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Advanced Millimeter Wave Chemical Sensor

N. Gopalsami

Energy Technology Division
Argonne National Laboratory, Argonne, Illinois 60439

Abstract

This paper discusses the development of an advanced millimeter-wave (mm-wave) chemical sensor and its applications for environmental monitoring and arms control treaty verification. The purpose of this work is to investigate the use of fingerprint-type molecular rotational signatures in the mm-wave spectrum to sense airborne chemicals. The mm-wave sensor, operating in the frequency range of 220-300 GHz, can work under all weather conditions and in smoky and dusty environments. The basic configuration of the mm-wave sensor is a monostatic swept-frequency radar consisting of a mm-wave sweeper, a hot-electron-bolometer or Schottky barrier detector, and a trihedral reflector. The chemical plume to be detected is situated between the transmitter/detector and the reflector. Millimeter-wave absorption spectra of chemicals in the plume are determined by measuring the swept-frequency radar return signals with and without the plume in the beam path. The problem of pressure broadening, which hampered open-path spectroscopy in the past, has been mitigated in this work by designing a fast sweeping source over a broad frequency range. The heart of the system is a Russian backward-wave oscillator (BWO) tube that can be tuned over 220-350 GHz. Using the Russian BWO tube, a mm-wave radar system was built and field-tested at the DOE Nevada Test Site at a standoff distance of 60 m. The mm-wave system detected chemical plumes very well; the detection sensitivity for polar molecules like methyl chloride was down to a concentration of 12 ppm.

I Introduction

Remote or standoff detection of airborne chemicals is gaining importance for arms control treaty verification and environmental monitoring. When compared with point detection or sampling techniques, the remote method is nonintrusive and can be used to monitor wide areas. Optical and laser techniques for sensing volatile organics and other hazardous chemicals are under active development in the infrared, visible, and ultraviolet regions of the electromagnetic spectrum.[1-3] The purpose of this work is to investigate the use of the mm-wave spectrum to remotely monitor chemicals. The mm-wave sensors use longer wavelengths than those of optics and thus can operate under all weather conditions and in smoky and dusty environments.

Millimeter-wave spectroscopy is a well-established laboratory technique for determining the structure and dynamics of molecules in the gas or vapor phase.[4] Millimeter-wave spectral lines are narrow and nearly 100% specific when analyzed in a gas cell under low pressures (<1 torr). However, when applied to open-air monitoring, the higher pressures cause the spectral lines to broaden because of molecular collisions. A typical air-broadening parameter of a molecule is 4 MHz/torr (half width at half height) and it is $\approx$4 GHz at 1 atm. Conventional detection methods that are capable of high detection sensitivities at low pressures, e.g., Stark modulation or phase lock techniques, are not directly applicable to open-air detection. Hence, new detection methods and systems are needed for remote detection of trace chemicals in air.

One way to overcome the pressure-broadening effect is to use a swept-frequency mm-wave source that can sweep over a broad frequency range in a short time. The wide-frequency sweep improves spectral line resolution and molecular selectivity, whereas the fast sweep allows for efficient baseline subtraction by direct video detection. The feasibility of open-air mm-wave spectroscopy was first demonstrated by using a monostatic, swept-frequency radar system in the 225-315 GHz range.[5] The mm waves were generated with a low-frequency sweeper and low-power frequency triplers. The narrow bandwidth of the triplers also limited the tuning range to within 50 GHz. The proof-of-principle of this system was tested by detecting D_2O in open air. In addition, the chemical selectivity of the technique was demonstrated by using a special deconvolution procedure.[6] Individual chemicals in a multicomponent mixture were determined from both simulated and experimental spectra.

With recently available backward-wave-oscillator (BWO) tubes (Model OB-30) from Istok Corporation, Russia, we developed a prototype radar system that can sweep the entire frequency range within 10 ms and generate

up to 10 mW of power.[7] This higher power allows a longer detection range and the wider tuning range improves the resolution of spectral lines. The radar system was recently field-tested at the DOE Nevada Test Site at a standoff distance of 60 m. Two chemicals, methyl chloride and butanol, were released from a wind tunnel at different concentrations. This paper describes the mm-wave sensor, the field test setup, and test results for methyl chloride and butanol releases.

