New Technique of Nitrogen Compounds Causing Secondary Aerosol Formation in Automobile Exhaust Based on IR – CRDS

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We report the accurate and precise measurement of nitric compounds such as NO2 in automotive exhaust gas by cavity ring-down spectroscopy (CRDS) using a thermoelectrically cooled, cw quantum cascade laser (QCL) as a light source. A mid-infrared QCL with a 6.2 μm wavelength was used to detect NO2. An effective optical path length of 2.1 km was achieved in a 50 cm long cell using high-reflectivity mirrors. In combination with a particle filter and purge gas to avoid mirror pollution, stable and sensitive measurement of NO2 in exhaust gas was achieved for more than 30 minutes with a time resolution of 1 s. The results of this work indicate that a laser based NO2 sensor can be used to measure NO2 in exhaust gas over a dynamic range of three orders of magnitude.

New Technique of Nitrogen Compounds Causing Secondary Aerosol Formation in Automobile Exhaust Based on IR – CRDS

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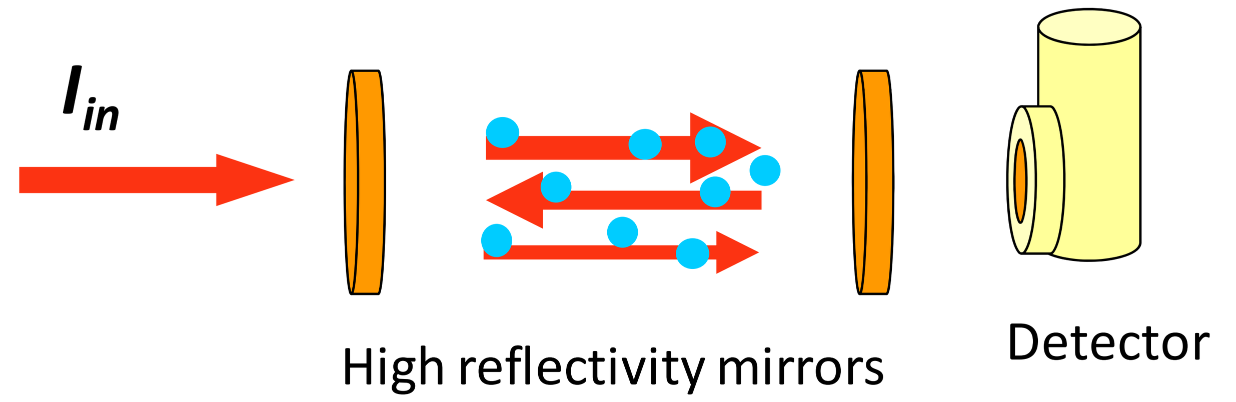
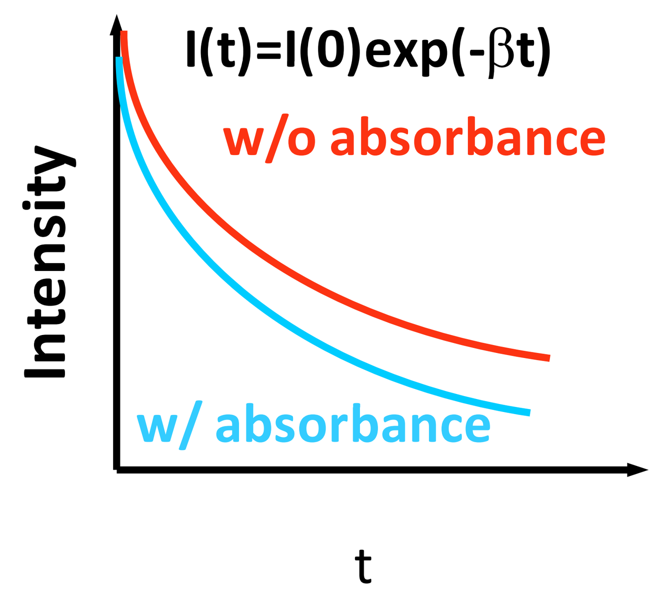
Japan started new atmospheric aerosol standard (PM2.5) to reduce secondary aerosol formation in atmosphere. It is known that the secondary aerosols are formed by the reactions of volatile organic compounds (VOC) with NOx. As for NOx, NO_2 is important because it has high toxicity and possibility to form nitro compounds which accelerate coagulation of particles. Usually NO_2 concentration is obtained from NOx concentration by subtracting NO. However this method often increases uncertainty. Thus new NO_2 measurement technique is required to study secondary aerosol formation process in atmosphere.

