

Application of quantum cascade laser absorption spectroscopy to studies of fluorocarbon molecules

S Welzel^{1,3}, S Stepanov², J Meichsner² and J Röpcke¹

¹Leibniz Institute for Plasma Science and Technology, Felix-Hausdorff-Str. 2, D-17489 Greifswald, Germany

²Institute of Physics, Ernst-Moritz-Arndt University, Felix-Hausdorff-Str. 6, D-17489 Greifswald, Germany

Email: welzel@inp-greifswald.de

Abstract. The recent advent of quantum cascade lasers (QCLs) enables room-temperature mid-infrared spectrometer operation which is particularly favourable for industrial process monitoring and control, i.e. the detection of transient and stable molecular species. Conversely, fluorocarbon containing radio-frequency discharges are of special interest for plasma etching and deposition as well as for fundamental studies on gas phase and plasma surface reactions. The application of QCL absorption spectroscopy to such low pressure plasmas is typically hampered by non-linear effects connected with the pulsed mode of the lasers. Nevertheless, adequate calibration can eliminate such effects, especially in the case of complex spectra where single line parameters are not available. In order to facilitate measurements in fluorocarbon plasmas, studies on complex spectra of CF₄ and C₃F₈ at 7.86 μm (1269 - 1275 cm⁻¹) under low pressure conditions have been performed. The *intra-pulse* mode, i.e. pulses of up to 300 ns, was applied yielding highly resolved spectral scans of ~ 1 cm⁻¹ coverage. Effective absorption cross sections were determined and their temperature dependence was studied in the relevant range up to 400 K and found to be non-negligible.

1. Introduction

Mid-infrared (IR) laser absorption spectroscopy (AS) has been known as a versatile tool for the detection of molecular species in their fingerprint region (3 - 20 μm) for years, whereas detection schemes employing interband and quantum cascade lasers (QCLs) have only recently been introduced owing to the increasing availability of this new type of lasers. QCLAS in the gas phase is now applied in various fields covering environmental trace gas detection [1-3], detection of toxic species or explosives [4,5], isotope ratio measurements [6], breath gas analysis [7,8] as well as industrial process monitoring [9] and plasma diagnostics [10-12]. The first demonstration of a QCL in 1994 [13], based on the idea of Kazarinov and Suris [14], and further development enable now pulsed or continuous wave, thermoelectrically (TE) cooled, single-mode distributed feedback (DFB-)QCLs to be used in spectrometers.

Different modes can be used to tune a QCL over the spectral transitions of interest. Particularly the *intra-pulse* mode is of high interest for time resolved measurements. For this tuning approach a relatively long laser pulse is used. The internal heating of the QCL causes a frequency down-chirped

³ To whom any correspondence should be addressed.

laser pulse which can be used to acquire a full absorption spectrum within the pulse width of typically a few hundred nanoseconds [15]. However, at low pressure conditions the measured absorption features are affected by an obstacle known as the "rapid passage effect" accompanied by potential power saturation effects [16,17]. Nevertheless, if a sensible normalisation [12] or calibration [9,11] is performed quantitative results can be obtained. This also addresses the required high resolution spectra of molecules with a complex structure which are typically absent or difficult to measure in jet cooled experiments. In this case a calibrated effective absorption cross section determined for a distinct spectral micro-window is also sufficient: Stancu et al. demonstrated this for SiF₄ where a temperature dependence was not observed, because the different contributions from several spectral lines tended to compensate each other [9].

In combination with TE cooled detectors QCL spectrometers became cryogen free and are hence particularly favourable for industrial applications and process monitoring. Moreover, the achievable time resolution with pulsed QCLs is theoretically limited to their pulse width on the nanosecond time scale and thus interesting for basic research on plasma chemical phenomena [11]. The QCL based detection and monitoring of stable and transient molecules in pulsed discharges is therefore an issue in both fields. Studies on pulsed discharges are essential for a better understanding of the plasma chemistry in usually complex industrial discharges such as fluorocarbon containing gas mixtures. IR tunable diode laser absorption spectroscopy in general provides an adequate means for measurements in these discharges [18-21] and QCLAS may facilitate a better time resolution.

