Guest Forum

Series of Lectures by Screening Committees of the Second Masao Horiba Awards

Applications of Laser Spectroscopy to Highly Sensitive Analyses

— Cavity Ring-Down Spectroscopy —

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Laser has been widely used for analysis of various molecules because laser has a variety of features from continuous-wave oscillation to ultra-short pulse. While introducing some examples of applications of lasers from vacuum-ultraviolet to near infrared region, Analysis techniques by laser-induced fluorescence (LIF) spectroscopy and photo-acoustic spectroscopy (PAS) with a pulsed dye laser are explained. Applications of cavity ring-down spectroscopy (CRDS) with a semiconductor laser are compared with LIF and PAS. Then, as an advanced analytical technique, fiber-CRDS with Bragg gratings and a gain-switch semiconductor laser is discussed. CRDS with an evanescent light device or an onboard waveguide is explained as future prospects.

Various Types of Lasers and their Applications

Analyses of Particles in the Air by Ultraviolet Lasers[1]

Irradiating a single particle with an ultraviolet laser pulse of megawatt peak power, the adsorbed molecules on its surface is evaporated, ionized and analyzed by means of mass spectrometry. In analysis of yellow sands by Nagoya University and National Institute of Environmental Studies, for example, it was found to contain sulfuric acid and nitric acid on silica surface. Particles coming from "over seas" are likely to have Cl anions, Na cations, etc. on the surfaces. On the other hand, particles in the urban air coming from Tokyo area are found to contain carbon element. Horiba and Nagoya University conducted a joint study to detect chemicals attached to the surfaces of small particles in the exhaust gases from automobiles.

Detection of Light Elements by Vacuum Ultraviolet Laser

With a vacuum-ultraviolet laser near 100 nm, it is possible to detect light element atoms from hydrogen atoms to halogen atoms.

Figure 1 shows an example of the experimental setup that was attached with a vacuum ultraviolet laser. By using simultaneously two dye lasers pumped by an excimer laser, vacuum ultraviolet laser light is generated due to the nonlinear optical effect of Kr or Xe gases. Then, using ozone as a sample gas, one can directly observe oxygen atom release from photodissociation reaction of ozone[2].

The tunable vacuum-ultraviolet laser enabled direct measurements of light atoms in the wavelength region, which was not possible before.

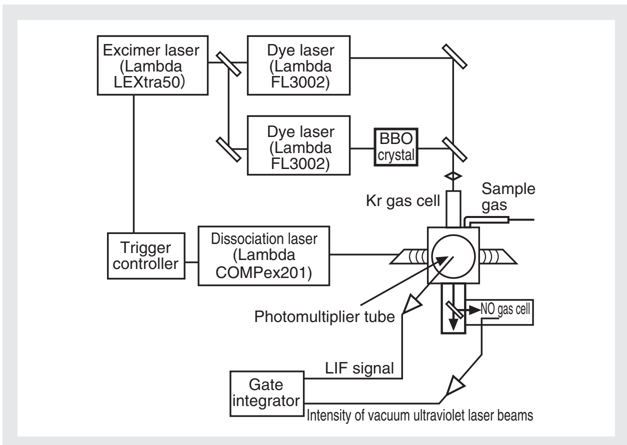


Figure 1 Experimental setup for Vacuum Ultraviolet Laser Specroscopy

Highly Sensitive Absorption Spectrometry using Optical-communication Semiconductor Lasers in the Near-infrared Region

High resolution semiconductor lasers have been developed as optical communication devices in the near-infrared region. Therefore, they are inexpensive, handy and suitable for spectroscopic applications. They are used for highly sensitive absorption spectroscopic analyses that is achieved by cavity ring-down spectroscopy (CRDS) with an effectively long optical path length or modulation of laser wavelength, and so on. For example, CRDS is applied to detection of carbon dioxide and water isotopes. Previously, only mass spectroscopy has been used to analyze isotopes.