II Description of mm-Wave Radar Sensor

The mm-wave sensor, shown in Fig. 1, is a monostatic radar system that operates in an atmospheric window in the frequency range of 225-315 GHz. Swept-frequency signals in the 225-315 GHz range are generated by a mm-wave sweeper that was built with a BWO tube (OB-30) from the Istok Company, Russia. The mm-wave radiation is transmitted through a chemical plume using a lens antenna. A corner cube, located behind the plume, returns the radar signals through the plume to a mm-wave detector situated next to the transmitter. Millimeter-wave absorption spectra of chemicals in the plume are determined by measuring swept-frequency radar signals with and without the plume in the beam path. A Fabry-Perot (F-P) cavity, that consumes a small part of the mm-wave energy, generates frequency markers for on-the-fly calibration of frequencies.[8] The F-P cavity markers allow accurate subtraction of baseline and also signal averaging.

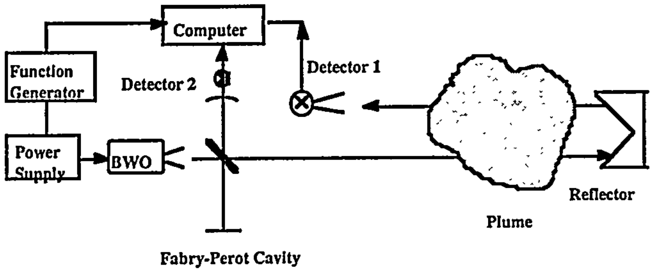

Figure 1. Schematic diagram of mm-wave radar system

III Field Test Setup

The mm-wave system was field-tested at the Nevada Test Site at Frenchman Flat near Mercury, Nevada. A wind tunnel capable of producing well-characterized open-air plumes was used to release desired concentrations of chemical vapors. The test of the mm-wave sensor was staged from a trailer 60 m away from the wind tunnel, in the cross wind direction. The trailer was fitted with an air conditioner and 110-V single-phase power supply. Figure 2 shows the mm-wave sensor trailer together with the wind tunnel and corner cube. The mm-wave radiation (≈10 mW of power) was transmitted through one of the trailer windows into the wind tunnel plume. The window was covered with a plastic film that was transparent to mm waves. A 6-in. lens, focused at infinity, was used to provide a highly directed beam. The cone angle of the beam is 0.37 °, with a footprint of 0.6 m at the wind tunnel. An aluminum corner cube with a 0.9 x 0.9 x 0.9-m opening was fabricated and mounted behind the plume to return radar signals. The return signals were collected by a 6-in. lens, coupled to a liquid-helium-cooled (hot electron) bolometer detector situated next to the transmitter.

For safety reasons, the trailer was not manned during the release, leaving the mm-wave sensor unattended during the test. Typically, an area sweep occurred at ≈11:30 AM at which time the final checks on the sensor were made and trailer was evacuated. Data were collected remotely from the wind-tunnel control room, 1.7 km away, via an RF link between a master computer in the control room and the data-acquisition (slave) computer in the trailer in master/slave fashion.

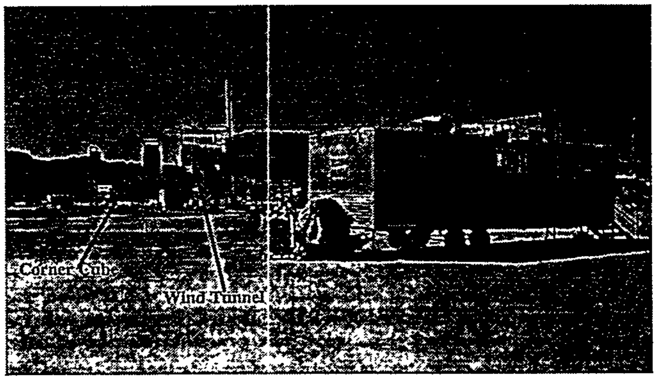

Figure 2. Millimeter wave system trailer, wind tunnel, and corner cube

IV Test Results

The mm-wave spectral data of methyl chloride and butanol were first measured in the laboratory with a 1.4-m gas cell. To simulate atmospheric pressure, a certain amount of each chemical was mixed with nitrogen to a pressure of 1 atm. Figure 3 shows the measured and model absorption spectra of methyl chloride in the frequency range of 230-298 GHz. The model lines were simulated with data from the JPL molecular database.[9]

