



Terahertz gas-phase spectroscopy of water and methanol isotopologues through difference-frequency generation in an intersubband polaritonic metasurface

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Abstract: We demonstrate room-temperature terahertz-frequency gas spectroscopy through difference-frequency generation in an intersubband polaritonic metasurface. This device has a strong $\chi^{(2)}$ nonlinearity and, when driven using a pair of mid-infrared quantum-cascade lasers, provides broad tunability (101.27 GHz) around a 4.7 THz center frequency. This enables the detection of the rotational–vibrational transitions of multiple gas-phase species simultaneously, including the overlapping spectral signatures of isotopologues of water and methanol vapors. We show that seven isotopologues (H_2O , HDO , D_2O , HD^{18}O , H_2^{18}O , CH_3OH and CH_3OD) can be distinguished within the spectral bandwidth. A calibration of the source tuning was achieved against 71 cataloged spectral lines, with a deviation of <80 MHz between the experimental and cataloged values. A minimum detectable absorption coefficient of $6 \times 10^{-4} \text{ cm}^{-1}$ was inferred, corresponding to a partial pressure of 100 μTorr ($6 \times 10^{12} \text{ particles/cm}^3$) of trace H_2^{18}O in a background measurement.

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1. Introduction

Terahertz-frequency (THz) gas spectroscopy is of interest across several disciplines, owing to its ability to probe rotational–vibrational transitions in numerous molecules with low molecular mass, or fine-structure transitions in atoms [1]. This presents important opportunities for atmospheric and astronomical measurements. For example, remote THz radiometric observations of the fine-structure transitions of atomic oxygen, OI, have been achieved, including from the OSAS-B high-altitude balloon mission [2] and from the GREAT instrument on the SOFIA aircraft [3]. In parallel, THz absorption-spectroscopy enables the cataloging of astronomical lines [4,5], or the potential for terrestrial applications including biomedical sensing [6,7], industrial process monitoring [8], greenhouse-gas monitoring [9], toxic gas detection [10], and food-quality inspection [11].

One key challenge in atmospheric chemistry is to determine the mechanisms and branching ratios of the complex photochemical reactions of Volatile Organic Compounds (VOCs) in the upper atmosphere. Isotopic labeling can be used as a strategy for this purpose in laboratory

experiments [12–15], in which a deuterium (D) atom at a known location on a molecule acts as a marker to track hydrogen transfer and reaction rates. However, the THz rotational–vibrational spectra of the species involved in H–D exchanges may be closely spaced or overlap in the frequency domain. Thus, a THz spectroscopy technique with a frequency resolution on the order of MHz and broad spectral coverage is required.

To date, photomixers and electronic multipliers are commonly used THz sources with linewidths on the order of MHz and milliwatt output powers, but their output power rolls off at frequencies above 2 THz, owing to the carrier dynamics within the device structures [16]. Quantum Cascade Lasers (QCLs) are a good alternative source for gas spectroscopy at higher frequencies [1,17]. These solid-state devices emit either mid-infrared (MIR) or THz radiation through electronic intersubband transitions within a multi-quantum-well structure. THz QCLs can be tailored to provide milliwatt continuous-wave output powers around a chosen frequency within the ~1.9–5.7 THz band [18,19]. MHz-scale frequency stability can be achieved with passive methods [2] and tuning ranges of ~5 GHz are typically obtained [20]. Significantly wider spectroscopic tuning bandwidths can be obtained using multimode QCLs (e.g., 72 GHz in [21]), or potentially tens of GHz in single-mode from coupled-cavity schemes [22,23]. However, high-powered THz QCLs require cryogenic cooling for continuous-wave applications, and their maximum emission-frequency is limited by the Reststrahlen absorption band within the device materials (8–9 THz for GaAs [19]).

Here, we demonstrate an alternative THz gas spectrometry scheme, which overcomes the above limitations by exploiting a recently developed difference-frequency generation (DFG) technique [24]. The output of two room-temperature MIR QCLs is focused onto an intersubband polaritonic metasurface, which exhibits strong $\chi^{(2)}$ nonlinearity across a large bandwidth and enables THz emission within the GaAs Reststrahlen band. This approach is distinct from THz photomixer spectroscopy, as THz radiation is generated through the fast polarization response of the metasurface elements, rather than the bulk carrier dynamics in a biased antenna structure. As such, much higher THz frequencies (extending into the Reststrahlen band) can be generated, with powers on the scale of 10 μ W. Here, we demonstrate the first THz sensing application based on these sources.

The experiments demonstrated in this work have a tuning bandwidth of ~100 GHz spanning 4.65–4.75 THz. We have distinguished the reagents and products involved in a deuterium exchange between H₂O and D₂O and between deuterated methanol (CH₃OD) and H₂O, in addition to ¹⁸O-containing isotopologues. We demonstrate a multi-species frequency calibration by fitting the data of low-pressure absorption lines to those in molecular spectroscopy catalogs [4,5,25].

We describe the structure and operation of the spectroscopy system in Section 2, followed by the spectroscopic analysis of the background atmospheric water spectrum and trace contaminants in Section 3. We then analyze H–D exchange reactions in D₂O and CH₃OD in Sections 4 and 5, respectively.

2. System configuration

2.1. Metasurface based down-conversion

The MQW heterostructure used in this work is fabricated from the In_{0.53}Ga_{0.47}As/GaAs_{0.51}Sb_{0.49} materials system, chosen for its narrow intersubband transition linewidths, which maximizes the achievable nonlinear response [24]. The metasurface used here shares the same growth run, layer design, and Y-shaped single-resonance nanoresonator geometry as the device optimized for the 4–6 THz band reported in the Supplement 1 of Ref. [24], and is therefore effectively identical to that device rather than a distinct redesign. The heterostructure comprises 23 repetitions of a coupled double-quantum-well unit with layer thicknesses, in nm, of **8.0**/4.9/**3.0**/5.6/5.0/**8.0**, where the GaAs_{0.51}Sb_{0.49} barrier layers are shown in bold and the underlined In_{0.53}Ga_{0.47}As quantum well is n-doped to a nominal electron density of $3.3 \times 10^{18} \text{ cm}^{-3}$. The resulting intersubband

structure is shown in Fig. 1(a). The intersubband transition energies were determined using angled absorption measurements, yielding $\hbar\omega_{01} = 116$ meV, $\hbar\omega_{02} = 128$ meV and $\hbar\omega_{12} = 12$ meV for the $0 \rightarrow 1$, $0 \rightarrow 2$ and $1 \rightarrow 2$ transitions, respectively. The resulting nonlinear response is described in the Supplement 1 of Ref. [24].

