

GAS ABSORPTION MEASUREMENT AT 50–70GHz AND 115GHz BAND FOR IN-SITU GAS SENSOR DEVELOPMENT

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ABSTRACT

Toward the realization of in-situ gas sensors for CVD diagnosis, air pollution control processes and laboratory measurement for atmospheric radiometry, the experimental gas sensor system consisting of a vector network analyzer and Fabry-Perot type gas cell is evaluated at 50–70GHz by ambient air oxygen and pure oxygen, and at 115GHz by CO gas. The measurement verifies the system having high reliability. By the comparative study of air and pure oxygen, a new spectrum model for pure oxygen is derived. The error in the estimate of temperature and pressure from the measured spectrum is analyzed for CO spectrum measurement.

INTRODUCTION

One of the attractive industrial applications of millimeter/submillimeter wave gas spectroscopy is the embodiment of in-situ gas sensors used for various gas processes ranging from air pollution gas emission control to CVD gas synthesis in the next generation semiconductors such as super-carbon, as well as used for laboratory measurements necessary for radiometry analysis. The conceived in-situ gas sensor, as depicted in Fig. 1, consists of a vector network analyzer (VNA) and a Fabry-Perot resonator gas cell [1][2][3]. The vector measurement of the input and output radio waves at the resonator is intended to subtract the direct coupling signal between the input-output ports in the vector space, so as to attain an accurate absorption spectrum measurement. Such in-situ gas sensors will be capable of simultaneous measurement of composition, temperature and pressure of extended gas sources on a real time basis, a great advantage over conventional gas sensors.

This paper is to present the outline of the experimental in-situ gas measurement system and the results of the performance evaluation in the 50–120GHz band using well-characterized gases such as ambient air oxygen and pure oxygen, which are used for the 50–70GHz band, and carbon monoxide for 115GHz. Both measured spectra of ambient air and pure oxygen show high repeatability. It is further shown that, while the air oxygen measurement agrees well with the Microwave Propagation Model (MPM92) [4], the case of pure oxygen measurement indicates that the line shape changes by the concentration and follows a different new model, which is discussed in this paper. The CO spectrum measurement at

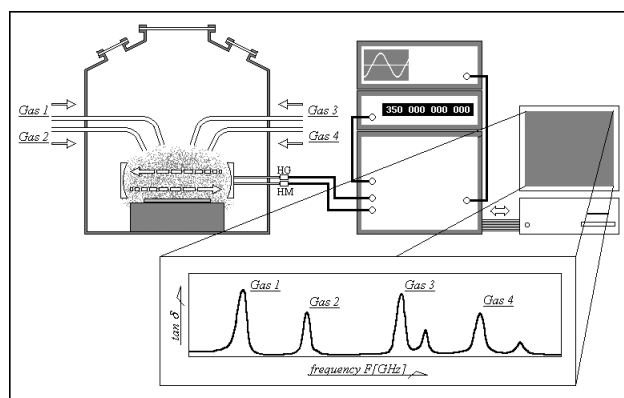


Fig. 1. Concept of in-situ gas sensor.

* This work was supported by the Sasakawa Scientific Research Grant from The Japan Science Society.

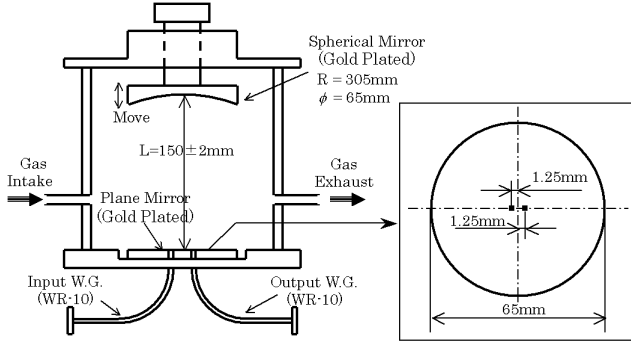


Fig. 2. Fabry-Perot resonator type absorption cell.

Table 1. Specifications.

Frequency : 8–350GHz
Resolution : $N \times 10\text{kHz}$ (N : harmonic rank)
Accuracy : Amplitude 0.1dB, Phase 0.4deg
Linearity : 110dB at 40–70GHz
95dB at 115GHz

115GHz also shows the system is highly reliable and the data fits better to the model by Colmont[5]. It is shown that the temperature and pressure can be accurately estimated.

MEASUREMENT SYSTEM

The Outline of Equipment

The measurement system consists of a vector network analyzer (VNA) and a Fabry-Perot resonator type gas cell. VNA employs frequency multipliers, and the major system characteristics are listed in Table 1. The 60–120GHz Fabry-Perot resonator is shown in Fig. 2. The quality factor is the maximum 136300 at 92GHz, 20000 at 60GHz and 60000 at 120GHz.