Figure 4 shows the measured absorption spectra (dashed line) of butanol obtained in the laboratory from 664 mtorr of butanol mixed with nitrogen to 1 atm. The signal fluctuations in the measured spectra correspond to basline variation due to the sweeper power change with frequency. The measured data were curve fitted to eliminate the basline fluctuation, as shown by the solid line. Because butanol is not in any of the known databases, the solid line is used as the model spectra of butanol for later data analysis.

Before the tests, the system frequencies were calibrated with a gas cell using acetonitrile. A triangular ramp of 40 ms period was used to sweep from 226 to 298 GHz and data were collected during up-ramp. The data acquisition procedure varied for methyl chloride and butanol. The release profile of methyl chloride was in the form of an on-off pattern, each pattern typically lasting ≈5 min. Reference and plume signals were taken with 100 averages each during the plume-off and -on periods, respectively. To minimize the DC drift due to sweeper instabilities, butanol data were collected continuously without averaging before and during the release of each butanol concentration. Three channels of data, 10,000 samples per channel, were collected: DC- and AC-coupled data from the bolometer and F-P cavity data. The AC-coupled channels worked well, but the DC-coupled channel drifted slowly, and eventually saturated ≈2 h after the start of each day of test. To interpret the spectral data, we will next develop the data analysis procedures for the DC- and AC-coupled cases.

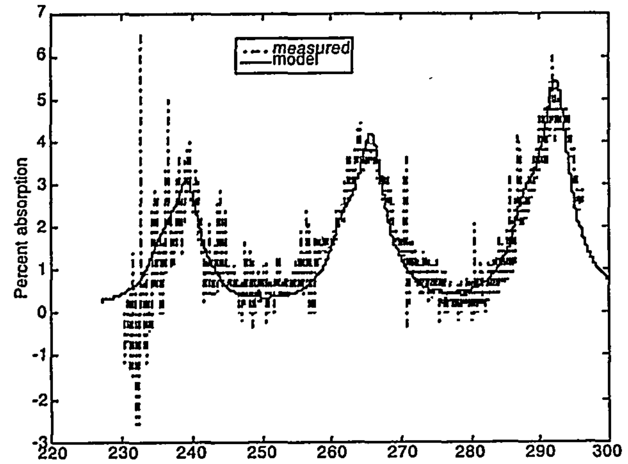

Figure 3. Methyl chloride spectra obtained in the laboratory from 377 mtorr of methyl chloride mixed with nitrogen to 1 atm in 1.4-m gas cell

DC-coupled data

The DC-coupled data collection refers to measurement of the absolute power of mm waves with respect to frequency. Let $P_0(\upsilon)$ be the output power of the transmitter as a function of frequency, and $P_1(\upsilon)$ and $P_2(\upsilon)$ the power measured by the detector without and with the plume, called reference and plume signals, respectively. Then

$$P_1(\upsilon) = P_0(\upsilon)\,T \qquad (1)$$

and

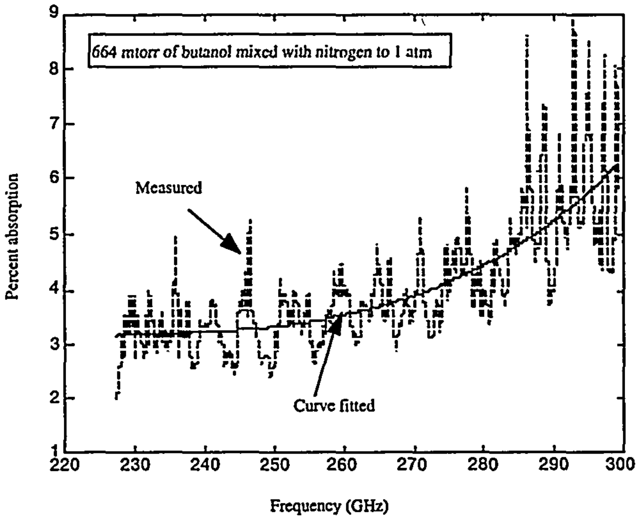

Figure 4. Butanol spectra obtained in the laboratory from 664 mtorr of butanol mixed with nitrogen to 1 atm in 1.4-m gas cell