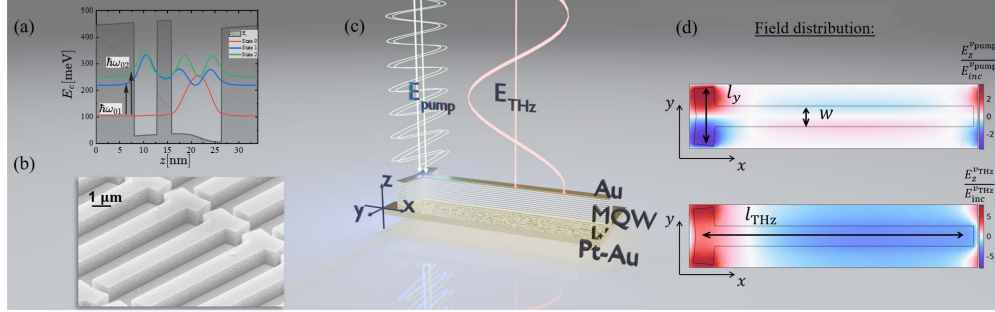


Fig. 1. DFG metasurface design. (a) Simulated conduction-band diagram of the employed multi-quantum-well (MQW) heterostructure. The transition energies $\hbar\omega_{01}$ and $\hbar\omega_{02}$ are designed to maximize $\chi_{zzz}^{(2)}$ at the mid-infrared pump wavelengths used in this work. (b) Scanning electron microscope image of the fabricated metasurface, showing the Y-shaped nanoresonator array. (c) Schematic of a single Y-shaped nanoresonator unit cell, showing the double-metal structure with the MQW layer sandwiched between the metal claddings. Pump fields, polarized along x , couple into the resonator head, while the elongated tail is tailored to radiate the generated THz field. (d) Simulated field distribution of the mid-infrared pump modes and the THz mode within the unit cell.

The effective second-order nonlinear susceptibility of the metasurface, $\chi_{\text{eff}}^{(2)}$, is enhanced relative to the intrinsic intersubband nonlinearity $\chi_{zzz}^{(2)}$ by a spatial overlap integral over the nanoresonator unit-cell volume V ,

$$\chi_{\text{eff}}^{(2)} = \chi_{zzz}^{(2)} \frac{1}{V} \int_V \frac{E_z^{v_1}}{E_{\text{inc}}^{v_1}} \frac{E_z^{v_2}}{E_{\text{inc}}^{v_2}} \frac{E_z^{v_{\text{THz}}}}{E_{\text{inc}}^{v_{\text{THz}}}} dV, \quad (1)$$

where $E_z^{v_i}/E_{\text{inc}}^{v_i}$ is the field enhancement at frequency v_i [24]. As illustrated in Fig. 1(b),(c) and (d), the Y-shaped nanoresonator geometry sets the mid-infrared and THz resonance positions independently via its head and tail dimensions, respectively: pump radiation couples into the resonator head, while the elongated tail is tailored to radiate the generated THz field. This device was designed to place its combined resonance response over the 2–6 THz band, encompassing the 4.7 THz operating point used in this work.

It is important to distinguish two different senses of “bandwidth” for this system. The metasurface itself supports DFG across the full 2–6 THz design band, set by its resonance structure; the >100 GHz tuning range demonstrated in this work (Section 2.2 onwards) is not a limitation of the metasurface but reflects the temperature-tuning range achievable with the two fixed-geometry QCL pumps used here. Access to a different sub-band within the metasurface’s 2–6 THz design range would require a different, discretely tunable or interchangeable pump-laser pair rather than a new metasurface.

At the 4.7 THz operating frequency used in this work, with the two pump photon energies chosen symmetrically about the intersubband transition manifold, the metasurface is expected to provide a peak mid-infrared-to-terahertz conversion efficiency of $\eta \sim 1 \text{ mW/W}^2$.

2.2. Spectrometer integration

Having established the design and expected performance of the metasurface itself, we now describe its integration into the complete source–detector spectroscopy system used in this work, in which two mid-infrared QCL pump lasers, optical beam-combining and delivery optics, and a THz detector are combined around the metasurface to form a tunable gas-phase spectrometer.

A system block diagram is shown in Fig. 2, including a simplified representation of the THz optical path (red shaded line) and MIR path (green and blue thin lines). This allows for wide tunability in a room-temperature system with a footprint of approximately $(30 \times 30) \text{ cm}^2$ and a minimal number of movable parts.

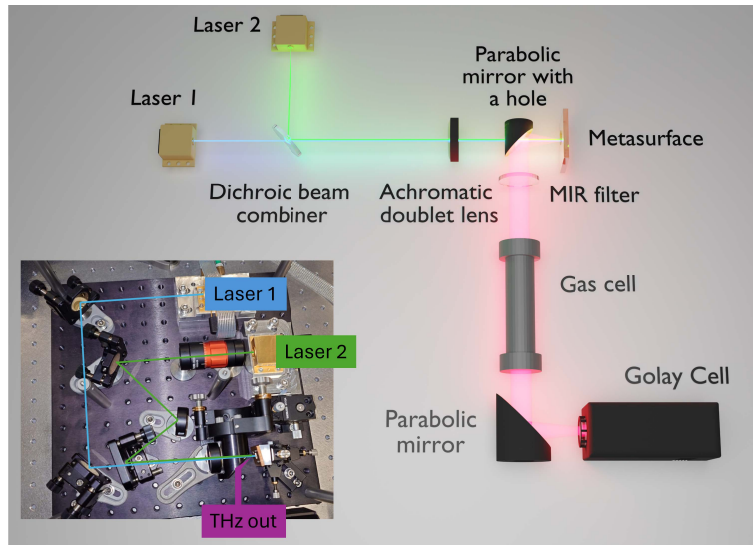


Fig. 2. A schematic illustration of the spectroscopy system (using simplified optical paths). Thin green and blue lines represent the MIR optical paths and the thicker shaded red path indicates the THz radiation. Inset: top-down photograph of the lasers and metasurface.

