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Kinetic and Diagnostic Studies of Molecular Plasmas Using Laser Absorption Techniques

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Abstract. Within the last decade mid infrared absorption spectroscopy between 3 and 20 µm, known as Infrared Laser Absorption Spectroscopy (IRLAS) and based on tuneable semiconductor lasers, namely lead salt diode lasers, often called tuneable diode lasers (TDL), and quantum cascade lasers (QCL) has progressed considerably as a powerful diagnostic technique for in situ studies of the fundamental physics and chemistry of molecular plasmas. The increasing interest in processing plasmas containing hydrocarbons, fluorocarbons, organo-silicon and boron compounds has lead to further applications of IRLAS because most of these compounds and their decomposition products are infrared active. IRLAS provides a means of determining the absolute concentrations of the ground states of stable and transient molecular species, which is of particular importance for the investigation of reaction kinetics. Information about gas temperature and population densities can also be derived from IRLAS measurements. A variety of free radicals and molecular ions have been detected, especially using TDLs. Since plasmas with molecular feed gases are used in many applications such as thin film deposition, semiconductor processing, surface activation and cleaning, and materials and waste treatment, this has stimulated the adaptation of infrared spectroscopic techniques to industrial requirements. The recent development of QCLs offers an attractive new option for the monitoring and control of industrial plasma processes as well as for highly time-resolved studies on the kinetics of plasma processes. The aim of the present article is threefold: (i) to review recent achievements in our understanding of molecular phenomena in plasmas, (ii) to report on selected studies of the spectroscopic properties and kinetic behaviour of radicals, and (iii) to describe the current status of advanced instrumentation for TDLAS in the mid infrared.

1. Introduction
Low-pressure, non-equilibrium molecular plasmas are of increasing interest not only in fundamental research but also in plasma processing and technology. Molecular plasmas are used in a variety of applications such as thin film deposition, semiconductor processing, surface activation and cleaning,
and in materials and waste treatment. The investigation of plasma physics and chemistry in situ requires detailed knowledge of plasma parameters, which can be obtained by appropriate diagnostic techniques. The need for a better scientific understanding of plasma physics and chemistry has stimulated the improvement of established diagnostic techniques and the introduction of new ones. Methods based on traditional spectroscopy have become amongst the most important because they provide a means of determining the population densities of species in both ground and excited states. The spectral line positions provide species identification while line profiles are often connected with gas temperature while relative intensities provide information about population densities. An important advantage of AS over Optical Emission Spectroscopy (OES) methods is that only relative intensities need to be measured to determine absolute concentrations, avoiding the problems of complete instrument calibration inherent in the OES methods. Absorption spectroscopy has been applied right across the spectrum from the Vacuum Ultra Violet (VUV) to the Far Infra-Red (FIR). Continuously emitting lamps (e.g. the Xe-lamp for the VIS and NIR, and the D$_2$-lamp for the UV) and tuneable narrow-band light sources (e.g. tuneable dye lasers, diode lasers) can be used as external light sources.

In the case where an external light source has much higher intensity than that of the plasma itself, the absorption of radiation can be described by the Beer-Lambert law which is,

$$I_v(l) = I_v(0) \exp(-\kappa(v)l)$$

$I_v(0)$ and $I_v(l)$ are the fluxes of the radiation entering and leaving the plasma, $l$ is the length of the absorbing (homogeneous) plasma column and $\kappa(v)$ is the absorption coefficient. Figure 1 illustrates this situation [1].

![Figure 1. Absorption of external radiation in a plasma according to the Beer-Lambert Law [1].](image)

With the development of tuneable, narrow band light sources such as tuneable dye lasers and infrared diode lasers, these have been substituted for continuous light sources in AS experiments. These narrow band laser sources have the advantage of high spectral intensity, narrow bandwidth, and continuous tuneability over the absorption profile.

