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Tunable Diode Laser Spectroscopy

— a High Resolution Analysing Technology for
Pollutant Trace Gases —

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(Pages 10–19)

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1. Introduction

Remote sensing of natural and urban atmosphere using spectroscopic techniques at infrared wavelengths, where every molecular species has characteristic absorption bands owing to its rotational and vibrational motions, greatly increased our knowledge of its detailed composition and structure. The sophisticated application of infrared absorption spectroscopy to the different problems in gaseous remote sensing provides a selective and sensitive means to monitor molecular concentrations in a direct and nondestructive way. This was possible due to two events: the first of these was and is up to now the development of sensitive, fast-response detectors, tunable laser light sources with high radiation densities, compatible optical materials and fast computers. The second was the discovery that man-made chemicals can affect a wide range of scales of environmental concern: from global (CO₂ - green house effects, N₂O - induced stratospheric ozone depletion and the overall radiation balance of our planet), through continental (SO₂ and NO_x - induced acid rain), to regional (NO_x - and unburned hydrocarbon -induced photochemical smog) and local events (CO-, NO - health effects, HCl and H₂SO₄ acid corrosion, C₆H₆ and 1,3 butadiene induced cancer, PAH and chlorinated hydrocarbon health effects a.s.o.).

The identification of the species from the measured absorption peculiarities in complex gaseous mixtures is based on the macroscopic absorption law by Lambert-Beer:

$$I(\nu, z) = I_0 \cdot \exp(-k(\nu) \cdot c \cdot z) \quad \dots\dots (1)$$

where I , I_0 denotes the absorbed and initial light intensities at wave number ν , $k(\nu)$ is the specific absorption coefficient normalized to the gas concentration c (dimension $\text{cm}^{-1} \cdot \text{cm}^3$) or the gas pressure ($\text{cm}^{-1} \cdot \text{atm}^{-1}$) and z is the thickness of the absorbing medium.

The further theoretical treatment splits the absorption coefficient of a single absorption line in the vicinity of a line center ν_0 in a product of the wave number independent line strength or the integrated absorption coefficient S and the normalized line shape function $\Phi(\nu - \nu_0, \Delta\nu)$, i.e.

$$k(\nu) = S \cdot \Phi(\nu - \nu_0, \Delta\nu_{L,D,V}(\text{FWHM})) \quad \dots\dots (2)$$

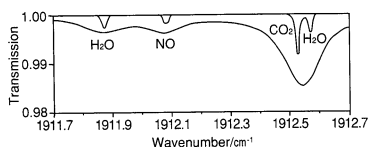


Fig. 1 Computed transmission spectra of exhaust gas with 15% CO₂, 15% H₂O and 10ppm NO for 20cm optical path length at atmospheric pressure (lower trace) and 38Torr (upper trace)

The line shape functions most commonly used are the Lorentz profile for natural and collisional broadened (index L) lines with full line width at half maximum $\Delta\nu_L$ (FWHM), the Doppler profile (index D) with $\Delta\nu_D$ (FWHM) and the convolution of both, the Voigt profile (index V) with $\Delta\nu_V$ (FWHM).

If more than one molecular species i contributes to the absorption of the radiation at



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- 1970-1976:
Low temperature physics in semiconductors.
- 1976-1986:
Crystal growth, fabrication and properties of lead chalcogenide diode lasers.
- 1987-:
Application of diode lasers in environmental research high resolution molecular spectroscopy of gaseous pollutants using diode lasers.

a given wavenumber, then $k(\nu)$ is taken over all species i , active at ν :

$$k(\nu) = \sum_i k_i(\nu) \quad \dots\dots (3)$$

Either the determination of the molecular parameters ν_0 , S , Φ and $\Delta\nu$ (FWHM) or of the gas concentration c for a given path length z in equ.1 and equ.2 for all absorption lines and gases requires precise spectroscopic transmission measurements within a range of specific absorption. This is demonstrated in Fig.1¹⁾. Without the knowledge of the spectroscopic line positions, line strengths and line broadening parameters the analysis of a measured transmission spectrum similar to the here computed simple gas mixture of H₂O, NO and CO₂ at atmospheric pressure would be impossible or very inexact. The interpretation of such complex spectra is more than ever a task involving basic research groups and essentially stimulates the further development of theoretical molecular physics .

Therefore in the last decade precise, quantitative measurements of molecular parameters and gas concentrations for groups of related molecular species were started. In Table I are listed some of the interesting molecules in earths atmosphere, detectable by infrared techniques. Typical concentrations of minor constituents are in the ppmv-, of trace gases in the ppbv- and subppbv- - regions.