$$P_2(\upsilon) = P_0(\upsilon)\,T \exp[-\,\alpha(\upsilon)\,C\,\ell], \qquad (2)$$

where T is the two-way transmission coefficient of the atmosphere between the transmitter antenna and receiver, $\alpha(\upsilon)$ is the absorption coefficient (cm^{-1}) of 1 ppm of chemical in the air at frequency υ, C is the concentration of the chemical (ppm), and ℓ is the path length (cm) of the plume. The difference between the reference and plume signals $D(\upsilon)$ is given by

$$D(\upsilon) = P_1(\upsilon) - P_2(\upsilon) = P_1(\upsilon)\left\{1 - \exp[-\alpha(\upsilon)\,C\,\ell]\right\}. \qquad (3)$$

Thus, in the DC-coupled case, the absorption coefficient $\alpha(\upsilon)$ can be determined by dividing Eq. 3 by the reference signal. For trace amounts of gases to be released in the open air, $\alpha(\upsilon)C\ell$ is small, and Eq. 3 becomes

$$D(\upsilon) = \alpha(\upsilon)\,C\,\ell\,P_1(\upsilon). \qquad (4)$$

AC-coupled data

The AC-coupled data refers to the ac-type signal (high-pass filtered signal) from the detector circuit that blocks the DC-level signals. This mode of data collection avoids saturation of the detector preamplifier if the detector signal drifts with time. Let a bar over the variables represent AC-coupled signal operation. For the AC-coupled case, Eqs. 1 and 2 become

$$\overline{P}_1(\upsilon) = \overline{P}_0(\upsilon)\,T \qquad (5)$$

and

$$\overline{P}_2(\upsilon) = \overline{P}_0(\upsilon)\,T - \overline{P_0(\upsilon)\,T\,\alpha(\upsilon)\,C\,\ell} + \frac{\overline{P_0(\upsilon)\,T\,\{\alpha(\upsilon)\,C\,\ell\}^2}}{2} - \ldots \qquad (6)$$

For gaseous absorption lines that are small and broad, the difference between the reference and plume signals, Eq. 5 - Eq. 6, becomes

$$\overline{D}(\upsilon) = \overline{P}_1(\upsilon) - \overline{P}_2(\upsilon) = \overline{P_0(\upsilon)\,\alpha(\upsilon)}\; C\,\ell\,T \cong \overline{P}_1(\upsilon)\,\alpha(\upsilon)\,C\,\ell \;. \quad (7)$$

Thus, the difference signal, (Eq. 7), represents an amplitude modulation of the reference signal by the plume absorption coefficient. As in Eq. 3 of the DC-coupled case, it is not possible to separate out the absorption coefficient by dividing the difference signal by $\overline{P}_0(\upsilon)$ because of its AC nature and possible zero crossings. However, the absorption coefficient $\alpha_m(\upsilon)$ of a chemical can be determined from one of the published molecular data bases, such as the JPL catalog, or by measuring it with a gas-cell spectrometer. In that case, $\overline{D}(\upsilon)$ in Eq. 7 can be fitted with a model $\overline{E}(\upsilon)$, given by

$$\overline{E}(\upsilon) = \alpha_m(\upsilon)\, C\,\ell\,\overline{P}_1(\upsilon), \quad (8)$$

where the constant C may be chosen such that it minimizes the values of the integral of the squared error, S(C), over the sweep frequencies f_1 to f_2. Thus,

$$S(C) = \int_{f_1}^{f_2} [\alpha_m(\upsilon)\, C\,\ell\,\overline{P}_1(\upsilon) - \overline{P}_1(\upsilon) + \overline{P}_2(\upsilon)]^2 d\upsilon . \quad (9)$$