The increasing interest in processing plasmas containing hydrocarbons, fluorocarbons or organosilicon compounds has lead to further applications of infrared AS techniques because most of these compounds and their decomposition products are infrared active. FTIR spectroscopy has been used for in situ studies of methane plasmas for a number of years, but it is generally insufficiently sensitive for detecting free radicals or ions in processing plasmas. TDLAS is increasingly being used in the spectral region between 3 and 20 $\mu$m for measuring the concentrations of free radicals, transient molecules and stable products in their electronic ground states. TDLAS can also be used to measure neutral gas temperatures [2] and to investigate dissociation processes of molecular low temperature plasmas [3-6]. The main applications of TDLAS until now have been for investigating molecules and radicals in fluorocarbon etching plasmas [2,5,7], in plasmas containing hydrocarbons [6, 8-14, 60,63] and nitrogen, hydrogen and oxygen [58,59,61,62]. A wide variety of low molecular weight free radicals
and molecular ions has been detected by TDLAS in purely spectroscopic studies e.g. Si$_2^+$ [15] and SiH$_3^+$ [16] in silane plasmas. Most of these spectroscopic results have yet to be applied in plasma diagnostic studies.

Molecular plasmas are increasingly being used not only for basic research but also, due to their favorable properties, for materials processing technology. These fields of application have stimulated the development of infrared spectroscopic techniques for industrial requirements. In order to exploit the capabilities of infrared TDLAS for effective and reliable on-line plasma diagnostics and process control in research and industry, compact and transportable tunable infrared multi-component acquisition systems (IRMA, TOBI) have been developed [17,18]). These systems are mainly focused on (i) high speed detection of stable and transient molecular species in plasmas under non-stationary excitation conditions and (ii) on sensitive (sub-ppb) trace gas detection with the aid of multi-pass absorption cells.

The main disadvantage of TDLAS systems, based upon lead salt diode lasers, is the necessary cryogenic cooling of the lasers (and also of the detectors), because they operate at temperatures below 100 K. Systems based upon lead salt diode lasers are typically large in size and require closed cycle refrigerators and/or cryogens like liquid nitrogen. The recent development and commercial availability of Quantum Cascade Lasers (QCL) offers an attractive new option for infrared absorption spectroscopy.

The present paper is intended to give an overview of recent achievements which have led to an improved understanding of phenomena in non-equilibrium molecular plasmas based on the application of TDLAS techniques. The paper is divided in three main chapters: In chapter 2 special attention is devoted to recent studies of plasma chemistry and reaction kinetics in gas discharges containing hydrocarbons, nitrogen, oxygen and hydrogen. Chapter 3 concerns recent results of spectroscopic properties and kinetic behaviour of selected radicals, which are of special importance for reaction kinetics and chemistry in molecular processing plasmas. The current status of advanced spectroscopic instrumentation is described in chapter 4.

2. Plasma Chemistry and Reaction Kinetics

2.1. General Considerations

Low temperature plasmas, in particular microwave and Radio Frequency (RF) plasmas, have high potential for applications in plasma technology. In molecular low temperature plasmas, the species and surface conversion is frequently governed by high degrees of dissociation of the precursor molecules and high amounts of chemically active transient and stable molecules present. For further insight into plasma chemistry and kinetics a challenging subject is to study the mainly electron induced plasma reactions leading to entire series of different chemical secondary reactions involving the whole group of substances making up the source gas molecules. Hydrocarbon precursors are of special importance, since they are used in a variety of Plasma Enhanced Chemical Vapour Deposition (PECVD) processes to deposit thin carbon films. In all cases, the monitoring of transient or stable plasma reaction products, in particular the measurement of their ground state concentrations, is the key to improved understanding of fundamental phenomena in molecular non-equilibrium plasmas which can in turn be applied to many other aspects of plasma processing.

