Long path length cw-THz spectrometer using a multipass cell

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***Abstract*—Multipass cells have been extensively used in the infrared. Their use at THz frequencies is minimal due to the difficulty of coupling the highly divergent THz beams. The divergence of a cw-THz photomixing source was characterized and included in a beam propagation calculation to match the THz beam to a multipass cell. Path lengths up to 20m have been realized. The spectra of carbonyl sulfide (OCS), vinyl chloride (CH_2CHCl) and dimethyl sulfoxide (DMSO), $(CH_3)_2SO$ are used to demonstrate the improved sensitivity of the spectrometer.**

I. Introduction And Background

THE fine spectral resolution and continuous coverage of the 0.3THz to 3THz band offered by photomixing sources has allowed them to provide a valuable contribution to spectroscopy applications in particular for gas phase studies. Such work has provided molecular parameters of gaseous many volatile polar molecules which present relatively intense THz signatures [1,2]. Improvements to the spectrometer sensitivity are key to allowing, a larger variety of molecules to be studied, trace detection, isotope identification, and measurement of low frequency molecular vibrations. Potential improvements include gains in the photomixer emission intensity, the minimum detectable power, and the interaction length of the THz beam with the gas phase subject. The propagation of the THz beam over long distances is hindered by its low power (typically ≈ 100nW) and highly divergent nature. Multipass cells have been successfully employed at infrared wavelengths allowing interaction lengths up to 50m to be achieved. In the THz band short (<1m) path lengths are generally used however multipass cells have been used with Time Domain Spectroscopy [3] and Fourier transform [4] instruments. A cw-THz spectrometer with a path length in the order of 10 m should allow Volatile Organic Compounds (VOC) such as vinyl chloride (CH_2CHCl) and dimethyl sulfoxide (C_2H_6OS) to be quantified.

II. RESULTS

The cw-THz beam is generated from an optical beatnote of two extended cavity laser diodes using a GaAs-LT photoconductive element with a log-spiral antenna, fig. 1. In order to successfully implement a multipass cell the focusing of the THz beam must be matched to the numerical aperture of the cell. To characterize the THz beam its intensity profile was measured using the knife edge technique at several frequencies and distances, allowing the beam waist of the source to be determined. A Gaussian beam calculation was performed to determine the beam radius at each mirror and aperture on the THz beam trajectory. The calculation allowed a parabolic mirror of focal distance of 152 mm to be selected in order to match the highly divergent THz beam to the low numerical aperture of a commercially available White cell (Infrared Analysis, 35-V).

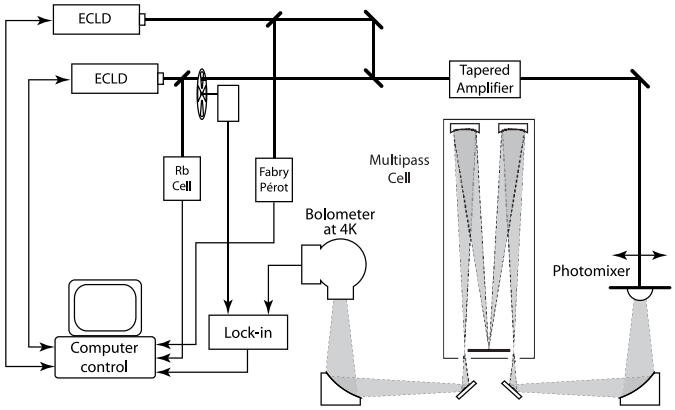

Fig 1. cw-THz spectrometer with multipass cell

The photomixer and Silicon lens are considered to be a single element located at d = 0 mm. The first parabolic mirror PM1 (f = 152 mm) is at d = 240mm and focuses the beam onto the entrance ENT of the multipass cell at 620mm. The beam propagates in the cell de-focusing and re-focsuing for every 2 passages. Path lengths corresponding to integer multiples of four passages (2.24m) may be realized. The entry and exit apertures have a diameter of 25mm, hence the optimization of the beam focusing is critical to prevent significant signal losses. A propagation path of four passages is illustrated in fig. 2 and includes a second parabolic mirror (PM2) at d = 3300 mm which focuses the exit beam onto the bolometer here positioned at 3540 mm.

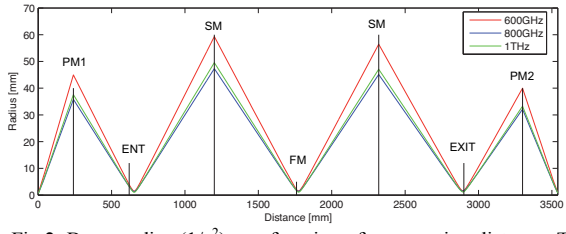

Fig 2. Beam radius ($1/e^2$) as a function of propagation distance. The spherical mirrors (SM), flat mirror (FM) are indicated.

Power transmission values of 40% have been realized at 1 THz for a path length of 2.24 m. The transmission decreases to 25% as the frequency is increased to 1.6 THz, decreased to 500 GHz, or the propagation distance lengthened to 6.72m. The path length of the multipass cell was verified by measurement of the intensity of a carbonyl sulfide (OCS) transitions, and examination of its free spectral range.

