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Terahertz continuous wave spectroscopy: a portable advanced method for atmospheric gas sensing

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Abstract: Motivated by the increasing demand to monitor the air-quality, our study proved the feasibility of a new compact and portable experimental approach based on Terahertz (THz) continuous wave high resolution spectroscopy, to detect the presence of the air's contaminants as greenhouse gases (GHG) and volatile organic compounds (VOCs). In this specific work, we first characterized, determining their molar absorption coefficient in the spectral region (0.06-1.2) THz, the pure optical response of the vapor of five VOCs: methanol, ethanol, isopropanol, 1-butanol and 2-butanol. In particular, 1-butanol and 2-butanol are characterized for the first time in literature at THz frequencies. Then we studied the optical response of their mixtures achieved with ambient air and ethanol. The results show that it is possible for a differentiation of single components by describing their spectral absorption in terms of the linear combination of pure compounds absorption. This proof of concept for this apparatus study and set-up paves the way to the use of THz Continuous wave high resolution spectroscopy for the environmental tracking of air pollutants.

1. Introduction

Volatile organic compounds (VOCs) belong to the family of toxic chemicals, such as hydrocarbons, alcohols, nitrogen-based compounds produced by natural and/or anthropogenic sources [1–3]. They are considered to be within the main indoor and outdoor air chemical contaminants [4–7] because, due to their low boiling points, they evaporate even at room temperature rapidly diffusing in the environment [5]. For this reason, they are now considered as an important risk factor for health and safety [6–9]. Therefore, the detection of VOCs for monitoring the indoor and outdoor air-quality is a topical issue. In these last years, the increasing demand for gas sensing systems and devices triggered the technological advances [10–13]. There are various conventional and innovative analytical methods for VOCs detection, based on chemical and physical principles, i.e. gas chromatography, mass spectroscopy [14–16], optical, electrochemical piezoelectric and

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chemo-sensors [11,17–21]. Many of the above-mentioned methods measure the exposure to chemical agents using static samplers and/or analytical techniques that require complex off-line procedures, time-averaged response with reduced sensitivity. The electrochemical piezoelectric and chemo-sensors have gained popularity thanks to their operational simplicity, suitability for point-of-care, their small size and high sensitivity. Nevertheless, high sensitivity is achieved for high operation temperature, see for example the electrochemical sensors [22,23], and this represents a risky condition for the detection of inflammable gases. VOCs' complementary detection methods are based on vibrational spectroscopy. The optical gas sensing systems based on vibrational spectroscopy guarantee detection limits comparable with gas chromatography and can overcome the issues related to chemo-resistive gas sensors [10,24]. Very recently, Terahertz spectroscopy (0.1-10 THz) attracted increasing interest, strongly encouraged by the rapid technological developments [25–28]. This spectroscopy, in fact, has been successfully applied in various technological and scientific fields e.g. biomedicine, condensed matter [29], analytical chemistry [30–34], including the gas sensing [10,35]. Compared to conventional infrared techniques used for gas sensing, THz spectroscopy shows many advantages: unique properties of high penetration in dielectric material, low aerosol scattering losses [36] and low photon energy (i.e. 4 meV @ 1 THz) which assures no molecules ionization and no combustion of inflammable materials. Moreover, THz spectroscopy is insensitive to the thermal background, showing a high Signal-to-Noise Ratio (SNR) and it does not require cooled detectors. Thanks to all these advantages THz spectroscopy may provide selective non-intrusive identification of gas molecules, through their molecular roto-vibrational modes, ensuring a high chemical selectivity and sensitivity and therefore it can represent a novel tool to probe the presence of VOCs in their gas-phase. The first experimental evidence to this issue was provided by a study on acetonitrile (CH_3CN) gas in the presence of smoke at atmospheric pressure. Many rotational transitions were resolved in the spectral range between (0.1-1) THz, without the influence of scattering and/or absorption by the smoke [37]. In addition, the detection of hazardous gases generated by the combustion process, such as hydrogen cyanide (HCN) and H_2O molecules due to a urethane foam block [38], suggested possible applications in remote locations. Choi et al. [39] detected the presence of low concentrations of di-nitrogen monoxide (N_2O, 25% in air) with a 1-m-long gas cell, while monitoring via remote detection, nitrogenous compounds (N_xO_y). The results opened the possibility of applying THz spectroscopy for the identification [39]. THz time-domain spectroscopy (THz-TDS) has been first applied in gas sensing, demonstrating a higher selectivity compared to infrared spectroscopy in the examination of various gases, such as acetaldehyde (C_2H_4O), acetonitrile (C_2H_3N), NH_3, propionaldehyde, propionitrile (C_3H_5N), and H_2O vapor in the range between (0.03–3.9) THz [40]. Although nowadays, THz-TDS has become the common tool for the material analysis, the achievable spectral resolution represents a limitation for some specific applications like gas-phase sensing in environment monitoring [10], human breath [41–43] and drugs and explosives detection [39,44], where high resolution THz continuous wave frequency-domain spectroscopy (THz-FDS) is highly demanded. THz-FDS is closely related to TDS in physical processes, measurement and detection schemes [45,46]. In comparison to the TDS, the main advantages of FDS are the high frequency resolution (~ MHz), the possibility to work at a fixed frequency or in a tunable frequency range and the relatively low cost. Moreover, THz-FDS systems do not require mechanical movements and therefore are more stable, compact and portable, thus suitable for real-time *in situ* measurements [47,48]. In this work, we experimentally investigated the optical response of a set of alcohols, belonging to the VOCs' family and of interest as toxic contaminants posing a risk to the human health, in gas-phase. We applied THz-FDS spectroscopy with a broad bandwidth (60-1200) GHz and high resolution of 0.1 GHz. Despite the great interest shown in THz gas-sensing, many gas-phase VOCs have never been spectrally characterized with high resolution in the THz frequency range (60-1200) GHz, and few research activities were focused on the detection in