By setting dS(C)/dC = 0, the equation for C becomes

$$C = \frac{\int_{f_1}^{f_2} \alpha_m(\upsilon)\,\ell\,\overline{P}_1(\upsilon)[\overline{P}_1(\upsilon) - \overline{P}_2(\upsilon)]d\upsilon}{\int_{f_1}^{f_2} [\alpha_m(\upsilon)\,\ell\,\overline{P}_1(\upsilon)]^2 d\upsilon} . \quad (10)$$

Figure 5 gives the AC-coupled data that correspond to 150 ppm of methyl chloride, for example, in which the dotted line represents the difference signal between the reference and the plume, and the solid line represents the model-fitted signal. The model fits the measured data well, eliminating the high frequency noise. To show that the difference signal is an amplitude modulation of the reference signal by the plume absorption coefficient, we have overlain an envelope of appropriately scaled model absorption curves. Figure 6 gives the corresponding AC-coupled data for butanol at 1200 ppm concentration.

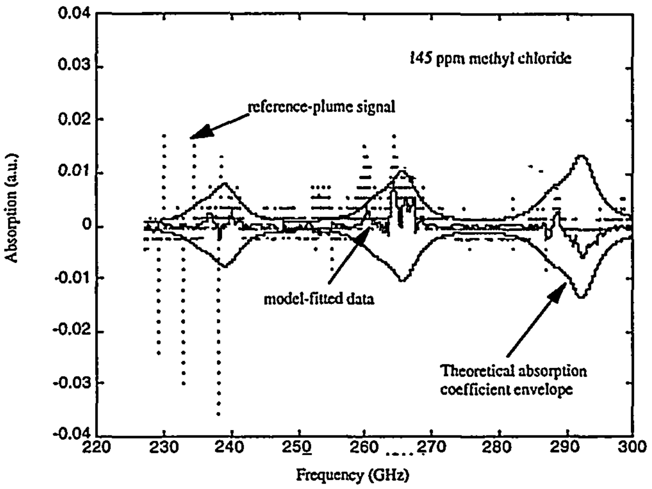

Figure 5. Difference signal between the reference and the plume (dotted line), model-fitted signal (solid line), and absorption coefficient envelope (solid line) for methyl chloride

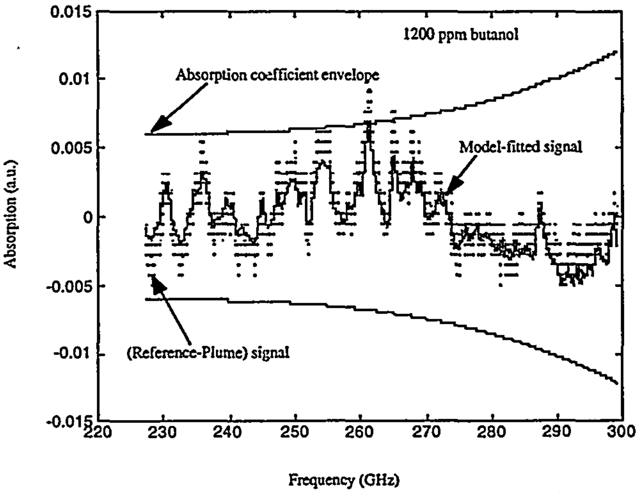

Figure 6. Difference signal between the reference and the plume (dotted line), model-fitted signal (solid line), and absorption coefficient envelope (solid line) for butanol

Figures 7 and 8 present plots of the model-fitted data for methyl chloride and butanol, respectively. These model data agreed well with the corresponding difference data between the reference and the plume. The corresponding values of C, from Eq. 10, are plotted in Figs. 9 and 10, respectively, with respect to the actual release concentrations. The value of C calculated from the model thus provides a good estimate of the release concentration.