An optical path length of 13.4m allowed rotational transitions of the $OC^{34}S$ and $O^{13}CS$ isotopes to be observed (natural abundancies are 4.2% and 1.0% respectively), fig 3.

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The $OC^{34}S$ transition at 521.7 GHz is distorted by an intense OCS line at 522.6GHz. The $O^{13}CS$ transition is observed at 520.9GHz and the line at 521.0GHz is the excited symmetric stretching ν_1 mode. The $O^{13}CS$ line has a tabulated intensity of $2x10^{-23}$ $cm^{-1}/(molecule.cm^{-2})$, indicating that for pure gases the spectrometer is capable of resolving line intensities as weak as 10^{-25} $cm^{-1}/(molecule.cm^{-2})$.

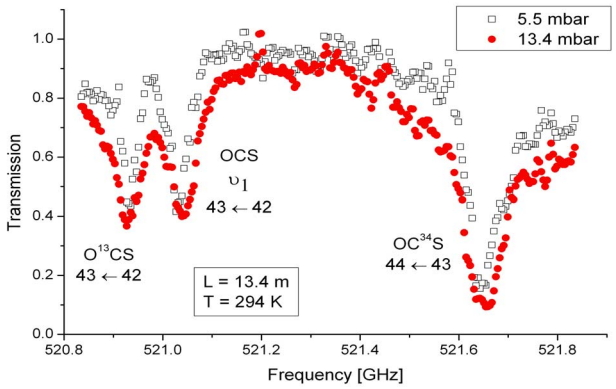

Fig 3. Rotational transitions of OCS isotopologues.

The increased sensitivity of the spectrometer is illustrated by the measurement of a VOC such as vinyl chloride (CH_2CHCl), fig. 4. In the case of the 24cm path length a pressure of 29mbar was required to observe an absorption signal, at this pressure the collisional broadening prevents the resolution of the individual transitions. At longer path lengths the increased sensitivity allows lower pressures to be used and the individual transitions may be isolated.

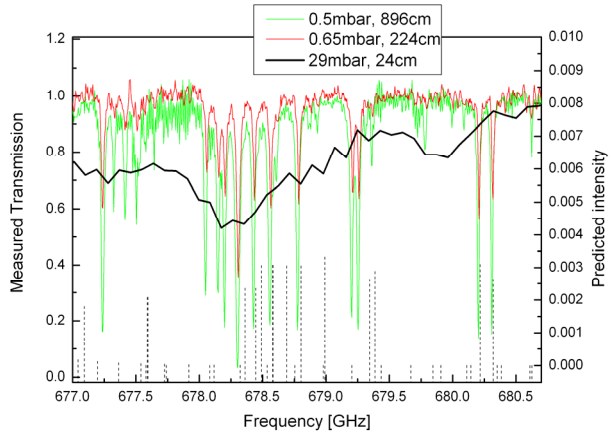

Fig 4. Spectra of CH_2CHCl for various path lengths at 294K. Dashed line indicates the predicted line positions and intensity.

A simulation of the ground state rotational spectra calculation has been performed to determine the position and relative intensity of the transitions of the $CH_2CH^{35}Cl$ isotopologue (75.8% natural abundancy). Comparison between the measured and predicted spectra reveals a similar structure with a frequency discrepency increasing from 0 to 400MHz as the measured frequency decreases. The frequency discrepancy results from the accuracy of the prediction which is based on molecular constants fitted by rotational lines measured below 30GHz [5]. As the path length is increased from 224cm to 896cm the weaker transitions can also be observed such as those at 677.3GHz. Preliminary measurements have also been performed on dimethyl sulfoxide (DMSO), $(CH_3)_2SO$ and at 580 GHz show weaker intensity transitions compared to vinyl chloride, fig 5. Nevertheless approximately 50 transitions have been identified and will be used to refine the molecular constants of this 10 atom molecule.

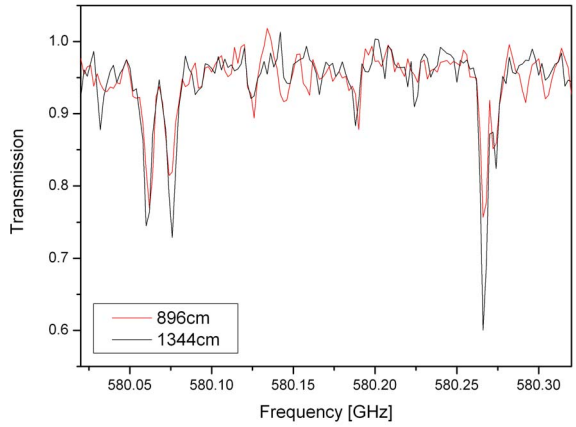

Fig 5. Measured spectra of DMSO for two various path lengths at 0.6mbar 294K.

CONCLUSION

A calculation of the propagation of the cw-THz beam has allowed a standard multipass cell to be used to extend the optical path length of the spectrometer to values up to 20m. The increased sensitivity of the instrument has been used to measure a number of weak OCS transitions and indicates that line intensities in the order of 10^{-25} $cm^{-1}/(molecule.cm^{-2})$ can be observed. This spectrometer opens up the possibility to examine larger variety of molecules demonstrated by the measured spectra of vinyl chloride and DMSO.

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