Transient molecular species, in particular radicals, influence the properties of nearly all molecular plasmas, both in the laboratory and in nature. They are of special importance in several areas of reaction kinetics and chemistry. The study of the behaviour of radicals together with their associated stable products provides a very effective approach to understand phenomena in molecular plasmas. Radicals containing carbon and oxygen are of special interest for fundamental studies and for applications in plasma technology.
2.2. Studies in Planar Microwave Reactors
In recent years several types of microwave discharge containing hydrocarbons as precursor gases have been at the centre of interest. The most recent applications of TDLAS for plasma diagnostic purposes include studies in which many different species have been monitored under identical plasma conditions [19,20]. This experimental data has frequently been used to model plasma chemical phenomena.

![Diagram of experimental setup]

**Figure 2.** Experimental arrangement of a planar microwave plasma reactor (side view) with White cell multiple pass optical arrangement and TDL infrared source. The laser beam path is indicated by dotted lines [20].

Although hydrogen and hydrocarbon containing plasmas with admixtures of oxygen and nitrogen have been extensively studied [1,20] there is still a lack of experimental data concerning the absolute densities of radicals in these discharges. The hydroxyl radical is known to be one of the main oxidising radicals. So far only a few studies have been reported on absolute OH concentrations in plasmas. Mostly, they were measured in the UV spectral region. In the present article quantitative measurements of OH in plasmas by means of TDLAS at 530 cm$^{-1}$ are reported.

The measurements were performed in a planar microwave reactor in Ar/CH$_4$/N$_2$/O$_2$- and Ar/H$_2$/N$_2$/O$_2$- discharges. The reactor was equipped with multi pass cell optics (White cell) in order to increase the absorption length (figure 2). A mirror spacing of 1.5 m and 40 passes gave an effective absorption length of 60 m. Details on the experimental setup, data acquisition and data processing can be found elsewhere [6,17,18,21]. The pressure was kept constant at 1.5 mbar during the experiments. With a typical input power of 1.5 kW and 420 sccm Ar two different gas mixtures were used: (0 ... 20) sccm H$_2$, 20 sccm N$_2$ + O$_2$ and 10 sccm CH$_4$, 10 sccm N$_2$, (0 ... 20) sccm O$_2$. In both cases the oxygen content in the discharge was varied. The molecules detected are summarised in table 1.
Table 1. Detected species and their line positions for two different gas mixtures.

| Molecule | ν [cm⁻¹] | Molecule | ν [cm⁻¹] |
|----------|----------|----------|----------|
| H₂O      | 1884.57  | CH₄      | 1327.07  |
| NH₃      | 965.50   | H₂O      | 1884.57  |
| NO       | 1884.30  | CO       | 2254.75  |
| OH       | 532.14   | CO₂      | 664.24   |
| NH₃      | 965.5    | NO       | 1884.3   |
| NO       | 1884.3   | HCN      | 1327.02  |
| H₂CO     | 2802.77  | OH       | 532.14   |

2.2.1. Ar/H₂/N₂/O₂ plasma

For an Ar/H₂ plasma H₂O and - depending on the oxygen flow - NH₃ or NO turned out to be the most abundant species (figure 3). The mole fraction of water was typically higher than 1 %.

![Figure 3. Concentrations of the most abundant species and of OH in an Ar/H₂/N₂/O₂ plasma (420 sccm Ar, 10 sccm H₂, (0...20 sccm) N₂ + O₂; 1.5 mbar). [NH₃] was below the detection threshold for oxygen flows higher than 6 sccm.](image)

Clearly the ammonia concentration is strongly affected even by quite small amounts of oxygen in the plasma, while the NH₃ concentration decreases as the NO and OH concentrations increase. This behaviour can be qualitatively understood in the light of three reactions (eq. (1) - (3)) which are most likely to occur [22]. Due to the impact of O and OH radicals (eq. (1) and (2)) NH₃ is effectively destroyed. When varying the hydrogen flow of the system (figure 4) the drop in [NH₃] is not so
pronounced for a higher hydrogen content than for a lower one. There is still a possibility to form NH₃ from NH₂ which is more probable for higher H₂ flows.