Photo-Acoustic Spectroscopy (PAS) by means of a Pulsed Dye Laser

Photo-acoustic spectroscopy (PAS) by means of a pulsed dye laser is practically useful. The photon energy of laser beams is absorbed by molecules and ultimately converted to the thermal energy. PAS enables the spectroscopic analysis with acoustic waves thus generated, which are detected by a microphone. To use a CW laser, a complicated design is required for a PAS cavity. When using a pulse laser, however, there is no need for such special design. Figure 2 shows an example of water isotope measurements by PAS and CRDS. There is no appreciable difference between two spectra for PAS and CRDS. Since light water, H_2O, is likely to evaporate, the isotopic ratios are changed in the vicinities of the Equator and the North/South poles. Therefore, the global water cycles can be identified by measurements of water isotope ratios.

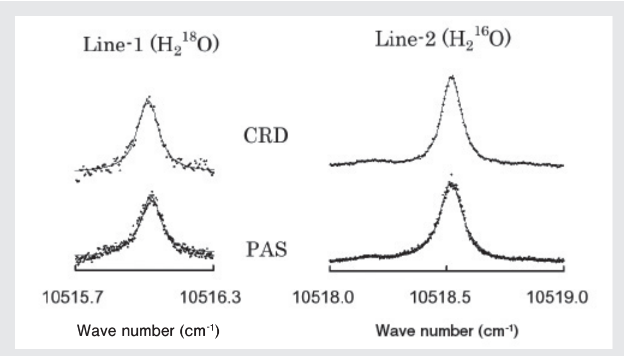


Figure 2 Measurements of Water Vapor Isotopes

Laser-Induced Fluorescence (LIF) of Ultra-low Volume Substances

Emission spectroscopy for molecules and atoms is extremely sensitive. A method to detect the number density of molecules by analyzing the fluorescence intensity generated by applying laser beams is called "Laser-Induced Fluorescence (LIF)". As for mercury that exists only small quantity in the air, if one uses the same wavelength (253.7 nm) for excitation and detection, the background signals caused by scattered laser beams reduce the sensitivity of analysis. Therefore, as is shown in Figure 3 by Prof. Hynes of University of Florida, Hg atoms are excited consecutively at 253.7 and 435.8 nm, and the detected at 546.1 nm corresponding to the transition between the electronically excited states to ensure high sensitivity in the measurements. This method makes it possible to detect ultra-low levels of Hg in the air within 1 - 2 seconds, and also enables online observation.

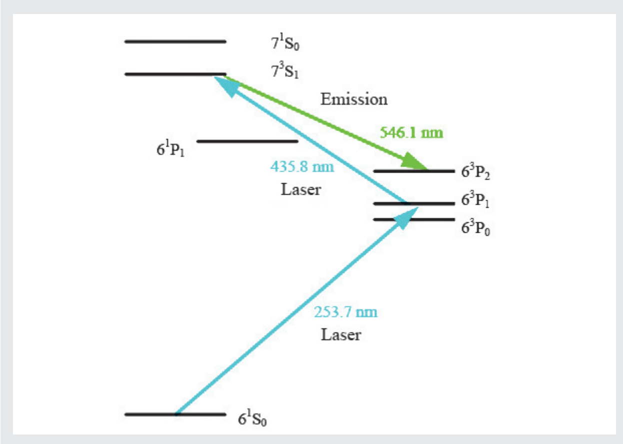
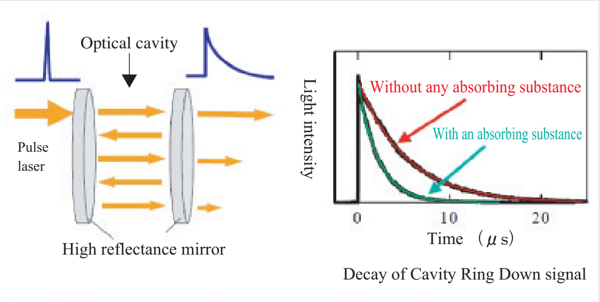


Figure 3 Energy Levels and Transitions of Hg Atoms
The upward arrow shows an excited laser beam, and the downward arrow shows an observation wavelength. 6^1S_0, 6^3P_1, etc. are atomic levels.