The QCLs are mounted in high-heat-load (HHL) packages controlled by thermoelectric coolers (TECs), and the laser outputs are coupled out of the packages using collimating lenses. The two QCLs are driven independently in continuous-wave mode using a pair of Thorlabs ITC4002QCL laser drivers. The first QCL (‘Laser 1’, Adtech Photonics), operated at a fixed driving current of $I_1 = 0.85 \text{ A}$ and was temperature-tuned over a wavelength range of $\lambda_1 = 10.52 - 10.56 \mu\text{m}$. The output power of Laser 1 is not modulated and exceeds 100 mW over the full tuning range used in this work. The second QCL (‘Laser 2’) was a distributed-feedback (DFB) QCL fabricated at the Walter Schottky Institute and operates at a fixed wavelength of $\lambda_2 = 9.04 \mu\text{m}$ with an output power of 176 mW. This operating point is obtained using a constant driving current of $I_2 = 1.05 \text{ A}$ and an operating temperature of $T_2 = 34^\circ\text{C}$. The radiation from Laser 2 is modulated using an optical chopper at 12 Hz, enabling signal recovery with a lock-in amplifier. To match the beam diameter to that of Laser 1, a twofold Gaussian beam expander was installed in the Laser 2 beam path.

The beams are combined using a dichroic beam combiner (Spectrogon LP 100000) and focused onto the metasurface using an achromatic doublet lens. Based on the conversion efficiency and pump powers described in Section 2.1, the metasurface is expected to generate approximately $1 \mu\text{W}$ of THz radiation at the 4.7 THz operating frequency. No independent, absolute-power calibration of the THz beam was performed for this experiment; however, the effective THz power delivered to the detector is estimated to be substantially lower, on the order of 400 nW. This

reduction relative to the expected source output is attributed to a partial loss of optical alignment sustained during transport of the system from Munich to Leeds, rather than to any change in the intrinsic performance of the metasurface source itself. Re-establishing full alignment, or engineering a more transport-robust optical mount, is expected to recover the full $\sim 1 \mu\text{W}$ source output and correspondingly improve the system signal-to-noise ratio.

The collimated THz radiation emitted from the metasurface is collected using an off-axis parabolic (OAP) mirror and directed through a gas cell. The outcoupled THz radiation is then focused using a second OAP mirror with a 2 inch diameter and a 4 inch focal length onto a Golay detector. The detector signal is demodulated using a Signal Recovery 7265 lock-in amplifier with a 2 s integration time constant.

The gas cell is 35 cm long and 1.5 inch in diameter, with 3 mm thick Polymethylpentene (TPX) windows. These allow THz radiation to pass through the cell but block MIR reflections from the metasurface. The gas cell is connected via a manifold to an Agilent TPS-compact turbomolecular pump. The spectroscopic target species is held in a liquid reservoir, and a vapor sample of the required pressure can be extracted through the manifold into the gas cell using an MKS Instruments pressure control system and a Mass Flow Controller (MFC). The manifold is constructed from standard aluminum vacuum tubing, with KF 16 and Swagelok fittings. Owing to the simple design of the cell, it is not possible to monitor the intra-cell pressure directly. However, the pressure in the manifold can be monitored before closing the gas cell using an Agilent a-Baratron capacitive pressure gauge, which has a minimum pressure reading of 3 mTorr.

The temperature of Laser 1 is adjustable incrementally over a $T_1 = 10 - 45^\circ\text{C}$ range as a method of tuning its MIR emission frequency and hence the THz difference frequency. Frequency tuning is limited by the QCL packaging, where temperatures above 45°C will melt the adhesive that bonds the lens to the HHL package and temperatures below 10°C will cause condensation on the lens and risk damaging the QCL. Condensation on the components could potentially be avoided by enclosing the DFG breadboard in a dry purge, which would enable a reduced minimum operating temperature and an increased THz bandwidth. The driving current for the QCLs was selected so that single-mode emission was achieved across the full tuning range of the experiments. It is important to emphasize that free-running QCLs were used in this work, without stabilization against a primary frequency reference and the emission frequency was tuned indirectly using laser temperature and current control. Slight variations in tuning occur between experiments, for example, through variations in chiller performance or in optical feedback through mechanical drifts. As such, there is an inherent reproducibility challenge, and the QCL tuning must therefore be calibrated against cataloged spectral lines for each spectral measurement. However, this could be overcome in future work through the use of an active stabilization scheme for the pump lasers.

3. Background spectral analysis

Our first experiment examined transmission through a nominally empty gas cell that was connected to the vacuum pump for 10 minutes and evacuated to a manifold pressure of <3 mTorr prior to cell closure. A spectroscopic scan was taken using a full $T_1 = 10 - 45^\circ\text{C}$ temperature sweep of Laser 1 in 1500 steps. A delay of 40 s was included in each increment to allow the temperature to stabilize. The normalized detector signal is shown as a function of temperature in Fig. 3(a). Here, a combination of background features is observable in the plotted data. Three broad dips in transmission are observable at temperatures of approximately 16.5°C , 23.5°C and $34.0\text{--}40.0^\circ\text{C}$. These correspond to pressure-broadened absorption features of water in the unpurged atmosphere outside the gas cell in the 4.7 THz region. In addition, residual low-pressure H_2O and other contaminants are present in the gas cell, resulting in individually resolvable narrow spectral features superimposed on the broadened atmospheric absorption bands. The atmospheric water absorption saturates the measurement in the range $34.0\text{--}40.0^\circ\text{C}$. The baseline shows a gradual

overall decrease as the temperature increases, as a result of the reduction in the output power of the QCL. As such, an accurate determination of the intensities of the experimental lines is challenging. This effect could be mitigated by using a vacuum or nitrogen-purged reference measurement, and in Section 5 we show that a numerical baseline-correction can be used as a post-process step. However, our focus at this stage is on analysis of the baseline and demonstration of broad spectral coverage rather than determination of molecular concentrations. As such, the uncorrected baseline is retained.