\[\text{NH}_3 + \text{O} \rightarrow \text{NH}_2 + \text{OH} \quad (1)\]

\[\text{NH}_3 + \text{OH} \rightarrow \text{NH}_2 + \text{H}_2\text{O} \quad (2)\]

\[\text{N} + \text{OH} \rightarrow \text{NO} + \text{H} \quad (3)\]

The longer NH₃ is present in the discharge the longer OH can build up. Finally, a slight maximum of the OH concentration was found for H₂/O₂ ratios of 1:1. For higher oxygen flows NH₃ can no longer act as a source for OH, especially at hydrogen flows lower than 20 sccm. So the decrease of [OH] should be mainly attributed to the loss channel (3) which may also explain the ambiguous behaviour of NH₃ and NO when increasing the oxygen content in the system.

![Figure 4](image_url)

**Figure 4.** Concentrations of OH (left panel) and NH₃ (right panel) for Ar/H₂/N₂/O₂-plasmas (420 sccm Ar, (0 ... 20) sccm H₂, (0 ... 20) sccm N₂ + O₂; 1.5 mbar) plasmas.

2.2.2. Ar/CH₄/N₂/O₂ plasma

Apart from the precursor molecule, the most abundant species in a methane containing plasma were determined to be H₂O and CO (figure 5). When comparing the amount of CH₄ added to the discharge and the measured CO concentration values it turns out that methane is mainly converted into CO and only to a lesser extent into HCN and CO₂. However, the CO₂ selectivity, i.e. [CO₂] / ([CO] + [CO₂]), is increasing with a higher amount of oxygen in the discharge.
In order to elucidate the underlying reactions one of the well known intermediate molecules for the conversion of CH₄, i.e. formaldehyde (H₂CO), and the concentration of OH were measured, too. For higher oxygen flows less H₂CO can be found in the discharge whereas the concentration of the OH radical is increasing.

The behaviour of the carbon containing molecules mentioned above can be understood qualitatively in terms of a model which was developed for a H₂/CH₄/O₂ plasma [6,23]. Although the bath gas was changed (Ar instead of H₂) the major reactions for the conversion of CH₄ (eq. (4)) should still be valid since mainly O or OH are involved. The prediction of the model calculation for the OH concentration is $5 \cdot 10^{11} \text{cm}^{-3}$ which agrees well with the values obtained in this study.

$$\begin{align*}
\text{CH}_4 & \rightarrow \text{CH}_3 \rightarrow \text{H}_2\text{CO} \rightarrow \text{HCO} \rightarrow \text{CO} \rightarrow \text{CO}_2 \\
\end{align*}\tag{4}$$

After the dissociation of CH₄ into CH₃ the main conversion path is terminated at H₂CO at low oxygen flows. With a higher oxygen content more radicals (O, OH) are available which first leads to a conversion into CO and finally into CO₂. Formaldehyde as the intermediate molecule is further converted leading to the observed maximum in [H₂CO] at lower oxygen flows. The more CO₂ is produced with higher oxygen flows - as the final product of the CH₄ conversion path - the more the CO₂ selectivity increases. However all the measurements were performed in a discharge regime which is still oxygen poor [6]. As a result CO remains the most abundant molecule due to an incomplete conversion of CH₄.

**Figure 5.** Most abundant molecular species and their concentrations in an Ar/CH₄/N₂/O₂-plasmas (420 sccm Ar, 10 sccm CH₄, 10 sccm N₂, (0 ... 20) sccm O₂; 1.5 mbar).
3. Kinetic Studies and Molecular Spectroscopy of Radicals

3.1. Line strengths and transition dipole moment of CH₃
This section describes a new measurement of μ₂ for the ν₂ fundamental band of the methyl radical in order to resolve the differences between earlier experimentally measured values and between experiment and theory. The method used for determining the absolute methyl radical concentrations was the same as that used by Yamada and Hirota [8]. However, integrated intensities and many more methyl radical lines were used. Furthermore the kinetic conditions were more precisely specified and the temperature determined more exactly. The resulting value of μ₂ is now in much better agreement with theory.