We report the accurate and precise measurement of nitric compounds such as NO_2 in automotive exhaust gas by cavity ring-down spectroscopy (CRDS) using a thermoelectrically cooled, cw quantum cascade laser (QCL) as a light source. A mid-infrared QCL with a 6.2 μm wavelength was used to detect NO_2. An effective optical path length of 2.1 km was achieved in a 50 cm long cell using high-reflectivity mirrors. In combination with a particle filter and purge gas to avoid mirror pollution, stable and sensitive measurement of NO_2 in exhaust gas was achieved for more than 30 minutes with a time resolution of 1 s. The results of this work indicate that a laser based NO_2 sensor can be used to measure NO_2 in exhaust gas over a dynamic range of three orders of magnitude.

Principle of Cavity Ring Down Spectroscopy (CRDS)





$I(t)=I(0)\exp(-\beta t)$

β: intensity decay rate

$\beta=\beta_0+\alpha c$ α: absorption coefficient

c: speed of light

Absorbance **= $(l/c)\,(\beta_{abs}-\beta_{base})$**

l: cavity length

Long path with small cell (over 1km)

No necessity to observe fluctuations of light souce

Experimental of continuous wave (CW) - CRDS

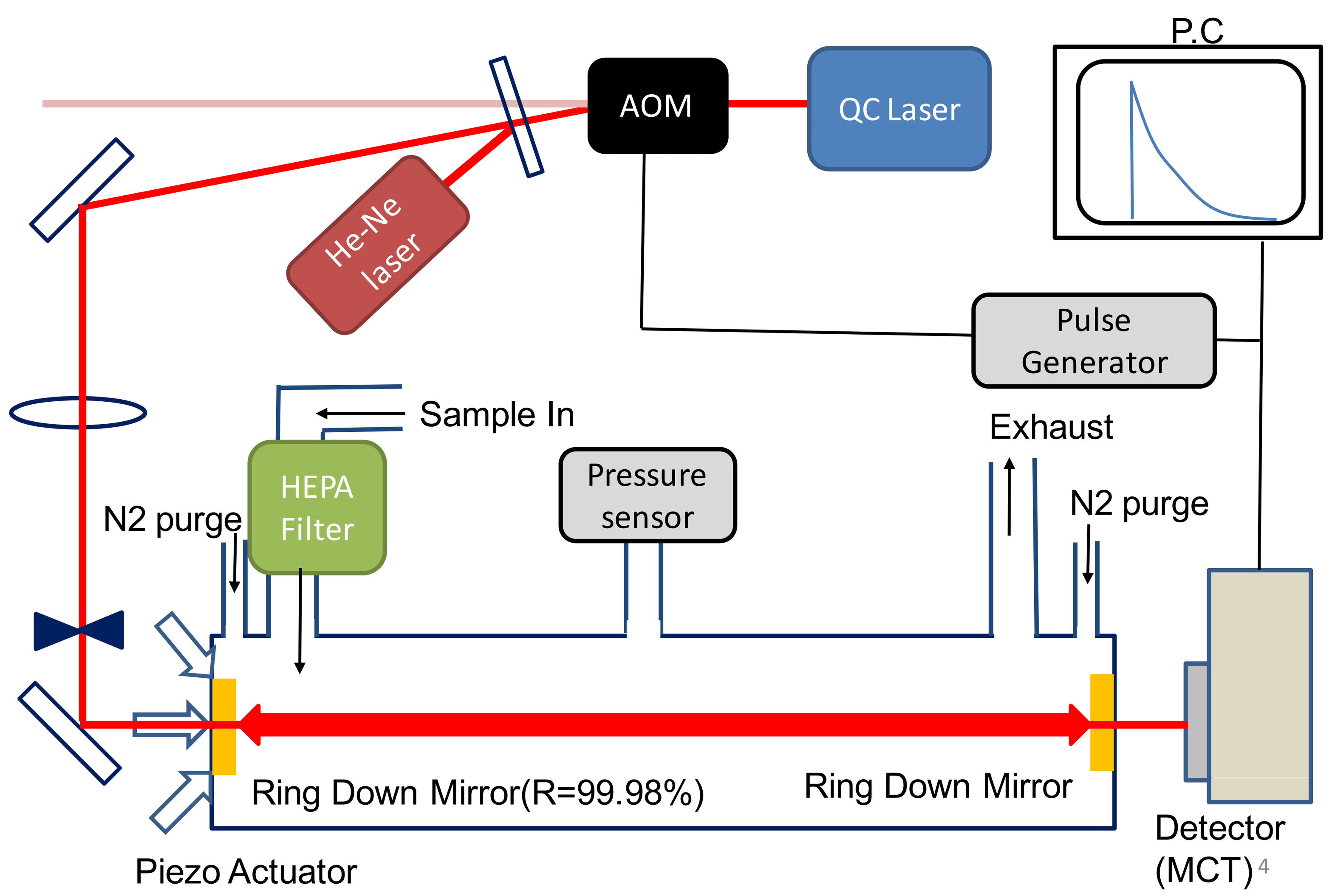
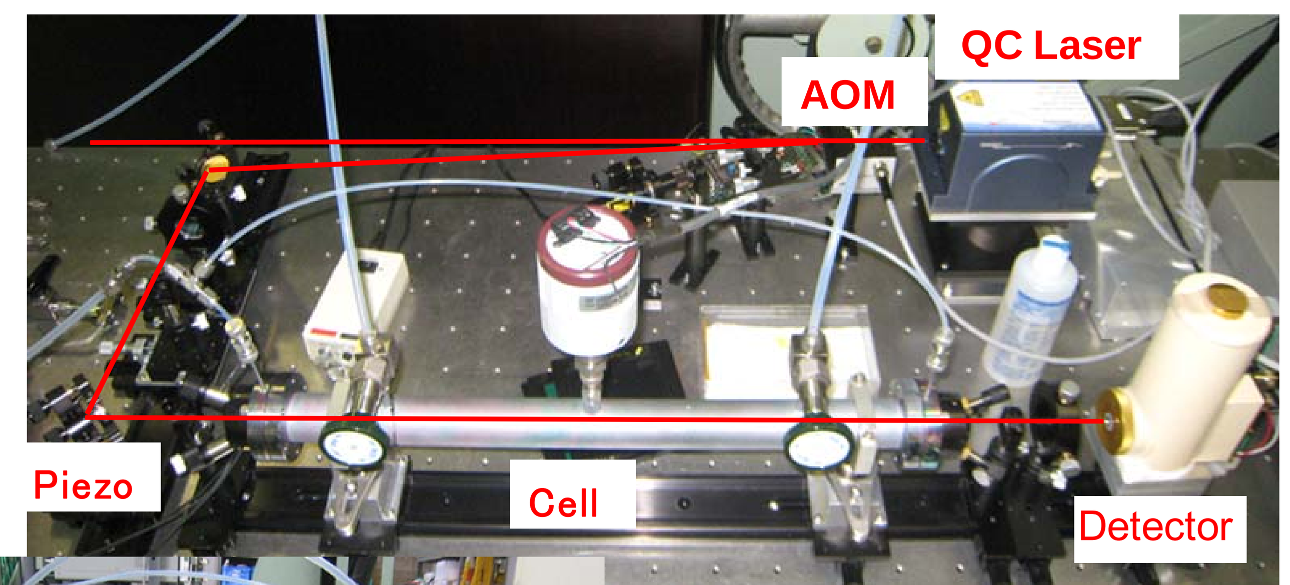
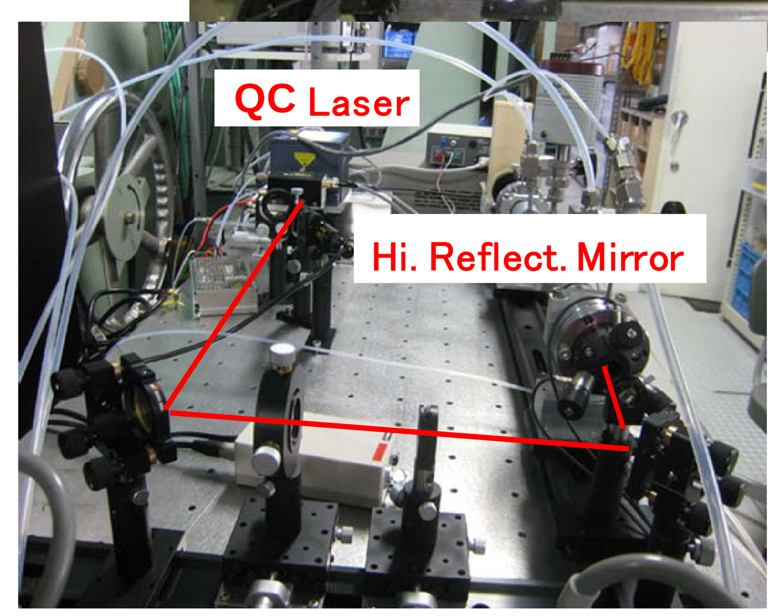