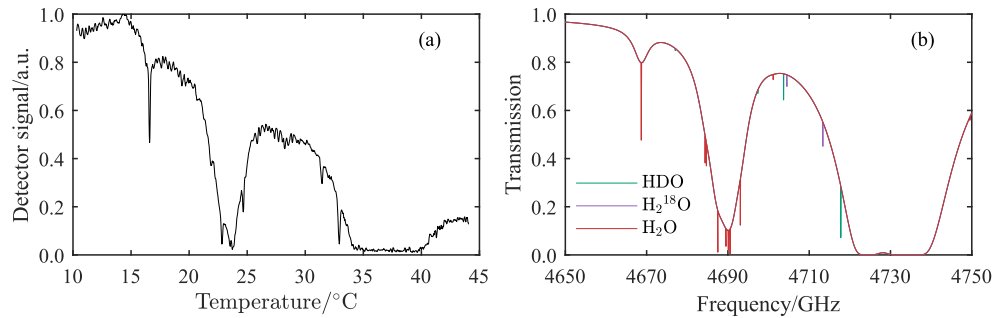


Fig. 3. (a) Normalized detector signal as a function of Laser 1 temperature, for THz radiation transmitted through a nominally empty gas cell and external (unpurged) air. A 5-point moving average filter has been applied to the detector signal. (b) Simulated transmission spectrum for 40% humidity outside the gas cell, and 50 mTorr H_2O within the cell. Additional isotopologue contributions are shown for HDO (2%) and H_2^{18}O (0.2%).

The distinctive shape of the background spectrum enables the calibration of the THz emission frequency as a function of T_1 . Initially, the broadened atmospheric water lines were used for coarse frequency calibration against H_2O data in the JPL spectroscopy catalog [4] by manually scaling the experimental temperature axis to the frequency range of the cataloged data. Figure 3(b) shows a simulation of the transmission spectrum in this range, through the gas cell and the external atmosphere. A Voigt lineshape was applied to the spectral lines, accounting for thermal Doppler broadening at room temperature and collisional broadening depending upon the environment (inside or outside the cell). The collisional broadening was modeled using a Lorentzian contribution to the overall lineshape. Half-widths at half-maxima of $0.1 \text{ cm}^{-1}\text{atm}^{-1}$ and $0.4 \text{ cm}^{-1}\text{atm}^{-1}$ were used for air-broadening and self-broadening respectively, in-line with typical values taken from the HITRAN catalog [26]. The atmospheric pressure outside the cell was assumed to be 760 Torr and the saturation pressure of water was taken as 26.6 Torr.

Initially, the cell was assumed to contain pure low-pressure water vapor as a result of outgassing. A cell pressure of 50 mTorr and the typical laboratory humidity of 40% were found to provide an acceptable match to the respective spectral contributions for the interior and exterior of the gas cell. Additional contributions were identified from the two most common naturally-occurring isotopologues of water (H_2^{18}O and HDO), whose rotational-vibrational spectra differ from those of H_2O owing to their different moments of inertia and molecular mass. Lines are shown in the simulated spectrum for H_2^{18}O , using its natural abundance of 0.2% and for HDO, using 2% abundance. The latter is significantly higher than the natural abundance of HDO (0.03%) and is the result of H-D exchange with trace D_2O contamination of the cell from previous experiments ($\text{D}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons 2 \text{HDO}$). No spectral contribution from D_2O itself can be resolved from the baseline at these concentrations.

This result can be understood by considering the equilibrium constant for the reaction, which has been evaluated as $K = [\text{HDO}]^2/([\text{H}_2\text{O}][\text{D}_2\text{O}]) = 3.85$ at room temperature [27], where the brackets denote the concentration (and hence partial pressure) of each species. Thus, the observed

[HDO] : [H₂O] $\approx$ 0.02 ratio in the background measurement implies a [D₂O] : [H₂O] $\approx 1 \times 10^{-4}$ ratio at equilibrium. As such, trace D₂O is effectively removed from the system by the H–D exchange process, and this explains the absence of its spectral features in this experimental result.

A final calibration of the QCL frequency was achieved by applying a linear fitting of the cataloged spectral line frequencies to the T_1 value at which the matching features were observed experimentally. Figure 4 shows that a linear relationship of the form $f = f_0 + kT_1$ provides a good fit to the data, where $f_0 = 4618.79$ GHz and $k = 3.00720$ GHz°C⁻¹. The confidence interval in the fitting is 71–80 MHz across the range of fitted values (i.e., <0.002% uncertainty) and detailed line assignments and associated quantum numbers can be found in Supplement 1. The frequency calibration shows that a tuning range of 4649.79–4751.06 GHz was achieved in this measurement, giving a total tuning bandwidth of 101.27 GHz and a step size of 67.5 MHz per sample.

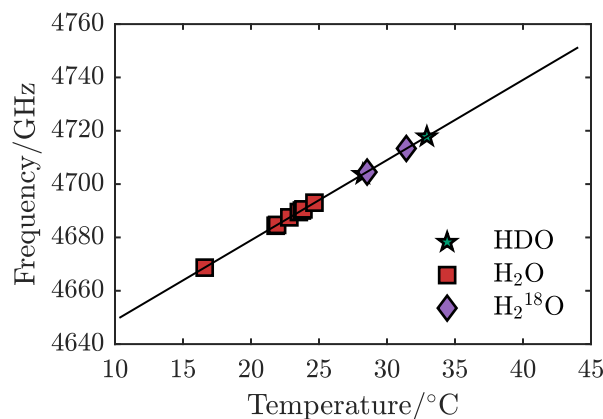


Fig. 4. Linear calibration of THz frequency against Laser 1 temperature, using residual water in an evacuated gas cell. Cataloged spectral line centre-frequencies are shown for H₂O, HDO and H₂¹⁸O.