The methyl radical has no electric dipole allowed rotational transitions because of its D₃h symmetry and so IR spectroscopy is one of the few suitable methods for its detection. The determination of methyl radical concentrations in terrestrial and astronomical sources using IR spectroscopy relies on the availability of accurate line strengths and transition dipole moments. The ν₂ band of CH₃ is the strongest of its IR active fundamentals and particularly useful for quantitative measurements. The need for a more accurate and precise value of μ₂ has been highlighted by the measurements of CH₃ in the atmospheres of Saturn [25], Neptune [26] and in the interstellar medium [27].

The experimental set-up of the planar microwave plasma reactor with the optical arrangements used for the methyl transition dipole moment study is comparable to that shown in figure 3. Details of the diode laser spectrometer, IRMA, and discharge absorption cell have been reported elsewhere [17,21]. The methyl radical was produced in mixtures of tertiary butyl peroxide ([CH₃]₃CO) and argon at total pressure of 1 mbar. Two kinds of experiments were performed: (a) time dependent measurement of the decay of the absorption coefficient when the discharge was turned off, to obtain absolute methyl concentrations and (b) measurements of the absorption coefficients of different rovibronic lines. In total ten lines were studied in the fundamental band, seven in the first hot band, and one from the second hot band. A survey spectrum of the Q-branch region of the ν₂ fundamental band is shown in figure 6.

![Survey spectrum showing several (J = K) Q branch lines of the ν₂ fundamental of the CH₃ free radical around the band origin. The spectrum represented by the dashed line is a calibration spectrum from N₂O and CO₂ [28].](image_url)

**Figure 6.** Survey spectrum showing several (J = K) Q branch lines of the ν₂ fundamental of the CH₃ free radical around the band origin. The spectrum represented by the dashed line is a calibration spectrum from N₂O and CO₂ [28].
In order to derive accurate line strengths and the transition dipole moment, it is necessary to obtain the absolute concentration of the methyl radical and its temperature in the discharge. The decay method was the experimental approach for methyl radical concentration measurements. The plasma was switched on and off for periods of ten seconds and the decay of the methyl radical signal measured during the off period with ms time resolution [29,30]. The absolute concentration was obtained from the decay of the integrated absorption coefficient and the recombination rate constant. It is well known from numerous kinetic studies that the main loss channel under the conditions used here is self recombination via a three body reaction. Hence by measuring the integrated absorption coefficient as a function of time and knowing the value of the recombination rate constant the absolute concentration of the methyl radical can be obtained.

The rate constant $k_1$ for the self recombination reaction of methyl radicals has been extensively investigated in experimental and theoretical work [31-38]. The selected value for $k_1$ was based on the compilation of Baulch et al. and was appropriate for the specific temperature and argon concentration [28,39]. The translational, rotational and vibrational temperatures of the methyl radical were measured. A near similarity of $T_{\text{trans}}$ and $T_{\text{rot}}$ was observed. Based on experimental results the vibrational temperature was found to be in equilibrium with the translational and rotational temperature within experimental uncertainties i.e. $T_{\text{vib}} = 600$ K. For details see refs. [28,40].

Figure 7 shows as an example of the temperature dependence of the line strengths of several transitions from the lower energy levels. The line strengths have been calculated from the experimental data. It should be mentioned, that the line strength dependencies can be used to determine the gas temperature when two absorption coefficients are measured. Measuring the ratio of two absorption coefficients is the same as the ratio of their line strengths. Taking a measured absorption coefficients ratio, the temperature for which their line strength ratio is the same determines the rotational temperature. In recent measurements (not shown here) which were done in a hot filament diamond deposition reactor [41,42] the gas temperature has been determined from the ratio of $Q(6,6)$ and $Q(12,12)$. The gas temperature was found to be about 800 K near the deposition substrate, which was essentially the same as the temperature measured by a thermocouple probe.

