The compound to be analyzed was injected into the bottom of the gas cell in its liquid state (natural state at room temperature and ambient pressure). Then, we monitored the vapor pressure by the Pirani gauge. Once the equilibrium (liquid-vapor) is reached, we collect the data (I_{sample}) for the sample. Each spectrum was acquired between 60 to 1200 GHz with a frequency resolution of 0.1 GHz and integration time of 30 ms. Raw data were processed and analyzed using algorithms written by the authors in MATLAB (ver. 2019a, MathWorks Inc., USA) as interpreter. The Beer–Lambert law is used to relate the amount of THz radiation transmitted through the gas cell. The experimental absorbance is calculated by

$$Absorbance = -log(I_{sample}/I_{cell}) \tag{1}$$

the absorbance is also directly proportional to the optical path d of the gas cell and the concentration of the sample, as follows

$$Absorbance = \alpha_M Cd \tag{2}$$

the inverse formula combined with the perfect gas law gives

$$\alpha_M = Absorbance/Cd = AbsorbanceRT/Pd \tag{3}$$

where α_M [cm^{-1}] is the molar absorption coefficient dependent on pressure and temperature, C is a molar concentration [M], d [cm] is the optical path of the gas cell, R the gas constant, T [K] the temperature and P [mbar] the pressure.

3. Results and discussions

3.1. Absorption of pure alcohols

The measured molar absorption coefficient α_M of the vapor of the pure MeOH, EtOH, IsoOH, BuOH-1 and BuOH-2 are displayed in Fig. 2(a and b). The absorption spectra are referred to the vapor concentration at equilibrium of 100 μl of the compound in its liquid state, injected inside the gas cell at the temperature of 20 °C. We monitored the equilibrium state by measuring the pressure.

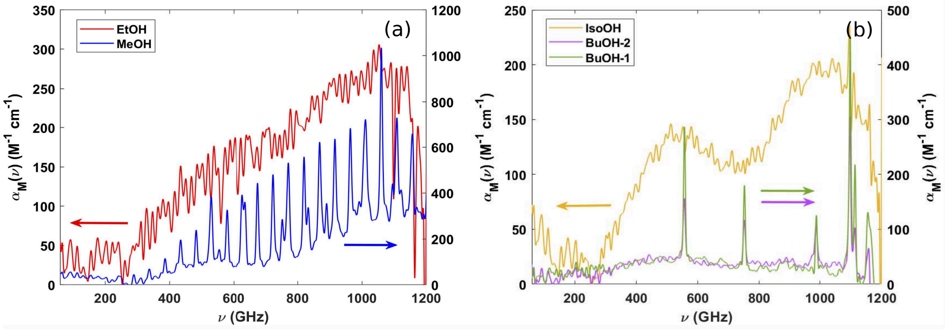

Fig. 2. Measured molar absorption coefficients of pure alcohols as a function of frequency: (a) MeOH and EtOH, (b) IsoOH, BuOH-1 and BuOH-2 in the spectral range (60-1200) GHz.