Fig.1 Experimental.





Results of Fundamental experiments

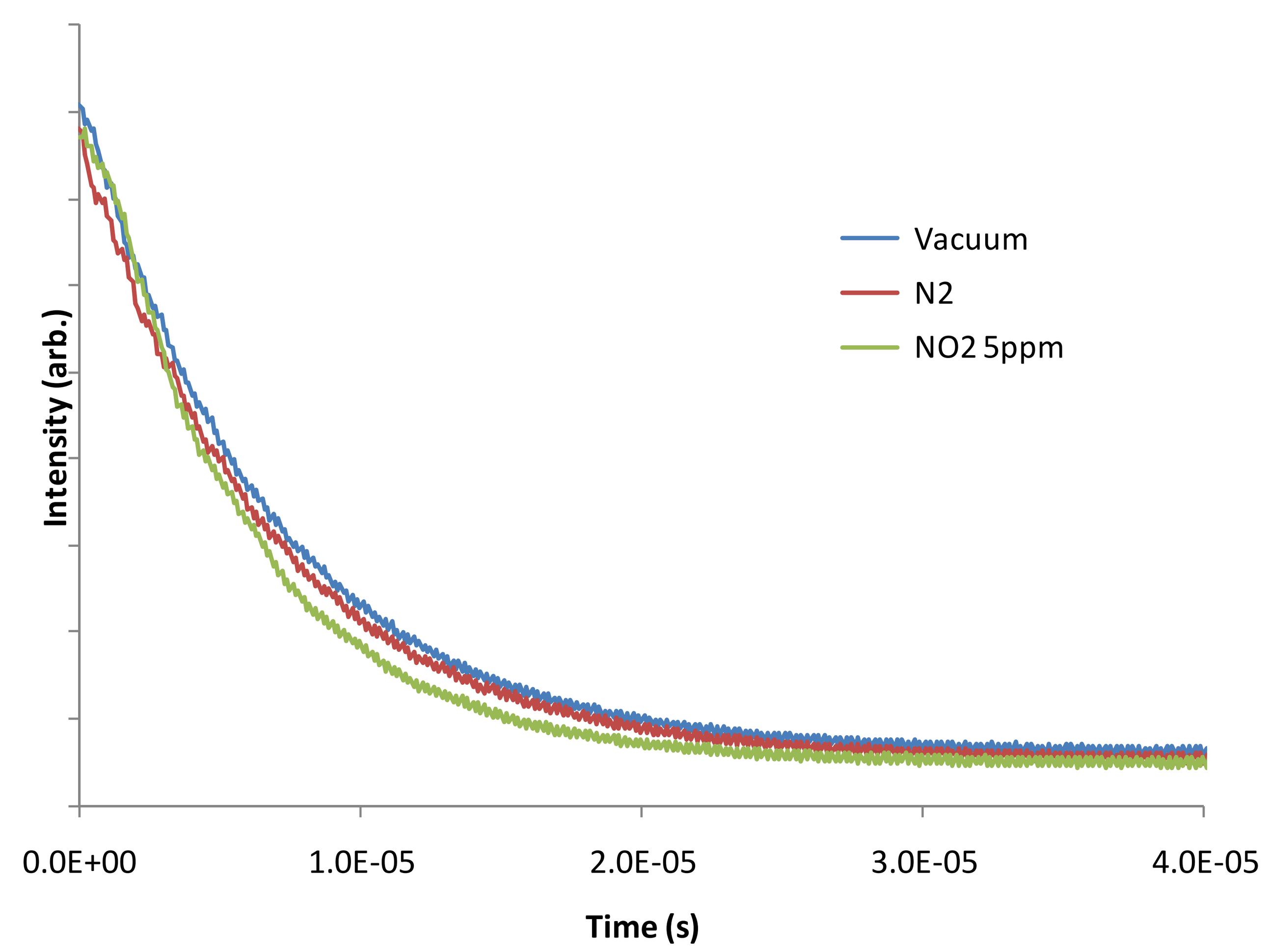