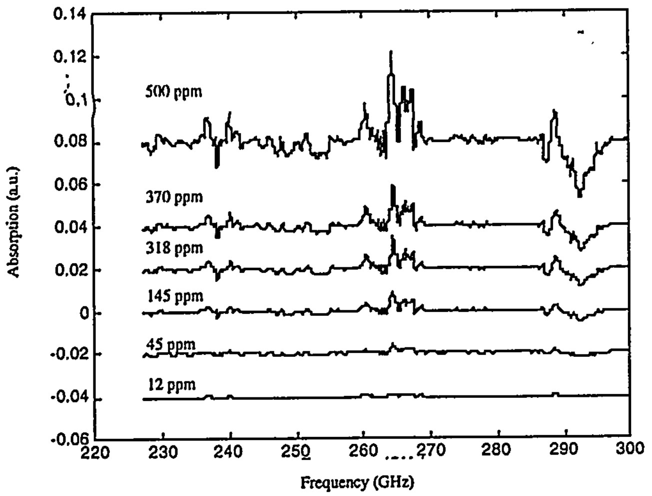

Figure 7. Plots of model-fitted spectra for various concentrations of methyl chloride

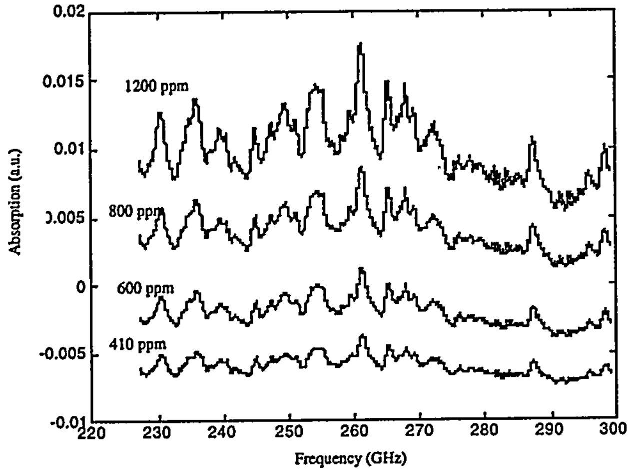

Figure 8. Plots of model-fitted spectra for various concentrations of butanol

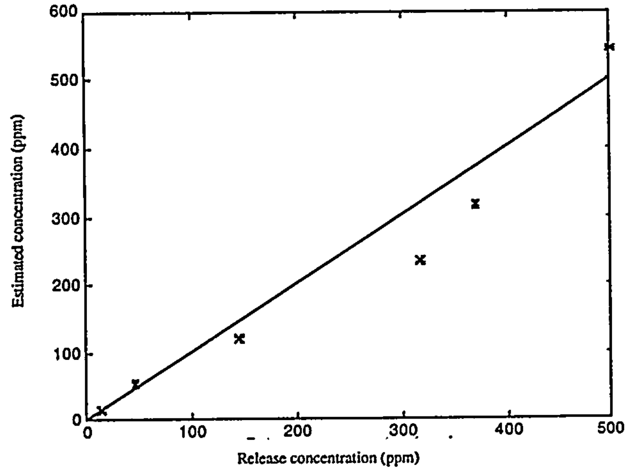

Figure 9. Estimated concentration of methyl chloride based on model fit

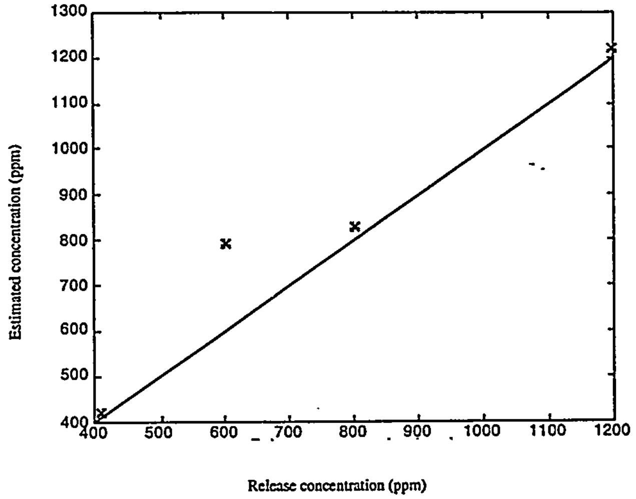

Figure 10. Estimated concentration of butanol based on model fit

V Conclusions

A millimeter-wave chemical sensor, developed at Argonne National Laboratory, was field tested at the Nevada Test Site. The objective of the test was to demonstrate the capability of the sensor to remotely detect chemicals that are pertinent to verification of the arms control treaty and environmental monitoring. The test of the sensor was staged from a trailer at a standoff distance of 60 m from the plume. The return of radar signals was provided by a 0.9-m corner cube mounted behind the plume.

