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Multiple component analysis of cigarette smoke using THz spectroscopy, comparison with standard chemical analytical methods

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ABSTRACT Terahertz time domain spectroscopy and photomixing have been used alongside one another for the detection and the quantification of small polar species in mainstream cigarette smoke. The broadband submillimeter source used in time domain spectroscopy allowed a rapid and simultaneous detection of several pure rotational transitions of hydrogen cyanide (HCN) and carbon monoxide (CO) in realistic conditions of pressure and temperature. The spectral purity of the continuous wave terahertz source produced by photomixing, permitted the concentrations of these molecules to be measured at pressures of tens of hPa. Moreover, at lower pressure, traces of formaldehyde (H_2CO) have been unambiguously identified at frequencies above 1 THz. A comparison with chemical analytical methods has been completed for each molecule highlighting the advantages of the direct measurement by THz spectroscopy.

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1 Introduction

The terahertz (THz) frequency domain is a transition region lying between the millimetre wave and the infrared portions of the electromagnetic spectrum. The submillimeter wavelengths and the far-infrared region extend from 1 mm to 30 μm, corresponding to frequencies from 300 GHz to 10 THz. This frequency range was considered as a "spectral gap" due to the considerable technological difficulties in producing a tunable source with sufficient power. Therefore the pioneer applications of THz radiation were dedicated to linear absorption spectroscopy. Terahertz radiation allows the pure rotational transitions of small polar compounds or the low-frequency vibrational modes of larger molecular systems to be probed. Benefiting the recent advances in the semiconductor research, linear absorption spectroscopy in the THz region is now currently being pursued in various scientific domains such as astrophysics, atmospheric chemistry and biochemistry [1].

Terahertz time domain spectroscopy (THz-TDS) experiments have been extensively employed to provide a useful method to study the absorption and dispersion of various samples. The time-gated coherent nature of THz-TDS makes it suitable for specific applications, including the determination of molecular parameters [2] or the interpretation of the dynamics of molecular systems [3]. The broadband THz pulse produced by subpicosecond optical pulses and short-lifetime semi-conductors allows the simultaneous and rapid measurement of many molecular transitions [4]. Moreover, although of limited spectral resolution, the capability of the pulsed source THz to obtain detection limits in the part-per-million concentration of gas phase species at low pressure was demonstrated in several previous studies [5, 6]. Improved spectral resolution can be achieved using continuous-wave (cw) difference-frequency generation [7, 8]. Terahertz radiation is generated by the mixing of two visible laser beams in a semiconductor based photomixer. The cw-THz spectrometer is well matched to the high quality factor of the resonances with the molecules in the gas phase in a large pressure range. Indeed, with a spectral purity of 2.5 MHz (HWHM) [8], the cw-THz radiation is generally narrower than the collisional linewidths. For ambient temperatures and at frequencies around 1 THz, the Doppler broadening of the spectral lines never exceeds tens of MHz ($\Delta\nu \sim 6.202 \times M^{-1/2}$ where $\Delta\nu$ is the Doppler broadening (HWHM) in MHz and M is the molecular weight in g/mol) [9]. So, at pressures in the order of 10 hPa or greater, the Doppler broadening can be, in a first approximation, neglected compared to the collisional broadening and cw-THz spectroscopy is capable of resolving the rotational fingerprints of a large variety of molecules [1]. In the THz region, molecular concentrations may be calculated by straightforward determination of the strengths of the rotational transitions. The translation of the measured fractional absorption into absolute concentration does not require the use of a calibration gas, provided that the spectral parameters are well known.

Although the propagation of THz radiation in the atmosphere is limited due to the presence of humidity it offers the possibility of obtaining information in environments that are dominated by scattering at shorter wavelengths. Pioneering experiments in a model random media built from teflon spheres have shown that THz-TDS could be employed in the study of propagation of waves in a scattering medium [10]. Environments contaminated by fog, rain, dust or smoke, which are opaque at visible wavelengths, may be suitable for investigation by THz radiation which does not suffer the same degree of energy loss by diffusion. Other media such as flames have been analyzed by THz spectroscopy: the

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simultaneous detection of molecules such as water, methylidyne (CH) and ammonia (NH_3) demonstrates the potential of a multi-detection in a complex matrix in the THz frequency range [11]. Cigarette smoke is a complex mixture containing a large variety of chemical species distributed between both the gas phase and aerosols [12]. This type of mixture has allowed THz spectroscopy to be applied to a scattering medium. Standard analytical chemistry techniques such as mass spectroscopy [13] and chromatography [14] are routinely employed for this kind of analysis and generally require a sampling method to capture the gas phase species. Optical spectroscopy in the infrared region has been used to make direct in situ measurements of the gaseous species with sources such as tunable diode lasers [15] or quantum cascade lasers [16] both of which present a limited tuning range.

Some preliminary results obtained by cw-THz spectroscopy were the subject of a recent short communication [17]. In the present paper the measurements realised by THz-TDS have been added in order to illustrate the complementarity of the two techniques in the context of a multiple components analysis of cigarette combustion gases. The two experimental set-ups and the main results are presented in the two first parts. A pressure of several hundred of hPa THz-TDS allowed rotational lines of multiple compounds such as H_2O, HCN, CO to be assigned quickly and simultaneously in the 0.1 THz–1.2 THz frequency domain. Formaldehyde (H_2CO) was observed only at lower pressure with the cw-THz spectrometer. Benefiting from the spectral purity of the cw-THz radiation produced by photomixing, quantitative information such as concentrations and detection limits has been obtained for HCN, CO and H_2CO. Finally, different standard chemical analysis has been performed on all identified compounds. In this way we show the main advantages and disadvantages offered by THz spectroscopy compared to standard analytical chemistry techniques specifically employed for the detection and the quantification of each molecule previously mentioned.

