Absorption Spectrum Measurement for Atmospheric Level Nitric Monoxide in γ-0 Band and Its Density Deduction

Ryuji KOGA*, Keiji HIRAO**, Megumi KOSAKA*

and Hiroya SANO*

Synopsis

   An absorption spectrum of Y-0 band of nitric monoxide of very dilute density was taken. An experimental electronic device showed a distinguishing power of 0.01 ppm through 10 m optical pathlength.

   By the aid of a data processing based on a principle developed by the authors, this sensitivity does not suffer from coexisting sulfur dioxide, which shares the absorption band with the nitric monoxide.

1. Introduction

   Many laser air-pollution monitoring methods have been proposed as a superior replacement for chemical methods and some of these are proved to be promizing for a real-time and remote monitoring purpose covering wide area [1][2][3]. A local and real-time monitoring is, however, required to study a microscopic air-pollution dynamics, which is concerned with a personal health.

   Double ended laser absorption method has been demonstrated for its high sensitivity and compatibility with existing chemical methods[4]. Its high performance owes, however, to a use of a long optical pathlength and the obtained data are averages over the path, which must be short for a local monitoring.

   A method which enables a local monitoring using a short optical pathlength ought to measure very little light-attenuation spectra. The authors have developed an electronic circuit system named as "the instantaneous difference compensation

* Department of Electronics

** Graduate School of Electronics

system", which cooperates with a data processing procedure executed by a computer [5][6]. A test for a measuring device build as trial proved that it can detect 4.2×10^{-3} Np with unity S/N, which promises a measurement of very low density of coloured gaseous air-pollutants over short optical path.

This report is concerned with a test in measuring a dilute NO gas spectrum and for a method to deduce its density from the spectrum.

2. Principles

An observed absorption spectrum $\tau(\lambda)$ of a mixture gas is written as

$$\tau(\lambda) = L \sum_{i=1}^{I} c_i s_i(\lambda) + n \qquad (1)$$

where

λ : wavelength,

c_i : density of i-th gas,

$s_i(\lambda)$: absorption coefficient spectrum,

L : optical path length

n : noise.

As has been reported previously[5], the density is deduced by a numerical operation expressed by an equation,

$$c_i = \frac{1}{L} \int_\Lambda s_i^*(\lambda) \tau(\underline{\lambda}) d\underline{\lambda}, \qquad (2)$$

where $\underline{\lambda}$ stands for a nominal wavelength, or a value found in the wavelength indicator of the device used. The weight $s_i^*(\lambda)$ is the adjoint spectrum.

After experiments, a systematic error, or an offset, was found in the indicated wavelength $\underline{\lambda}$. Let $\Delta\lambda$ denote this departure from the true value. Two methods A and B to compensate the offset were tested.

Method A is to introduce a tentative $\Delta\lambda$ into the nominal wavelength $\underline{\lambda}$. An optimal $\Delta\lambda$ is chosen so as that a relative residual

$$R = \frac{\int_\Lambda \{ \bar\tau(\lambda) - \hat\tau(\lambda) \}^2 d\lambda}{\int_\Lambda \{\bar\tau(\lambda)\}^2 d\lambda} \qquad (3)$$

be minimum, where the $\hat\tau(\lambda)$ is a reconstructed spectrum by Eq.(1).

Method B is based on a fact that the Eq.(1) is modified as

$$\tau(\lambda) = \frac{1}{L}\sum_{i=1}^{I} c_i [s_i(\lambda) + \frac{d}{d\lambda} s_i(\lambda) \cdot \Delta\lambda] + n \qquad (4)$$

By preparing adjoint spectra for $s_i(\lambda)$ and $\frac{d}{d\lambda}s_i(\lambda)$, the offset $\Delta\lambda$ can be known.

3. Experiments

Experiments were made to obtain absorption spectra at $\lambda=226$ nm where γ-0 band of NO and SO_2 absorption band overlaps[7]. Spectra of the NO with various densities are shown in **Fig.1**. A wavelength offset are recognized between the curves. The spectrum of blank cell are subtracted except for that shown at the lowermost. A base spectrum was generated by compensating the wavelength offset by normalizing, by averaging over the different measurement and by smoothing. Obtained base and adjoint spectra are shown in **Fig.2**. The associated density-distance products in Fig.1 are calculated by this procedure.

