto the fast detector (IRDM-600, neoplas control) using an OAP of 40 mm focal length ($d = 25.4$ mm). The detector module contains a temperature controller, which is specifically adjusted to the fast detector element (VIGO, PDI-2TE-10/12), a fast pre-amplifier (bandwidth: 600 MHz, rise time: 2 ns), and a non-switched temperature controller. These parts are included into a nickel-plated aluminium box to shield external noise sources. The pre-amplified detector signal is acquired with an oscilloscope (SDA735Zi, LeCroy, bandwidth: 3.5 GHz, sample rate: 40 GS/s). A computer records the data from the oscilloscope and performs the data analysis as detailed below. A function generator (33120A, Hewlett Packard) and a delay generator (DG535, Stanford
Research Systems) provide an appropriate trigger regime for multiplexing the radiation of the QCLs (Fig. 1).

III. DATA PROCESSING AND ANALYSIS TECHNIQUE

Figure 3 shows an entire spectrum as recorded by the oscilloscope. The three laser pulses centred around 2207 cm\(^{-1}\), 1900 cm\(^{-1}\), and 1615 cm\(^{-1}\) along with corresponding absorption features of N\(_2\)O, NO, and NO\(_2\) can be clearly seen. Begin and end of the laser pulses are typically characterised by a fast increase and decrease of the emission. The leading edge is often followed by damped transient oscillations (e.g., QCL 1). Strictly speaking, the emission follows the behaviour of the QCL current as detailed in Ref. 13. The QCL current in turn follows from the match or slight mismatch between the QCL impedance and the laser driver. The response of a QCL to the laser beam is as short as the repetition frequency of the laser pulses. It is omitted for the spectral analysis. From Fig. 3, it is obvious that the response of the laser also affects the end of the pulse. Hence, at least 20 ns around the onset and the end of the laser emission is omitted for the spectral analysis. From Fig. 3, it is obvious that information about the concentration of all three molecular species can be gained in less than 800 ns. This, however, requires proper selection and adjustment of the individual laser pulse length in conjunction with the trigger regime. Note that single absorption features are observed in less than 10 ns. In case of ultra-fast periodic events, this might be considered as lower limit time-resolution of this method.

For single, non-periodic events, a burst mode can be applied, which acquires entire spectra after receiving a trigger pulse for a limited time period, typically only part of a second, see Chap. IV. This implies an inherent time-resolution, which is as short as the repetition frequency of the laser pulses. It should be pointed out that in this case all spectra are acquired without any signal averaging. In case of reduced laser pulse widths of about 50 ns, a repetition rate of up to 400 kHz may be applied corresponding to a minimum time resolution of 2.5 \(\mu\)s. This mode of operation fits to the 2\% duty cycle limit specified by the laser manufacturer (Alpes Laser).

As one can see from Fig. 3, the line width of an absorption feature is of the order of several ns. To measure an absorption line correctly, the sample rate of the oscilloscope should be \(\approx\) depending on the tuning rate of the QCL \(\approx\) at least 10 GS/s. The acquisition of all three spectra along with the required high sample rate leads to a significant number of data points, i.e., of the order of several 10000 data points. Therefore, an on-line data treatment becomes difficult within the available time frame of the plasma pulse(s). In general, the spectra were first subsequently acquired and stored on a standard personal computer hard drive, whereas the data treatment was performed afterwards.

The determination of the number density of absorbing species using laser absorption spectroscopy is based on the relation between the change in the laser intensity \(dl\) along the laser beam \(dz\). This is expressed by the Beer-Lambert law,

\[
dl = -k_\nu \cdot n(z) \cdot I \cdot dz,
\]

where \(k_\nu\) is the absorption cross section at a wavenumber \(\nu\) and \(n(z)\) is the density (per unit volume) of the absorbing species. Assuming an effective number density \(n_{\text{eff}}\) and temperature \(T_{\text{eff}}\) along the line of sight, Eq. (1) can be integrated over the entire absorbing length \(L\) \((l(z = 0) = l_0, l(z = L) = l)\). Integration over a single line yields the expression,

\[
\frac{1}{L} \int_{\text{line}} \ln \left( \frac{l_0}{T} \right) d\nu = - \int_{\text{line}} k_\nu \cdot n_{\text{eff}} d\nu = n_{\text{eff}} \cdot S(T_{\text{eff}})
\]

\[= K(T_{\text{eff}}), \tag{2}\]

where \(K(T_{\text{eff}})\) denotes the integrated absorption coefficient and \(S(T_{\text{eff}})\) denotes the line strength of a particular transition. The line strength can be taken from databases such as, e.g., HITRAN.\(^{14}\) Using Eq. (2), the effective number density connected to an absorption line can be calculated. If nonlinear absorption occurs, the relation \(n_{\text{eff}} = K(T_{\text{eff}}) S(T_{\text{eff}})\)
FIG. 4. The measurement of the pulse jitter $J_1$ and of the line jitter $J_2$ (upper panel) and principle of the determination of the jitter time distribution (lower panel).

