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Real-Time Terahertz Absorption Spectroscopy of Methanol and Deuterated-Methanol Vapour, using a TeraFET Detector Array

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Here we have demonstrated the potential of terahertz (THz) spectroscopy using a THz-frequency quantum cascade lasers coupled with a THz field-effect-transistors detector as a tool for probing chemical reactions, by observing distinct transitions in methanol and deuterated methanol (CH₃OD) in the 3.35, 3.4 and 3.45 THz region.

I. INTRODUCTION

GAINING an in depth understanding into a chemical reaction can be useful in a plethora of applications, from optimization of industrial relevant syntheses, to insight into the atmospheres of celestial bodies. A wide range of spectroscopic techniques have been developed taking advantage of the properties of different parts of the electromagnetic spectrum to interrogate chemical reactions, such as ultraviolet/visible to see electronic transitions, infrared to see bond vibrations or radio waves to observe the fine splitting in nuclear spin states in a magnetic field.

The terahertz band (1–10 THz) offers unique insights, owing to its absorption by rotational modes, rovibrational modes, low energy vibrational modes and absorptions from radical species. These absorptions give each molecule a unique and distinct absorption profile in the THz region allowing for great clarity in tracking individual chemical species in complex mixtures without convolution from other species present [1]. However, until recently there has been a lack of good quality sources and detectors in this band, resulting in poor signal-to-noise ratios, and detection rates too slow to resolve reactions.

Terahertz-frequency quantum cascade lasers (THz QCL) [2] have emerged as attractive sources to overcome these challenges, owing to their high-intensity, and narrowband emission. THz field-effect-transistors (TeraFETs) have also been shown to provide narrowband, high-speed, sensitive and low-noise detection of QCL emission at room temperature [3].

Here, we demonstrate the potential for THz spectroscopy of chemical reactions using a THz QCL coupled with a TeraFET array detector, to observe the distinct transmission spectra of methanol (MeOH) and deuterated methanol (MeOD, CH₃OD) in the gas-phase, and resolve changes in concentration over millisecond timescales.

II. RESULTS

The THz QCL used in this work has lasing modes at 3.35, 3.40 and 3.45 THz depending on temperature (20–60 K) and drive current (350–1000 mA). The emitted light was collimated and passed through a 95 cm long glass cell, whose windows are made of polymethylpentene (TPXTM) and held at the Brewster angle to allow for maximum THz transmission and eliminate any reflections; this also eliminates light coupling back into the QCL. The cell was filled with either MeOH or MeOD at a pressure of 0.5 Torr. The transmitted light was collected by an

8 × 8 TeraFET array with an integrated low-noise preamplifier with ~500 kHz bandwidth. The QCL bias was ramped from 350–1000 mA *via* external modulation by a sawtooth wave with a fundamental frequency of 230 Hz. The detector signal was sampled at a rate of 150 kHz, providing a ~1 mA current step per sample. A total of 13,800 current sweeps were taken and averaged together, for both an evacuated cell and with the sample present; these are then converted into a transmission spectrum.

The resulting transmission spectra are shown in Fig. 1 for the 3.40 THz mode. MeOH (Fig. 1a) displays several strong peaks in agreement with simulated data from the Jet Propulsion Laboratory (JPL) Molecular Spectroscopy catalogue [4], [5] (Fig. 1b). Interestingly, MeOD spectrum (Fig. 1c) shows significantly more peaks, we believe this is due to the isotopic effect on the transitions, shifting more peaks into our probe window that appear elsewhere for MeOH. As can be seen, the distinct transmission profiles of MeOH and MeOD can be discerned. We also note that in the MeOH data while the most intense peak positions agree with the JPL catalogue, relative peak intensity differs; this is likely due to uncertainties within the simulation model. Furthermore, significantly more minor