Major constituents	N ₂ , O ₂
Minor constituents	H ₂ O, CO ₂ , O ₃ , N ₂ O, CO, CH ₄
Trace gases:	
nitrogen oxides	NO, NO ₂ , N ₂ O ₅ , HNO ₃ , HO ₂ NO ₂
halogens	CCl ₃ F, CCl ₂ F ₂ , CHClF ₂ , CCl ₄ , CF ₄ , SF ₆ , HF, HCl, CH ₃ Cl, ClONO ₂ , COF ₂ , HOCl
sulphur oxides	OCS, SO ₂
others	H ₂ S, HCN, NH ₃ , C ₂ H ₂ , C ₂ H ₄ , C ₆ H ₆ ,

Table 1 Atmospheric molecules detectable by IR remote sensing²⁾

The ability to determine the concentrations of these various species simultaneously, in-situ, nonintrusive and with fast response are some of the most important advantages of high resolution infrared absorption techniques. The Infrared Tunable Diode Laser Absorption Spectroscopy (IR-TDLAS) and the Infrared Fourier Transform Spectroscopy (IR-FTS) in the best way fulfil the demands, mentioned above. While the IR-FTS is widely used for overall view spectra in the multi-component gaseous analysis (spectral resolution of instruments not better than 10^3 cm^{-1} at reasonable dimensions and prices), the IR-TDLAS is a spectroscopic finger print method. It allows to determine very low molecular concentrations of different species in smaller wavelength regions, with high spectral resolution better than 10^4 cm^{-1} , fast response times better than 10^{-3} s, comparable small dimensions of the instruments and enables open path sensing.

The aim of this paper is to give a short report of modern trends in TDLAS and its applications in the last semi-decade.

2. Principles of TDLAS

Principles, instrumentation and performance of the TDLAS - technique are determined by the properties of the diode lasers, of course. To demonstrate the principles of TDLAS in Fig.2 and Fig.3 the experimental arrangements for an inexpensive, portable ammonia monitoring system based on GaAs diode lasers³⁾ and a high resolution diode laser spectrometer operating with different diode laser compounds are compared.⁴⁾

In Fig. 2 the GaAs diode operating near 1.5 μm (Mitsubishi ML 9702) is mounted on a Peltier cooling element (ILX LDM-4412). The temperature and current were regulated by a commercial diode controller (ILX LDC-3742). After focussing by plastic lenses the laser beam was splitted through a sample cell (30 cm length) and a reference cell (100cm length). The beams were detected by In GaAs photodiodes, the signals preamplified and sent to lock-in amplifiers. The diode laser controller and so the photosignal lock-ins were connected to a computer or a single micro-processor with the necessary control software. By current tuning the laser temperature was changed and the most intensive rovibrational line of ammonia near 6400 cm^{-1} was chosen and calibrated with a confocal etalon and the known HDO and D₂O absorption lines. In order to achieve maximum sensitivity frequency modulation for the diode laser and 2f detection for the sample beam was utilized. Because of temperature fluctuations the laser frequency was stabilized by third derivate line-locking to the reference gas cell. Thus a stable zero base line was obtained. The sensitivity and the stability of the system were tested. At atmospheric pressure the sensitivity was 2.2×10^{-2} Torr. m (29ppm), the measurements were carried out with a time constant of 1 s and a S/N - ratio of 1. The line locking was stable over several days. The material cost of such an ammonia monitor were below 6000 Dollars (1992).

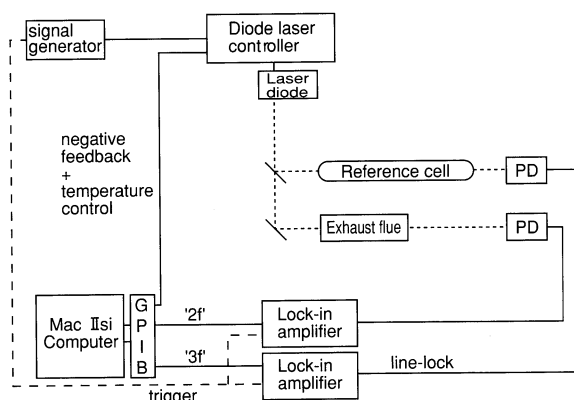


Fig. 2 Experimental arrangement for the near-infrared ammonia monitoring system. PD's, photodiodes.