Fig.2 Sample of Ring Down Signal

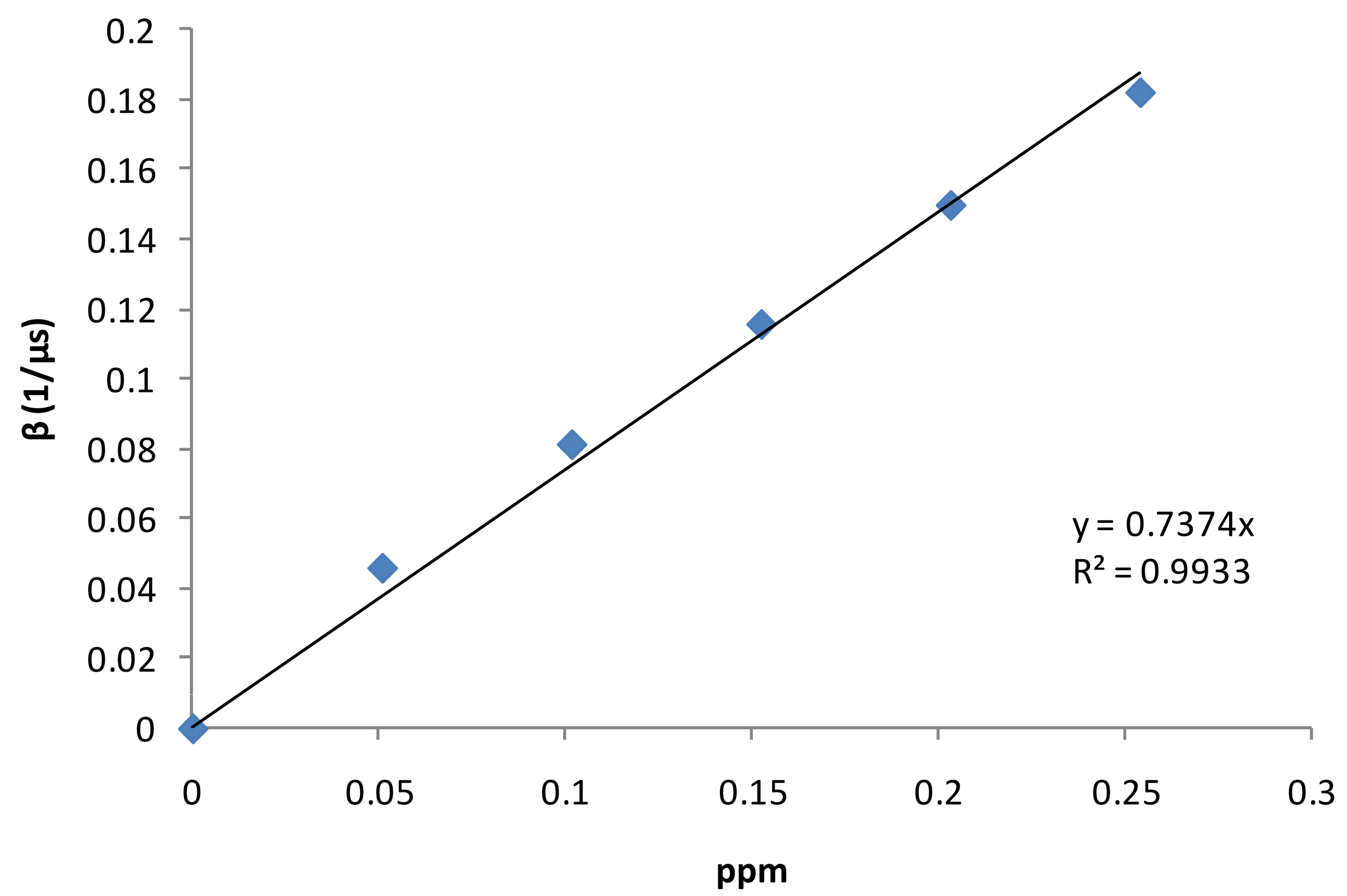


Fig.3 Correlation between ring down time and NO2 concentration