Fig.3 shows spectra of very diluted nitrogen dioxides, where a curve for blank cell is cited as well. The drops found in the blank-cell curve on the both wings arise from the limited photo-diode aperture and the spacial distribution of the incident laser beam across its cross-sectional plane, which moves up and down according to the wavelength tuning because of the wavelength dependence of the phase matching angle of the used frequency-doubling crystal, the potassium penta borate.

The noise in the measured value of τ was 6×10^{-4} Np in standard deviation for a single laser shot. Taking account of this and the result of Fig.3, it is concluded that the sensitivity of our system is 0.014 ppm for 10 m pathlength, the value can be more reduced when multiple laser shots are used and the values are averaged. This result promises a real-time monitoring of the suburban atmospheric pollution monitoring.
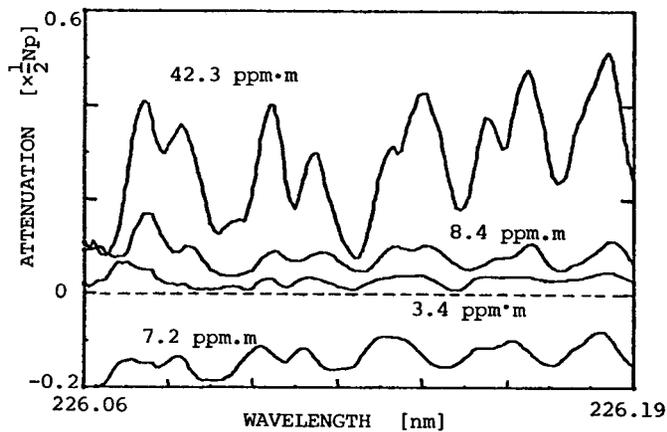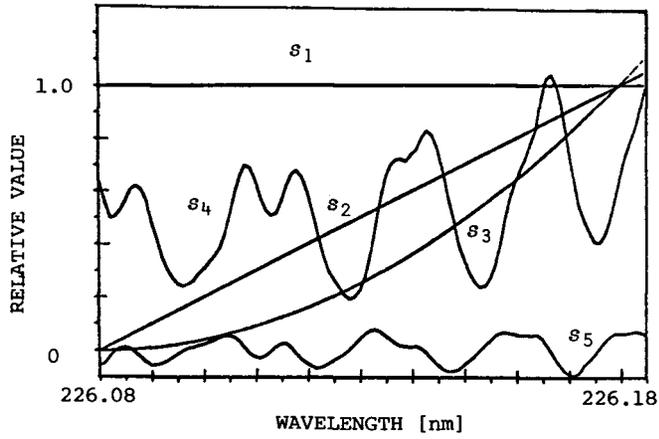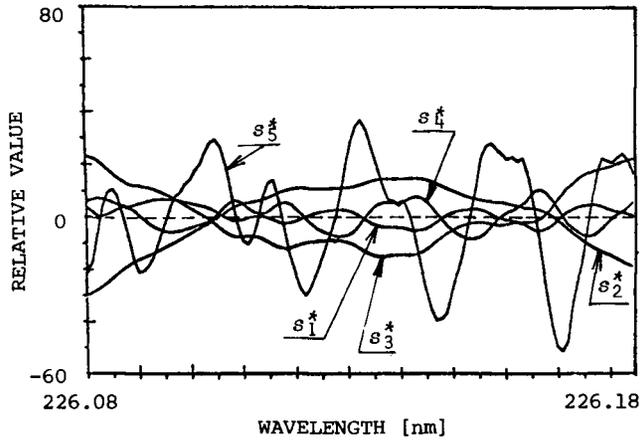

Fig.1 Absorption spectra of nitric monoxide in γ-0 band taken by the test system.