2 Experimental

2.1 *Time domain spectrometer*

A typical pump–probe THz configuration has been used for TDS experiments. Two identical ultrafast dipolar antenna formed from a metallic layer photolithically deposited on a low temperature-grown gallium arsenide (LT-GaAs) epilayer have been used for the THz emission and detection. The dipolar antennae had an electrode separation of 5 μm providing an optimal compromise between bandwidth and sensitivity. This short gap is located in the middle of a long transmission line consisting of two parallel lines separated by 37.5 μm. The THz radiation was generated by femtosecond pulses at a wavelength of 800 nm focused onto the emitter antenna biased by a voltage of 20 V. The laser used in this work was a Ti:sapphire (Coherent, MIRA 900) laser pumped by a 6 W frequency doubled Nd:YVO_4 (Coherent, Verdi) producing 10 nJ pulses with a FWHM of 100 fs at a repetition rate of 76 MHz. The average power of the broadband THz emission was estimated to be in the order of 70 nW using a silicon cryogenic bolometer (4 K) and an average incident power of 50 mW. Estimation of power measurement precision is problematic due to the lack of calibrated sources at THz frequencies. The detection dipole is biased by THz pulse and a current is collected when the probe optical pulse is also present, the current being dependent on the THz field. A delay line is implemented on the probe pulse allowing the photoconductive sampling of the THz field. The bias voltage applied to the emitting antenna was modulated at 30 kHz allowing signal recovery by a phase-sensitive amplifier (lock-in amplifier) with a low noise pre-amplifier section. The temporal form of the THz pulse shows that the time separation between the maximum and minimum of the THz field was 1.1 ps, with an estimated signal to noise ratio (SNR) of 5000 with an integration time of 100 ms. The broadband spectrum obtained by a numerical Fourier transform of the THz pulse extends from around 100 GHz to in excess of 1200 GHz hence permitting the simultaneous detection of multiple molecular transitions in a few minutes. The spectral resolution was estimated to be 2.2 GHz and is a fundamental limit determined by the maximum pump–probe delay, here restricted to 450 ps in order to conserve a sufficient signal to noise ratio.

2.2 *Continuous-wave spectrometer*

One way to generate cw-THz radiation is by the spatial overlapping of two cw lasers with a THz beat note in a semiconductor material used as a photomixer. A conventional planar structure photomixer [18] consisting of an interdigital electrode array coupled to a log-spiral antenna and deposited on an active layer of LT-GaAs allows an efficient photocurrent conversion. The main characteristics of the planar photomixer and of the spectrometer have been described in details previously [8, 17]. The difference frequency generation was performed using two cw Ti:sapphire (899-29 Autoscan) laser pumped by a 10 W frequency doubled Nd:YVO_4 (Coherent, Verdi) both emitting around 800 nm. The total incident power exciting the semiconductor charge carriers was limited to 30 mW with a bias voltage of 15 V applied across the photomixer. The detection of the cw-THz radiation was performed using a helium-cooled silicon bolometer with a responsivity of 12 kV/W calibrated at 275 GHz using a black-body source and a band-pass filter [8]. A mechanical chopper was used to modulate one of the cw lasers at a frequency of 270 Hz. A phase sensitive detection system was used to extract the cw-THz signal from the bolometer output. The detected power was estimated to be around 2 nW at 1 THz, this decreases with increasing frequency at a rate of 12 dB/octave. Above 2 THz the detected power is lower than 100 pW. Nevertheless, absorption spectroscopy may be performed beyond 3 THz because of the good noise characteristics of cryogenic detectors with a noise equivalent power (NEP) equal to 2.8 pW $Hz^{-1/2}$. Taking into account this value and an integration time of 1 s, the evaluation of the dynamic range of the cw-THz spectrometer give an estimation of the spectrometer sensitivity from $1.1 \times 10^{-5}\,cm^{-1}$ at 1 THz to $2.2 \times 10^{-4}\,cm^{-1}$ at 2 THz.

The potential of the cw-THz set-up for spectroscopic applications has been investigated previously with the study of the pure rotational spectrometer of hydrogen sulphide H_2S. A large tunability from 100 GHz to 3000 GHz and a relatively good spectral purity around 2.5 MHz (HWHM) close to the Doppler widths are obtained thanks to the performance of the two Ti:sapphire lasers [8]. This spectral purity was directly obtained from the measurement of a beat note in the microwave region using a photodetector and a spectrum analyser [8]. The source spectral width is mainly due to high frequency fluctuations (laser jitter) which were too fast for the frequency locking system (piezo electric mirror). A slow thermal drift of the frequency of the fixed laser (30 MHz/h) occurred due to the locking on a Perot–Fabry interferometer but its effect on the line shape remained negligible. A recent study showed the capabilities of the cw THz spectrometer for the absolute determination of line strengths in the pure rotational spectrum of carbon sulphide OCS [19]. With the OCS rotational lines, the minimal detectable absorption was estimated to be $10^{-3}\,\text{cm}^{-1}$ at 500 GHz, and to be $4 \times 10^{-5}\,\text{cm}^{-1}$ at 900 GHz. Due to the very distorted baseline at low frequencies, the optimal range for this spectrometer was above 700 GHz. Self-broadening coefficients and absolute intensities of OCS rotational lines have been measured with a relatively weak standard deviation (typically 2%). Contrary to this study, the analysis of the lineshape at pressures lower than 5 hPa required the instrumental line shape and the Doppler broadening to be taken into account. The instrument HWHM was set to 3 MHz and the Doppler width was fixed at the value corresponding to the experimental temperature and the line frequency. In this work, the zero crossing of the pressure broadening extrapolation of the 73 → 74 rotational $J \rightarrow J+1$ line of OCS clearly shows than the instrument line width may be neglected in the collision broadened limited case [19].

