Gas-Absorption Spectroscopy with Electronic Terahertz Techniques

Daniel W. van der Weide, *Member, IEEE*, Janusz Murakowski, and Fritz Keilmann

***Abstract*—In this paper, we present the first gas-absorption spectra measured with an all-electronic terahertz spectrometer. This instrument uses phase-locked microwave sources to drive GaAs nonlinear transmission lines that produce picosecond pulses, enabling measurement of broad-band spectra. By sweeping the fundamental excitation, however, the spectrometer can also measure single lines with hertz-level precision, a mode of operation not readily available with optoelectronic terahertz techniques. Since this system is based on integrated circuits, it could ultimately function as an inexpensive gas-sensing system, e.g., for vehicle emissions, an application for which we analyze the sensitivity of a prototypical system.**

***Index Terms*—Electronic terahertz, environmental monitoring, gas absorption, nonlinear transmission line, spectrometer.**

I. INTRODUCTION

THERE IS A strong need for multispecies gas sensing to monitor automotive and factory emissions, particularly in the presence of particulates (e.g., soot from diesels) that scatter near-infrared radiation (NIR) used in current gas sensors.

For wavelengths longer than the NIR, Fourier-transform infrared (FTIR) spectroscopy is the dominant method for measuring multiple gas-absorption spectra [1]. While this technique is employed to accurately measure the millimeter-wave regime with specialized equipment [2], the relative weakness of the black-body source (usually a mercury vapor arc lamp) below 10 cm^{-1} (300 GHz) requires prohibitively long scans and averaging times.

In this study, we employ a spectroscopic method that is not only compact, but also free of the need for a coherent detector so that an incoherent (e.g., photoconductive or bolometric) detection mechanism can be used (Fig. 1). This eliminates the noise inherent in a sampling detector and establishes a baseline for future fully integrated implementations that would use sampling detectors.

II. EXPERIMENTAL SETUP

In the spectrometer we use here, we spatially combine the freely propagating beams from two coherent picosecond pulse generators (which have discrete spectra ranging from 6 to $>$450 GHz), resulting in a compact, reliable, and easy-to-implement microwave and millimeter-wave source for spectroscopy. Since this dual-source interferometer (DSI) modulates each harmonic of one source with a precisely offset harmonic from the other source—both sources being driven with stable phase-locked synthesizers—the resultant beat frequency can be low enough for detection by a standard composite bolometer [3]. Room-temperature detection possibilities for the DSI include antenna-coupled Schottky diodes. An integrated frequency translator [4], [5] will further improve the portability and reduce the cost of this system.

A. Spectroscopy Using Nonlinear Transmission Lines

To generate broad-band (discrete) spectral energy, we use nonlinear transmission line (NLTL) pulse generators coupled to broad-band planar antennas. The GaAs integrated circuit (IC) NLTL's used in this study consist of series inductors (or sections of high-impedance transmission lines) with varactor diodes periodically placed as shunt elements. On this structure at room temperature, a fast (∼1–2 ps) voltage step develops from a sinusoidal input because the propagation velocity u is modulated by the diode capacitance , $u(V) = 1/\sqrt{LC(V)}$, where L is the line inductance and $C(V)$ is the sum of the diode and parasitic line capacitance [6], [7]. Limitations of the NLTL arise from its periodic cutoff frequency, waveguide dispersion, interconnect metallization losses, and diode resistive losses. Improvements in NLTL design have resulted in sub-picosecond pulses at room temperature [8].

In the DSI, the output of each NLTL feeds an integrated bow-tie antenna (Fig. 2) mounted at the focus of a hyperhemispherical high-resistivity silicon lens [9]. These lenses in turn are mounted at the foci of off-axis paraboloidal mirrors. The beams collimated by the mirrors are either transmitted (Source "A") or reflected (Source "B") by a wire-grid polarizing beamsplitter (PB). Each beam then equally contributes to the final linearly polarized beam by arrangement of a final wire-grid polarizer mounted at 45° to the beamsplitter. Note that while the prototype construction is already small (∼170-mm long, 120-mm wide, and 80-mm high), it would be possible to fabricate two antennas and their circuitry on the same substrate, making the whole system more compact [10]. We also note that other workers have described similar ideas using laser-triggered photoconductive switches [11]–[13], but one advantage of the current system is its all-electronic approach, which offers