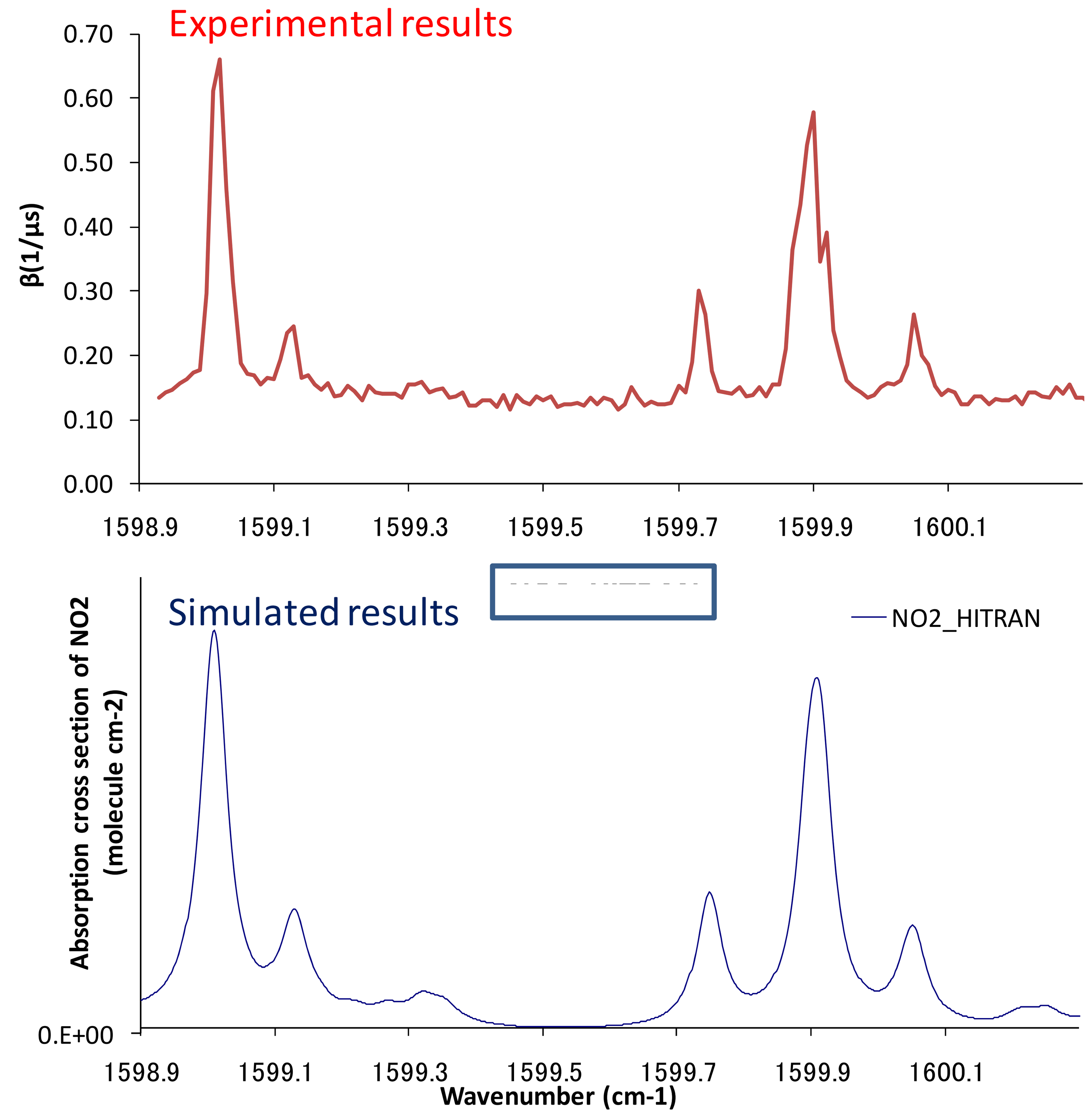


Fig.4 Spectrums of NO2, experiments and simulation (HITRAN).