4. Isotopologues of water

A more detailed study of H–D exchange in water was carried out by injecting a sample of D₂O into the gas cell. This provides a simpler spectral analysis than that of H–D exchange in methanol (see Section 5) owing to the relatively sparse spectra of the water isotopologues and high line strengths. When D₂O is introduced into the gas cell in high concentration, the H–D exchange reaction with residual H₂O results in an equilibrium yield of HDO, in addition to the equivalent reaction for H₂¹⁸O, producing HD¹⁸O.

For this measurement, D₂O vapor (Sigma–Aldrich, 99.9%D) was introduced into the gas cell at a manifold pressure of 5 Torr and the spectrometer was temperature tuned over the range $T_1 = 10.3 - 23.8^\circ\text{C}$ in 1000 steps. The temperature range was truncated to avoid the saturated atmospheric water band at higher frequencies. Figure 5 shows that a different set of spectral peaks are observable from those in the background sweep. The calibration in Fig. 5(a) uses 13 cataloged spectral lines to determine a linear tuning range of 4653.5–4693.6 GHz with a fitting uncertainty of 90–100 MHz across the band. Here, slightly different tuning parameters $f_0 = 4622.63$ GHz and $k = 2.98584$ GHz°C⁻¹ were obtained and an increment of 40.3 GHz between experimental samples was inferred.

Several key differences are apparent in comparison to the background scan. Two strong HDO lines are seen at 4677 GHz and 4683 GHz and a very weak D₂O line at 4689 GHz, which were not resolved in the background scan. A weak additional spectral feature was observed at 13.3 °C, which may correspond to the cataloged HDO line at 4661 GHz. However, there are no other

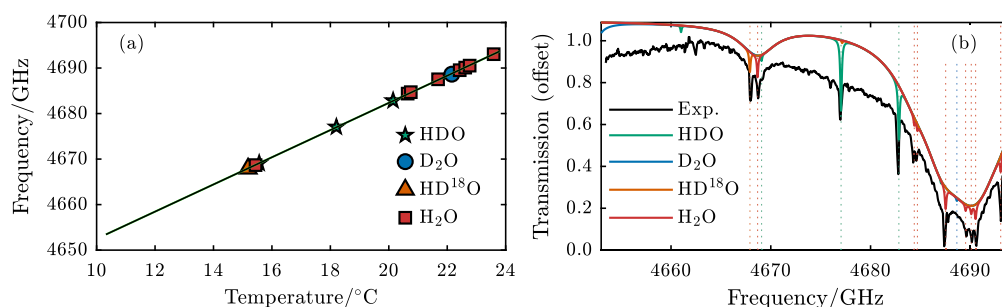


Fig. 5. (a) Spectral calibration using cataloged lines observed following injection of D₂O into a gas cell. (b) Comparison between frequency-calibrated experimental data (black line) and simulated spectral contributions of cataloged species. Vertical dashed lines indicate frequencies of cataloged lines used for fitting. For readability, the simulated spectra are offset vertically by 0.1 transmission units from the experimental spectrum.

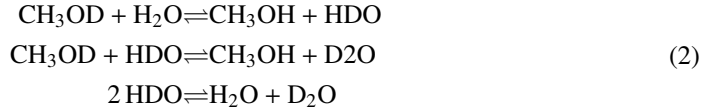
measurable lines in the lower-frequency part of the spectral band. In Section 5, we show that a piecewise linear fit is needed for accurate calibration of data in the low-frequency region, owing to a possible laser mode-hop. As such, the feature at 13.3 °C cannot be assigned reliably in this dataset and was excluded from the analysis. An additional HD¹⁸O line is present at 4668 GHz, as a product of the H–D exchange with H₂¹⁸O. The presence of these additional lines compared with the background is a result of the much higher D₂O concentration in this experiment and the correspondingly higher HDO production. A simulated set of spectral lines for each identifiable species is shown in Fig. 5(b) along with the experimental data. Partial pressures of ~1 Torr and ~200 mTorr were found to provide an acceptable match to the experimental transmission for D₂O and H₂O respectively. An equilibrium with $K = 3.85$ produces a corresponding partial pressure of 830 mTorr for HDO. Taking the 0.2% natural abundance of H₂¹⁸O and assuming identical equilibration yields a concentration of 1.7 mTorr for HD¹⁸O. Under the assumption of negligible initial HDO concentration, the equilibrium expression implies initial partial pressures of 1.4 Torr and 600 mTorr for D₂O and H₂O respectively.

The simulated spectral lines using the calculated equilibrium partial pressures provide overall agreement with the experimental data, albeit with two apparent anomalies. First, the sum of the simulated partial pressures of the equilibrium lines is 2 Torr, whereas the experimental manifold pressure and collision-broadened linewidth imply a total cell pressure of 5 Torr. The additional pressure contribution in the experimental results may be the result of trapped air within the system or additional volatile contaminants without spectral lines in the frequency range under study. Second, the inferred initial partial pressure of D₂O is only 70% of the isotopologue distribution, although nominally pure D₂O was used as the source. Although a cannula transfer process was used to extract D₂O from its storage vessel, its purity will have degraded over time through gradual ingress of atmospheric water. Small amounts of H₂O in the transfer line and manifold will also have reduced the concentration of D₂O prior to injection into the cell. However, the simulation confirms that four isotopologues of water can be identified simultaneously within a single THz frequency sweep and with relative concentrations that correspond reasonably well with theoretical values.

5. Isotopologues of methanol

More complex H–D exchange processes occur between methanol and water isotopologues. To demonstrate this more challenging spectroscopic scenario, we take CH₃OD as our starting point, in which a deuterium atom has replaced hydrogen in the OH group. This isotopologue has low natural abundance and undergoes H–D exchange with residual water, yielding a series of

reversible reactions:



An equilibrium therefore forms between CH_3OD , CH_3OH , D_2O , HDO and H_2O in addition to equivalent H–D exchanges with H_2^{18}O . The combined THz transmission spectrum contains numerous lines with overlapping spectral signatures for each species.