Cavity Ring-Down Spectroscopy[3] Outline

Since Cavity Ring-Down Spectroscopy (CRDS) is based on optical absorption, it is applicable to analysis of any substances including non-luminous species. As is indicated in Figure 4, a laser beam pulse is introduced into an optical cavity equipped with high reflectance mirrors (Reflectance $\simeq$ 99.99%). One can measure the absorbance of a sample in the cavity by observing attenuation of leaked light intensity as a function of time.

Generally, there are three choices to improve the sensitivity in absorption spectroscopy:
(1) Long optical path length (up to 10 m)
(2) Multi-path cell (up to 100 m): Make use of the multi-reflection in the light path
(3) Light trap (up to 10 km): Using a optical cavity equipped with high reflectance mirrors r
Item (3) is compatible with an effective optical path length of 10 km maximum, with which sensitivity is enhanced by a factor of 1,000 compared with Item (1).



$$I(t) = I_0 \exp(-t/\tau) = I_0 \exp(-t/\tau_0 - \sigma nct)$$

Figure 4 Principle of Cavity Ring-Down Spectroscopy
$I(t)$, I_0: Time t, and light intensity at t = 0
τ: Ring down time when there are absorbing substances (Decay lifetime of light intensity attenuated in optical cavity)
τ_0: Ring down time in vacuum
σ: Absorption cross-section of substances
n: Number density of substances per unit volume
c: Speed of light

Table 1 shows the advantages of Cavity Ring-Down Spectroscopy and their reasons. Generally, a pulse laser has an intensity fluctuation about 1%. However, CRDS analysis is not influenced by the variation of the laser output because optical absorbance is measured from the decay of the CRDS signal intensity as a function of time. This is a greatest advantage of CRDS. Further, since it offers high sensitivity as well as high resolution over the wide pressure range, it is applicable in the gas, liquid, solid phase, and to thin membranes.

Table 1 Advantages of Cavity Ring-Down Spectroscopy

Advantage	Reasons
High sensitivity	Detection limit of absorbance is below 10^{-8}, due to effective long optical path length (up to 10 km).
Quantitative	Not affected by variation of laser intensity.
Wide pressure range	Molecular beam*, Atmospheric pressure, Liquid phase, Thin membrane
High resolution	10^{-2}-10^{-5} cm^{-1}

*The flow of molecules in a vacuum in the form of a straight beam

Table 2 shows some examples of applications of Cavity Ring-Down Spectroscopy.

Table 2 Examples of Applications of Cavity Ring-Down Spectroscopy

Gas phase	Radical
	Metal cluster
	N_2^+, Si and SiH^3 in plasma
	Isotopes ($H_2{}^{18}O$, CO_2)
Liquid phase	Benzene in hexane solvent
	Rhodamine dye in organic solvent
	Acetyl copper in organic solvent
Solid phase	Amorphous silicon film
	C_{60} film
	Iodine monolayer

Comparison with Other Methods

Laser-Induced Fluorescence (LIF)

Table 3 shows a comparison between CRDS and LIF. LIF, is an emission spectroscopy, offers high sensitivity as shown in the aforementioned mercury atom. However, it does not provide information on the absolute density, whereas CRDS, an absorption spectroscopy, can do from an absorption cross section. LIF requires considerable efforts to measure minor constituents at normal pressures due to optical quenching caused by collisions with surrounding molecules. Also, LIF cannot analyze substances that do not emit, including H_2O and CO_2. Further, it cannot be used for molecules that photodecompose.

Table 3 CRDS vs. LIF

	CRDS Long optical path absorption spectroscopy	LIF High sensitivity emission spectroscopy
Absolute density calculation	Possible	Not possible
At normal pressures	Possible	Nearly impossible
Non-emission radical	Possible	Not possible
Position resolution	Low	High
With variations in refractive indices	Not possible	Possible

Mass Spectroscopy

In the case of analyzing $H_2{}^{18}O$ in natural water (natural abundance 0.2%) by Mass Spectroscopy, if water is directly supplied to the sample transfer system, it is not possible to obtain accurate isotopic ratios due to the isotope exchange reactions. Therefore, it is necessary to convert water to CO_2 based on the equilibrium relation ($H_2{}^{18}O + C^{16}O_2 \leftrightarrow H_2{}^{16}O + C^{16}O^{18}O$). CRDS can analyze the isotopomers without any sample preparation procedure, thus, save analysis time and amount of samples.