2.3 *Mainstream cigarette smoke sampling*

The two spectrometers were used to investigate mainstream cigarette smoke. Firstly, the cell and connecting tubes were evacuated by a turbo molecular pump (10^{-5} hPa). The cigarette was then lit and the smoke generated was naturally aspirated in the evacuated cell. The gas pressure was measured with a capacitance manometer directly in the cell. Stainless steel absorption cells with 50 mm clear diameter polytetrafluoroethylene (PTFE, or teflon) windows were used for the THz-TDS and cw-THz experiments. Two different cell lengths of 580 mm and 1280 mm were respectively used for THz-TDS and cw-THz studies. Due to the low-resolution of THz-TDS, the initial pressure close to the atmospheric pressure was used during the acquisition of these spectra. In the case of cw-THz, the isolation of the rotational lines was optimised by reducing the pressure to 20 hPa at which the lines are fully resolved as the instrument spectral resolution is at least five times smaller than the FWHM.

3 Results

3.1 *Multiple component detection of cigarette combustion gases*

The juxtaposition of the THz-TDS and cw-THz spectroscopies have been employed for a multi-detection of polar compounds contained in the complex matrix of mainstream cigarette smoke. With a scanning time of a few minutes, the THz-TDS was initially used in order to rapidly obtain a preliminary identification of the detectable polar compounds contained in the smoke and to localize the most intense absorptions within the frequency range of 100 GHz to 1200 GHz. A typical spectrum of the mainstream cigarette smoke recorded by THz-TDS is shown in Fig. 1. This transmission spectrum results from the ratio between the THz broadband spectrum in the presence of cigarette smoke at a pressure of 950 hPa in the cell, and the THz broadband spectrum obtained without smoke. The spectrum of cigarette smoke by THz-TDS, Fig. 1, shows several strong and clearly defined absorptions of water. At frequencies exceeding 1100 GHz many water transition lines are present and limit the useful spectral coverage, so it is difficult to discriminate between individual transitions. Although the reference spectrum is removed from the gas spectrum, variation of the laboratory atmosphere humidity prevents the total elimination of the free space propagation water absorption. The water transitions in the spectrum therefore originate from the moisture generated by the combustion process and the ambient humidity. The spectrum also shows nine equally spaced absorptions with a mean frequency interval of 88.4 GHz. This value corresponds to approximately twice the rotational constant of the linear molecule of hydrogen cyanide (HCN). The measured results where compared to a simulated spectrum based on an estimated HCN concentration of 180 ppm and the published values for line intensities, line positions and air broadening coefficients [19]. The comparison shows a qualitative agreement between the line positions and intensities, unambiguously attributing all the HCN $J \rightarrow J+1$ transitions with $4 \leq J \leq 12$. Carbon monoxide (CO) has permanent dipole moment around 27 times weaker than that of HCN [21] and as the observed line intensities are dependent on the square of its value, the ability of THz-TDS to measure CO is much lower than for HCN. Nevertheless CO was detected by THz-TDS thanks to its relatively high concentration in the cigarette smoke. Carbon monoxide is a linear molecule ($B = 57.636$ GHz) and so should present equally spaced lines by an interval larger than those of HCN

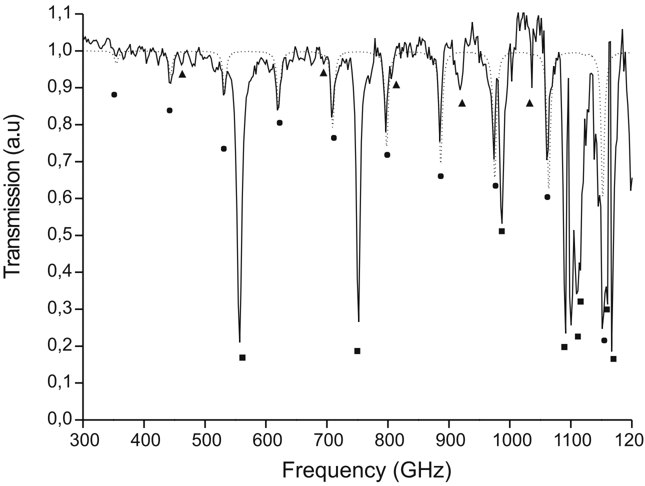

FIGURE 1 *Full line*: Transmission spectrum of mainstream cigarette smoke obtained by THz-TDS at 950 hPa. *Dots*, *squares* and *triangles* denote the strongest pure rotational transitions of HCN, H_2O and CO, respectively. *Dotted line*: theoretical spectrum of HCN issue from the HITRAN spectroscopic database ($P = 950$ hPa, [HCN] = 180 ppm) [20]