Inspection of Fig. 2 reveals grouping of the gas-phase components with strong rotational absorption features, such as MeOH and EtOH (Fig. 2(a)) that dominate the spectra compared to BuOH-1 and BuOH-2 (Fig. 2(b)). MeOH is one of the most abundant oxygenated VOCs present in the atmosphere [53]. We selected methanol as the gas sample to demonstrate the capability of the THz-FDS system to simultaneously probe multiple absorption lines, as made in other works [37,40,42]. The rotational spectral shape is evident and the lines corresponding to rotational transitions are spaced approximately every 50 GHz. MeOH is a prolate symmetric top molecule and the frequency spacing approaches 2B=49.38 GHz [54]. EtOH has a lower α_M than MeOH and shows periodic features distributed at approximately equal distance, see Fig. 2(a). As well as for MeOH, EtOH is a prolate asymmetric top molecule with rotational constants A=34.02 GHz, B=9.19 GHz and C=8.10 GHz [55]. As the difference 2B-2C ~ 1.09 GHz (degeneracy) is lower than the Full Width at Half Maximum FWHM ~ 9 GHz of the rotational transitions, in Fig. 2 the spectra do not allow discriminating between the two features. Due to the same degeneracy effect the rotational pattern connected to the A rotational constant is likely to be superimposed to the other two (B,C). In Fig. 2(b), we show α_M for alcohols with a long carbon chain (≥3), including IsoOH, BuOH-1 and BuOH-2. All of them exhibit a low α_M compared to MeOH. The rotational constants for the IsoOH, A=8.49 GHz, B=8.04 GHz and C=4.77 GHz, suggest that the molecule can be considered as an oblate asymmetric top [56]. The experimental frequency spacing of the spectral lines is ~ 16 GHz. As before, the difference 2A-2B ~ 0.45 GHz (degeneracy) is lower than the FWHM ~ 5 GHz of the rotational transitions and again in Fig. 2(b), thus we cannot discriminate the two. Due to the same degeneracy effect the rotational pattern connected to the C rotational constant is again superimposed to the other two (A,B). BuOH-1 and BuOH-2 show a lower absorption with respect to the other three examined alcohols. Despite the butanol isomers share the same chemical formula (C_4H_9OH), their physical properties such as melting point and molar volume are different from those of the other isomers. The butanol isomers have different chemical configurations due to the arrangement of the methyl groups with respect to the carbon attached to the hydroxyl group. The chemical structure results in different spectral shapes, as demonstrated in the IR spectral region [57]. Here, for the first time, we observed different absorption characteristics between BuOH-1 (green line) and BuOH-2 (purple line), (Fig. 2(b)) by THz-FDS. We evaluated their main THz frequency positions using the second-derivative analysis [58,59], that shows a negative peak for each band and a shoulder in the absorption spectrum. Very strong bands appear at 556.9, 751.9 and 988 GHz for BuOH-1. For BuOH-2, these peaks are shifted at 556.5, 751.4 and 987.4 GHz, as evident in the limited frequency interval of Fig. 3(a). These bands can be associated to hydroxyl groups rotational modes. The relative shifts of the main peaks of BuOH-1 and BuOH-2 are even more evident if we refer to their second-derivatives for the three sub-band frequencies, as reported in Fig. 3(c)-e. For each single compound, the second-derivatives are given, and the negative peaks identify the main absorption bands for BuOH-1 and BuOH-2, respectively. A significant shift of 500 MHz is observed in BuOH-2, attributable to the different isomeric molecular structure of BuOH-1 compared to BuOH-2. In addition, as the background line for the BuOH-1 and BuOH-2 is comparable, we can give a quantitative estimation of the absorption values: α_M at 557 and 752 GHz for BuOH-1 is 2-fold greater than for BuOH-2, instead for the absorption at 988 GHz they are at 132 $M^{-1}cm^{-1}$ and 102 $M^{-1}cm^{-1}$ for BuOH-1 and BuOH-2, respectively.

3.2. Absorption of binary mixture of BuOH-2 and air

To further investigate the applicability of the THz-FDS system as a valid alternative tool for gas sensing in a system approaching those found in ambient air, we performed the absorption measurements for the BuOH-2/air mixtures. We fixed the concentrations of BuOH-2 gas into the gas cell and varied progressively the air content, injecting fixed volumes (3 ml and 6 ml) at 40% RH and 20°C room temperature. In Fig. 4(a), we report the experimental absorbances for the mixtures of BuOH-2/air. Increasing the air content, it is possible to observe different absorption behaviours.