![Figure 7. Line strengths, $S$, for different Q branch transitions of CH$_3$ as a function of temperature. Values calculated from the reference temperature values at 296K [28].](image-url)
The line strengths of the nine Q branch lines in the \( \nu_2 \) fundamental band of the methyl radical in its ground electronic state were used to derive a more accurate value of the transition dipole moment of this band: \( \mu_2 = 0.215(25) \) Debye. Improved accuracy over earlier measurements of \( \mu \) was obtained by integrating over the complete line profile instead of measuring the peak absorption and assuming a Doppler line width to deduce the concentration; and the derivation of more accurate temperatures by examining a large number of lines. In addition a more precise value for the rate constant for methyl radical recombination than available earlier was employed. The new value of \( \mu_2 \) is in very good agreement with high quality \textit{ab initio} calculations. Furthermore, the ratio of the transition dipole moments of the \( \nu_2 \) and \( \nu_3 \) fundamental bands in the gas phase is now in highly satisfactory agreement with the ratio determined for the condensed phase. Figure 8 shows the chronological summary of calculated and measured values of \( \mu_2 \) the transition dipole moment of the \( \nu_2 \) fundamental band.

\[
\mu_{(\nu=1-0)} \text{[D]}
\]

0.00 0.05 0.10 0.15 0.20 0.25 0.30 0.35 0.40 0.45

C. Yamada, E. Hirota and K. Kawaguchi
\textit{estimated} (1981) [24]

C. Yamada and E. Hirota
\textit{measurement} (1983) [8]

P. Botshwina, J. Flesch and W. Meyer
\textit{wavefunctions calculation} (1983) [43]

J. Wormhoudt and K. E. McCurdy
\textit{measurement} (1989) [44]

J. Pacansky, W. Koch and M. D. Miller
\textit{theoretical calculations} (1991) [45]

G. D. Stancu, P. B. Davies, J. Röpcke
\textit{measurement} (2005) [28]

\( k_1 \) - new data

Figure 8. Chronological summary of calculated and measured values of \( \mu_2 \) the transition dipole moment of the \( \nu_2 \) fundamental band of CH\(_3\) [28].

3.2. Molecular spectroscopy of the CN Radical

The CN radical is of fundamental importance in laboratory spectroscopy and in astrophysics. Electronic emission spectra arising from the red (A\(^{2}\Pi \rightarrow X^{2} \Sigma^+\)) and violet (B\(^{2} \Sigma^+ \rightarrow X^{2} \Sigma^+\)) band systems excited in flames and discharges have been studied in the laboratory over decades while CN spectra have been detected in the atmospheres of stars and in the interstellar medium. Most recently the electronic band systems have been very extensively measured and analysed in emission [46,47] using high resolution Fourier transform spectroscopy.

Rotationally resolved spectra of the fundamental band of the CN free radical in four isotopic forms have been measured using tuneable diode laser absorption spectroscopy [126]. The source of the radical was a microwave discharge in a mixture of isotopically selected methane and nitrogen diluted
with argon. The lines were measured to an accuracy of $5 \times 10^{-4}$ cm$^{-1}$ and fitted to the formula for the vibration rotation spectrum of a diatomic molecule, including quartic distortion constants. The band origins of each of the isotopomers from the five parameter fits were found to be $^{12}$C$^{14}$N: 2042.42115(38) cm$^{-1}$, $^{13}$C$^{14}$N: 2000.08479(23) cm$^{-1}$, $^{12}$C$^{15}$N: 2011.25594(25) cm$^{-1}$, $^{13}$C$^{15}$N: 1968.22093(33) cm$^{-1}$ with one standard deviation from the fit given in parenthesis. Some of the lines showed a resolved splitting due to the spin rotation interaction. This was averaged for fitting purposes. The average equilibrium internuclear distance derived from the $v = 0$ and $v = 1$ rotational constants of the four isotopomers is 1.171800(6)Å which is in good agreement with the value determined from microwave spectroscopy. Figure 9 shows a stick diagram of all the lines measured in the four isotopic forms and their intensities calculated for a rotational temperature of 950K [48].