A sample of CH_3OD (Alfa Aesar, 99.5% D) was introduced at 2 Torr manifold pressure into the gas cell and residual water resulted in H–D exchange. For consistency, and to avoid the H_2O saturation band at higher frequencies, the QCL bias and tuning parameters remained the same as in our analysis of H–D exchange in water. Figure 6 shows that a much larger number of spectral lines was observed, compared with water isotopologues alone. This is consistent with the co-existence of the multiple species identified above. It is much more challenging to assign cataloged spectral lines than in the investigations described in the previous sections and a baseline-correction process was therefore used to simplify analysis. The uncalibrated detector signal was initially normalized against the maximum value of a 10-point moving window and then filtered using a 3-point moving average. The atmospheric-absorption baseline was approximated by initially taking the 10-point moving maximum of the smoothed signal (such that the sampling window is larger than the linewidth of any given line) and then smoothing this using a 10-point moving average. The filtered signal was finally divided by the baseline to obtain an approximation to the transmission spectrum of the gas mixture within the cell.

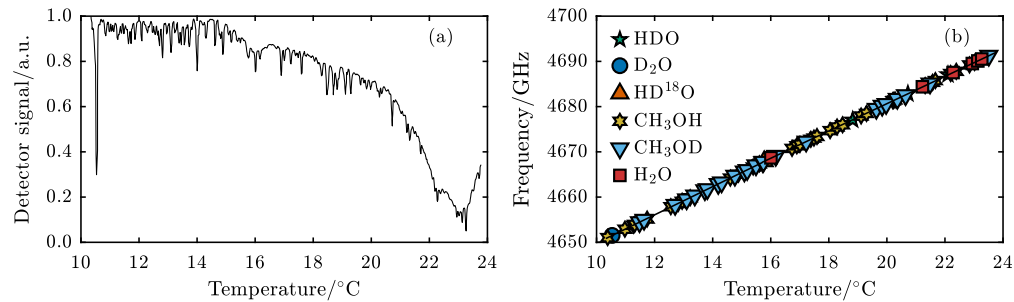


Fig. 6. (a) THz detector signal as a function of T_1 for transmission through a cell containing the equilibrium mixture resulting from H–D exchange between CH_3OD and residual H_2O . A 3-point moving average filter has been applied. (b) Spectral calibration against cataloged line frequencies.

A search was performed for all cataloged spectral lines of the relevant water and methanol isotopologues in the 4650–4695 GHz range with an intensity greater than a cut-off value of $1 \times 10^{-4} \text{ nm}^2 \text{ MHz}$. Data for H_2O , D_2O , HDO , HD^{18}O and CH_3OH were taken from the JPL spectroscopy catalog [4] and those for CH_3OD were supplied as supplementary data by the authors of Ref. [25]. The cataloged line frequencies were tabulated manually against the T_1 value at which the matching experimental features were observed, starting with the highest intensity and most spectrally isolated lines. Strongly overlapping or very weak lines were omitted from the assignments. In the case of indistinguishable spectral doublets in the cataloged data, a single calibration temperature was used. In total, 71 spectral lines were used from the six different species in the final calibration (81 including doublets). The calibration fitting is shown in Fig. 6(b) and a detailed spectral assignment is given in Supplement 1. Unlike the investigations above, a significant number of lines were present at low QCL temperatures ($f < 4670 \text{ GHz}$). It was found that continuous linear or low-order polynomial calibrations

were inadequate and a small, ~ 56 MHz step in the DFG source frequency was identified at a temperature of $T_1 \approx 15.7^\circ\text{C}$, which was at the lower limit of the previous calibration range. A discontinuous two-part piecewise linear calibration was found to give a good match to the data in Fig. 6(b), using $f_0 = 4618.66\text{ GHz}$, $k = 3.11809\text{ GHz}^\circ\text{C}^{-1}$ for $T_1 < 15.7^\circ\text{C}$, and $f_0 = 4620.30\text{ GHz}$, $k = 3.01721\text{ GHz}^\circ\text{C}^{-1}$ for $T_1 \geq 15.7^\circ\text{C}$ (i.e., a 3% change in the tuning coefficient). The origin of this discontinuity in the tuning characteristics is unclear; however, the effect is very weak and may be attributed to small changes in optical feedback or chiller performance over the ~ 16 hour duration of the experiment. It is also well below the frequency resolution of standard FTIR spectrometry and therefore would not be observable in standard characterization of the QCLs. A fitting uncertainty of ~ 40 MHz was found across the full range of temperatures, and the calibration mapped all experimental lines to within 80 MHz of their assigned cataloged values.

In principle, a least-squares fitting process could be used to determine the partial pressure of each species. However, this is very challenging, owing to the crowded spectrum, relatively low spectral resolution, and a lack of experimental data for pure isotopologue samples. As such, a manual adjustment of the simulated partial pressure was made to each species to find an approximate agreement with the experimentally observed spectrum. Figure 7 shows the baseline-corrected transmission spectrum. For easy comparison, the normalized experimental transmission measurement (P/P_0) is shown on the same axes as an inverted simulation ($2 - P/P_0$). Spectral contributions for individual species are shown as colored traces, with the total simulated and experimental traces shown as black lines. Vertical colored lines are shown for each line frequency used in the calibration, and symbolic markers indicate the corresponding experimental peak for which the QCL temperature was tabulated. Colors and symbols take the same meaning in this plot as the definitions in Fig. 6. Several notable features are apparent in the experimental spectrum, including a strong D_2O line at 4651.5 GHz and multiple moderate-intensity CH_3OH and CH_3OD lines overlapping in the $\sim 4651\text{--}4680$ GHz band. Near complete mapping of experimental spectral peaks to cataloged lines was achieved.

Here, partial pressures of 100 mTorr (H_2O), 30 mTorr (D_2O) and 107 mTorr (HDO) were found to provide good agreement with the experimental water lines, while constrained to the expected $K = 3.85$ equilibrium. An HD^{18}O partial pressure of 200 μTorr was also found to agree with the observed line intensities, in line with the natural 0.2% abundance. Approximate partial pressures of 300 mTorr for both CH_3OH and CH_3OD were found to give broad agreement with the experimental observation. The CH_3OD concentration was expected to be significantly larger than that of CH_3OH , owing to the trace H_2O concentration within the gas cell. However, as before, the purity of the injected sample is likely to have been reduced significantly by gradual H–D exchange with atmospheric water during storage, and with residual water within the manifold.