Examples of Applications

Observation of CO_2 Density Distributions

To obtain altitude distribution of atmospheric CO_2 from satellite measurements, pressure broadening coefficients are essential data, which are obtained by measuring degree of spread of the CO_2 near-IR spectra due to collisions of air gas molecules.

Figure 5 shows pressure broadening of CO_2 near-IR spectra measured by CRDS.

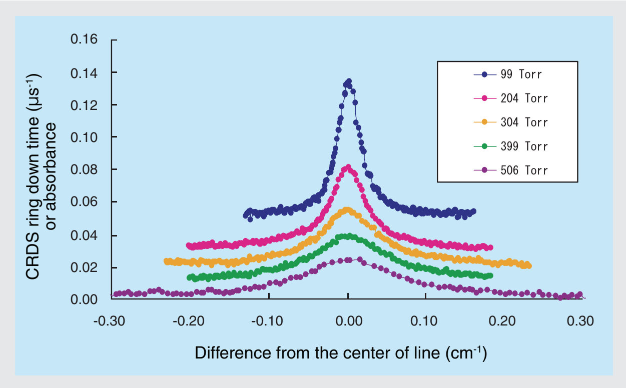


Figure 5 Pressure Broadening of CO_2 Near-IR Spectrum

Other Applications

Shown below are examples of some applications of CRDS with semiconductor lasers.

- Detection of trace gases (CO (1.55 μm, CH_4 (1.65 μm), NH_3 (1.5 μm), HCHO (1.76 μm))
- Determination of isotope ratios ($^{12}CO_2/^{13}CO_2$ (1.6/2.0 μm), $H_2{}^{16}O/H_2{}^{18}O$ (0.9/1.1 μm), $HD^{16}O/H_2{}^{16}O/H_2{}^{18}O$ (2.5 μm))

There are many substances including NH_3 and H_2O, which can be observed in the near infrared region. The absorption of these compounds is higher at around 2 μm. From now on, I would like to pay more attention to the mid-infrared region analysis that uses a quantum cascade laser (QCL).

Advanced CRDS Spectroscopy

CRDS Spectroscopy with Fiber Bragg Gratings (FBG) and a Gain-switch Semiconductor Laser[4]

Figure 6 shows an experimental setup of CRDS with Fiber Bragg Gratings (FBG). The analysis cell is attached with high reflectance FBGs in an optical fiber by preparing the grating directly in the fiber core glass. As indicated in the figure, the small sample cell is inserted in the fiber rink for a trace amount of substances, and then, Ring-down waveform is observed. Figure 7 shows the pattern diagram of FBG that is prepared by melting an optical fiber core with an excimer laser.

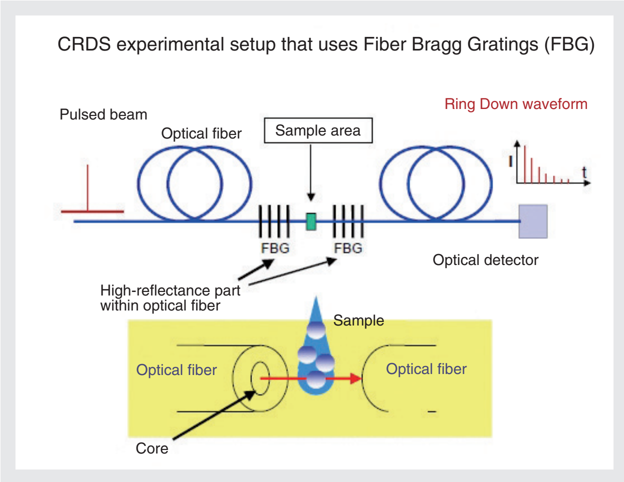


Figure 6 CRDS experimental setup and Fiber Bragg Gratings (FBG)