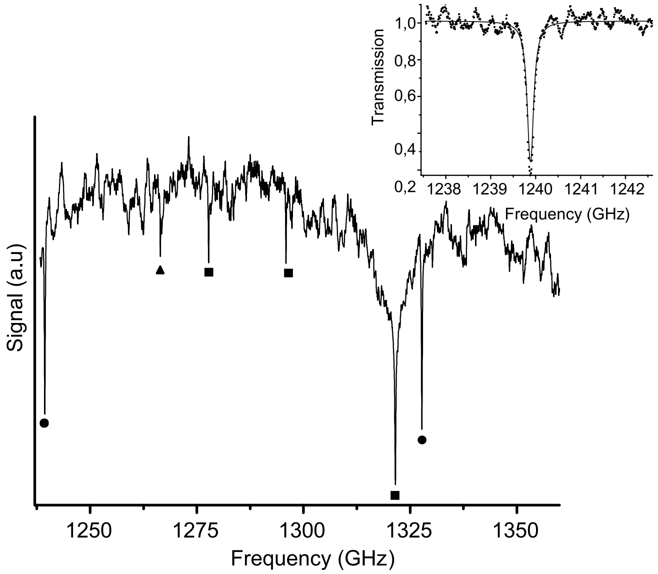

FIGURE 2 The cw-THz spectrum of cigarette smoke ($T = 294\,\mathrm{K}$, $P = 20\,\mathrm{hPa}$) in the 1300 GHz frequency region. *Dots*, *squares* and *triangles* denote the rotational transitions of HCN, H_2O and CO, respectively. *Insert*: Absorption spectrum of the $J = 12 \leftarrow J = 11$ pure rotational line of HCN centred at 1063.0 GHz. The Lorentzian fit (*solid line*) used for the concentration determination is superimposed on the experimental curve (*dots*)

($B = 44.316\,\mathrm{GHz}$) [21]. With the assistance of a spectroscopic database providing the CO line positions [21], a number of weak transitions can be suggested as shown in Fig. 1. Nevertheless the weakness of the transitions and the presence of HCN and H_2O lines in the spectrum prevent some of the predicted CO transitions from being observed, such as for example the $4 \rightarrow 5$ transition expected at 576.3 GHz [21]. At a pressure of 950 hPa, a selective measurement of the absorption intensities is difficult due to the important overlapping between the absorption lines belonging to different species. Moreover at this pressure, the various line profiles are not fully resolved with the spectral resolution of 2.2 GHz. Therefore the quantitative information on the detected species was obtained at lower pressure by the improved spectral purity of the cw-THz source [17].

The cw-THz spectrometer was initially used to perform a systematic search of all rotational lines of HCN and CO at a pressure of 20 hPa. All the HCN transitions $J \rightarrow J+1$ with $6 \leq J \leq 25$ have been unambiguously assigned in the 620 GHz–2300 GHz frequency range. A straightforward assignment of the $J \rightarrow J+1$ transitions of CO with $5 \leq J \leq 19$ has been done too in the 690–2300 GHz frequency range. The rotational transitions $13 \rightarrow 14$ and $14 \rightarrow 15$ for HCN centred respectively at 1239.9 GHz and 1328.3 GHz and $10 \rightarrow 11$ centred at 1267.0 GHz for CO are shown on the spectrum of the Fig. 2. Whereas the THz-TDS allows an instantaneous measurement of all absorptions including the broad band spectrum, this spectrum results from the cw-THz signal detected by a long scan of 100 GHz obtained after thirty minutes of accumulation. The molecule of formaldehyde (H_2CO) was detected in the mainstream cigarette smoke only at low pressures of less than 5 hPa. In Fig. 3 a transmission spectrum of cigarette smoke obtained at a pressure of 0.5 hPa is shown. The pure rotational spectrum of the asymmetric top H_2CO shows a large number of $J'_{\mathrm{Ka}',\mathrm{Kc}'} \leftarrow J''_{\mathrm{Ka}'',\mathrm{Kc}''}$ transitions in the frequency domain available by the cw-THz spectrometer. In Fig. 3, the lines centred at 1471.3 GHz and 1473.8 GHz have been assigned respectively to the rotational transitions $20_{1-19} \leftarrow 19_{1-18}$ and $20_{3-17} \leftarrow 19_{3-16}$ of formaldehyde. For this molecule, only the transitions with the strongest intensities have been detected and assigned to the 1000–1500 GHz frequency range.

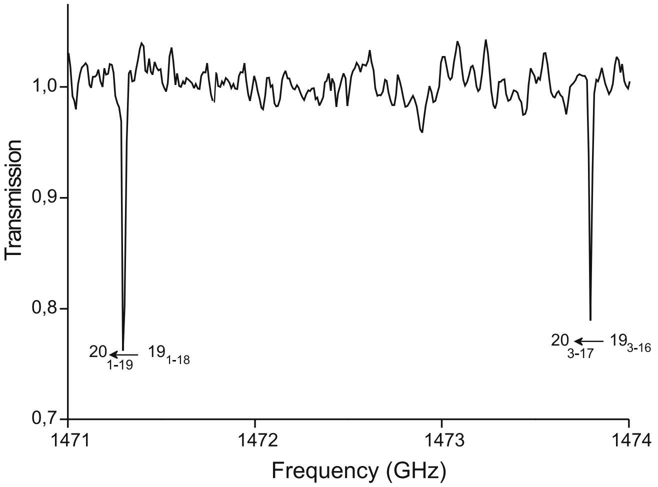

FIGURE 3 The cw-THz transmission spectrum of cigarette smoke ($T = 294\,\mathrm{K}$, $P = 0.5\,\mathrm{hPa}$) showing two rotational lines assigned to two $J'_{\mathrm{Ka}',\mathrm{Kc}'} \leftarrow J''_{\mathrm{Ka}'',\mathrm{Kc}''}$ transitions of formaldehyde H_2CO

3.2 *Concentrations measurements and detection limits*

The cw-THz set-up is a powerful instrument for concentration measurements of chemical species detected in the gas phase at low pressure. Two main reasons explain this point. Firstly, as the absorption coefficient of a rotational line depends on the permanent dipolar moment and angular quantum mechanics, its exact determination is possible and therefore, the absolute integrated intensity of the line can be translated into absolute concentration by straightforward calculation. Secondly, any of the many isolated rotational lines can ordinarily be used for quantitative purposes. Consequently, the good spectral purity of the cw-THz radiation gives a large selectivity for spectroscopic measurements and allows elimination of the possibility of interfering and overlapping lines [17, 19].