Results of Exhaust gas analysis

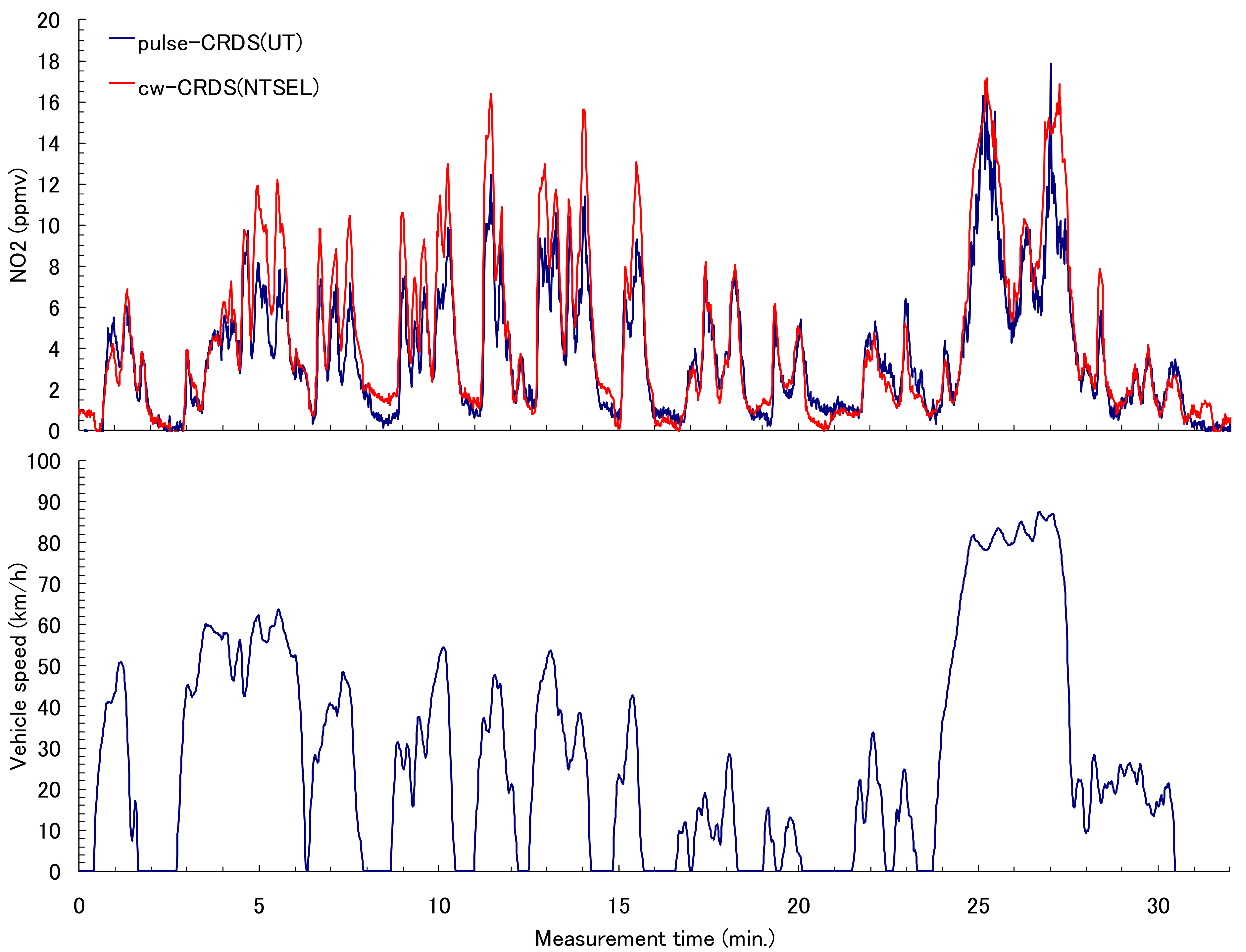


Fig.5 NO2 measurements with CW-CRDS and pulsed-CRDS with dryer

Engine Type	L4 DI
Intake air management	NA, EGR
Displacement(L)	4.8
Max. power (kW/rpm)	96 / 3000
Injection System	Common rail
Aftertreatment	DOC
GVW (kg)	4485
Emission Regulation	03 Japan

Conclusion

Developed CW-CRDS system achieved steady observation of NO2 for over 30 minutes.

CW-CRDS can detect NO2 without interferences from other species

Results indicates potential of CW-CRDS expecting application to various measurements