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ambient air [31,42,49–51]. Thus, we first studied the optical response of these pure compounds in gas-phase: methanol, ethanol, isopropanol, 1-butanol and 2-butanol, indicated in the following text and figures, respectively, as MeOH, EtOH, IsoOH, BuOH-1 and BuOH-2. Then we studied the optical behavior of BuOH-2/air mixtures by increasing progressively the air content and BuOH-1/EtOH mixture. To our knowledge, this is the first high resolution characterization for BuOH-1, BuOH-2 and the mentioned mixtures in this THz spectral region. The results of this study prove that this methodology can be capable of gas sensing in a fashionable and compact set-up which can be carried on for *in situ* atmospheric measurements.

2. Materials and methods

2.1. Materials

The following liquid VOC samples were used: methanol (CH_3OH - Sigma Aldrich - Purity ≥99.8%), ethanol (C_2H_6O - Sigma Aldrich - Purity ≥99.8%), isopropanol ($CH_3CH(OH)CH_3$ - Sigma Aldrich - Purity ≥99.9%, 1-butanol ($CH_3(CH_2)_3OH$ - Sigma Aldrich - Purity ≥99.5%) and 2-butanol ($CH_3CH(OH)CH_2CH_3$ - Sigma Aldrich - Purity ≥99.5%). The binary mixture of BuOH-1 and EtOH was prepared blending 50% in volume of both alcohols. The mixture of BuOH-1/EtOH was injected into the absorption gas cell, waiting for the equilibrium liquid-gas condition to be reached. The total pressure of 15 mbar was measured. Concerning the BuOH-2/air mixtures, we injected the liquid VOCs into the absorption gas cell, waiting for the equilibrium condition (liquid-vapor) to be reached. This condition was monitored by the Alcatel Pirani CA 111 gauge. Subsequently, different volumes of ambient air (relative humidity RH=40%) were added to the gas cell.