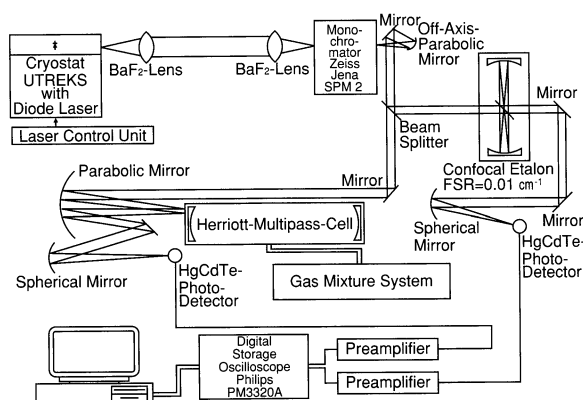


Fig. 3 Experimental setup of the diode laser spectrometer.

Compared with this simple arrangement the prototype of a diode laser spectrometer in Fig.3 is more sophisticated. It allows the spectroscopic analysis of very dif-

ferent molecular gases and their mixtures with resolutions about 10^4 cm^{-1} . In the case discussed here the spectrometer optics consist of BaF_2 lenses, a grating monochromator for mode separation and two optical channels with sample and reference cells and two Mercury Cadmium Telluride (MCT) photodiodes (time constant about 100 nsec). The laser diodes are mounted in a helium cryostat with a temperature control unit, which allows to select any temperature between 10K and 300K within 3×10^{-3} K precision and are driven in pulsed mode (pulse lengths up to 2 ms, duty cycle 100Hz, current pulses up to 2A).

The reference channel was used for wave number calibration and, if necessary, for DL frequency stabilization with the help of a boxcar signal averager. The boxcar windows were set to sample the absorption line at half-maximum points on both sides of the line center, their outputs were differentially amplified and the resulting error signal was added to the laser current in negative feedback. Temperature drifts during signal averaging could be reduced drastically. This driving mode for the lasers can be used for lead salt diodes as well as for III-V diodes⁵⁾. The relative wave number calibration was done with an internally coupled confocal etalon with a free spectral range of $\text{FSR} = 0.0104 \text{ cm}^{-1}$ or an Ge etalon. The first type of etalon can also be used as an open path cell for accurate calibration or analysis of the atmosphere demanding low optical path lengths.

The sample cell was of Herriot-multipass-type with different geometrical and optical path lengths up to 10 m, but small cell volumes. The resolution of the spectrometer was $4 \times 10^4 \text{ cm}^{-1}$.

In lead salt lasers a rough tuning of the emission wave number by some 100 cm^{-1} is possible, varying the operating temperature at a rate of 2 to $4 \text{ cm}^{-1}/\text{K}$. The ultimate fine tuning uses the transient pn-junction heating during applied current pulses. Typical for all Fabry-Perot diode lasers is a continuous fine tuning over 1 to 3 cm^{-1} , followed by a mode jump. So a photodiode signal represents a transmission spectrum of one of the optical channels. This is demonstrated in Fig.4 showing a detail of an absorption spectrum for SO_2 within a $200 \mu\text{s}$ long laser pulse⁶⁾ (page 249,1992).

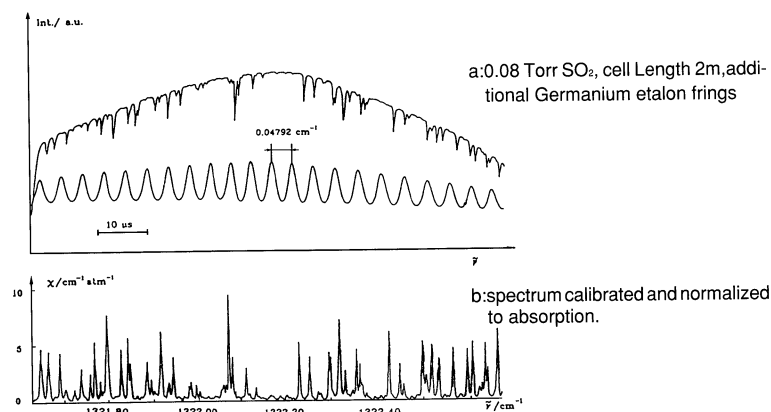


Fig.4 Part of the SO_2 spectrum near 1322 cm^{-1}

For data acquisition and analysis in this case the spectra were recorded in single-shot mode. Taking at least 50 shots of the absorption spectrum and the reference channel, the signal-to-noise ratio was strongly improved. Each single shot was linearised using the appropriate etalon spectrum and accumulated according to the peak of a selected absorption line. This procedure provided a better wavenumber and line shape accuracy than others. For the analysis of measured lines were used special fitting procedures OPTIMIZE 4.0 (nonlinear least-squares fit, blind search, evolution fit strategy). Up to five lines could be fitted simultaneously with line position ν_0 , line strength S , Doppler - $\Delta \nu_D$, Voigt- $\Delta \nu_V$ and collisional widths $\Delta \nu_L$.