Since pulsed fluorocarbon plasmas are of high interest in industry and as a model system for plasma chemical investigations the present study is concerned about the detection of stable fluorocarbons, among them the precursor CF₄. Measurements were carried out in pulsed radio-frequency (rf) discharges at 7.86 μm (1269 - 1275 cm⁻¹) by means of a pulsed QCL. The experimental arrangement is discussed in section 2. Both fluorocarbons, CF₄ and C₃F₈, with absorption features in this spectral range exhibit complex spectra [22-25]. For C₃F₈ only coarse spectra or band integrated absorption cross sections are available in literature. For CF₄ a few IR tunable diode laser measurements, i.e. highly resolved spectroscopic data, around the band origin at 1283 cm⁻¹ exist, but these studies provide only line positions [26,27] or relative absorption cross sections [28]. Measurements around the band origin of CF₄ were presently not feasible because of the almost total absorption of the IR radiation by the precursor molecule under the present experimental conditions. For that reason effective absorption cross sections have been determined for both molecules which is described in detail section 3. This comprises also the definition of two different spectral ranges for the plasma measurements in order to facilitate a discrimination between the contributions from the different species. Furthermore the temperature dependence of the absorption cross sections has been studied which is also discussed in section 3. The results are summarised in section 4.

2. Experimental

The focus of the present study was twofold: (i) the design of a IR spectrometer for time resolved QCLAS measurements in pulsed radio-frequency (rf) discharges [29] and (ii) the determination of necessary calibration data for the absorption features of CF₄ and C₃F₈. Although not necessary in terms of a high time resolution or special trigger events all calibration data have been recorded under identical trigger conditions as for the plasma measurements. This approach was required, since changes in the trigger frequency (e.g., to speed up the data acquisition) also affect the heat sink temperature and hence the output frequency of the QCL.

The entire optical set-up including triggering devices is shown in figure 1. The QCL optics was located on an optical board (OB I) and provided a collimated IR beam which was co-aligned to an existing tunable diode laser arrangement (OB II) [21]. A part of this beam shaping optics was used to guide the QCL beam in double pass configuration (~ 90 cm) through the plasma reactor. A fast TE cooled detector (D₂, neoplas control, VIGO element PDI 3TE-10/12) was placed close to the beam exit at the plasma chamber where the transmitted light was collected with an off-axis parabolic mirror (OAP) (25.4 mm diameter, f/0.64). First, the emitted QCL radiation was collected with an OAP

(50 mm diameter, $f/0.99$). Next, in order to transmit a maximum of the laser output power through the shared ~ 30 mm entrance and exit port of the reactor, the beam diameter was reduced by means of an OAP telescope by a factor of almost 4.

For further analysis of QCL spectra acquired during a chirped laser pulse reliable triggering is essential because a single absorption line typically spreads over less than 5 ns. A jitter of ~ 1 ns between the electrical trigger of the power supply and the detected laser signal induces thus a non-negligible error on the results. In order to tackle this jitter a second fast TE cooled detector (D_1) has been installed in a reference path. The rising edge of the laser pulse deflected by a ZnSe beam splitter onto this detector provided a stable trigger for data acquisition with a fast digitising oscilloscope (LeCroy, WR104Xi).

The pulsed room-temperature DFB-QCL (Alpes Lasers) emitting between 1269 and 1275 cm^{-1} (7.86 μm) was operated with a QCL measurement and control system (Q-MACS, neoplas control) in a water cooled laser housing. All measurements were carried out in the *intra-pulse* mode with a laser pulse width of 300 ns, i.e. a spectral coverage of ~ 1 cm^{-1} , and repetition frequencies between 200 Hz and 1 kHz. The trigger to the QCL power supply was provided by a frequency generator (Hewlett Packard) activated by a master pulse generator (MPG, BNG 555) which normally also served as the trigger for the rf discharge. More details on the trigger scheme can be found in [29]. The measurements were performed at two spectral positions around 1271 cm^{-1} and 1274 cm^{-1} requiring a QCL heat sink temperature of $+17$ $^\circ\text{C}$ and -15 $^\circ\text{C}$ respectively. Relative and absolute calibration of the laser frequency was provided by the fringes of a germanium etalon (25.4 mm, 0.0485 cm^{-1} free spectral range) and interpolation as well as the spectral features of CH_4 and N_2O .

