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Spectral analysis of a gas-phase reaction using self-mixing in a terahertz quantum cascade laser

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***Abstract*—We demonstrate a terahertz gas spectroscopy technique based on self-mixing in a multimode quantum cascade laser (QCL). The spectral parameters of the H/D exchange reaction between water (H_2O) and deuterated water (D_2O) have been measured between 3.36–3.37 THz.**

I. INTRODUCTION

TERAHERTZ-FREQUENCY quantum-cascade lasers (THz QCLs) are attractive sources for gas spectroscopy, owing to their compact size, narrow linewidth and high output power. Many gases have rotational modes that occur within the THz range, which has established THz spectroscopy as a desirable technique for use in atmospheric and space research. Measuring the chemical composition and dynamics, particularly of gases that appear in the Earth's upper atmosphere, can allow for more accurate climate models and aid understanding of anthropogenic climate change. Self-mixing interferometry (SMI) is a technique whereby radiation is intentionally reflected back into the laser cavity, causing interference and inducing a change in the QCL terminal voltage, which is sensitive to both amplitude and phase of the reflected radiation. As such, the laser acts as both a radiation source and detector, enabling compact, coherent sensing. This technique has been used for analysis of stable gases across multiple emission modes of the QCL simultaneously [1].

A common method for monitoring chemical reactions is to use isotopic markers to provide trackable spectral signatures. One of the most common markers is a deuterium (D) atom in the place of hydrogen (H) within a molecule, *i.e.* R–D *vs* R–H. The extra mass of the D atom causes a frequency shift compared with the non-deuterated molecule. By mapping the progression of the D atom during the reaction, greater insight can be gained into the overall reaction mechanism. Here, we demonstrate the capability of THz-SMI to monitor an H/D exchange reaction between H_2O and D_2O to form HDO.

II. RESULTS

The QCL used was a multimode QCL which was mounted within a precision micromachined copper block, with an integrated diagonal feedhorn [2]. In order to validate the SM method, the QCL emission spectrum was measured and compared to results obtained from Fourier-transform infrared (FTIR) spectroscopy with a Michelson interferometer (*Fig.1*) In both spectras, the two main QCL emission lines at 3.365 THz and 3.425 THz can be identified with very minimal frequency shift seen between the two different methods.

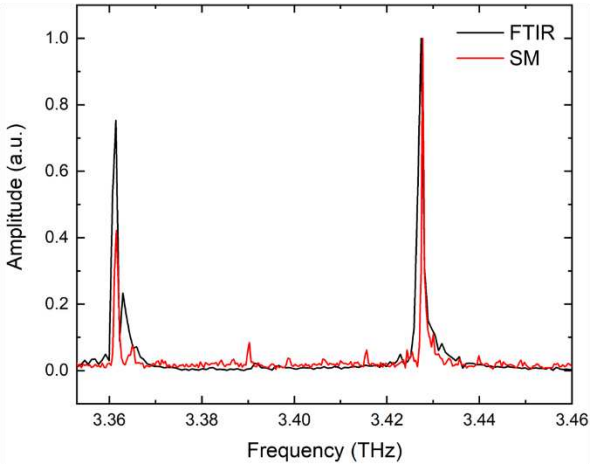

Fig. 1 THz QCL emission spectras measured using SMI and FTIR spectroscopy.

To further demonstrate SM capabilities in spectroscopy, a H/D exchange reaction was monitored using The THz radiation emitted from the feedhorn was collimated and directed through a 96.5-cm-long gas cell containing a gaseous sample before being reflected back into the QCL using a planar reflector mounted on an optical-delay stage. The QCL voltage perturbations were recorded as the length of the optical-delay stage was varied to produce an interferogram and hence measure the QCL emission spectra over a range of QCL biases. The current is changed at set increments, which in turn changes the available laser modes in the laser cavity. A FFT of each interferogram was used to infer the emission spectrum. The transmission spectrum for a D_2O/H_2O mixture at a pressure of 1 Torr between 3.36-3.37 THz was obtained between 110.0mA to 140.0mA with a current-sweep step of 0.2mA (*Fig.2).* Every 10 iterations were averaged to minimise noise. A reference measurement was taken with the gas cell evacuated to a base pressure of 0.03 Torr. High purity (>99.5%) D_2O and H_2O were used.

Within this frequency range, no H_2O spectral lines appear. Good agreement is shown between the experimental data and the simulation data extracted from the JPL molecular spectral catalogue [3]. The absorption peaks of D_2O can be identified at 3.3651 THz, 3.3656 THz, 3.3673 THz, and 3.3677 THz. The peak at 3.3667 THz corresponds to the catalogued absorption line of the product of the deuteration reaction, HDO.

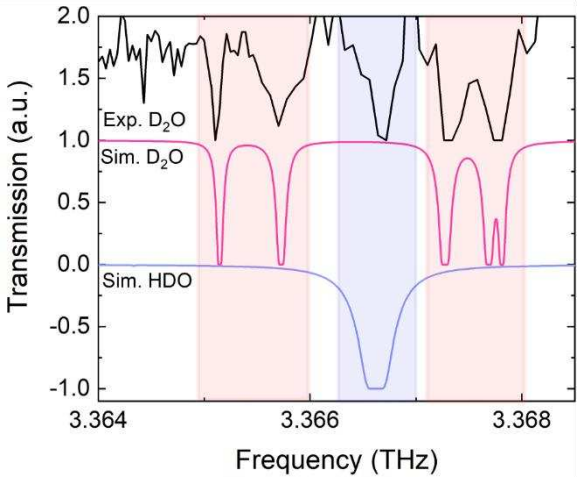

Fig. 2 THz transmission spectrum of the H/D exchange at 1 Torr at 298 K.

III. Summary

Here, SMI was used to measure the H/D exchange reaction between H_2O and D_2O using a THz QCL. SMI has shown to be a promising technique for spectroscopy and the results are in good agreement with the simulated data, showing the formation of the product- HDO. The signal-to-noise ratio and hence molecular detectivity may be enhanced in future work, with higher laser powers, and extended interaction pathlengths. Nevertheless, this work demonstrates the potential of THz-QCL spectroscopy for analysis of gas-phase reaction processes.

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