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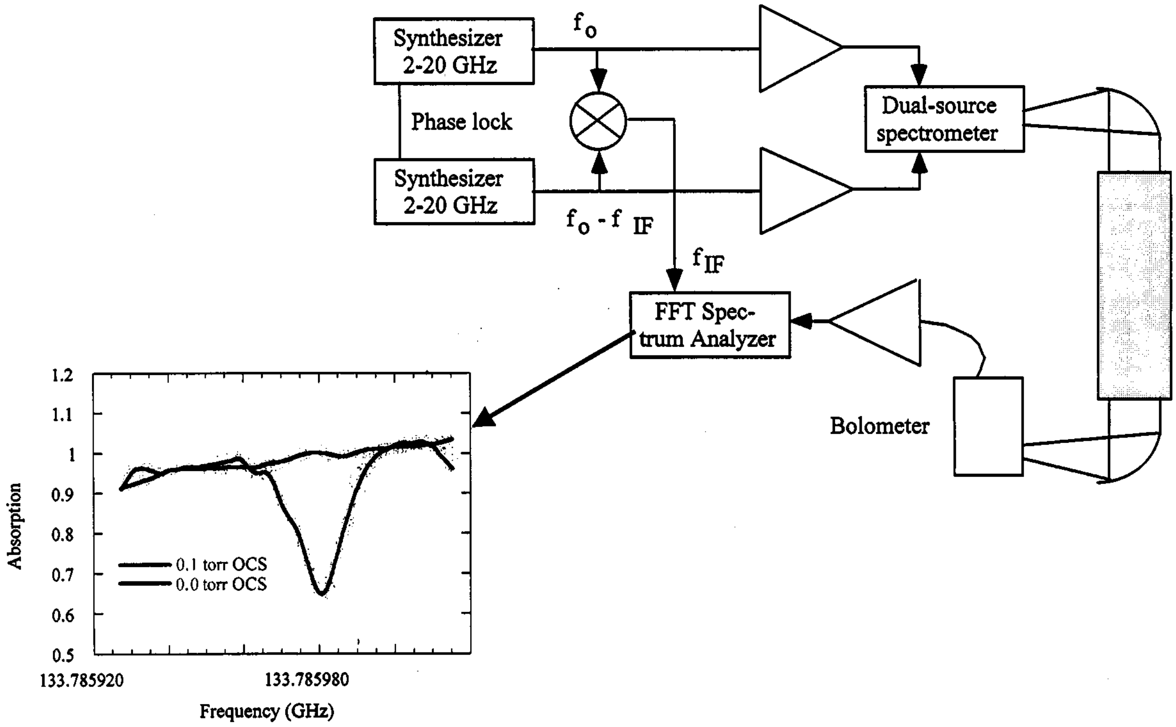

Fig. 1. Dual-source spectrometer system configured for gas-absorption measurements. Inset shows raw and smoothed data from 0.1-torr carbonyl-sulfide (OCS) versus vacuum from a 760-mm-long cell, uncorrected for background power slope. Horizontal scale is 20 kHz per large division.