In order to determine effective absorption cross sections σ_{eff} for CF_4 and C_3F_8 corresponding gas mixtures were measured in the plasma reactor. However, the temperature dependence $\sigma_{\text{eff}}(T)$ could not be deduced with this procedure, because a homogeneous external heating of the gas phase in the reactor volume of 20 l was not feasible. Therefore a 25 cm long metallic reference cell wrapped with a heating tape was filled with the studied fluorocarbons and placed inside the beam path (figure 1).

3. Results and discussion

3.1. Basic spectroscopic issues

For measurements in the discharge a spectral position with reduced interferences from other plasma produced transient or stable fluorocarbons was required. Figure 2 (upper panel) shows normalised FTIR spectra for three stable C_xF_y molecules in the considered spectral range. Taking into account the fact that the precursor CF_4 could not be measured at the maximum of its absorption band, since the transmission through the reactor would have been too weak in this case, the spectral window between 1269 and 1275 cm^{-1} has been chosen. Other stable molecules than C_3F_8 may not interfere in this target range. The CF_3 and CF radicals (figure 2, lower panel) would only give minor contributions due to weak absorption lines or low concentrations of CF .

Highly resolved absorbance spectra of CF_4 and C_3F_8 measured in the considered spectral range by means of QCLAS are shown in figure 3. These overview scans consist of several successively acquired parts obtained by tuning the heat sink temperature of the QCL while keeping pulse width and repetition frequency constant. C_2F_6 was also checked but exhibited no considerably absorption in this range. While the C_3F_8 absorbance appears to be smooth over the mapped frequency range strong fluctuations on the CF_4 data are observed. As shown in the inset of figure 3, in the case of CF_4 single lines or a group of lines can still be resolved. In combination with the ringing features of the "rapid passage effect" this spectrum appears as "noisy" whereas the C_3F_8 spectrum is very dense and the mentioned effects smooth out.

Furthermore, two spectral micro-windows (R_1 , R_2) around 1271 cm^{-1} and 1274 cm^{-1} , respectively, are marked in figure 3. As can be clearly seen from the graph the ratio of the absorption cross sections of both stable molecules is reversed for R_1 and R_2 . Thus, if absorption spectra are acquired in these micro-windows under identical discharge conditions this provides a means to distinguish between CF_4

and C_3F_8 contributions and to derive their concentrations. Details on this approach can be found in [29]. In what follows the effective absorption cross sections are calibrated for R_1 and R_2 .

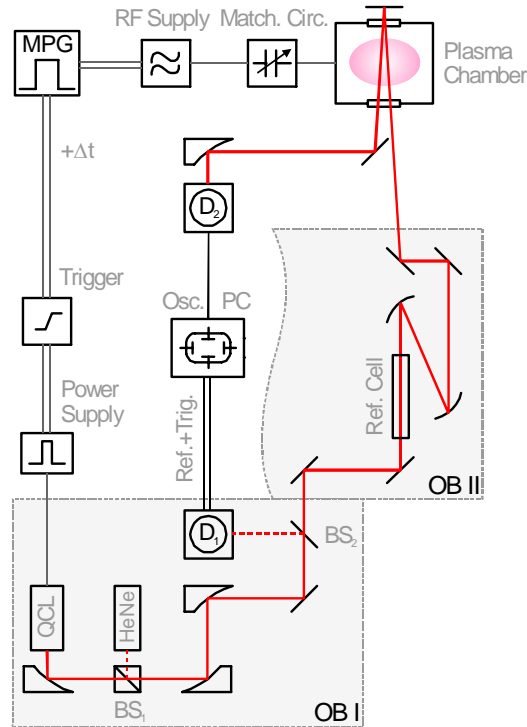


Figure 1: Schematic diagram of the apparatus used for calibration measurements and subsequent plasma diagnostic studies (cf. [29]). Double lines represent trigger lines. (OB - optical board, BS - beam splitter, D - detector, MPG - master pulse generator, Osc. - oscilloscope)