Concentrations measurements of HCN and CO have been realized from the analysis of the line profiles on different rotational transitions for each molecule. The fitting procedure of the rotational lines has been described in detail in the previous publication [17]. In this paper, the main results concerning the concentration measurements by cw-THz spectroscopy are reported. At pressures of around 20 hPa, the collision broadened limiting is reached. The Doppler and the instrument contribution to the linewidth may be neglected in a first approximation. Hence a pure Lorentzian fit with the line position ν_0 and the air-broadened halfwidth (HWHM) $\Delta\nu$ fixed with the published values [20] has been used in order to measure the total absorbance A_{tot} of the rotational line. In addition to the knowledge of the spectral line intensity S available in the spectroscopic database [20] and the cell length L, the density N of absorbing molecules could be deduced with the expression

$$A_{\text{tot}} = \int_{\text{line}} \frac{\text{SNL}}{\pi} \left[\frac{\Delta\nu}{(\nu-\nu_0)^2 + (\Delta\nu)^2} \right] d\nu = \text{SNL} \,. \qquad (1)$$

The ratio between the quantity of the absorbing molecules to the total number of molecules present in the cell gives the average concentration of the targeted compound. The insert of Fig. 2 shows an example of the Lorentzian fit of the $J = 12 \leftarrow J = 11$ pure rotational line of HCN centred at 1063.0 GHz. The Lorentzian fits yielded a HCN average concentration of 210 ± 11 ppm. Based on the measured noise feature of the cw-THz spectra, the detection limit of HCN was estimated to be 7 ppm×m. This result shows the unique opportunity given by the THz sources using photomixing devices for trace gas detection of highly polar compounds. For a weakly polar molecule such as CO the results are largely less satisfactory in terms of the relative uncertainty and detection limit. Using the same procedure as HCN, the carbon monoxide concentration and the detection limit have been determined as $1.7 \pm 0.3\%$ and 0.08%m, respectively.

Due to the weakness of the measured intensities, only a rough estimation of the formaldehyde concentration could be deduced. A concentration of 386 ppm has been measured from a spectrum obtained at a pressure of 2.1 hPa with the Lorentzian fit of a line centred at 1047.5 GHz and assigned to the $15_{1-15} \leftarrow 14_{1-14}$ transition. Taking into account the fact of detecting H_2CO only at low pressure, consistent with the hydrophillicity and therefore the strong tendency for the molecule to adsorb on surfaces [22], this concentration measured do not represent the real concentration of formaldehyde due to the full combustion of one cigarette but a lower limiting value.

The same remark concerning the hydrophillicity and the adsorption tendency of H_2CO may be made for ammonia (NH_3) but this molecule was not detected by THz spectroscopy even at very low pressure. The absence of an ammonia (NH_3) spectral signature in the THz spectra was a surprise considering the numerous strong rotational transitions in the THz frequency range [23] and its previous detection and quantification in the mainstream cigarette smoke by infrared spectroscopy [16, 22]. As an example a strong transition of NH_3 was expected at around 1214.9 GHz and never detected. By a direct comparison between the intensity of this expected transition and the intensity of the HCN transition observed at 1239.42 GHz (Fig. 2), a predicted detection limit equal to 64 ppm×m was determined. A similar approach could be done by comparison between the $15_{1-15} \leftarrow 14_{1-14}$ transition of H_2CO centred at 1047.5 GHz and the $12 \leftarrow 11$ transition of HCN centred at 1063.0 GHz. In this case a predicted detection limit equal to 89 ppm × m has been estimated. All quantitative results deduced from the cw-THz analysis are summarized in Table 1.

Molecule	Average concentration	Standard deviation	Detection limit[a]
HCN	210 ppm	11 ppm	9 ppm
CO	1.7%	0.3%	0.1%
H_2CO^b	> 386 ppm	-	114 ppm
NH_3^c	-	-	82 ppm

[a] Detection limit estimated for a length cell equal to 1280 mm. For H_2CO and NH_3, the detection limits has been estimated by comparison with the intensity of a HCN spectral line (see text)

[b] Only a lower limiting value of the formaldehyde concentration could be done (see text)

[c] Ammoniac has not be observed by CW-THz spectroscopy

TABLE 1 Quantitative measurements of CO, HCN, H_2CO and NH_3 contained in the mainstream smoke of one cigarette deduced from the analysis of the rotational lines recorded by the cw-THz spectrometer

3.3 *Comparison of* THz *spectroscopy with chemical analytical methods*

Standard analytical chemistry techniques are currently employed for the detection and the quantification of molecular compounds in complex media. In this work, four different methods, currently employed in analytical chemistry, have been performed in order to estimate the quantities of CO, HCN, H_2CO and NH_3 issued from the full combustion of a cigarette. The aim of these measurements was the validation of the quantitative results deduced from the cw-THz spectra and the highlighting of the potential of the THz spectroscopy compared to more classical analytical techniques. Table 2 summarizes the four different analytical methods employed and their results are compared to masses per cigarette deduced from the cw-THz concentration measurements. It is important to notice that the mainstream cigarette smoke was prepared in identical conditions for chemical and optical analysis. Contrary to THz spectroscopy, the concentration measurements of HCN, H_2CO and NH_3 requires a sampling method (sorbent cartridge or impinger) to capture the gas phase species, the comparison with a standard of calibration and a detection technique adapted to the molecular system studied (IR, colorimetry, UV or conductimetry). The following description of the four measurements illustrates these three points.