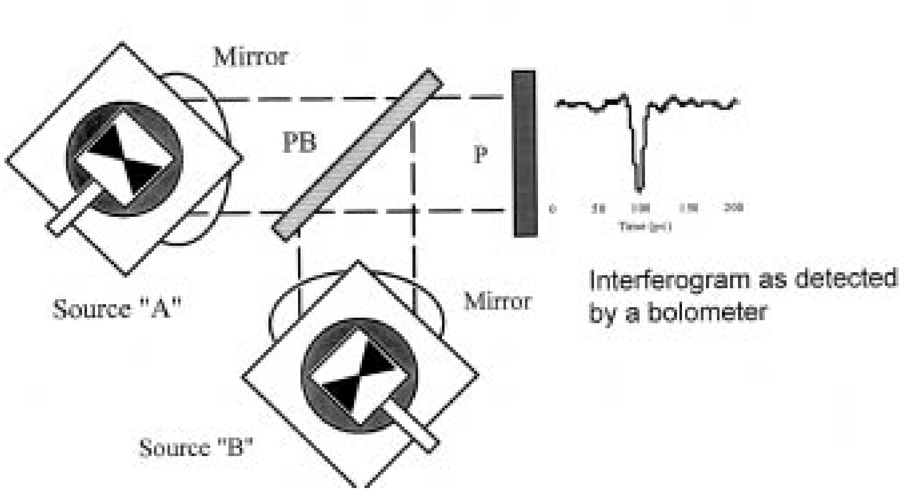

Fig. 2. DSI configuration. Each source/antenna combination is at the focus of a paraboloidal mirror and radiates a polarized beam, which is transmitted ("A") or reflected ("B") by the PB. The output wire grid polarizer (P) selects half the power of each beam. The output waveform is that detected by a bolometer [3].

precise amplitude (0.01 dB) and frequency (1 Hz) control of the fundamental excitation.

Each source is fed by a 100–500-mW sinewave generated by one of two microwave synthesizers, both of which share a common 10-MHz timebase. The output of one synthesizer is offset by $\Delta f \ll f_o$ ($\Delta f \sim 100$ Hz, ; $f_o = 3$–10 GHz), and this offset is used as a trigger for a fast Fourier transform (FFT) spectrum analyzer or digital lock-in amplifier. While the synthesizers and broad-band power amplifiers used in the present demonstration are expensive, they could be replaced by an inexpensive single source combined with a new NLTL-based frequency translator [4], [5].

III. RESULTS

As shown in Fig. 1, the DSI can illuminate a single-pass absorption cell using off-axis paraboloidal mirrors to collimate the radiation and collect it for detection by the bolometer. Using a digital lock-in amplifier, we could measure a single harmonic of the DSI, in this case, at 133.785 980 GHz, the twentieth

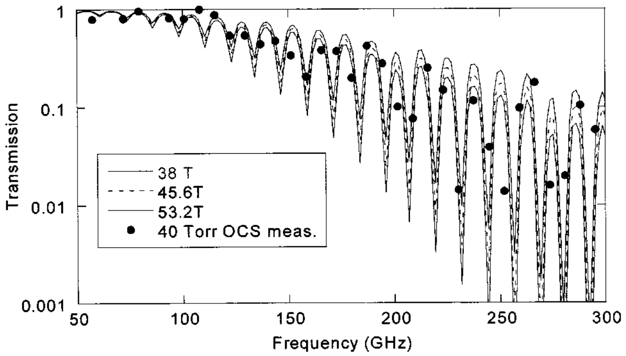

Fig. 3. 40-torr OCS broad-band absorption data from a 4-m cell (points) compared to HITRAN database predictions for 38-, 45.6-, and 53.2-torr OCS.

harmonic of the fundamental of 6.689 299 GHz. To measure the data shown, we used a third synthesizer to provide the 10-MHz timebase for the microwave synthesizers, and then varied this 10-MHz signal to continuously sweep the harmonics of the DSI. This enabled the extremely narrow linewidth of 0.1-torr OCS to be resolved, with an equivalent $Q(f_o/\Delta f)$ of >8 × 10^9. We have also measured CO and NH_3 lines using the same method. This represents the first such lines to be resolved at this precision.

By measuring nominally 40-torr OCS absorption in the conventional fixed-fundamental mode (Fig. 3), we observed good correspondence with the predictions of the HITRAN molecular database, though some effects of standing waves were apparent.

IV. ANALYSIS

In order to set a baseline for comparison of future all-electronic terahertz systems to be used for diagnostics of emissions, here we establish limits of sensitivity for pollutants commonly found in car exhaust. Rather than use the DSI configuration with a bolometric detector, which would be impractical for automotive on-board diagnostics, future systems may employ sampling detectors at possibly lower sensitivities. Thus, we analyzed system uncertainties versus frequency in a conventional sampling detector configuration [14]–[16]. We performed detailed measurements and analysis of the transmission coefficient uncertainty in a system with moderate performance, and found it to be <0.5 dB, (in the range of 0–200 GHz, similar to the ~0.2–0.4 dB reported by Konishi *et al.*[17], and the 0.2–0.3 dB of the DSI configuration), rising at ~2 dB/100 GHz (in the range of 200–500 GHz).