requires a correction and a calibration function has to be determined.\textsuperscript{15, 16}

The detection of a sequence of several QCL pulses on one detector requires a careful trigger regime for the individual lasers and, additionally, the consideration of uncertainties in timing with respect to the master trigger. In the case when only one QCL pulse is present, such phenomena are less important. Fluctuations, usually called jitter, are inherent to the laser and are, therefore, inevitable. In what follows two terms are distinguished (Fig. 4), (i) pulse jitter $J_1$: variation of the time between the master trigger and the rising edge of the laser emission and (ii) line jitter $J_2$: variation of the time between the rising edge of the light signal and the absorption line. $J_1$ is mainly caused by the response of the laser driver to the master trigger, while $J_2$ is directly linked to the response of the laser to the applied current pulse, i.e., influenced by ohmic heating and impedance matching. For a characterisation of these two jitter phenomena, the pulse jitters as well as the line jitters of all three lasers were established separately. For this purpose, 1000 spectra of static gas compositions were analysed. It transpires that both jitter effects form a distribution, which can be approximated by a fit function. The lower panel of Fig. 4 shows two typical examples of the time distribution of $J_1$ and $J_2$, respectively. The specific distribution functions of all three QCLs used in these experiments are shown in Figs. 5 and 6. It is clear that the width of the distribution of the pulse jitter, $J_1$, is of the order of a few ns, whereas the width of the distribution of the line jitter, $J_2$, is about one order of a magnitude smaller. From Figs. 5 and 6, it is quite obvious that QCL 3 (NO$_2$ at 1615 cm$^{-1}$) behaves entirely different concerning its jitter distributions compared to QCL 1 and 2 (N$_2$O and NO at 2207 and 1900 cm$^{-1}$).

Particularly the pulse jitter phenomenon prevents the direct application of constant limits for the baseline fitting routine as well as for the calculation of the integrated absorption coefficient $K(T_{ef})$. Hence, at first, the position of the rising edge of each pulse is identified by means of a software algorithm. The first data point of each pulse, which exceeds 10% of the pulse maximum, served to define the edge of the laser emission. Once this point is determined, the main process of the algorithm continues as follows:

1. \textbf{Calculate baseline $I_0$:}
   The baseline $I_0$ has been calculated by fitting a second order polynomial function to the spectrum. Only the ranges of the spectrum which are marked in Fig. 7 have been taken into account for the fitting routine.

2. \textbf{Calculate absorbance:}
   The absorbance $AB$ has been calculated from the baseline ($I_0$) and the pulse spectrum ($I$) using $AB = \ln(I_0/I)$. 

An example is given in Fig. 8. Subsequently, all values of the absorbance AB, which turned out to be smaller than zero, have been set equal to zero, Fig. 8.

Calculate integrated absorption coefficient $K$: The integrated absorption coefficient $K(T_{eff})$ is calculated from absorbance $AB$ using Eq. (2) within the limits of integration given in Fig. 8. It has been validated that the line jitter of about 0.5 ns falls always within these limits. It, therefore, has no influence on the calculation of $K(T_{eff})$.

The integrated absorption coefficient $K(T_{eff})$ is usually considered to be directly proportional to the line strength $S(T_{eff})$ documented in, e.g., HITRAN. It should be mentioned that this is not the case for these experiments, since the absorption line is strongly affected by nonlinear effects, e.g., rapid passage or saturation effects. Therefore, the relation $n \cdot S(T_{eff}) = K(T_{eff})$ requires a correction and a calibration function has to be determined. For this purpose, a gas mixture of 1% of $N_2O_y$ diluted in $N_2$ was filled in the discharge tube at different pressures. The calibration experiments also enable the detection limits of the species of interest to be determined. For the experiments performed in the present study, the detection limits of NO, NO$_2$, and N$_2$O were found to be $4 \times 10^{13}$, $3.4 \times 10^{13}$, and $0.5 \times 10^{13}$ molecules cm$^{-3}$, respectively.

IV. VALIDATION OF THE SYSTEM PERFORMANCE

The performance of the multi-channel spectrometer was validated by absorption spectroscopy measurements of $N_2/O_2$ plasmas with admixes of 0.8% $N_2O_y$. Such fundamental investigations are important to improve the understanding of the chemistry of plasma induced pollution abatement and to verify modelled species concentrations. Therefore, the fast detection of the concentration is of increasing interest for the
FIG. 9. Schematic diagram of the burst mode applied to record the temporal evolution of $N_xO_y$ absorption spectra in pulsed dc plasmas: the spectra of all three QCLs are recorded at once after a master trigger event; where $N$ (max. 3000) of such combined spectra is stored in the memory of the oscilloscope; master trigger pulses are separated by 50 $\mu$s ($f_{\text{Rep}} = 20$ kHz).

study of the temporal evolution of key molecules and their total concentration.