Acquisition of Absorption Coefficient

Absorption measurement comprises two-step Q measurements. Measuring the unloaded Q_0 by N_2 gas and the loaded Q , the absorption coefficient is given as

$$\alpha = 10^4 \log_{10} e \times \frac{2\pi f}{c} \left(\frac{1}{Q} - \frac{1}{Q_0} \right) \quad [\text{dB/km}] \quad (1)$$

where f is the frequency, e is the base of the natural logarithm, and c is the speed of light.

O₂ SPECTRUM MEASUREMENT AND NEW SPECTRUM MODEL

Results

At first, the atmospheric oxygen is measured. In Fig. 3 the black points represent the data, and the chain line indicates MPM92 that is the atmospheric oxygen spectrum model[4]. The data shows small standard error and agrees well with MPM92. Hence, the measurement is considered accurate and reliable.

At second, the pure oxygen is measured. In Fig. 3 the white points represent the data, and the dashed line indicates the converted value from MPM92 with $\alpha/0.21$ as the predicted. The data shows small standard error, so that the reliability of the measurement is regarded as high as the atmospheric measurement. Comparing with the converted MPM92, the data shows lower around the peak at 60GHz. This fact indicates that the line shape changes according to the composition, in addition that the intensity is proportional to the concentration.

Derivation of Pure Oxygen Absorption Model

As the pure oxygen spectrum measurement is considered to be accurate, a new spectrum model for the pure oxygen is derived based on MPM92. The atmospheric oxygen spectrum model introducing the line mixing parameter Y_k was first formulated by Rosenkranz in 1975[6]. According to the latest model so-called Microwave Propagation Model 92, MPM92, the line shape F_k'' is expressed as the following.

$$F_k'' = \gamma_k (\eta_+ + \eta_-) - Y_k \{ (f_k - f)\eta_+ + (f_k + f)\eta_- \} \quad (2)$$

where f_k is the line center, γ_k is the line width, Y_k is the line mixing parameter, and η_{\pm} is

$$\eta_{\pm} = f [f_k \{ (\pm f_k - f)^2 + \gamma_k^2 \}]^{-1}. \quad (3)$$

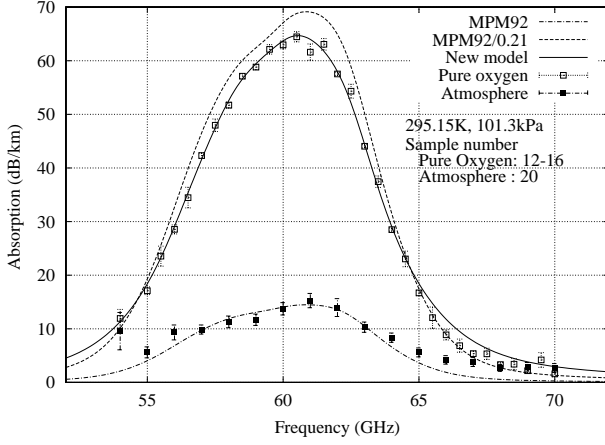
Table 2. y_k for O_2 model.

Fig. 3. Pure and atmospheric oxygen spectrum at 60GHz band.

Q# N	N-		N+	
	Line center f_k GHz	Mixing y_k $10^2/\text{kPa}$	Line center f_k GHz	Mixing y_k $10^2/\text{kPa}$
1	118.750343	-0.017	56.264775	0.139
3	62.486260	-0.199	58.446590	0.280
5	60.306061	-0.311	59.590983	0.322
7	59.164207	-0.220	60.434776	0.162
9	58.323877	0.003	61.150560	-0.084
11	57.612484	0.175	61.800154	-0.247
13	56.968206	0.257	62.411215	-0.313
15	56.363389	0.276	62.997977	-0.318
17	55.783802	0.177	63.568518	-0.210
19	55.221367	0.004	64.127767	-0.032
21	54.671159	-0.146	64.678903	0.118
23	54.130000	-0.233	65.224071	0.203
25	53.595749	-0.276	65.764772	0.245
27	53.066907	-0.309	66.302091	0.275
29	52.542394	-0.340	66.836830	0.305
31	52.021410	-0.365	67.369598	0.328
33	51.503350	-0.382	67.900867	0.344

The parts to be changed for the derivation of a new model are the line strength, the line width γ_k and the line mixing parameter Y_k . The line strength is proportional to the number of molecules. γ_k is different for the pure oxygen(O_2-O_2) and the atmospheric oxygen(O_2-N_2), because of γ_k 's dependence on the collision of each molecule. The O_2-O_2 line width is given in the [7]. Y_k is derived from the measurement data by the fitting method described in the [4]. The resultant Y_k are given by

$$Y_k = y_k \times 10^{-2} P (T/300)^{0.8} \quad (4)$$

where y_k are normalized forms of the Y_k and listed in Table 2, P is pressure in kPa and T is temperature in K. These parameters are applied to MPM92. The derived new model is shown in Fig. 3 with the solid line.