2.2. Methods

In order to investigate the spectral features of gaseous samples in the frequency range (60-1200) GHz, we used a commercial THz-FDS (TeraScan 1550, TOPTICA Photonics AG, Germany) system, as shown in Fig. 1. The system includes two distributed feedback (DFB) lasers (#LD-1550-0040-DFB at 1533 and at 1538 nm), one THz transmitter (TX) and THz receiver (RX), four off-axis parabolic mirrors (PMs) and a signal processing unit. The lasers are coupled by optical fibers into a laser combiner (Fib-MIX) to generate a beat signal which is divided into two beams with the same average power approximately of 35 mW. One of the two beat signals pumps the TX, a low-temperature grown InGaAs photoconductive antenna (PCA), generating THz radiation though photomixing technique [35,52]. The generated THz beam signal is collimated by a PM and then recollected and focused on the RX which is also coupled by a silicon super hemisphere lens. The detected THz signal drives the photo-carriers pumped by the other laser beat to form a photocurrent amplified by a lock-in amplifier (LIA). The TX is biased by an AC modulation frequency of ∼ 39.67 kHz and voltage 0.9 V. The detected continuous wave (CW) THz spectrum covers the range (60-1220) GHz with an intensity I(ν) decreasing with increasing frequency as shown in Fig. 1(c) blue curve (bands for the blue curve are related to water vapor absorption). This decreasing behavior is an intrinsic characteristic of the TX/RX emitter/detector response [35]. The homemade gas cell was designed and realized in order to meet the requirements of the system. It is equipped with 2 mm thick Teflon windows, which were located perpendicular to the collimated radiation transmission direction, and with a Pirani sensor as vacuum gauge. The gas cell is 50 mm long and has an inner diameter of 30 mm, enabling the collimated THz beam to completely pass through the cell without clipping losses.

We performed the measurements at room temperature (measured 20 °C). To minimize the water vapor absorption due to the THz beam path outside the gas cell, we closed the optical set-up in an acrylic box, containing a drying air system that maintained the humidity at 20%. Background collections (I_{cell}: empty gas cell) were performed immediately prior of each sample.

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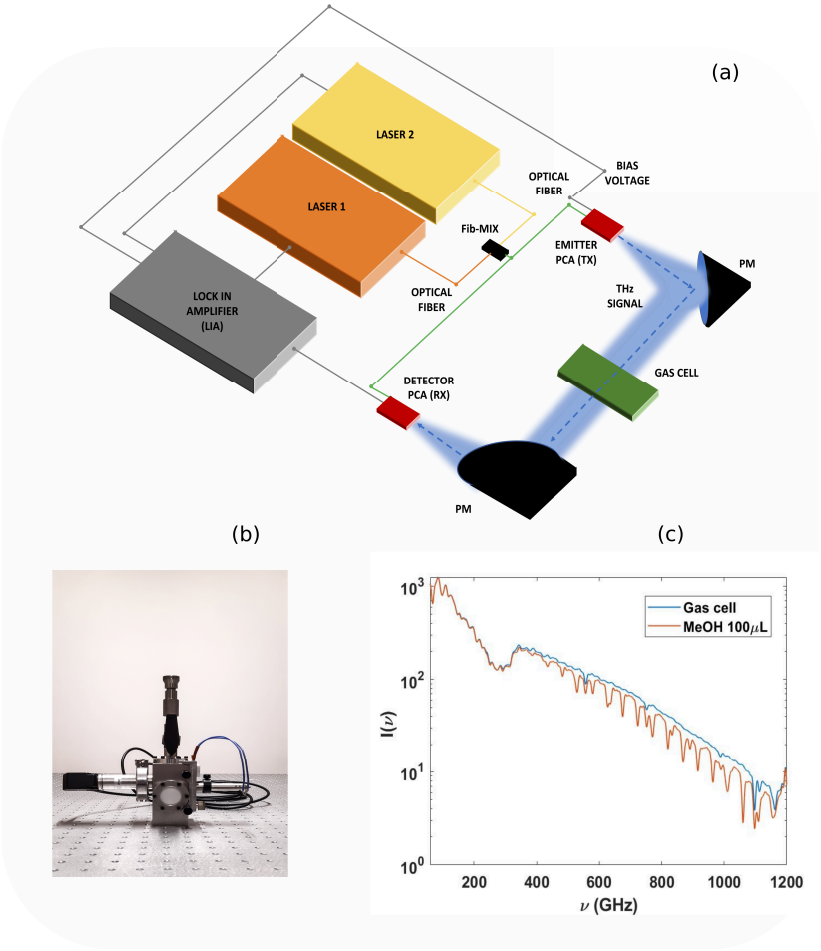

Fig. 1. (a) Schematic layout of THz-FDS system for gas detection. (b) Home-made gas absorption cell. (c) THz intensities as a function of frequency of empty (blue) and filled gas cell with MeOH (red), respectively. The minima appearing in the blue curve are related to water vapor absorption, for the red line to the MeOH absorption.