Carbon monoxide concentration measurements were performed using a commercial instrument (Hartmann and Braun, Model URAS 10P) based on infrared absorption around 4.67 µm, requiring a gas flow rather than a static smoke sample. Particles and moisture were eliminated from the flow by a heated dust filter and a cooling system [24]. The concentration of CO is deduced from a comparison with a calibrated mixture. A controlled 25% dilution with the ambient air was required in order to avoid any saturation of the absorption signal. Finally, an average mass of carbon monoxide equal to 17.8 mg per cigarette was deduced from the infrared absorption analysis. With a standard error of 4.9 mg, this measurement agrees well with the CO mass equal to 13.4 mg ± 2.4 mg deduced from the concentrations measured by cw-THz spectroscopy. Nevertheless, for the CO detection, taking into account the detection limit of 0.1% in the Table 1 equivalent to a mass of 0.1 mg, the sensitivity of the cw-THz spectrometer is actually weaker than the ultimate sensitivity of the commercial instrument estimated at 5 ppmv corresponding to a mass per cigarette equal to 17.4 µg.

In order to measure the concentration of HCN in the mainstream smoke, the CN^- ions were trapped by bubbling in a NaOH solution (0.1 N) and dosing by a colorimetric method.

Molecule	Chemical analysis method	Mass of the compound measured by chemical analysis	Mass of the compound measured by cw-THz spectroscopy	Mass of the compound measured in tobacco research*
CO	Commercial instrument based on infrared absorption measurement	17.8 mg ± 4.9 mg	13.4 mg ± 2.4 mg	11.5 mg ± 2.4 mg[a]
HCN	Dosage of the anions CN^- by a colorimetric method	> 13.4 µg	160.1 µg ± 8.4 µg	200.0 µg ± 22.0 µg[b]
H_2CO	HPLC with UV detection in a DNPH solution	103.7 µg ± 2 µg	> 2.5 µg	101.9 µg ± 2.3 µg[c]
NH_3	Dosage of the cations NH_4^+ by ion chromatography using conductivity detectors	< 0.4 µg	< 39.4 µg	3.0 µg ± 1.0 µg[d]

* All these studies used the standard conditions specified by the American F.T.C under which cigarettes should be smoked and are performed for different reference cigarettes. [22]

[a] See reference 25: measurements using a Filtrona ATCOM 302 non-dispersive IR analyser

[b] See reference 15: measurements on whole smoke using FTIR spectroscopy

[c] See reference 14: HPLC measurements using DNPH and Impinger method

[d] See reference 16: measurements using quad quantum cascade laser infrared spectroscopy

TABLE 2 Masses of CO, HCN, H_2CO and NH_3 compounds measured in the full mainstream smoke produced by the combustion of a cigarette: comparison between chemical analysis methods and cw-THz spectroscopy. Average values found in the tobacco research literature are cited for each compound

From the NaOH solution, a coloured dye was produced following several reactions previously described [26]. A UV-Visible spectrometer was finally used in order to measure the absorbance at 612 nm and to determine the CN^- concentration by comparison to a calibrated mixture. Although this is a standard analytical method for the dosage of HCN in gas phase, a concentration of cyanide ions corresponding to an equivalent mass of HCN equal to 13.4 µg per cigarette has been detected. This value is very weak compared to the HCN mass of 160.1 µg ± 8.4 µg deduced by THz spectroscopy. This large discrepancy seems to be due to the chemical method where interferences occur between the CN^- anions and other compounds in the mainstream cigarette smoke in the reaction mechanism used to produce the coloured dye. The mass of 13.4 µg deduced from the CN^- dosage has to be considered as the lower limiting value for the mass of HCN contained in the mainstream smoke produced by the combustion of a cigarette. The detectable concentration limit CN^- ions by this technique has been estimated previously to be 5.7 µmol/L [26]. In the present case, this concentration corresponds to a mass of around 3.1 µg of HCN per cigarette. This value is close to a mass of 6.9 µg deduced from the detection limit of HCN by the cw-THz spectrometer. For a highly polar and reactive molecule as HCN, quantitative measurements by THz spectroscopy appear to be a good alternative to standard chemical analytical methods.

A standard analytical method for the determination of aldehydes and ketones in air ambient has been used in order to quantify the formaldehyde contained in the cigarette mainstream smoke [14]. This technique is based on reacting H_2CO in gas phase with 2,4-dinitrophenylhydrazine (2,4-DNPH) followed by separation and analysis of the hydrazone derivative by high performance liquid chromatography (HPLC) with ultraviolet detection at 360 nm. By comparison with a standard mixture, the concentrations of the main aldehydes contained in the cigarette smoke have been calculated. A mass of 103.7 µg ± 2 µg per cigarette of H_2CO has been deduced from HPLC measurements, this value reveals a good agreement with similar measurements in a previous work [14] and does not refute the lowest limit value of 2.5 µg deduced from the concentration measurement by cw-THz spectroscopy. Moreover, the results obtained by HPLC showed the presence of a large number of aldehydes and ketones in the mainstream cigarette smoke in agreement with the previous study of Wang et al. [14] This study shows that very weak concentrations of aldehydes and ketones are detectable with this analytical chemical method. In particular, the limit of detection for H_2CO has been estimated equal to 0.43 ng/mL for an injection volume of 10 µL [14]. This concentration corresponds to a mass of 0.09 µg lower than the mass of 0.74 µg deduced from the detection limit of HCN by the cw-THz spectrometer. For the H_2CO detection, the sensitivity of the current THz spectrometer has to be increased in order to rival the ultimate sensitivity of the HPLC measurements.