(a) base spectra

$$s_1(\lambda)=1, \quad s_2(\lambda)=\lambda-\lambda_0, \quad s_3(\lambda)=(\lambda-\lambda_0)^2, \quad s_4(\lambda)=s_{NO}(\lambda), \quad s_5(\lambda)=\frac{d}{d\lambda}s_{NO}(\lambda)$$

(b) adjoint spectra

Fig.2 Base spectra and adjoint spectra for NO simplex.
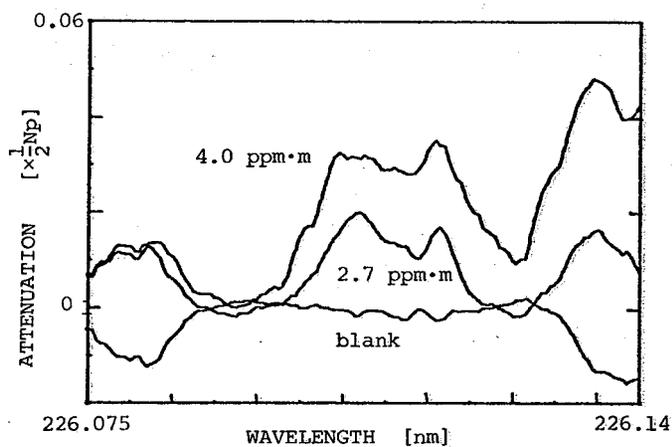
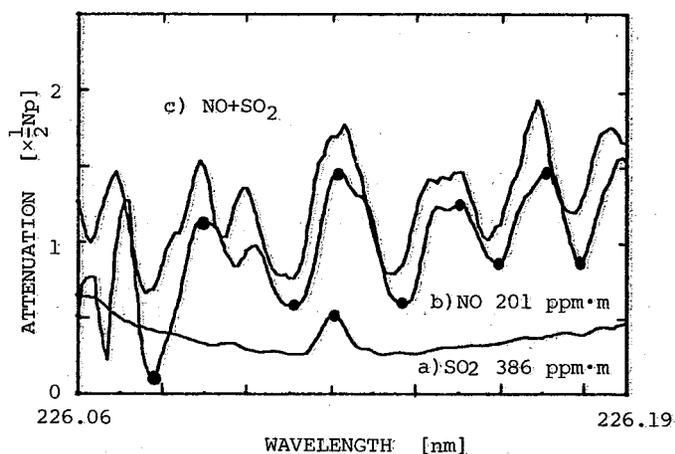Fig.3 Absorption spectra of very dilute nitric monoxide.

Fig.4 Absorption spectra of (a) sulfur dioxide, (b) nitric monoxide,
and (c) their mixture.

Spectra of NO and SO_2 mixtures are shown in Fig.4. There is significant difference between the spectrum of NO and that of SO_2, which leads to an accurate density deduction for NO, but poor for SO_2. It should be noted that the density of NO can be deduced still under heavy SO_2 interference.

Both wavelength compensation methods were tested. Method A was carried out by a desktop computer. The involved representative data are shown in Fig.4 by solid circles. The method B was executed by a large sized computer, requiring many

storage capacity and involving whole data. No difference between results of these methods were found. This is attributed to the cause that the wavelength compensating power of the method B is cancelled by a poorer immunity for noise, because amplitudes of adjoint spectra become larger with increasing number of base spectra.

4. Concluding remarks

By experiments, it has been shown that the use of the specifically developed system shows the possibility of measuring a very low density, 0.014 ppm, of NO, which may exist in local atmosphere. The immunity for a possible SO_2 absorption overlap has been also demonstrated.

References

[1]W. B. Grant, R. D. Hake Jr., E. M. Liston, R. C. Robbins, and Proctor Jr.: Appl. Phys. Lett., Vol.24, No.11(1974)550.

[2]T. Tsuji, H. Kimura, Y. Higuchi and Kenya Goto: Jap. J. Appl. Phys., Vol.15, No. 9(1976)1743.

[3]K. Asai, T. Itabe, and T. Igarashi: Appl. Phys. Lett., Vol.35, No.11(1979)60.

[4]K. Asai, H. Kuroiwa, and T. Igarashi: in Proceedings of the 8th Int. Laser Radar Conference, Drexel University, Philadelphia, Pa., 1977; Trans. IECE J.60-C, 624 (1977)(in Japanese).

[5]H. Sano, R. Koga, Y. Tanada, and M. Kosaka: Memoirs of the School of Engineering, Okayama Univ., Vol.13(1979)181.

[6]Ibid., 195.

[7]B. A. Thompson, P. Harteck, and R. R. Reeves Jr.: J. Geophysical Res., Vol.68, No.24(1963)6431.

[8] T. Tajime, T. Saheki, and K. Ito: Appl. Opt., Vol.17, No.8(1978)1290.