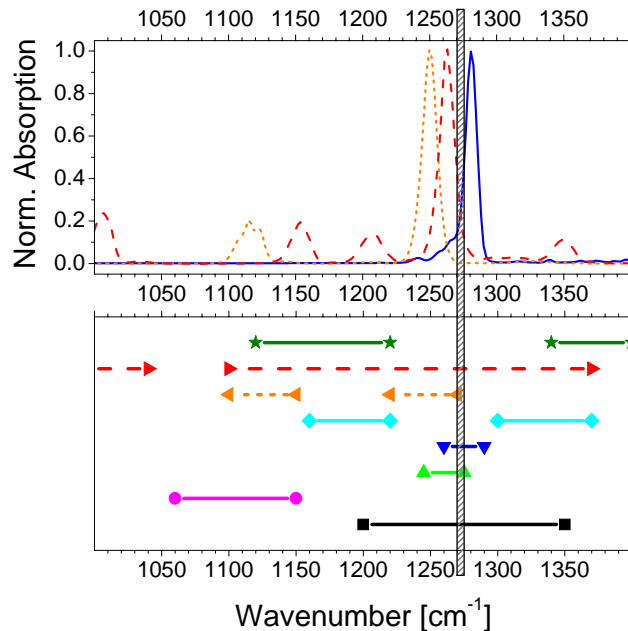


Figure 2: Spectral ranges with absorption features of different fluorocarbon molecules and selected spectral window for the present study (shaded area). Upper: Normalised FTIR spectra of CF_4 (solid line), C_3F_8 (dashed line) and C_2F_6 (dotted line). Lower: Potential interferences of C_xF_y absorption bands (■ - CF , ● - CF_2 , ▲ - CF_3 , ▼ - CF_4 , ◆ - C_2F_4 , ▲ - C_2F_6 , ▲ - C_3F_8 , ★ - CHF_3) [22,25,30,31]

The recorded absorption spectra were affected by three main noise sources: i) noise from the preamplifier of the detector, ii) QCL pulse to pulse intensity fluctuations, and iii) noise induced from the RF generator during plasma measurements, particularly, at the transition points of the pulsed discharge. Averaging over 25 QCL pulses provided a sufficiently smoothed signal for further analysis. For calibration measurements, however, averaging was performed over 600 pulses, mainly to keep the trigger scheme (i.e. the duty cycle) and thus the heat sink temperature and spectral output of the QCL stable. An example for several overlaid single shot spectra and an averaged spectrum (over 600 pulses) is given in figure 4.

3.2. Determination of effective absorption cross sections

In absorption spectroscopy the number density n is inferred from Beer-Lambert's law for a single line from the ratio of the incident and transmitted intensity I_0 and I in a sample with an absorption length L

$$\ln(I_0(\nu)/I(\nu)) = n\sigma(\nu)L \quad (1)$$

where $\sigma(\nu)$ is the absorption cross section. Equation (1) is often used in its integral form over the transition of interest where the frequency dependence of $\sigma(\nu)$ is replaced by an integral value, i.e. by the line strength S

$$\frac{1}{L} \int_{\text{line}} \ln(I_0(\nu)/I(\nu)) d\nu = nS. \quad (2)$$

In the case of dense or complex spectra like CF₄ or C₃F₈ definition (2) is not applicable and $\sigma(\nu)$ should be used. Since literature values with the required spectral resolution and studies on their temperature dependence above room temperature for application to plasma diagnostics were not available the absorption cross sections had to be calibrated. Following (1) the approach is straightforward for stable molecules provided L and the number density n in the sample is known. In this case σ can directly be calculated from the measured $\ln(I_0/I)$. However, due to the influence of the rapidly chirped QCL pulse the deduced absorption cross sections should be considered as effective values σ_{eff} . Typically the measured absorbance and hence σ_{eff} is underestimated in comparison to experiments without "rapid passage effect".