After individual line fits for various pressures the collisional broadening line widths for every line can be plotted against the total pressure p and allow to determine the individual line broadening coefficient γ for different collision partners X with the partner Y : $\Delta \nu_L$ (FWHM) = $\gamma_{X-Y} \cdot P_Y$. The parameter γ strongly changes even for neighboring absorption lines of the same gas (up to 20% or more) and can have a strong influence on the form of the envelope (see Fig.1) of the absorption lines at atmospheric pressure.

The experimental arrangement in Fig.3 made it possible to measure and calculate for selected, best suitable absorption lines (single lines or well pronounced absorption structures and strong intensities) and its known γ_{X-Y} - values the product of the minimum detectable molecular concentration and the optical pathlength $c_{\min} \times z$. Some results are shown in Table II and compared with the values for the Air Quality Standards TA LUFT IW1 and IW2 and the Maximum Working Concentrations (MAK - values), valid for Germany⁷⁾ and the most countries of the EC.

Gas	TA LUFT IW1		TA LUFT IW2		MAK		(C . Z)	Wavenumber
	mg/m ³	ppm	mg/m ³	ppm	mg/m ³	ppm		
SO ₂	0.14	0.05	0.40	0.150	5.0	2.0	1.1	1382
CO	10.00	8.73	30.00	26.200	33.0	30.0	0.15	2150
NO ₂	0.08	0.04	0.20	0.110	9.0	5.0	0.20calc	1600
NO	-	-	0.15	0.120	-	0.40	-	1900
O ₃	-	-	0.10	0.050	0.2	0.1	0.75calc	1055
H ₂ S	-	-	0.10	0.070	15.0	10.0	15.6	1180
C ₆ H ₆	-	-	0.01	0.003	cancerogen		31.1	1038
Toluen	20.00*	5.3*	-	-	380.0	100.0	-	-
Xylen	-	-	-	-	440.0	100.0	-	-
CF ₂ Cl ₂	-	-	-	-	5000.0	1000.0	0.1	1161
N ₂ O	-	-	-	-	200.0	100.0	-	-

Table II Experimentally determined (c.z) values, obtained for a S / N ratio of 100 in and best suitable wavenumber in comparison with air quality standard values TA Luft⁷⁾ from 1986 for annual mean values IW1 stress values IW2 and maximum working concentration MAK; *-VDI values.

Besides the pulse measuring techniques discussed above traditional amplitude modulation and more recent frequency modulation (FM) techniques, demanding higher quality diode lasers in cw tuning regime are widely used⁶⁾. The competition for the best system approach is still undecided and will surely differ for the various analysing tasks. Ultrasensitive detection limits for FM spectroscopy arising from the quantum

statistics of the photodetection process itself are already reported⁸⁾. Experimentally determined sensitivities of 10^{-7} in a 1Hz bandwidth have been demonstrated for the detection of CO and CO₂ at 4.8 μ m and a lead salt laser with high spectral quality.

3. State -of- the - art of Tunable Diode Lasers

Tunable Diode Lasers (TDL) are characterized by the high monochromacy of a single mode (spectral line width (FWHM) much smaller than the Doppler line widths of any molecule) and its rapid tunability. These two properties are used to identify the absorption line of a gaseous species even in a gas mixture with high absorption line density and to measure its concentration.

Recently, three groups of diode lasers became of particular interest for TDLAS : the **near -infrared III-V compound diode lasers, the first MCT-diode lasers and the lead salt compound diode lasers in the MIR.** By this, a wide spectrum of infrared diode lasers manufactured mainly by HWE - (hot wall epitaxy), LPE - (liquid phase epitaxy) and MBE - techniques (molecular beam epitaxy) as double heterostructures or multi quantum well structures is now available. An survey is given in Table III.