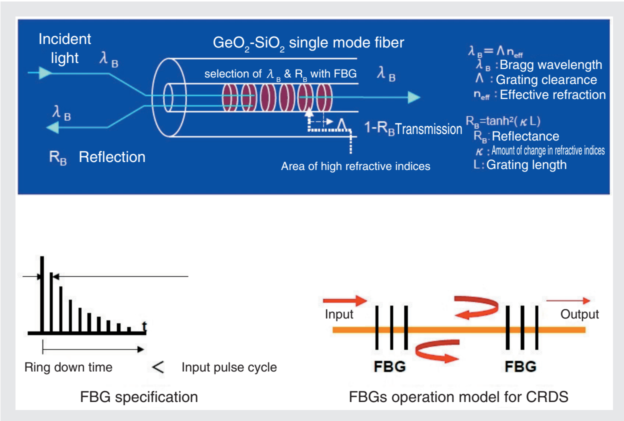


Figure 7 FBGs for Cavity Ring-Down Spectroscopy

On the other hand, the gain-switch semiconductor laser is not a system that uses a CW semiconductor laser attached with an optoacoustic modulator (AOM), but is a system that a semiconductor laser beams is operated by the Gain Switching Method. When this gain-switch single pulse (up to 30 ps) is introduced into the cavity, the pulse train lasts up to around 500 ns, and CRDS decay measurement becomes possible.

With this fiber CRDS with FBGs of 30 dB (Reflectance: 99.9%) and the gain-switch semiconductor laser, Ring Down pulse train lasts 200 or more times. We were able to analyze a trace amount (100 pL) of liquid samples (Figure 8).

CRDS that uses an Evanescent Wave Device

To use evanescent light effect, that is, an optical leakage effect from fibers, one removes the external cover of an optical fiber by heating until exposing the core. As for application to fiber CRDS any connection loss caused by the formation of gaps can be ignored. In our experiments, we put the evanescent device into a glass tube, and measured the difference in CRDS signals between water and ethanol. The refractive index of ethanol is higher by 0.03 than water, hence, ethanol showed larger optical leakage and the faster attenuation of Ring Down decay waveform. One application could be measurement of absorption spectra within a living cell along its depth direction.

Lab-on-a-Chip (LOC) Device with the Ultra-high Sensitivity Absorption Spectroscopic System Integrated on a Substrate

Based on the advanced CRDS that uses FBGs and the gain-switch semiconductor laser, we are currently studying further possibilities of CRDS-LOC (Lab-on-a-Chip) with an optical waveguide circuit directly prepared on a silicone tip board (Figure 9).