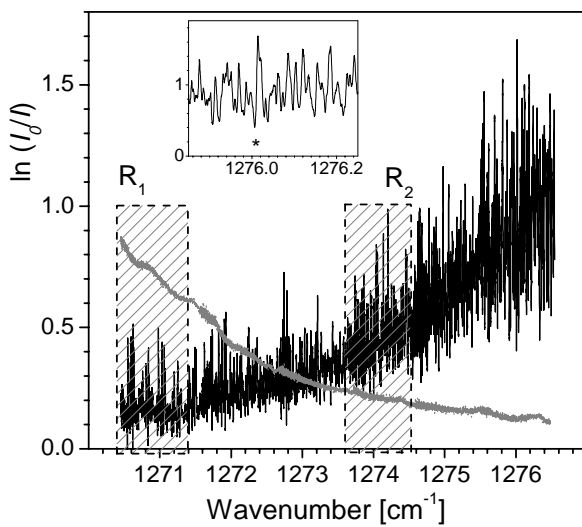


Figure 3: QCL overview spectra of CF₄ (black) and C₃F₈ (grey) measured at 10 Pa with 90 cm absorption length. The spectral micro-windows (R₁, R₂) have been defined for further analysis to discriminate absorption contributions from these two molecules. Inset: Detailed view on partly resolved CF₄ lines with indication of the "rapid passage effect" (asterisk).

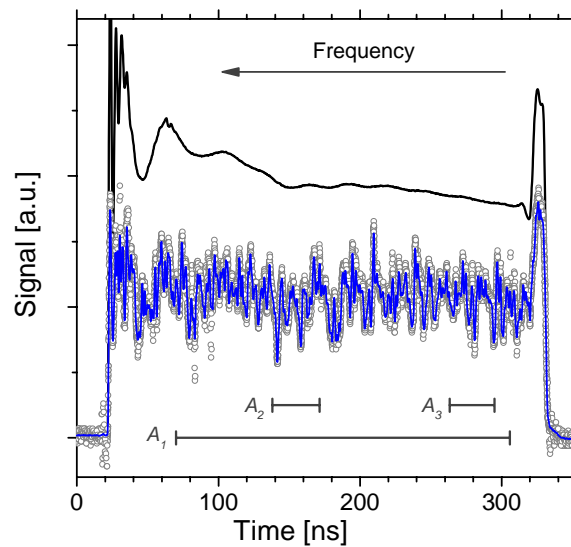


Figure 4: QCL spectra at micro-window R₂ (1274 cm⁻¹). Grey points represent single shot measurements; solid lines represent averages over 600 spectra (baseline and 70 % CF₄ at 10 Pa respectively). For the determination of σ_{eff} the three indicated ranges A₁ - A₃ have been analysed. Note: the frequency scale increases from the right to the left due to the frequency-down chirp.

As discussed in section 2 even a small inevitable jitter of less than 1 ns in the trigger may cause a non-negligible error, since not the peak but the wing of an absorption feature would be analysed at a fixed temporal position in a spectrum. This error can be markedly reduced, if not a distinct point in the spectrum is analysed, but a carefully defined range, i.e. a spectral range $\Delta\nu$ in the order of a few 0.1 cm⁻¹ [9], which is in fact an additional averaging

$$\sigma_{\text{eff}}(\langle\nu\rangle) = \frac{1}{nL} \ln\left(\frac{I_0(\langle\nu\rangle)}{I(\langle\nu\rangle)}\right) = \frac{1}{nL} \ln\left(\frac{\langle I_0(\nu) \rangle \cdot \Delta\nu}{\langle I(\nu) \rangle \cdot \Delta\nu}\right) = \frac{1}{nL} \ln\left(\frac{A_0}{A}\right). \quad (3)$$

Instead of calculating the absorbance from the transmitted intensities I at ν the area (or integral) $A \approx I\Delta\nu$ can be employed in predefined ranges. For the calculation of σ_{eff} the contribution of $\Delta\nu$ cancels out in equation 3. In order to estimate the error caused by this approach three ranges $A_1 - A_3$ of different size have been defined for further analysis (figure 4).