The power of a microwave signal traveling through length z of gas at temperature T and pressure p is

$$P(z) = P_0 \exp\left(-\sigma \frac{A_0 p}{RT} z\right)$$

where R is the gas constant, $R = 8.314$ J/(mol K), σ is the cross section of the molecule, $A_0 = 6.023 \times 10^{23}$ mol^{-1} is Avogadro's number, and P_0 is the incident power of the microwave signal. If we have a mixture of gasses, the above formula then becomes

$$P(z) = P_0 \exp\left(-\frac{A_0 z}{RT} \sum_i \sigma_i p_i\right)$$

where the sum is over the gas species in the mixture, and σ_i and p_i are the cross section and the partial pressure, respectively, of the each gas component.

TABLE I
DETECTION LIMITS FOR COMMON EXHAUST GAS SPECIES

Species	Detection limit (concentration)
H_2O	0.0081
CO	0.025
N_2O	0.018
NO	0.0084
NO_2	0.0080
H_2CO	0.00019
SO_2	0.00034

What is measured experimentally is the ratio P/P_0. The information about the composition of the gas mixture is obtained by fitting the linear combination $\sum_i \sigma_i p_i$ to the experimental absorption spectrum by adjusting the partial pressures p_i. If we measure the ratio $r = P/P_0$ at frequencies f_j enumerated by a discrete index j to get a vector r_j of absorptions at frequencies f_j, the partial pressures of the gasses in the mixture can be expressed as

$$p_i = -\frac{RT}{A_0 z} \sum_j A_{ij} \ln r_j$$

where the matrix A_{ij} is given by $A = (ss^T)^{-1} s$, and s is the matrix of cross sections σ_i of the gasses in the mixture at frequencies f_j; the superscript ^{T} in s^T denotes matrix transposition. Extracting information about partial pressures from the absorption spectrum is possible if and only if $\det(ss^T) \neq 0$, which formally requires that the number of frequencies at which we measure the absorption is not less than the number of gas species present in the mixture. In practice, the number of analyzed frequencies in our system is much greater than the number of detected gas species.

The sensitivity of the method depends on:

- absorption spectrum of the particular substance in the frequency range generated by the system;
- presence of other absorbers;
- accuracy of the measurement of the absorption spectrum;
- in case of gasses, the ambient pressure and temperature.

The effect of the absorption spectrum uncertainty on the sensitivity measurement can be analyzed as follows. Assume that the uncertainty of the measurement of the absorption r_j at the jth frequency is Δr_j. The uncertainty of the partial pressure of the ith gas is then

$$\Delta p_i = \frac{RT}{A_0 z} \sqrt{\sum_j \left(A_{ij} \frac{\Delta r_j}{r_j}\right)^2}$$

assuming that other quantities have negligible uncertainties. The uncertainty of the partial pressure Δp_i is essentially the detection limit, or sensitivity, for the ith gas.

Using measured uncertainties with an achievable <100 ms averaging time and the $T = 400$ K, $P = 1$ atm HITRAN gas spectra typical of automotive tailpipe conditions, we obtain the following detection limits for common exhaust gas species shown in Table I.

Improvements in these sensitivities will come with frequency modulating the source (as demonstrated above) to continuously sweep through absorption lines rather than use the fixed frequencies of this analysis.

V. CONCLUSION

We have described and demonstrated a technique for gas-absorption spectroscopy using a new all-electronic terahertz interferometer having no moving parts, but rather one whose phase is controlled electronically via a frequency offset between its two identical sources. This enables extremely high quality-factor measurements of low-pressure absorption while ensuring absolute accuracy set by phase-locked synthesized sources.

This study lays the foundation for multispecies gas spectroscopy using multiple-resonant cavities and fully integrated terahertz sources and detectors.

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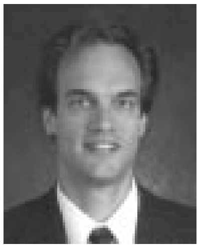

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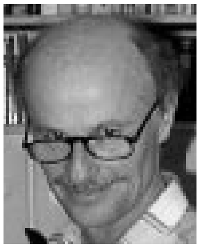

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