# Gas filter correlation instrument for air monitoring at submillimeter wavelengths

**G. Mouret, W. Chen, and D. Boucher**

*Laboratoire de PhysicoChimie de l'Atmosphère, Université du Littoral, 145 Route du Pertuis d'Amont, 59140 Dunkerque, France*

**R. Bocquet**

*Laboratoire de Physique des Lasers Atomes et Molécules, Université des Sciences et Technologies de Lille, 59655 Villeneuve d'Ascq Cedex, France*

**P. Mounaix and D. Lippens**

*Institut d'Electronique et de Microélectronique du Nord, Avenue Poincaré, B.P. 69, 59652 Villeneuve d'Ascq Cedex, France*

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A gas filter correlation (GFC) instrument for air monitoring at submillimeter wavelengths has been developed. We used a high-power terahertz radiation source in combination with a specific gas filter cell to obtain a highly selective instrument to differentiate species present in an unknown mixture. This approach provides a new method for survey measurements in the spectrum from 100 to 1000 GHz, in which many molecular rotational lines appear. Basic operational considerations and preliminary experiments with hydrogen sulfide are described. © 1999 Optical Society of America

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Air monitoring by means of IR, visible, and UV spectroscopy has a long and respectable history. Investigation by use of submillimeter-wave spectroscopy has a shorter history, even though these wavelengths are rich in spectral lines of atmospheric molecules. Nondispersive gas filter correlation (GFC) in the IR region has been known for many years and has been widely used in gas monitoring.[1–4] Very high selectivity can be achieved, and survey measurements of a single compound in a gas mixture are practical. Radiation sources used in such instruments include hot wires, globars, heated gas, and the Sun. Very low spectral radiance of these conventional thermal sources in the terahertz (THz) frequency range can be troublesome for GFC applications at these wavelengths. Over the past decade, generation of freely propagating THz radiation has been a subject of considerable interest.[5] Pulsed electromagnetic radiation with a THz bandwidth has been produced by means of femtosecond optical pulses incident upon a dipole antenna. The corresponding mean power level of this radiation is ~30 nW.[6] This THz generation technique has proved its efficiency in many important applications, especially in gas sensing.[7,8] A detailed description and many other applications in time-domain spectroscopy are reviewed in Ref. 9. Also, similarly to the approach reported here, Jacobsen *et al*. used another approach for real-time chemical recognition of gases and gas mixtures.[10] For the GFC application a higher power is desirable, since we employ a standard bolometer detector. We have developed a high-power THz source by use of a large-aperture photoconducting antenna in combination with a regenerative amplifier, as reported in Ref. 11. THz pulses have their central frequency in the millimeter-wave range, with a radiated signal up to THz frequency. The maximum mean power of these pulses has been estimated to be roughly a few hundred microwatts in the overall frequency band. Based on these achievements, we report for the first time to our knowledge an experiment based on the GFC technique in the region from 100 to 1000 GHz.

The basic idea of the GFC instrument is to use a sample of the gas to be detected as a spectral filter (a so-called target gas) and to measure the broadband correlation between the target gas and the pollutant to be monitored. In our experiment the incoming THz radiation was split in two beams by a tilted chopper (Fig. 1). One beam was directed to the gas filter channel, while the second was used for the reference channel and was fed through an adjustable attenuator. The gas filter cell, which contained the compounds to be detected, introduced absorption lines into the initial spectrum, ideally with no transmitted light at the absorption frequencies. The adjustable attenuator in the reference channel allowed us to balance and then to equalize the transmission in both channels in the absence of the target gas in the sample cell. When the sample cell was filled with the target gas, the two channels became unbalanced. Indeed, although the transmission of the gas filter channel did not change appreciably, the intensity transmitted by the reference channel decreased. As a consequence a signal appeared on the detection system at the switching frequency and could be easily processed by a lock-in amplifier. The presence of other species whose absorption lines do not match those of the target gas reduced the energy by the same amount in each channel. So, in principle, the presence of other compounds (interfering gases) does not affect the measurements. Note that the GFC technique

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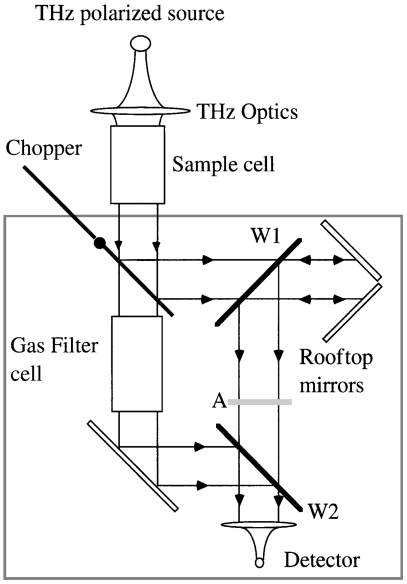