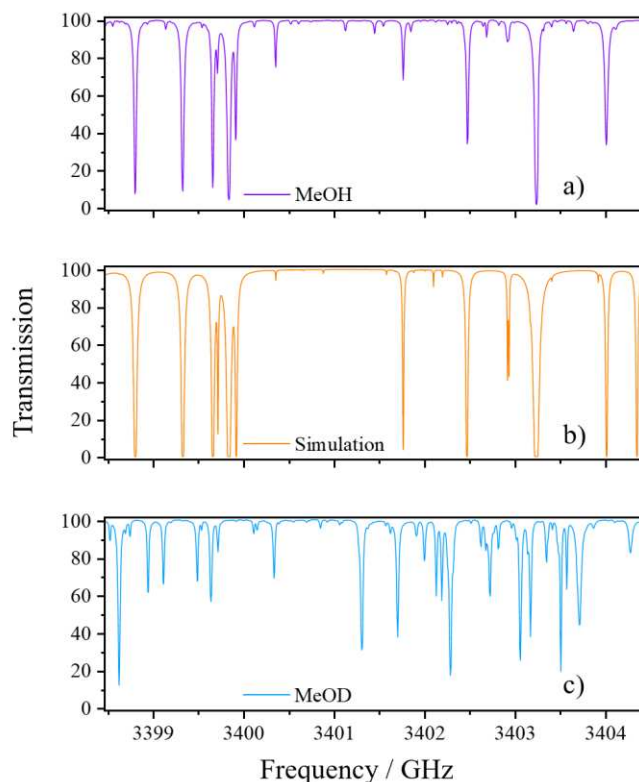


Fig. 1. Terahertz transmission spectra of MeOH (a), simulated MeOH (b) and MeOD (c) between 3399.5 and 3404.5 GHz, at a pressure of 0.5 Torr with a path length of 95 cm.

Conflict of interest

The authors have no conflicts to disclose.

Author contributions

M. D. Horbury: writing (original draft); data curation; investigation (lead); methodology (equal); visualization. N. K. North: investigation (supporting); methodology (equal). J. Holstein: investigation (supporting); methodology (equal). H. Godden: investigation (supporting). L. H. Li: resources; investigation (supporting). J. R. Freeman: fundings acquisition (supporting); conceptualization (supporting); methodology (equal). E. H. Linfield: funding acquisition (supporting); conceptualization (supporting). H. Roskos: funding acquisition (lead); conceptualization (supporting). A. Lisauskas: funding acquisition (supporting); conceptualization (lead); methodology (equal); supervision (equal). A. Valavanis: writing (review & editing); funding acquisition (supporting); conceptualization (supporting); methodology (equal); supervision (equal).

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peaks are observed than predicted. This trend is also seen at the 3.35 and 3.45 THz lasing modes. From our transmission data, we have determined that the minimum pressure of MeOH we can observe within our probe window is ~ 0.0025 Torr, when probing the strongest transition.

In addition to the static transmission spectra, we have also performed kinetic measurements of MeOH diffusing into the cell to demonstrate the time-resolved capabilities of the system. A kinetic trace is shown in Fig. 2., which was taken by probing the 3442.62 GHz absorption line, every 1 ms for 17 s, as MeOH entered the gas-cell to a total pressure of 0.25 Torr. The resulting kinetic fit gave a time-constant of 2.335 ± 0.003 s for diffusion.

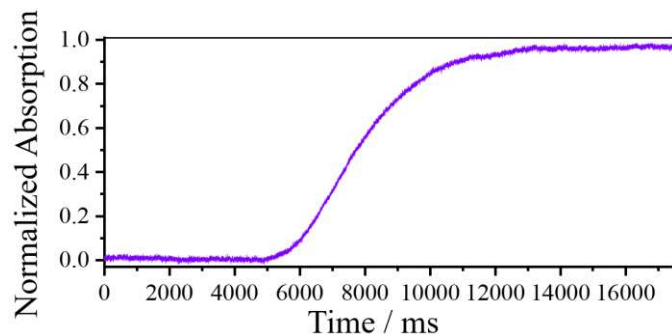


Fig. 2. Kinetic trace of MeOH at 3442.62 GHz as it diffuses into a 95 cm long cell.

III. SUMMARY

We have taken the terahertz (THz) transmission spectrum of methanol (MeOH) and deuterated methanol (MeOD, CH_3OD), using a quantum cascade laser with lasing modes at 3.35, 3.40 and 3.45 THz with a total frequency bandwidth of 10 GHz, coupled with a TeraFET detector array. Furthermore, we have shown the chemical selectivity of this technique, by taking a transmission spectrum of MeOH and MeOD, where the distinct transmission spectrum of each species are easily distinguished. Finally, we have demonstrated the time-resolved capability of this system. We believe that this demonstrates the great potential of THz spectroscopy for chemical applications, such as atmospheric chemistry and astrochemistry. Specifically, due to the ability to distinguish between different chemical species.

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DATA AVAILABILITY

The data associated with this paper are openly available from the University of Leeds Data Repository <https://doi.org/10.5518/1321>