![Figure 9](image_url)

**Figure 9.** Stick diagrams showing the detected absorption lines from the fundamental band of CN and their intensities at 950 K: (a) $^{12}$C$^{14}$N and $^{13}$C$^{14}$N (dotted lines) and (b) $^{12}$C$^{15}$N and $^{13}$C$^{15}$N (dotted lines) [48].

4. Quantum cascade laser absorption spectroscopy for plasmas diagnostics and control

4.1. Plasma Diagnostics with high time resolution

The recent development of pulsed QCLs and their commercial availability offer promising new possibilities for infrared absorption spectroscopy [49-51]. Pulsed QCLs are able to emit mid infrared radiation at near room temperature operation. Compared to lead salt laser systems, QCL systems are very compact mid infrared sources characterized by narrow line width combining single-frequency operation and considerably higher powers, i.e. tens of mW. The output power is sufficient to combine them with thermoelectrically cooled infrared detectors, which permits a decrease of the apparatus size and provides an opportunity to design compact cryogen-free mid infrared spectrometer systems. The positive features of quantum cascade laser absorption spectroscopy (QCLAS) opens up new fields of application in research and industry. Recently a compact quantum cascade laser measurement and control system (Q-MACS) has been developed (figure 10 and 11) for time-resolved plasma diagnostics, process control and trace gas monitoring which can be used as platforms for various applications of QCLAS [1,52].
Nowadays QCLAS has been used to detect atmospheric trace constituents or trace gases in exhaled breath. Furthermore, it has already been successfully applied to the study of plasma processes, e.g., of microwave and RF discharges [53, 54]. Of special interest for all hydrocarbon-based processes is the capacity to detect transient molecules like the CH$_3$ radical, as the supposed key growth species, by means of QCLAS (figure 12).

![Figure 10. Q-MACS Basic with optical collimation module.](image1)

![Figure 11. New generation of compact QCLAS equipment.](image2)

The scan through an infrared spectrum is commonly achieved by two different methods. In the inter pulse mode a bias DC ramp is applied to a series of short laser pulses of a few ten nanoseconds [30, 55]. Another option is the intra pulse mode, i.e., the scanning in single, longer pulses acquiring an entire spectrum [56]. Since this scan is performed in tens up to a few hundred nanoseconds a time resolution below 100 ns has become possible for quantitative in-situ measurements of molecular concentrations in plasmas for the first time. Therefore it fits very well to measurements of rapidly changing chemical processes. Based on this new approach for fast in-situ plasma diagnostics the time decay of NO in single discharge pulses has been studied (figure 13). At the centre of interest was the kinetics of the destruction of NO in a pulsed DC discharge. It transpired that the QCLAS

![Figure 12: Detection of the CH$_3$ radical ($v_2$ band) by means of QCLAS (solid) using the intra pulse mode. For comparison a reference spectrum of N$_2$O (dashed) and the line strengths at 650 K are given [28].](image3)

![Figure 13: Decay of the NO absorbance in a pulsed DC discharge containing 0.91 % NO in an Ar - N$_2$ mixture for static (full) and flowing (open) gas conditions [57].](image4)
measurements, accompanied by simplified model calculations, serve as a powerful non-invasive temperature probe with a remarkable time resolution up to the sub-microsecond time scale giving insight into the gas heating dynamics [57].

4.2. In situ monitoring of silicon plasma etching

During the last forty years plasma etching has become a fundamental feature for processing integrated circuits. The optimization of the plasma chemistry of the etching processes includes the identification of the mechanisms responsible for plasma induced surface reactions combined with the achievement of uniformity in the distribution of molecules and radicals for homogeneous wafer treatment.

