Conference or Workshop Item:
Nuttall, E, Han, YJ, Brewster, N et al. (9 more authors) Analysis of deuteration reactions using self-mixing in a terahertz quantum-cascade laser. In: Infrared Terahertz Quantum Workshop (ITQW 2019), 15-20 Sep 2019, Ojai, California, USA.

Analysis of deuteration reactions using self-mixing in a terahertz quantum-cascade laser

Eleanor Nuttall[1], Yingjun Han[1], Nick Brewster[2], Matthew Oldfield[2], Lianhe Li[1], Giles Davies[1], Edmund Linfield[1], Brian Ellison[2], Paul Dean[1], Daniel Stone[3], Julia Lehman[3] and Alexander Valavanis[1*]

[1] School of Electronic and Electrical Engineering, University of Leeds, Leeds LS2 9JT, UK
[2] RAL Space Department, URKI–STFC, Harwell Campus, Didcot OX11 0QX, UK
[3] School of Chemistry, University of Leeds, Leeds LS2 9JT, UK
*Contact Email: a.valavanis@leeds.ac.uk

Short Abstract We present a THz-QCL spectroscopy technique, for analyzing deuteration reactions in gases. This is an important analytical chemistry technique, underpinning mechanistic studies. We use a self-mixing interferometry approach, in which radiation from a multimode QCL is fed-back into the device, via a gas cell, causing perturbations to the QCL voltage. This enables "detector-free" sensing over a 17-GHz range, allowing speciated measurements of reactions involving H_2O, D_2O, HDO, CH_3OH and CH_2DOD.

1. Introduction

THz QCLs are attractive sources for analytical and atmospheric chemistry, owing to their ability to probe strong and narrow spectral modes of a wide range of gas-phase species, which cannot readily be distinguished in the infrared or microwave regions. For example, atomic oxygen (O, 4.7-THz) and hydroxyl radicals (OH, 3.5-THz) are key constituents of the mesosphere and lower thermosphere region of the Earth's atmosphere, and the variation in their global concentrations is understood to be a highly-sensitive indicator of climate-change phenomena [1]. A number of approaches for THz QCL spectroscopy have been demonstrated [2], including direct-detection of transmitted radiation, frequency-comb spectroscopy, frequency modulation and photoacoustic spectroscopy. There is, however, great potential for THz radiation to study reaction processes, rather than stable mixtures, e.g., oxidation of volatile organic compounds in the atmosphere, or analysis of automotive combustion processes. The use of deuterated reagents (i.e., molecules with a deuterium substituted for hydrogen) is a key technique in mechanistic studies, as these species represent molecular "markers", enabling determination of precise reaction pathways. To realize this in the THz band, spectroscopy techniques must be developed, providing high spectral bandwidth (to observe multiple gas species simultaneously), sensitivity, and frequency resolution.

In this work, we use a recently developed THz-QCL spectroscopy technique, based on multi-mode self-mixing interferometry to analyze deuteration processes for the first time. Here, the radiation from a ~3.4-THz QCL is directed through a gas cell and reflected back into the QCL, via an optical delay path [3] (Fig. 1, top). The resulting interference with the intra-cavity field causes perturbations to the QCL voltage, which are proportional to both the magnitude and the phase of the reflected field. By recording this perturbation while adjusting the optical delay, an interferogram is obtained. A Fourier transform is then used to determine the emission spectrum of the QCL. The measurement is repeated at a range of QCL bias currents to obtain a range of THz probe frequencies, and to infer the spectral features of the gas within the cell.

2. Results

The products of an exemplar deuteration reaction (between water and fully-deuterated "heavy" water) are shown in Fig. 1 (bottom-left):

$$H_2O + D_2O \rightarrow 2HDO$$

The spectra of the reactants have been obtained individually, with the gas-cell being purged with dry nitrogen between each measurement, with characteristic absorption lines being observed within the THz spectrum. When D_2O is added slowly to H_2O vapor, an additional spectral line is observed, corresponding to the HDO product (c.f., NASA JPL Molecular Spectroscopy Catalog), as highlighted in blue in the figure. This technique has also been applied to organic molecules (methanol and partially-deuterated methanol), with spectral discrimination between at least five gas species obtained from the measurement. Fig. 1 (bottom-right) illustrates the dependence of the measured THz absorption of gas species, as a function of partial pressure, underpinning the use of this technique in future analytical chemistry measurements.

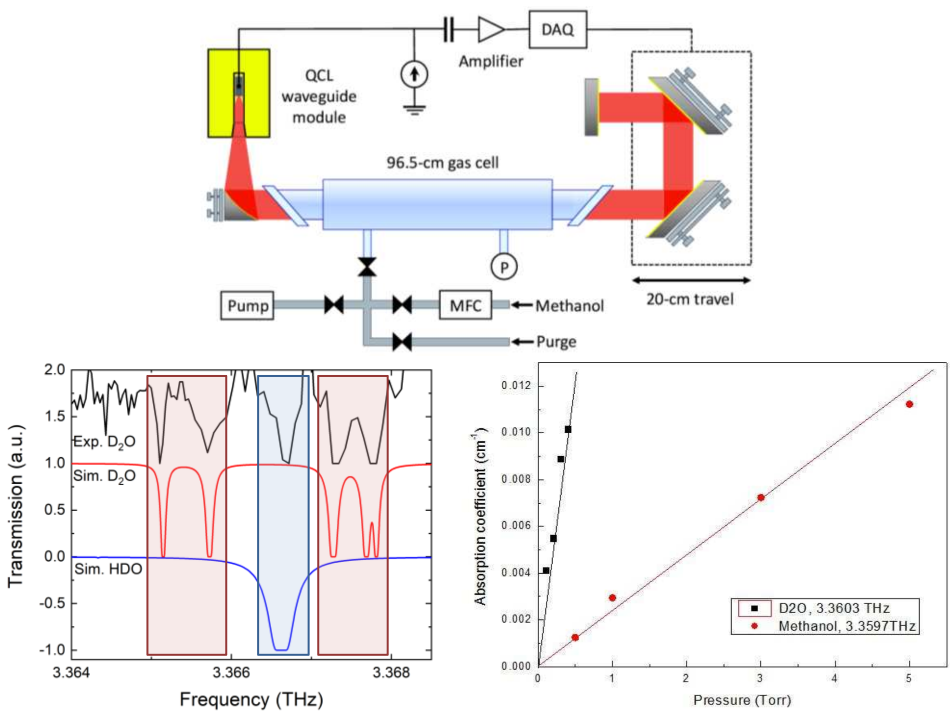

Figure 1 (top) Schematic of self-mixing gas spectroscopy apparatus, (bottom-left) THz spectrum of reaction products from water deuteration, highlighting features of D_2O in red and HDO in blue (bottom-right) Inferred absorption coefficients of D_2O and methanol with respect to partial pressures.

References

[1] G. Beig et al., 'Review of mesospheric temperature trends', Rev. Geophys., vol. 41, no. 4, p. 1015, Dec. 2003.

[2] H.-W. Hübers, H. Richter, and M. Wienold, 'High-resolution terahertz spectroscopy with quantum-cascade lasers', Journal of Applied Physics, vol. 125, no. 15, p. 151401, Apr. 2019.

[3] Y. J. Han et al., 'Gas spectroscopy through multimode self-mixing in a double-metal terahertz quantum cascade laser', Opt. Lett., OL, vol. 43, no. 24, pp. 5933–5936, Dec. 2018.