A final analysis of the ammonium cations (NH_4^+) produced by the trapping in an acid solution of HCl (0.1 N) of the ammonia contained in the cigarette smoke has been performed in order to explain the absence of NH_3 on the THz spectra. The cations NH_4^+ have been quantified with an ion chromatography using conductivity detectors. From the comparison with a calibration mixture, this analytical technique showed a detection limit of 0.06 ppmv for a signal of 0.01 Siemens. This limit was insufficient to detect the NH_4^+ ions issued from the ammonia present in the cigarette smoke. Only a superior limit value of 0.4 µg per cigarette for the NH_3 mass may be deduced from this analysis. With a mass of 39.4 µg deduced from the detection limit of 64 ppm×m estimated previously, the sensitivity of the cw-THz spectrometer is lower than the ultimate sensitivity of the chemical technique and therefore it does not allow observation of ammonia traces in the mainstream cigarette smoke.

Finally, Table 2 gives the quantities of each compound measured previously with different and specific experimental techniques by several laboratories specialising in tobacco research. The comparison with their measurements reveals a rather good agreement especially when we take into account the differences between the combustion processes used in the experimental protocols. Indeed, the American Federal Trade

Commission (FTC) specifies the standard conditions under which cigarettes should be smoked as a 35 mL puff volume of 2 s duration at an interval of 60 s [22]. Typically, in our experiments, the full combustion of one cigarette required around thirty seconds which is very quick compared to the precedent conditions. The cigarette smoke sampling protocol used in this work did not respect the true inhalation of a smoker: the combustion process was performed at an average continuous flow of at least 5 l/min, as a human breathes 10 l/min of air at rest, but in a discontinuous way. For a smoker these inhalations are even more discontinuous. With a better control of the combustion processes, THz spectroscopy should be an accurate tool for the control of the rates of toxic compounds inhaled by the smoker.

4 Conclusion and future prospects

The aim of this study was to demonstrate the abilities of THz spectroscopy in the detection and the quantification of multiple combustion products in cigarette smoke. The juxtaposition of THz-TDS with cw-THz spectroscopy provided rapid an unambiguous identification and an absolute quantification of several polar compounds such as HCN, CO or H_2CO. Contrary to chemical analytical methods, THz spectroscopy does not require a sampling method to capture the gas phase species, nor a comparison with a calibration standard, and an adapted detection technique to the molecular system studied. Nevertheless, due to the limited sensitivity of the pulsed and the continuous-wave spectrometers, only a small variety of molecules among the thousands of species presents in cigarette smoke may be detected. As an example, for the detection and the quantification of the different aldehydes and ketones contained in large amount in the cigarette smoke, the sensitivity of the current THz spectrometer has to be increased in order to rival the ultimate sensitivity of the HPLC measurements. Additional polar components present in large concentrations in mainstream cigarettes, such as acetaldehyde, acrolein, formic acid, and acetone should be good candidates for detection with more sensitive THz spectrometers.

Three fundamental steps are needed in order to improve the THz spectrometer sensitivity: the THz radiated power, the detection scheme and the interaction length between radiation and molecules. The increase in the THz power requires advances in the photomixer technology. In the lower part of the spectrum (< 1200 GHz), a vertically integrated spiral antenna which radiated at least twice the power of the present interdigited photomixer, should raise the potential of the cw-THz spectrometer [8]. A resonant dipole antenna should improve ultimate sensitivity at higher frequencies [27]. Travelling-wave THz photomixer based on a free-space optical-THz phase-matching scheme offers great potential in terms of bandwidth and output THz power and should be a good compromise between the two latter photomixer antennas [28]. However, such a mixer based on a photoconductive process is limited in the μW range. In a recent study, cw-THz generation using antenna-integrated uni-travelling-carrier (UTC) photodiodes demonstrate the possibility of obtaining more than 10 μW of radiated power at 1 THz [29]. A such mixer associated with a helium-cooled silicon bolometer with an NEP in the $10^{-15}\ \mathrm{W/Hz^{1/2}}$ which are now available [30] should improve the ultimate sensitivity by several orders of magnitude. Finally, the increase in the propagation lengths appears as the following step of the improvement of the THz radiated. Very sensitive techniques using multipass cells with optical paths up to 50 m [31] or cavity-enhanced absorption spectrometers [32] were already used in THz spectroscopy and allow very weak absorptions. A THz radiated power in the order of one μW with an improved bolometer NEP of $10^{-15}\ \mathrm{W/Hz^{1/2}}$ and an optical path of 100 m may reduce the cw-THz minimal detectable absorption to $10^{-12}\ \mathrm{cm^{-1}}$, predicting the detection of a highly polar molecule such as HCN at concentrations in the order of 1 part per trillion.