In etch plasmas used for semiconductor processing concentrations of the precursor gas NF₃ and of the etch product SiF₄ were measured on-line and in situ using a new experimental arrangement, designated the Q-MACS Etch System, which is based on quantum cascade laser absorption spectroscopy (QCLAS). In addition, the etch rates of SiO₂ layers and of the silicon wafer were monitored including plasma etching endpoint detection. For this purpose the Q-MACS Etch System functioned in an interferometric mode. The experiments were performed in an industrial dual frequency capacitively coupled magnetically enhanced reactive ion etcher (MERIE), which is a plasma reactor developed for dynamic random access memory (DRAM) technologies. The absorption cross sections of SiF₄ and NF₃ have been determined to be \( \sigma = 7.7(±0.7) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1} \) and \( \sigma = 8.7(±0.8) \times 10^{-20} \text{ cm}^2 \text{ molecule}^{-1} \), respectively, in the spectral range 1028 ± 0.3 cm⁻¹.

**Figure 14.** Experimental arrangement of the MERIE plasma etching reactor and the 3 channels Q-MACS Etch system: a) side access and b) top access monitoring [55].

The quantum cascade laser system Q-MACS Etch consists of a pulsed infrared QCL source with the laser wavelength tuneable in the range 1027 - 1032 cm⁻¹, optical components, detectors and data acquisition cards controlled by a PC. The laser driver used was a Q-MACS Basic [1,52].
MACS Basic provides a laser pulse width tuneable between 10 - 255 ns and a repetition frequency between 100 Hz - 1 MHz. From figure 14 it can be seen that the IR beam is split into three channels using two IR transparent ZnSe beam splitters (BS). The main part of the beam is coupled into an IR fibre using an off axis parabolic (OAP) mirror, and then collimated into the plasma reactor using either lenses or OAPs. The second channel, operating as a pulse normalisation channel, is used to reduce the fluctuation intensities of the QCL from pulse to pulse. In the third channel a reference spectrum of C2H4 is measured through a reference gas cell in order to calibrate the spectral region and to correct drifts of the laser frequency due to temperature instability of the laser chip. Industrial requirements, such as (i) no open optical path and (ii) the availability of just one optical access port makes coupling the infrared beam into the reactor a challenging task. The solution presented here is based on the use of (a) mid infrared fibres and (b) internal reflections in the reactor chamber.

In figure 15 an example of on-line in situ monitoring of the SiF4 absorbance during a deep trench etch processes is shown. Figure 15 (c) shows the enlarged temporal behaviour of the measured concentration. Changes of the concentration due to plasma density over the wafer are clearly visible and further prove the sensitivity and time resolution of the method.

This first application of a quantum cascade laser arrangement for monitoring of industrial etch processes has opened up a challenging new option for control of demanding semiconductor production applications. Focused on sensitive and fast concentration measurements of key molecular components, while ensuring compactness, robustness and long term stability, this new class of process control equipment has the potential to become implemented into other fields of plasma technology [55].

Figure 15. SiF4 absorbance monitoring using QCLAS for: a) a complete plasma etching process; b) complete plasma etching process with injection of 2% SiF4; c) SiF4 concentration variation due to changes of the magnetic field. The experiments were performed using a process wafer [55].

5. Summary and conclusion
During the past few years a variety of phenomena in molecular non-equilibrium plasmas in which many short-lived and stable species are produced have been successfully studied based on diode laser absorption techniques in the mid infrared spectral range, with which the present review article is
concerned. It has been possible to determine absolute concentrations of ground states using spectroscopy thereby providing a link with chemical modelling of the plasma, the ultimate objective being to better understand the chemical and reaction kinetic processes occurring in the plasma. The other essential component needed to reach this objective is to determine physical parameters of the plasma, as for example, temperatures, degrees of dissociation and dynamics of reaction kinetic processes. The present article discusses methods for achieving this. The need for a better scientific understanding of plasma physics and chemistry has stimulated the application of TDLAS, which has proven to be one of the most versatile techniques for studying molecular plasmas. Based on the recent development of quantum cascade lasers the further spread of this method of high resolution mid infrared spectroscopy to industrial applications has become a reality.

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