Fig. 1. Schematic of the THz GFC. W1, W2, and the attenuator (A) are polarizer wire grids. The dotted box outlines depict the detection section. The window material is Teflon, and the length of the filter cell is ~50 cm.

derives its sensitivity and selectivity from the large throughput, high degree of multiplexing, and very high degree of spectral resolution, which is limited only by the width and shape of the spectral lines. The down side of this method is the problem of the containment of some gases.

The broadband THz generation experiment is described in Ref. 11. Briefly, we used a large-aperture photoconducting GaAs antenna that consisted of two periodically biased dc pads short circuited by ultrashort optical pulses. The applied bias was provided by a high-voltage generator. We used no more than 1400 V to avoid damage to the wafer. The pad spacing was 3.5 mm for a typical pad length of 10 mm. Ultrashort optical pulses were obtained from a Ti:sapphire femtosecond laser pumped by a 25-W ionized argon laser tuned to 800 nm and subsequently amplified by a regenerative amplifier. At the output the optical pulse duration was 200 fs and the pulse energy was 4.5 $\mu$J. The repetition rate could be varied easily from 10 to 300 kHz. We detected the THz radiation by use of a liquid-helium-cooled composite bolometer. The THz intensity depended as a square of the dc emitter bias voltage, and above 750 V the bolometer was overloaded. By extrapolation, we estimated that the mean power radiated at the maximum bias voltage of 1400 V was ~600 $\mu$W over the whole frequency band. Because of the high level of the detected signal, we also used a standard pyroelectric detector to roughly confirm this value.[11] In the subsequent demonstration we preferred to exploit the low-noise characteristic of the bolometer. The maximum amplitude was centered around 200 GHz, with the radiated signal up to 1.2 THz, as shown in Fig. 2. The THz polarized radiation was collimated and subsequently passed through a 10-cm sample cell filled with the mixture to be analyzed (Fig. 1). A six-blade chopper was used to switch the submillimeter-wave radiation at 200 Hz. Wire grid W1 was oriented such that the incident THz radiation was fully transmitted and then fully reflected after rotation of the THz polarization vector by the rooftop mirror. Wire grid W2 recombined the THz beam from the filter and the reference channels to the detector without losses. The variable attenuator was provided by a third wire grid. The wire grids were fabricated from 10-$\mu$m-diameter tungsten wire with 30-$\mu$m spacing to operate at up to 5 THz.[12]

The spectral radiance at the output of the sample cell can be written as

$$E(\nu)T_i(\nu)T_{\text{target}}(\nu), \tag{1}$$

where $E(\nu)$ is the spectral radiance of the THz source, $T_i(\nu)$ is the attenuation that is due to interfering gases, and $T_{\text{target}}(\nu)$ is the attenuation that is due to the target gas. This incoming radiation contains the spectral signature of the target gas and is split between the reference channel and the gas filter channel. The signal produced at the detector is the difference between the contributions of the two channels, and the detector receives an integrated value over the spectral range covered by the THz pulses. Therefore, from the mean-value theorem, we expect the following detected signal:

$$S_{\Delta\nu} = \langle E\rangle\langle T_i\rangle(\langle T_{\text{target}}T_0\rangle - \langle T_{\text{target}}\rangle t), \tag{2}$$

where $t$ is the transmittivity of the variable attenuator and $T_0(\nu)$ is the transmittivity of the gas filter channel. Recall that $T_{\text{target}}(\nu)$ and $T_0(\nu)$ are strongly correlated, since they represent the spectral transmission that is due to the same gas. The angle brackets denote average value. It can be seen from Eq. (2) that major improvements in the detection system can be obtained by use of a high-power radiation THz source in the Rayleigh–Jeans spectral band, in which the brightness of a conventional blackbody source is poor. However, the sensitivity of the system is moderated by the presence of interfering gases. Recall that the power balance between the reference and the filter beams in the absence of the target gas in the sample cell reduces problems that are due to the stability of the THz source. Therefore, ideally all common mode noise