In addition to the cataloged lines, we observed a strong anomalous line at 4676.71 GHz, which corresponds to a doublet of torsion–rotational $\nu_t = 2 \rightarrow 1$ transitions, which are identified in Ref. [28]. Three other anomalous absorption features at 4662.32 GHz, 4679.87 GHz and 4691.85 GHz do not correspond to the cataloged lines of any relevant species but may be transitions between higher-order states in CH_3OH or CH_3OD .

6. Conclusion

We have demonstrated a THz gas spectrometer with a single-mode tuning range of > 100 GHz around 4.7 THz. This tuning range is limited by the MIR QCL pump sources, whereas the polaritonic metasurface device enables several THz tunability. It has previously been shown to be capable of producing microwatt THz power in the Reststrahlen band when combined with an appropriate difference frequency. This approach presents significant potential advantages compared with alternative THz frequency-domain spectroscopy methods. The bandwidth and upper tuning range exceed those of existing photomixer, electronic multiplier, and THz QCL

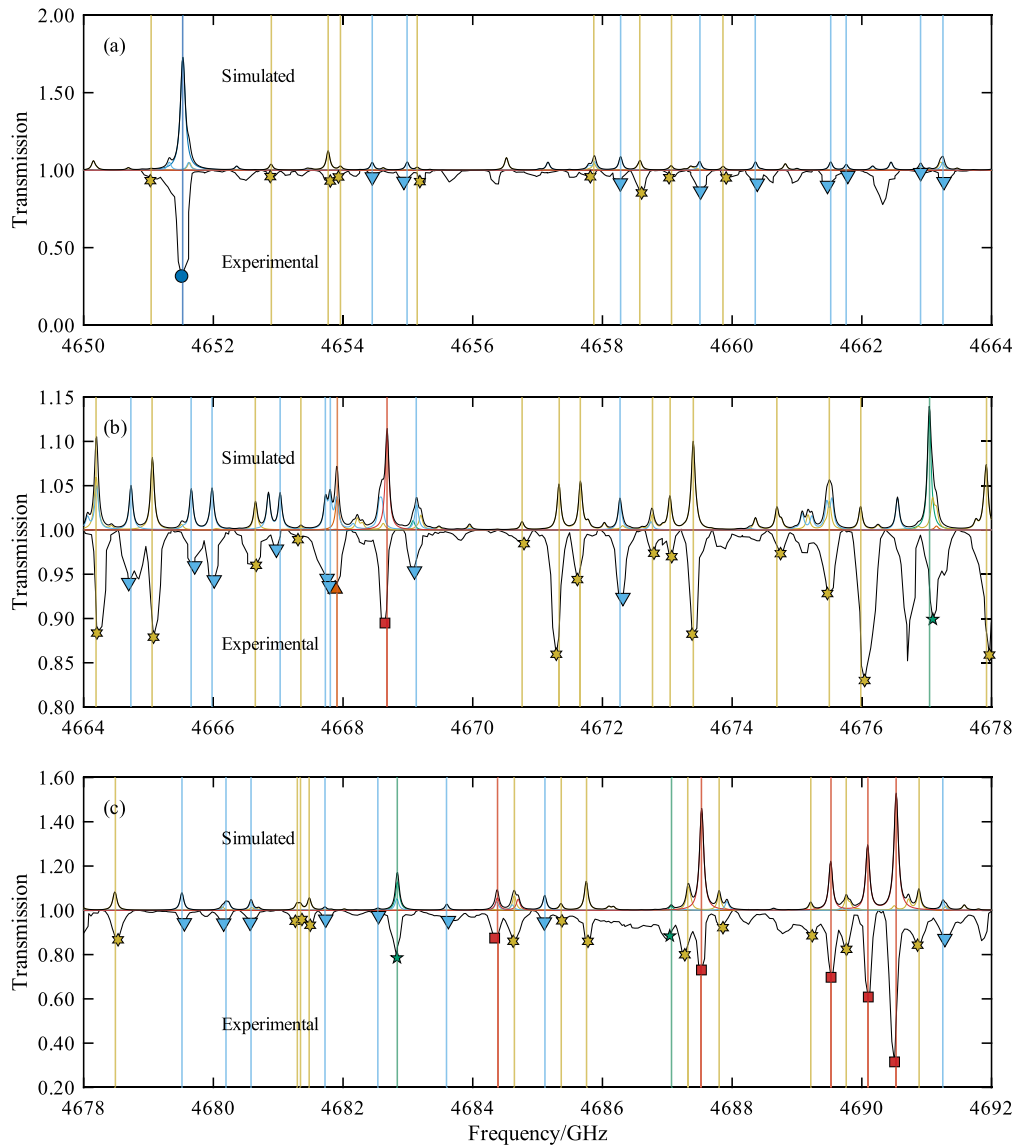


Fig. 7. Calibrated CH₃OD/H₂O H-D exchange transmission spectrum with baseline correction. Data are shown for the ranges (a) 4650–4664 GHz, (b) 4664–4678 GHz and (c) 4678–4692 GHz. Simulated spectral lines are shown on an inverted $2 - P/P_0$ scale, while vertical lines indicate the frequencies of the cataloged spectral lines used in calibration. Symbols have the same meaning defined in Fig. 6 and indicate the center of the experimental line corresponding to each calibration point.

sources, while also operating at room temperature. The (30×30) cm² footprint of the THz source is also potentially well-suited to portable field-deployable system integration.