The experiments to deduce σ_{eff} were carried out under flowing gas conditions at two different pressures (10 and 25 Pa) and at room temperature (296 K) in the plasma chamber. The results are shown in figure 5. For the precursor CF_4 effective absorption cross sections σ_{eff} of $4.2 \times 10^{-18} \text{ cm}^2$ and $1.5 \times 10^{-18} \text{ cm}^2$ are gained at 1271 cm^{-1} and 1274 cm^{-1} respectively. Conversely, $1.5 \times 10^{-18} \text{ cm}^2$ and $3.4 \times 10^{-18} \text{ cm}^2$, respectively, are deduced for C_3F_8 . All these values should be considered as average values with a total error of about 15 %. This includes uncertainties in the pressure and gas flow measurements as well as in the data acquisition from the detector, e.g., baseline stability over time. It can be also clearly seen in figure 5 that values obtained from the fairly extended range A_1 appear between those from A_2 and A_3 . Moreover, the σ_{eff} values deduced from A_2 and A_3 reproduce the general trend in the absorbance (figure 3) for all molecules, e.g., $\sigma_{eff}(A_2) > \sigma_{eff}(A_3)$ for CF_4 since A_2 was defined in all cases at higher wavenumber and thus located closer to the band origin than A_3 .

3.3. Temperature dependence

The absorption cross section is typically temperature dependent which has to be considered for plasma measurements. Therefore the relative change of σ_{eff} with temperature has been studied for all ranges $A_1 - A_3$ in both spectral micro-windows, R_1 and R_2 (figure 6).

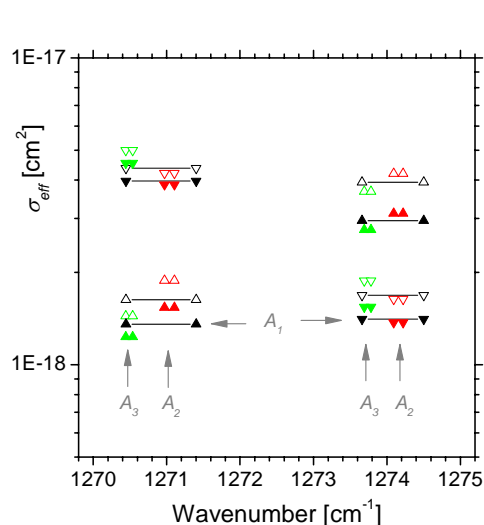


Figure 5: Calculated effective absorption cross section σ_{eff} for CF_4 (triangle up) and C_3F_8 (triangle down) at 10 Pa (open symbols) and 25 Pa (full symbols). The three analysed spectral ranges A_1 (solid line) and A_2, A_3 are indicated by arrows.

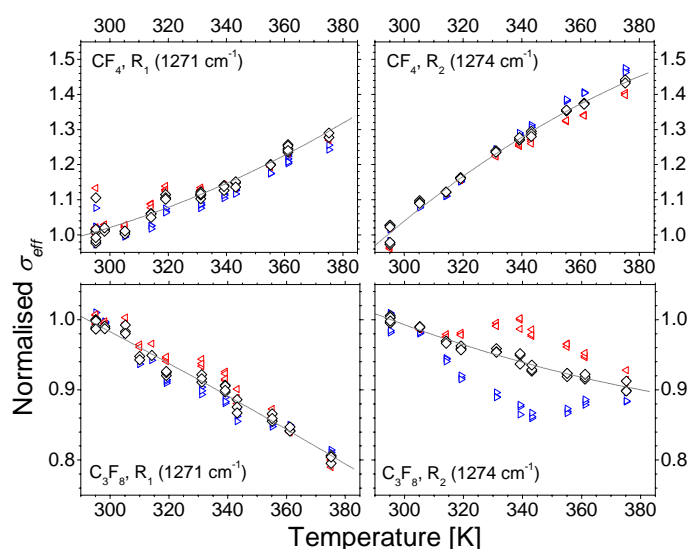


Figure 6: Relative temperature dependence of the calibrated effective absorption cross sections $\sigma_{eff}(T)$ measured at 25 Pa in a 25 cm long reference cell. All three ranges A_1 (\diamond), A_2 (\triangle), and A_3 (\square) were analysed separately. Dashed lines show a parameterisation by second order polynomials.