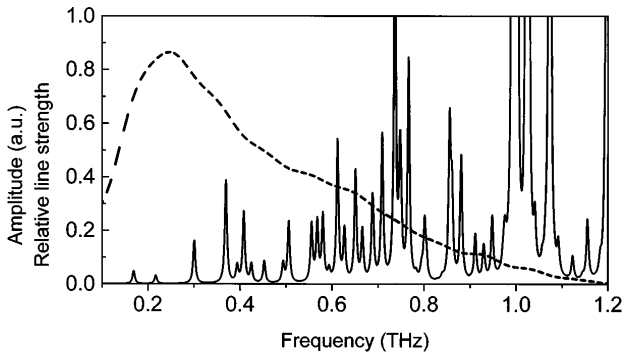


Fig. 2. Amplitude spectrum of the generated THz pulse (dashed curve) compared with the calculated $H_2S$ absorption spectrum at atmospheric pressure.

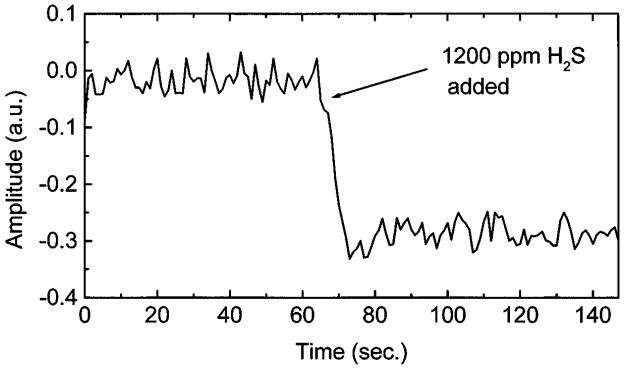


Fig. 3. Experimental record of the output of the lock-in amplifier of the gas correlation detection of $H_2S$.

should be canceled, and the experimental signal-to-noise ratio is limited only by the performance of the detector (NEP) and by the stability of the optical alignment, which is affected by mechanical vibrations of the chopper. Unfortunately, the high bias voltage in the emitter section produces a large amount of noise that is subsequently picked up by the detector. This noise is one of the tedious limiting factors in the present experimental arrangement.

To demonstrate the feasibility of our GFC scheme in the THz spectrum band we performed preliminary experiments on the $H_2S$ molecule. Within the broad spectral band covered by the THz pulse, this molecule has several rotational absorption lines (Fig. 2). We filled the sample cell with the target gas and backfilled it with dry nitrogen to obtain a known specific gas concentration. No attempt was made to calibrate the system in this short demonstration. Based on the measured noise feature, the detection limit of $H_2S$ was estimated to be ~30 parts in $10^6$ (ppm) per meter (Fig. 3). By use of another approach, Gopalsami *et al*. expected to reach a $H_2S$ detection limit of 167 ppm/m.[13] A frequency-tripled millimeter source was used to measure an absorption line of $H_2S$ near 300 GHz.[13] The higher detection sensivity in our experiment seems to be the result of the very high degree of multiplexing of the GFC technique. Indeed, all absorption lines from 100 to 1000 GHz were observed simultaneously. However, we detected the appearance of a low signal magnitude rather than a small change in a large signal.

We tested selectivity by filling the sample cell with carbonyl sulfide, which acted as an interfering gas. At first, no signal was detected under low-pressure conditions (50 Torr) even at high concentrations (a few percent). However, for atmospheric pressure, interfering signals were recorded. A concentration of 5000 ppm of carbonyl sulfide produced a spurious signal of the same order of magnitude as that recorded for the target gas ($H_2S$), owing to the well-known pressure-broadening effect. Indeed, under atmospheric conditions, line broadening induces a severe overlap between the spectra of the target and the interfering gases, so gas sensing in the THz frequency range usually requires measurements by use of an absorption cell at reduced pressure.[8,10] Under these conditions, the GFC technique offers the great advantage of an almost unlimited degree of spectral resolution. The linewidths are proportional to the pressure. When the pressure is reduced to 50 Torr, more than 15,000 individual lines can be resolved from 100 to 1000. So, cross correlation that is due to overlap between spectra of the target gas and the interfering gases drastically decreases and tends toward zero. In practice, no spurious signal was recorded below 100 Torr.

In conclusion, these experiments have demonstrated the feasibility of a system for detection of pollutants in submillimeter waves that is based on GFC and uses the new high-brightness THz source. It is believed that further improvements in accuracy and sensitivity can be achieved by an increase in the spectral radiance of the THz emitter and by use of a multipass cell.

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