Both DC- and AC-coupled bolometer data were collected remotely from a control room. Reference and plume signals were collected by using 20-ms sweeps and 100 averages, with the plume on and off for 2 to 5 min intervals. Whereas the DC-coupled signals saturated the preamplifier $\approx$2 h after the start of the experiments, the AC-coupled mode of data collection worked well during the entire test period of $\approx$7 h. The meteorological conditions during the tests were somewhat benign: 35°C, 8% relative humidity, and winds of 5-10 m/s. At times, wind gusts produced a blowing sand storm.

A model-based analysis procedure has been developed to interpret and quantify the acquired AC-coupled data. The analysis shows that the difference between the reference and plume signals is essentially an amplitude modulation of the reference signal by the plume absorption function. The correlation constant between the measurement and model data provides a quantitative estimate of the chemical concentration. Good agreement between the measured and model data was obtained for various release concentrations of methyl chloride and butanol. A linear fit was obtained between the estimated and actual concentrations. The detection sensitivity of the sensor, for example, was 12 ppm for methyl chloride.

Because of generally poor long-term stability of the mm-wave sweepers, it was necessary to keep the time interval between the reference and plume signals short, within ≈2 to 3 min, to obtain reproducible results. One approach to further improve the detection sensitivity is to use two reflectors, one in the front and another in the back of the plume, and to steer the mm-wave beam between the two reflectors. This allows for long signal averages, while the time interval between the collection of reference and plume signals remains short.

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References

[1] W. B. Grant, R. H. Kagann, and W. A. McClenny, "Optical remote measurement of toxic gases, J. Air Waste Manage. Assoc., vol. 42, pp. 18-30, 1992.

[2] S. P. Levine and G. M. Russwurm, "Fourier transform infrared optical remote sensing for monitoring airborne gas and vapor contaminants in the field," trends in analytical chemistry, vol. 13, pp. 258-262, 1994.

[3] J. V. Cernius, D. A. Elser, and J. Fox, "Remote active spectrometer," SPIE Laser Applications in Metrology and Earth and Atmospheric Remote Sensing, vol. 1062, pp. 164-171, 1989.

[4] W. Gordy and R. L. Cook, *Microwave Molecular Spectra*, John Wiley, New York, 1984.

[5] N. Gopalsami, S. Bakhtiari, A. C. Raptis, S. L. Dieckman, and F. C. DeLucia, "Millimeter-wave measurements of molecular spectra with application to environmental monitoring," IEEE Trans. Instrum. Meas., vol. 45, pp. 225-230, 1996.

[6] N. Gopalsami, S. Bakhtiari, A. C. Raptis, and S. L. Dieckman, "Millimeter-wave sensor for monitoring effluents," U.S. patent No. 5468964, November 1995.

[7] N. Gopalsami, S. Bakhtiari, and A. C. Raptis, "Open-path millimeter-wave spectroscopy in the 225-315 GHz range," Proc. Int. Conf. on Millimeter and Submillimeter Waves and Applications III, SPIE, vol. 2842, pp. 274-283, 1996.

[8] A. Dryagin, V. V. Parshin, A. F. Krupnov, N. Gopalsami, and A. C. Raptis, "Precision broadband wavemeter for millimeter and submillimeter range," IEEE Trans. Microwave Theory Techniques, vol. 44, pp. 1610-1613, 1996.

[9] L. Poynter and H. M. Pickett, "Submillimeter, Millimeter, and Microwave Spectral Line Catalog," JPL Publication 80-23, Revision 2, 1983.