

4A1) 파장가변 다이오드 레이저 흡수 분광학을 사용한 대기환경분석

Tunable Diode Laser Absorption Spectroscopy for Environmental Monitoring

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1. Introduction

Tunable diode laser absorption spectroscopy (TDLAS) has been widely used in environmental monitoring of gaseous species in the past decade. TDLAS is a direct measurement technique for pollutants such as NO_x without any interference from other species. Because of its superior spectral purity ($\sim 0.001 \text{ cm}^{-1}$), absorption linewidths with resolvable rotational structure can be studied in the mid infrared region where strong fundamental vibrational transitions of molecules appear. The TDLAS technique has much higher sensitivity (<ppb) with longer optical path lengths than conventional Fourier transform infrared measurements. In U.S.A. an open path remote sensor based on TDLAS could be operated with an optical path length of $\sim 100 \text{ m}$ to measure the NO_x emissions of on-road vehicles. A detection limit less than $\sim 1 \text{ ppb}$ of trace gaseous species was reported using a 200 m path length multiple-pass absorption cell in the laboratory. Recently developed non-cryogenic, quantum cascade laser-absorption spectroscopy in the mid-infrared region is expected to have a great potential for practical approach of trace gas detection in the atmosphere.

2. Methods

The lead-salt diode lasers are used to study the fundamental vibrational transitions of gaseous molecular species. Table 1 shows the specification of our diode laser spectrometer. Tuning of our diode laser spectrometer is achieved by varying the temperature and current. A typical threshold current is around 100-500 mA.

Table 1. Specification of a diode laser spectrometer

Part	Specification
Laser Diodes	PbSnSe, PbSnTe, PbSSe
Operating Temperature	40-160 Kelvin
Spectral Range	4-30 μm (2500-350 cm^{-1})
Window	KRS-5, BaF ₂
Collimating Lens	IRTRAN-2
Detector	HgCdTe (liquid N ₂ cooled)

The Diode laser beam has to be collimated because of its large divergence. KRS-5 or BaF₂ is used as an optical window in the mid-infrared region. A photoconductive HgCdTe detector is used with a combination of lead salt diodes. Its detectivity is in the range of 10^9 - $10^{11} \text{ cm Hz}^{1/2}/\text{W}$

3. Results and Discussion

We currently have more than 15 laser diodes to study atmospheric chemistry in the spectral region between 1080-2520 cm^{-1} . Table 2 lists wavenumber regions of each diode laser. One diode laser can usually cover a spectral region of $\sim 100 \text{ cm}^{-1}$ with many mode gaps. Due to these mode

gaps, we cannot scan a certain spectral region continuously however. In practice one diode laser mode can span $\sim 1 \text{ cm}^{-1}$. Also it is often found that the optical characteristics of diode lasers may be slightly changed after a certain elapse of time.

Table 2. Spectral region of 15 lead-salt diode lasers. (Unit: cm^{-1})

1084-1220	1166-1404	1181-1291	1189-1278	1321-1341
1354-1501	1390-1405	1539-1675	1790-1805	1802-2039
1980-2060	2071-2238	2160-2175	2192-2257	2510-2520

The mid-infrared spectral region has an advantage of containing strong fundamental vibrational bands. The infrared absorption signal is proportional to the ratio of the absorbed intensity ΔI to the initial intensity I

$$\Delta I / I = n \sigma l$$

where n is the number density. l is the optical path length and σ is the absorption cross section. For a transition of $n \sim 10^{10} \text{ cm}^{-3}$, $\sigma = 10^{-17} \text{ cm}^2$, and $l = 100 \text{ cm}$, $\Delta I / I \sim 10^{-5}$ is required to observe its spectrum with a detection limit of less than 1 nmol/mol ($< 1 \text{ ppb}$). Environmentally interesting species can be studied with resolvable rotational-vibrational structure in both open and closed path. On the basis of our previous experience of high resolution spectroscopy of gaseous species including reactive molecular ions and free radicals in the laboratory, we plan to study atmospheric chemistry under a variety of environmental conditions using the TDLAS technique.

References

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