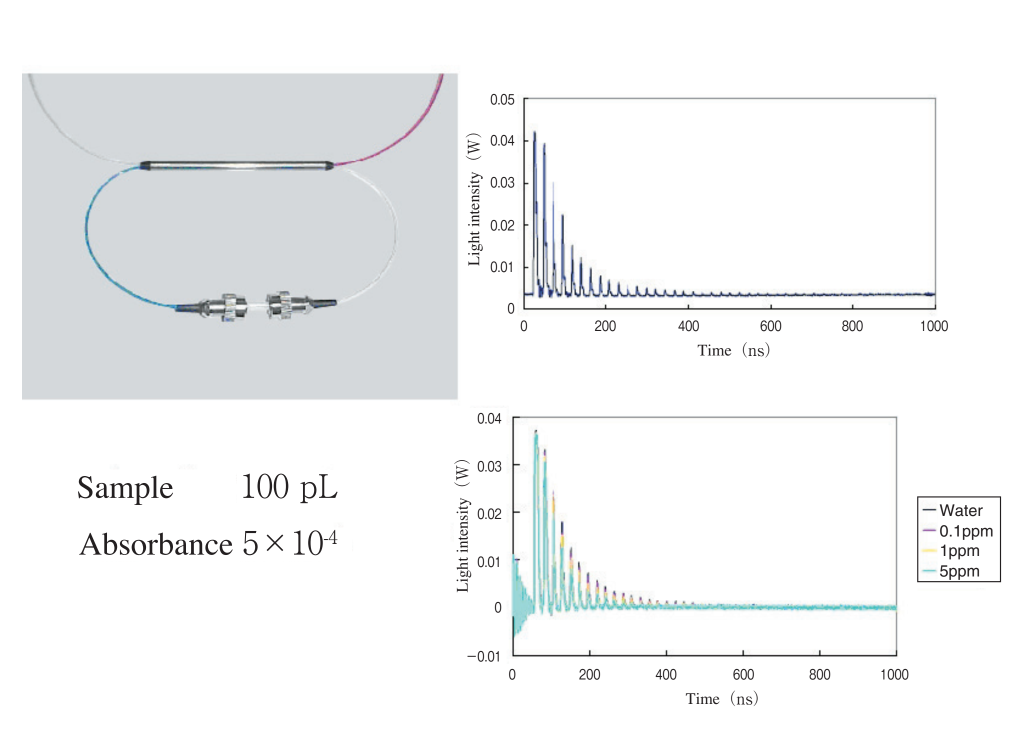


Figure 8 Trace-sample Detection Device for Methylene-blue with CRDS

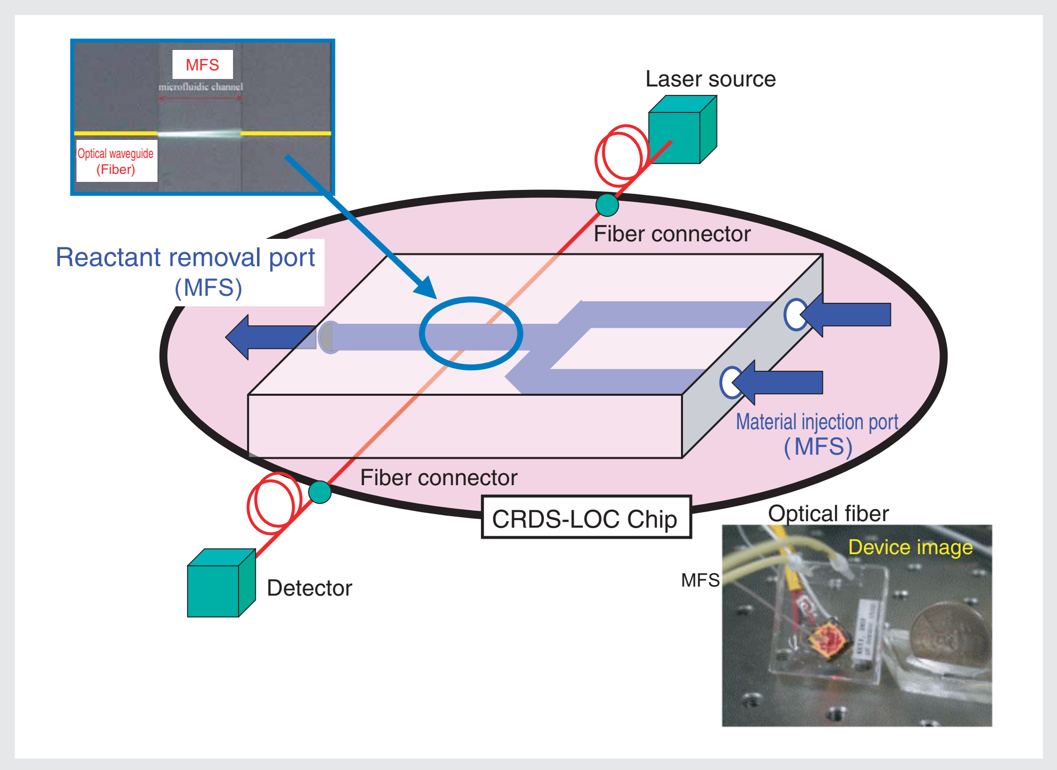


Figure 9 CRDS-LOC Chip (Cavity Ring Down Spectroscopic Instrument that uses a Flat WaveGuide)

Conclusion

I have explained about various highly sensitive analytical techniques for various wavelength regions. Due to rapid progress in the near-infrared technologies, I think, Cavity Ring-Down Spectroscopy , which is one of the highly sensitive analytical techniques, will be used widely in the future, especially in analysis of liquid samples.

<Excerpt from the Screening Committee Lecture for Masao Horiba Awards, May 30, 2005 (Publication members have responsibility for the translation)>

Reference

[1] Yabushita K, Matsumi Y, *Geophys. Res. Lett.*, 33, L07876, 10.1029/2006GL025782 (2006).
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