The low-pressure discharge chosen for the performance test here was ignited in a Pyrex tube with an inner diameter of 20 mm and a total length of 60 cm. A detailed description of the geometry and equipment can be found in Ref. 18. The sensitivity limits have been improved by a multi-pass alignment of the laser. Using a set of mirrors outside of the vacuum tube, the laser radiation could pass the plasma three times. The lasers were operated in the burst mode of the system, Fig. 9, applying a pulse repetition frequency of $f_{\text{Rep}} = 20$ kHz. In other words, after 50 $\mu$s a new full spectrum, consisting of the three laser pulses, could be detected. The spectra were recorded into the internal memory of the oscilloscope. The memory size allowed saving up to 3000 spectra.

From the repetition frequency $f_{\text{Rep}}$ and the number of spectra recorded, the total duration of the spectroscopic measurement was 150 ms. From the saved spectra, the species concentration was calculated as described above. No additional spectral averaging was applied.

In Figs. 10 and 11, two examples of the temporal evolution of the concentration of $N_xO_y$ molecules in low-pressure pulsed air plasmas ($p = 1.33$ mbar) are shown. The discharges were ignited with an initial concentration of 0.8% $N_2O$ (Fig. 10) and 0.8% $NO_2$ (Fig. 11) admixed to the dry air. The plasma was ignited 8 ms after the spectroscopic measurements, i.e., the first burst was started. In this way, molecular concentrations are available before, during, and after the plasma pulse. In both discharges, NO is formed as a reaction product. Two pronounced steps are detected during the formation of NO. In both examples (Figs. 10 and 11), the NO density during the plasma pulse levels off at about 50% of the value that is measured in the afterglow phase. After a rapid depletion of the precursor molecules ($N_2O$ and $NO_2$) within about 1 ms, these densities remain constant throughout the plasma pulse. In the afterglow, a relatively fast increase in the $N_2O$ and $NO_2$ ground state densities can be observed within 3 ms. The temperature dependency on the line strength has been taken into account, too. For this purpose, a correction factor has been determined following Ref. 19.

V. ACCURACY AND LIMITATIONS

In general, molecular densities obtained by QCL spectrometers applying the intra-pulse mode under low-pressure conditions are affected by the uncertainties of the calibration routine and by a variety of noise sources. The main error sources are summarized here briefly: First, instabilities of the laser emission, among them the stability of the output power and the tuning rate, the stability of the spectral properties (single or multi-mode emission), and the stability of the spectral position of the emission (i.e., the line jitter mentioned above), increase the uncertainties. Second, the design of the optical

FIG. 10. Time dependence of the $N_2O$ (triangles) and NO (circles) concentrations before, during, and after a single plasma pulse of 5 ms length corresponding to an energy of 1.23 J in a $N_2O$/air dc discharge ($p = 1.33$ mbar). A data point smoothing is applied to guide the eyes (solid lines).
subsystem may induce etalon effects, which complicate the analysis of the baseline. Third, the stability and linearity of the detector module and digitising equipment have to be carefully checked: the noise level of the pre-amplifier, local variations in the sensitivity of the detector element, and possibly saturation effects of the detector element can reduce the general sensitivity of the system. Additionally, the entire system can be sensitive to mechanical vibrations, which can also cause a modulation of the detector signal. Finally, for the examples shown above, a reference gas mixture with a specified \( \text{N}_2\text{O} \) mixing ratio was injected to the tube reactor and controlled by mass flow controllers. Usually, these devices have an accuracy of about 2%.

Since it is quite difficult to estimate the influence of a single parameter, the total error of the system was determined. For that reason, the same spectra used for scrutinising the jitter phenomena were analysed again. The integrated absorption coefficient \( K_{\text{eff}} \) of \( \text{N}_2\text{O} \) at line 2207.62 cm\(^{-1} \), \( \text{NO} \) at line 1900.52 cm\(^{-1} \), and \( \text{NO}_2 \) at line 1615.15 cm\(^{-1} \) were calculated for static gas conditions. The spectra were taken at a repetition frequency of \( \text{f}_{\text{Rep}} = 5 \text{ kHz} \). This analysis yields total relative errors for each molecule, i.e., 15% for \( \text{N}_2\text{O} \) and \( \text{NO} \) as well as 10% for \( \text{NO}_2 \).

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