The measurements were performed under static conditions at 25 Pa for both molecules, CF_4 and C_3F_8 . The reference cell was temperature stabilised by a heating tape which enabled temperatures up to 100 K above room temperature to be achieved. The analysis was made on average spectra (over 150 pulses) for each of the predefined ranges $A_1 - A_3$. Except for C_3F_8 at 1274 cm^{-1} the relative change

of σ_{eff} yielded the same results at these three ranges (figure 6). For CF_4 a monotonic increase of σ_{eff} by 30 % and 50 % is observed in R_1 and R_2 , respectively, for a temperature increase from room temperature to 390 K. In contrast, σ_{eff} decreases with temperature for C_3F_8 , however much less pronounced than for CF_4 . The decrease is less than 20 % up to 390 K. The typical error, mainly caused by uncertainties in the baseline measurements, is about 10 %. The difference in the relative temperature dependence for C_3F_8 at 1274 cm^{-1} between the micro-windows A_2 and A_3 is not clear, but might be still within the general measurement error. In order to discriminate conversion or hysteresis effects a few measurements were repeated during the cooling phase, but no significant difference was found compared to the values obtained during the heating of the cell. In order to apply the obtained temperature dependencies to the calculation of absolute number densities in forthcoming plasma measurements $\sigma_{eff}(T)$ was parameterised by second order polynomials (figure 6). Due to the monotonic behaviour an extrapolation up to 400 K or potentially 425 K might also be regarded as valid.

4. Summary

Spectroscopic studies for time resolved QCLAS measurements on fluorocarbon containing plasmas have been performed, among them the calibration of effective absorption cross sections for CF_4 and C_3F_8 at 1271 cm^{-1} and 1274 cm^{-1} . Since results of measurements with pulsed QCLs are affected by the rapidly chirped laser a careful calibration of effective absorption cross sections σ_{eff} is necessary. It was shown that defining σ_{eff} for a distinct spectral micro-window is preferable because the inherent averaging effect reduces the calibration uncertainties. Calibration in two different spectral ranges is required for the discrimination between CF_4 and C_3F_8 in a discharge. Although the determined σ_{eff} values are expected to be underestimated due to the "rapid passage effect" the order of magnitude for CF_4 ($\leq 5 \times 10^{-18}\text{ cm}^2$) stays in good agreement with non-highly resolved literature values [23,32]. It should be noted that the absolute σ_{eff} values cannot directly be transferred to other QCL systems. Every change in the chirp rate, due to another QCL, or the bandwidth of the detection system (i.e. detector, preamplifier, digitiser) may alter the observed absorbance. Nevertheless, the normalised values still enable quantitative results to be obtained [12] or may be transferred to other systems. Furthermore, a pronounced temperature dependence of σ_{eff} was deduced for CF_4 . The absorption cross section rises by up to 50 % for a 100 K temperature increase above 296 K. While the absorption cross section integrated over the entire band is temperature independent [33] the present results correlate with the tendency of σ which was found below 296 K at the current spectral position [23]. In contrast to CF_4 , the temperature dependence of C_3F_8 is less pronounced and σ_{eff} is decreasing with temperature. The highly resolved C_3F_8 spectra appear as a pure drop of the baseline where no spectral feature can be recognised.

Acknowledgements

This work was supported by the German Research Foundation (DFG) within the framework of the Collaborative Research Centre Transregio 24 "Fundamentals of Complex Plasmas" (SFB-TR 24), projects B2 and B5. The authors thank D Gött, P Druckrey, U Meißner, S Saß, C Senske and F Weichbrodt for valuable technical assistance. The authors are further indebted to Alpes Lasers for their support and S Glitsch for valuable discussions.