Traditionally the **lead salt diode lasers** are more generally used for high -sensitivity detection of molecules because they emit in their fundamental rotation - vibrational bands in the middle infrared (MIR). However, lead salt diode lasers several disadvantages: (1)they still operate below 200 K (in cw regime), (2) they are low

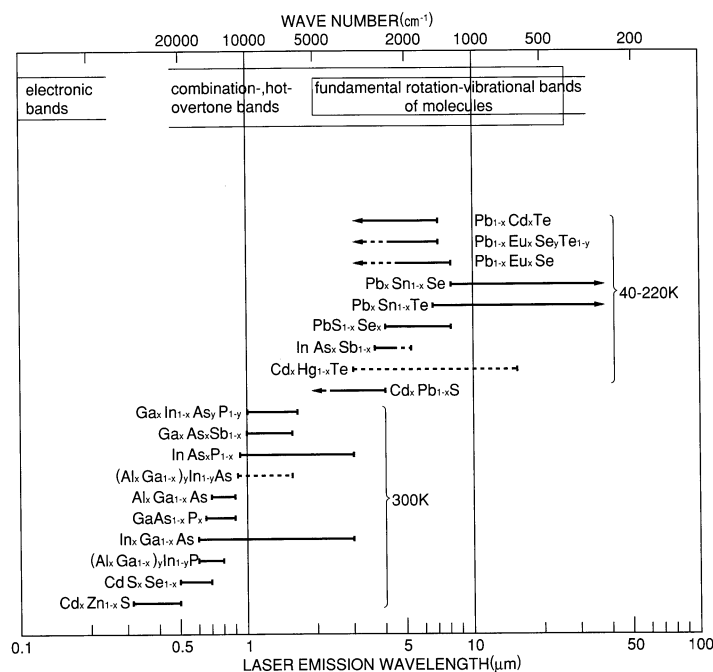


Table III Molecular absorption bands and laser emission wavelengths either presently (full line) or potentially (dotted line) available with III-V, II-VI, IV-VI hetero-structure lasers /20 and this work /

power devices ($< \text{mW}$), usually with multimode characteristics, (3) they are more expensive than the III-V diode lasers in the NIR-region, (4) they are available only from a small number of suppliers.

Since 1963⁹⁾, large efforts were made to manufacture sophisticated diode laser structures from lead salts alloyed with group IV-VI elements, with emission in the MIR spectral region from 3 to 30 μm and maximum operating temperatures around 250 K in pulsed current regime¹⁰⁾. Lasers emitting at even longer wavelengths were not manufactured, because of the very low density of states that can participate in the lasing process in such small energy band gap materials ($E_G < 0.04 \text{ eV}$) and due to the strong free carrier absorption losses at these wavelengths.

Besides the lead salts and their classic alloys many recent studies were concentrated on their alloys with rare earth monochalcogenides, especially with europium and strontium. The europium compounds, e.g. EuTe, has a large energy band gap about 2 eV and the best stability of its +2 state, its lattice constant differs from that of PbTe only about 2%. Similar properties has EuSe. Therefore double heterostructure diodes in stripe geometry and with corrugated end surfaces for monomode emission, single or multiple quantum well diode lasers have been manufactured in the PbEuTe-PbTe¹¹⁾, PbEuSnSe-PbSnSe¹²⁾ and PbSnTe-PbSeTe¹³⁾ systems and have operated up to 170 K cw and 243 K pulsed, to 165 K cw and 220 K pulsed and 130 K cw and 204 K pulsed, respectively. Single mode operation with a power of 1.7 mW at 50 K and operating temperatures 105 K cw and 144 K pulsed was reported, too¹⁴⁾. The record value 270 K for pulsed PbEuSeTe diodes at 3.9 μm was reported in 1988¹⁰⁾.

The two desirable properties of diode lasers are obtained for the lead salts, too: single mode operation combined with a wider continuous tuning range (about 10 to 20 cm^{-1}) and operating temperatures for pulsed diodes above 200 K. The first one enables the application of the laser as a local oscillator in the heterodyne detection for the analysis of distant gaseous sources. The second one is an essential step to the critical 220K mark, which allows the diode operation with thermoelectric coolers and meets the interests of instrument makers. It should be mentioned, that the number of publications and institutions dealing with the growth and optimization of lead salt diode lasers decreased in the last five years, while the number of publications attached to their spectroscopic applications is strongly and steadily increasing (see e.g. J.of Molecular Spectroscopy).

Due to their widespread use in optical communication industry, the **III-V diode lasers** used in TDLAS¹⁵⁾ are now not longer fixed to some selected wavenumbers. They are available in a variety of structures, operate at ambient temperatures and have a wider tunable wavenumber region in single mode regime. The last property was obtained by employing lasers with distributed feedback (DFB) or distributed Bragg reflector (DBR) structures. In many cases, high power (mW) single mode III-V

lasers are available at relatively low costs.