At low frequencies, between 100-350 GHz, the absorbance tends to increase compared to the pure compound. This may be due to strongest water vapor rotational lines and pressure broadening effects [51]. Moreover the 10 GHz periodicity, which is characteristic of the pure BuOH-2 compound, tends to disappear and a new frequency modulation approximately at 20

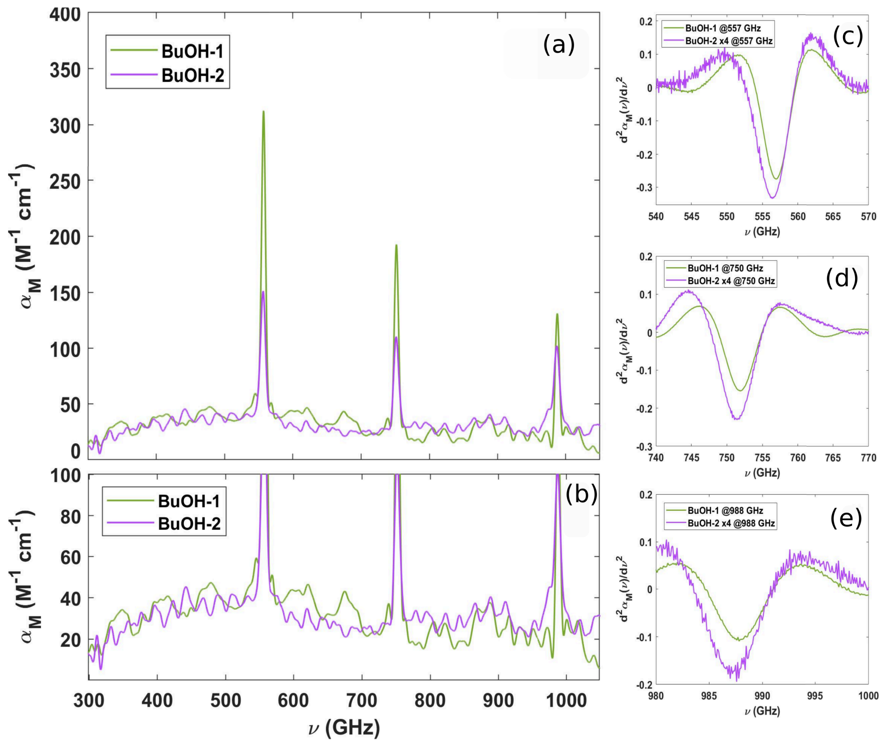

Fig. 3. (a) The frequency sub-bands of α_M for BuOH-1 (green line) and BuOH-2 (purple line) between (300-1000) GHz. (b) Enlargement of the lower intense spectral components in this spectral region. (c) (d) and (e) Second-derivatives of the absorption spectra of BuOH-1 and BuOH-2 in the frequency positions close to 557 GHz, 752 GHz and 988 GHz, respectively.

GHz appears. Concerning the most intense absorption lines, located around 556.5, 751.4 and 987.4 GHz, we do not observe appreciable shifts, but only a change in their intensity. For the sub-bands at 556.4 and 751.4 GHz we note a progressive increase in intensity as a function of the increase in the air content in the mixture, evident in Fig. 4(b) and 4(c), where the integrated areas of the main peaks (after subtraction of the background) are reported. The subtraction has been performed with a spline curve [59]. A different behaviour is observed for the absorption band located at 987.4 GHz (Fig. 4(d)). In fact, this band tends to be split into three sub-bands at around 973.7, 986.9 and 997 GHz when the air content increases up to about 6 ml.

3.3. Absorption of binary mixture of BuOH-1 and EtOH alcohols

We have prepared 200 μl of solution mixing equal volumes of components, but with molar fractions, 0.6129 ± 0.0001 and 0.3907 ± 0.0001 of EtOH and BuOH-1, respectively. The experimental net absorbance of the gaseous mixture is the sum of the contribution of the linear absorbance of each component, when the interaction among components can be considered negligible; this is known as the multiple absorbers approach [51]. The experimental absorbance for non-interacting compounds can be written as

$$A_{mix}^{exp} = \sum A_i \tag{4}$$

where A_{mix}^{exp} is the experimental mixture absorbance and A_i is the estimated pure absorbance due to each species i, at the same pressure and temperature conditions. The measured net absorbance