Around 60GHz the data fits to the derived new model, while at the both wing sides the data fits to the converted MPM92. The F test is used to two models. The results are $F = 2.78$ for the new model and 8.48 for the converted MPM92[8], and thus the new model fits better to the data.

CO SPECTRUM MEASUREMENT AND ESTIMATE OF CONDITION

The measurement of the CO spectrum at 115GHz is shown in Fig. 4. The data shows small standard error and hence the reliability of the measurement. Two lines in Fig. 4 are the spectrum models. The solid line is based on the line width $\Delta\nu$ with $T^{-0.5}$ proportionality [9][10], and $\Delta\nu$ is given as

$$\Delta\nu = 3.85 \times 10^5 P T^{-0.5} \quad (5)$$

where P is pressure in Pa. The dashed line is the model by Colmont [5][11], where the line width can be expressed as

$$\Delta\nu = 2.52 \times 10^4 P (T/300)^{-1.03} \quad (6)$$

The results of F test are $F = 3.24$ for the model by (5) and $F = 1.63$ for the Colmont model, so it is considered that the shape of the spectrum is closer to the Colmont model.

Furthermore, the error in the estimate of the temperature and pressure due to the discrepancy between a spectrum model and a measured spectrum is evaluated by a so-called spectrum diagram [2][10]. The spectrum diagram is constructed by the contour plots of the maximum intensity and the half-maximum full-width (HMFWM) for various temperature and pressure for a given spectrum model, so that it shows the correspondence between the set of the temperature and pressure and the set of the maximum intensity and HMFWM. Fig. 5 is the spectrum diagram based on the Colmont model. For the current measured values, the maximum intensity 122.6dB/km and HMFWM 5.254GHz, the corresponding temperature and pressure are estimated and they are listed in Table 3, along with the result with the model by (5). The Colmont model results in good estimate as 3.5% error for temperature and 2.8% for pressure.

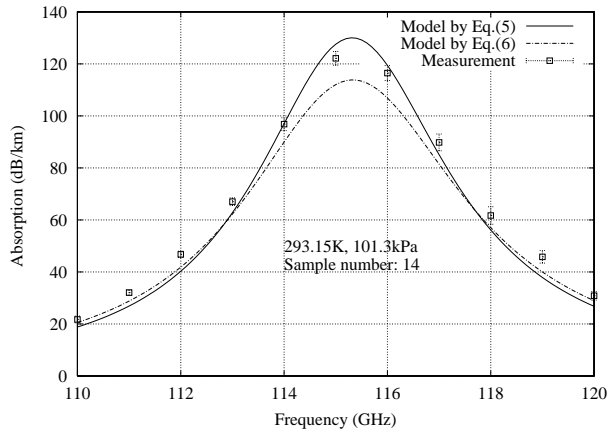


Fig. 4. CO spectrum at 115GHz band.

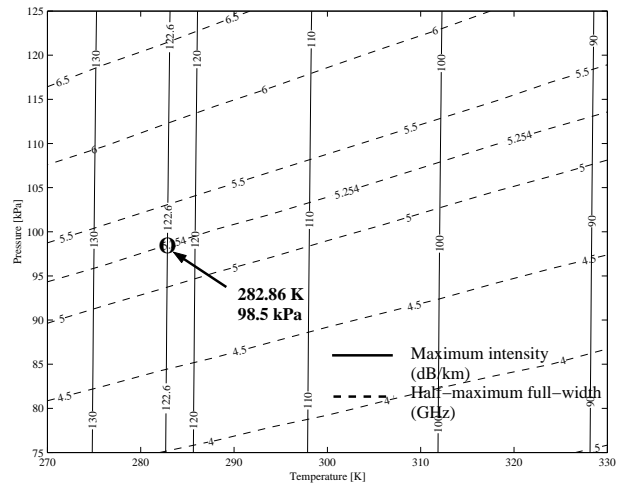


Fig. 5. CO spectrum diagram for Colmont model.

Table 3. Estimate by two models.

	Temperature (K)	error (K)	Pressure (kPa)	error (kPa)
Condition	293.15	—	101.3	—
Model by (5)	300.24	+7.09	117.7	+16.4
Model by (6)	282.86	-10.29	98.5	-2.8

CONCLUSION

The experimental gas sensor system utilizing vector measurement realizes reliable spectrum measurement. The comparative measurement of the atmospheric and pure oxygen at 50–70GHz shows the dependence of the spectrum on the composition, and a new model for the pure oxygen has been developed. The measurement of CO gas spectrum at 115GHz also shows good accuracy. The current quality of measurement coupled with well-established spectrum models will result in good estimate of temperature and pressure.

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