Therefore, in the last years the analysis of gases in the weaker overtone and combination bands in the near infrared (NIR) from 0.6 to 3 μ m became of growing interest¹⁶⁾. However for spectroscopic applications, the III-V lasers are restricted to a relatively small number of molecules with low molecular weights, that have overtone and combination bands in the NIR spectral region. But as already discussed in Fig.2, interesting applications at low costs for special gases are to be expected.

In contradiction to earlier theoretical predictions, which principally rejected the preparation from this bulk material diode laser structures, in 1991 on the **first mercury -cadmium - telluride double heterostructure injectionlaser** at 2.86 μ m and 77 K was reported¹⁷⁾. The diode laser was obtained by MBE and operated under pulsed current at temperatures between 40 and 90 K. Similar results were obtained by LPE from other groups¹⁸⁾.

For HgCdTe injection lasers in the short wavelength region the situation is different compared with that of the III-V lasers. The industrially use of MCT for photodiodes and focal plane arrays operating at liquid nitrogen temperatures at 10 μ m is based on low carrier concentrations in the material. In contradiction, for diode lasers relatively high carrier concentrations in the active region are necessary.

In MCT the Auger recombination is proportional to the cube of the carrier concentration. Even in active layers with quantum well structures and lower carrier concentrations the Auger process, which is a nonradiative one, will dominate the radiative recombination above a critical operating temperature. It will depend on further success in basic research, especially on the realization of optimum confinement structures in MCT, to obtain high operating temperatures for the diode lasers and to demonstrate their application in TDLAS.

4. Conclusions

Since the first demonstration of high resolution spectroscopy using lead tin telluride diode lasers by Hinkley and co-workers at MIT Lincoln Laboratory¹⁹⁾ in 1970 IR -TDLAS has become a standard technique for the chemical analysis of gases²⁰⁾ and complex gas mixtures in various environment²¹⁾. TDLAS systems are now available for a wide wavelength range from 0.67 to 30 μ m, with detection limits as low as 25 pptv and a dynamic range of more than 4 orders of magnitude. The rapid time response has been used to make eddy correlation flux measurements and to get good spatial resolution from fast moving aircraft. TDLAS measurements have been carried out in very clean troposphere and in the stratosphere, in polluted urban and rural air, smog chambers, coal mines, industrial sites, in indoor work places and automobile exhaust, on mobile vans, ships, aircraft, balloons and rockets (see, e. g. ⁶⁾) Recently, the spectroscopic analysis of free radicals and ions²²⁾, as well as of isotopomers²³⁾,

were reported. There is no doubt that with further success in the optimum confinement of the laser parameters for the different groups of diode lasers, the spectrum of possible technical applications for environmental analysis, discussed here, becomes a wide field for instrument makers.

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波長可変型ダイオード・レーザ・スペクトロスコピー
—大気汚染性微量ガス成分の高分解能分析—

波長可変ダイオード・レーザを使った赤外線吸収分光分析法 (IR-TDLAS) は、1970年にMIT Lincoln LaboratoryのE.D.Hinnkleyらにより報告されて以来、有力な環境中のガス状物質の分析方法として発展してきた。

TDLASの高感度・高選択・高速応答などの優れた特性は、大気中の微量ガス成分の遠隔測定にとくに威力を発揮し、現在では、 $0.67\sim 30\mu\text{m}$ の波長領域にわたり、最小検出感度として25ppt/vのものが達成されている。

TDLASの中核をなす波長可変型ダイオード・レーザ素子は、①Ⅲ-V族の4元系半導体化合物、②水銀-カドミウム-テルル系 (MTC)、③鉛塩系化合物の3つのグループが開発・市販化されてい

る。中赤外用として広く使われている鉛塩系は、シングルモードで可変幅が最大 50cm^{-1} のもの、動作温度が200K (パルス発振) のものなどが報告されている。一方、液体窒素温度以上で使える2重ヘテロ構造の注入型のMTC系は、室温作動は難しいだろうが、検出器と一体化するなど、新たな応用展開が期待される。

最近、フリー・ラジカルやイオン、同位体の分析なども報告されており、今後、TDLASの応用がますます拡大していくことは間違いないだろう。本稿では、IR-TDLASとその応用に関する最近の研究成果を紹介する。

(文責 編集部)