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REFERENCES

1 F.C. De Lucia, *Spectroscopy in the THz spectral region*, in: D.M. Mittleman, *Sensing with terahertz radiation* (Springer, Berlin, 2003)
2 H. Harde, D. Grischkowsky, J. Opt. Soc. Am. B **11**, 1018 (1994)
3 B.L. Yu, Y. Yang, F. Zeng, X. Xin, R.R. Alfano, Appl. Phys. Lett. **86**, 101 108 (2005)
4 R.H. Jacobsen, D.M. Mittleman, M.C. Nuss, Opt. Lett. **21**, 2011 (1996)
5 G. Mouret, W. Chen, D. Boucher, R. Bocquet, P. Mounaix, D. Lippens, Opt. Lett. **24**, 351 (1998)
6 S.A. Harmon, R.A. Cheville, Appl. Phys. Lett. **85**, 2128 (2004)
7 A.S. Pine, R.D. Suenram, E.R. Brown, K.A. McIntosh, J. Mol. Spectrosc. **175**, 37 (1996)
8 G. Mouret, S. Matton, R. Bocquet, F. Hindle, E. Peytavit, J.F. Lampin, D. Lippens, Appl. Phys. B **79**, 725 (2004)
9 C.H. Townes, A.L. Schawlow, *Microwave Spectroscopy* (Dover, New York, 1975), Chapt. 13, p. 337
10 J. Pearce, D.M. Mittleman, Opt. Lett. **26**, 2002 (2001)
11 R.A. Cheville, D. Grischkowsky, Opt. Lett. **20**, 646 (1995)
12 R.R. Baker, *Smoke Chemistry* in *TOBACCO Production, Chemistry and Technology*, ed. by D.L. Davis, M.T. Nielson (Blackwell Science, London, 1999), Chapt. 12, p. 398
13 B.D. Morrical, R. Zenobi, Atmosph. Environ. **36**, 801 (2002)
14 T.L. Wang, H.W. Tong, X.Y. Yan, L.Q. Sheng, J. Yang, S.M. Liu, Chromatographia **62**, 631 (2005)
15 S. Plunkett, M.E. Parrish, K.H. Shafer, D. Nelson, J. Shorter, M. Zahniser, Vibrat. Spectrosc. **27**, 53 (2001)
16 R.E. Baren , M.E. Parrish, K.H. Shafer, C.N. Harward, Q. Shi, D. Nelson, J.B. McManus, M. Zahniser, Spectrochim. Acta A **60**, 3437 (2004)
17 D. Bigourd, A. Cuisset, F. Hindle, S. Matton, E. Fertein, R. Bocquet, G. Mouret, Opt. Lett. **31**, 2356 (2006)
18 E.R. Brown, K.A. Mc Intosh, K.B. Nichols, L. Dennis, Appl. Phys. Lett. **66**, 285 (1995)
19 S. Matton, F. Rohart, R. Bocquet, G. Mouret, D. Bigourd, A. Cuisset, F. Hindle, J. Mol. Spectrosc. **239**, 182 (2006)
20 L.S. Rothman, D. Jacquemart, A. Barbe, C.D. Benner, M. Birk, R.L. Brown, R.M. Carleer, C. Chackerian, K. Chance, L.H. Coudert, V. Dana, M.V. Devi, J.M. Flaud, R.R. Gamache, A. Goldman, J.M. Hartmann, K.W. Jucks, A.G. Maki, J.Y. Mandin, S.T. Massie, J. Orphal, A. Perrin, C.P. Rinsland, M.A.H. Smith, J. Tennyson, R.N. Tolchenov, R.A. Toth, J. Vander-Auwera, P. Varanasi, G. Wagner, J. Quantum Spectrosc. Radiat. Transf. **96**, 139 (2005)
21 H.M. Pickett, R.L. Poynter, E.A. Cohen, *Submillimeter, Millimeter and Microwave Spectral Line Catalog*, access via World Wide Web. (http://spec.jpl.nasa.gov) from the Jet Propulsion Lab., Pasadena, CA
22 S. Plunkett, M. Parrish, K. Shafer, D. Nelson, J.B. McManus, J.L. Jimenez, M. Zahniser, Proc. SPIE **3758**, 212 (1999)

23 H. Harde, J. Zhao, M. Wolff, R.A. Cheville, D. Grischkowsky, J. Phys. Chem. A **105**, 6038 (2001)

24 N.N.M. Masalehdani, J.L. Potdevin, F. Cazier, D. Courcot, Int. Conf. on coal fire research 2005, pp. 101–103

25 A.M. Calafat, G.M. Polzin, J. Saylor, P. Richter, D.L. Ashley, C.H. Watson, Tobacco-Control **13**, 45 (2004)

26 A.E. Lindsay, A.R. Greenbaum, D. O'Hare, Anal. Chim. Acta **511**, 185 (2004)

27 I.S. Gregory, W.R. Tribe, C. Baker, B.E. Cole, M.J. Evans, Appl. Phys. Lett. **86**, 204 104 (2005)

28 S. Matsuura, G.A. Blake, R.A. Wyss, J.C. Pearson, C. Kadow, A.W. Jackson, A.C. Gossard, Appl. Phys. Lett. **74**, 2872 (1999)

29 H. Ito, F. Nakajima, T. Furuta, T. Ishibashi, Semicond. Sci. Technol. **20**, S191 (2005)

30 J. Bock, D. Chen, P.D. Mauskopf, A.E. Lange, Space Sci. Rev. **74**, 229 (1995)

31 V.B. Podobedov, D.F. Plusquellic, G.T. Fraser, J. Quantum Spectrosc. Radiat. Transf. **91**, 287 (2005)

32 R. Schiwon, G. Schwaab, E. Bründermann, M. Havenith, Appl. Phys. Lett. **86**, 201 116 (2005)