References

- [1] McManus J B, Shorter J H, Nelson D D, Zahniser M S, Glenn D E and McGovern R M 2008 *Appl. Phys. B* **92** 387
- [2] Hay K G, Wright S, Duxbury G, Langford N 2008 *Appl. Phys. B* **90** 329
- [3] Tittel F K, Bakhirkin Y, Kosterev A A and Wysocki G 2006 *Rev. Laser Eng.* **34** 275
- [4] Bauer C, Sharma A K, Willer U, Burgmeier J, Braunschweig B, Schade W, Blaser S, Hvozدارa L, Müller A and Holl G 2008 *Appl. Phys. B* **92** 327
- [5] Miller J H, Bakhirkin Y A, Ajtai T, Tittel F K, Hill C J and Yang R Q 2006 *Appl. Phys. B* **85** 391

- [6] Tuzson B, Mohn J, Zeeman M J, Werner R A, Eugster W, Zahniser M S, Nelson D D, McManus J B and Emmenegger L 2008 *Appl. Phys. B* **92** 451
- [7] McCurdy M R, Bakhirkin Y, Wysocki G, Lewicki R and Tittel F K 2007 *J. Breath Res.* **1** 014001.
- [8] Cristescu S M, Persijn S T, te Lintel Hekkert S and Harren F J M 2008 *Appl. Phys. B* **92** 343
- [9] Stancu G D, Lang N, Röpcke J, Reinicke M, Steinbach A and Wege S 2007 *Chem. Vap. Deposition* **13** 351
- [10] Cheesman A, Smith J A, Ashfold M N R, Langford N, Wright S and Duxbury G 2006 *J. Phys. Chem. A* **110** 2821
- [11] Welzel S, Gatilova L, Röpcke J and Rousseau A 2007 *Plasma Sources Sci. Technol.* **16** 822
- [12] van Helden J H., Horrocks S J and Ritchie G A D 2008 *Appl. Phys. Lett.* **92** 081506
- [13] J, Capasso F, Sivco D L, Sirtori C, Hutchinson A L and Cho A 1994 *Science* **264**, 553
- [14] Kazarinov R F and Suris R A 1971 *Sov. Physics Semicond.* **5** 707
- [15] Beyer T, Braun M and Lambrecht A 2003 *Journ. Appl. Phys.* **93** 3158
- [16] Duxbury G, Langford N, McCulloch M T and Wright S 2005 *Chem. Soc. Rev.* **34** 921
- [17] McCulloch M T, Duxbury and Langford N 2006 *Mol. Phys.* **104** 2767
- [18] Haverlag M, Stoffels W W, Stoffels E, den Boer J H W G, Kroesen G M W and de Hoog F J 1996 *Plasma Sources Sci. Technol.* **4** 260
- [19] Haverlag M, Stoffels E, Stoffels W W, Kroesen G M W and de Hoog F J 1996 *J. Vac. Sci. Technol. A* **14** 380
- [20] Gabriel O, Stepanov S and Meichsner J 2007 *J. Phys. D: Appl. Phys.* **40** 7383
- [21] Gabriel O, Stepanov S, Pfafferott M and Meichsner J 2006 *Plasma Sources Sci. Technol.* **15** 858
- [22] NIST Chemistry WebBook (URL = <http://webbook.nist.gov/chemistry>)
- [23] McDaniel A H, Cantrell C A, Davidson J A, Shetter R E and Calvert J G 1991 *Journ. Atm. Chemistry* **12** 211
- [24] Hurley M D, Wallington T J, Buchanan G A, Gohar L K, Marston G and Shine K P 2005 *Journ. Geophys. Res.* **110** D02102
- [25] Poll H U, Hinze D and Schlemm H 1982 *Appl. Spectrosc.* **36** 445
- [26] Suzuki T, Okada H and Fujiyama T 1979 *Bull. Chem. Soc. Japan* **52** 2505
- [27] Takami M 1981 *J. Chem. Phys.* **74** 4276
- [28] Höjer S and May R D 1996 *J. Mol. Spec.* **178** 139
- [29] Stepanov S, Welzel S, Röpcke J, and Meichsner J 2008 *J.Phys.: Conf. Ser.* submitted
- [30] Yamada C and Hirota E 1983 *J. Chem. Phys.* **78** 1703
- [31] Ballard J, Knight R J and Newnham D A 2000 *J. Quant. Spectrosc. Rad. Transf.* **66** 199
- [32] Cruden B A, Rao M V V S, Sharma S P and Meyyappan M 2002 *Plasma Sources Sci. Technol.* **11** 77
- [33] Nemtchinov V and Varanasi P 2003 *J. Quant. Spectrosc. Rad. Transf.* **82** 461