It is instructive to compare the present work with the performance of THz-QCL-based spectrometers, which are the only other compact frequency-domain spectroscopy systems to have been demonstrated around 4.7 THz. Our DFG approach provides much greater continuous single-mode tunability, compared with ~5–12 GHz in THz QCLs [29,30]. FTIR analysis of

a rapidly-chirped multimode 4.7 THz QCL can extend the spectral coverage to 72 GHz, but this is at the expense of much lower (transform-limited) 1.5 GHz resolution [21]. Conversely, the output power of the present system (400 nW) is much lower than the 8 mW achievable with a 4.7 THz QCL [30], and therefore a commensurate difference in signal-to-noise ratio and molecular detection limit is expected. It is important to note, though, that THz QCLs only operate at cryogenic temperatures, whereas our system is entirely at room temperature. The speed of measurement achieved in the present system is also significantly lower than that of THz QCL spectroscopy, owing to the thermal tuning method used in this work. A single-frequency-point sampling rate of 25 mHz was used here to allow for temperature stabilization, although rates of 150 kHz have been demonstrated for electrically-tuned THz-QCL gas spectroscopy using a FET-based detector [31]. This is not a fundamental limitation of the DFG approach, and fast electrical modulation of the mid-IR pump laser will be applied in future work.

We have shown that it is possible to sample H₂O, D₂O, HDO, HD¹⁸O, CH₃OD, and CH₃OH within a single hydrogen–deuterium exchange experiment. Although these measurements used a reduced tuning bandwidth, to avoid saturation by atmospheric water, we have shown that H₂¹⁸O is also measurable at higher THz frequencies. This demonstrates the ability to distinguish a range of isotopologues with overlapping spectral features, underpinning future THz analysis of VOCs through isotopic labeling. The emission frequency of the temperature-tuned system has been calibrated against 71 cataloged spectral lines, resulting in a fitting uncertainty of ~40 MHz across the full spectral range. The calibration has been shown to drift between experiments as a result of using free-running QCL pump lasers. For example, at an operating point of 20 °C, the calibrated emission frequencies are 4678.93 GHz, 4682.35 GHz and 4680.64 GHz for the experiments in Sections 3, 4 and 5 respectively. This is likely to be caused by a combination of effects including adjustments to system alignment and drifts in chiller performance, and provides a motivation for either direct frequency monitoring (e.g., by heterodyne mixing with a stable reference oscillator [20]) or active control of the frequency (e.g., by locking to a microwave reference [32]).

The partial pressures of each species were fitted manually to experimental data using cataloged line intensities and the relative concentrations of water isotopologues were shown to fit the expected $K = 3.85$ equilibrium constant. The ¹⁸O-containing isotopologues of water were also shown to have the expected natural abundance relative to ¹⁶O. In practice, this manual approach to spectral decomposition is impractical and laborious. A nonlinear least-squares fitting of the partial pressures, linewidth and baseline is a more desirable option, although a higher frequency resolution and improved system noise performance would be required for reliable implementation.

The smallest partial pressure inferred for a species observed in this work was 100 μTorr partial pressure for H₂¹⁸O in the background spectral scan, which corresponds to 3.2×10^{12} particles/cm³. In more general terms, the system noise level limits the minimal resolvable transmission drop to $\Delta P/P_0 \approx 0.02$ and hence a minimum absorption coefficient of 6×10^{-4} cm⁻¹. Although this is much higher than the typical values for millimetre-wave spectrometers, it is important to note that this first demonstration employs free-running QCL sources and a broadband Golay detector with no filtering. Background thermal inputs to the THz detection could be mitigated, and detection speed could be increased through the use of a narrowband Schottky-diode or FET-based detector [33]. This, in turn, would enable frequency-modulation spectroscopy (and hence avoidance of $1/f$ noise contributions) through rapid electrical modulation of one of the QCL pumps. An enhancement of the source power (and hence decrease in detection limit) could also be achieved through the use of a CO₂ pump laser. The detection limit could potentially be reduced further using a long-path or multi-pass sensing configuration, and by active stabilization of the pump lasers. In summary, the DFG approach demonstrated in this work enables a compact, room-temperature and widely tunable THz spectrometer, underpinning multi-gas detection and potential future applications in isotope-labeled VOC spectroscopy.

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Data availability. The data associated with this work is openly available in the Zenodo data repository [34].

Supplemental document. See [Supplement 1](#) for supporting content.

References

1. H. W. Hübers, H. Richter, and M. Wienold, “High-resolution terahertz spectroscopy with quantum-cascade lasers,” *J. Appl. Phys.* **125**, 151401 (2019).
2. M. Wienold, A. D. Semenov, E. Dietz, *et al.*, “OSAS-B: A balloon-borne terahertz spectrometer for atomic oxygen in the upper atmosphere,” *IEEE Trans. Terahertz Sci. Technol.* **14**(3), 327–335 (2024).
3. H. Richter, C. Buchbender, R. Güsten, *et al.*, “Direct measurements of atomic oxygen in the mesosphere and lower thermosphere using terahertz heterodyne spectroscopy,” *Commun. Earth Environ.* **2**(1), 19 (2021).
4. H. M. Pickett, R. L. Poynter, E. A. Cohen, *et al.*, “Submillimeter, millimeter, and microwave spectral line catalog,” *J. Quant. Spectrosc. Radiat. Transf.* **60**(5), 883–890 (1998).
5. H. S. P. Müller, S. Thorwirth, D. A. Roth, *et al.*, “The Cologne Database for Molecular Spectroscopy, CDMS,” *Astronomy Astrophysics* **370**(3), L49–L52 (2001).
6. N. Rothbart, V. Stanley, R. Koczulla, *et al.*, “Millimeter-wave gas spectroscopy for breath analysis of COPD patients in comparison to GC-MS,” *J. Breath Res.* **16**(4), 046001 (2022).
7. V. Vaks, V. Anfertev, M. Chernyaeva, *et al.*, “Sensing nitriles with THz spectroscopy of urine vapours from cancers patients subject to chemotherapy,” *Sci. Rep.* **12**(1), 18117 (2022).
8. F. J. Müller, M. Jaidl, D. Theiner, *et al.*, “Water vapor quantification in raw product gas by THz quantum cascade laser,” *Energy Convers. Manag. X* **26**, 100906 (2025).
9. A. Cuisset, F. Hindle, G. Mouret, *et al.*, “Terahertz rotational spectroscopy of greenhouse gases using long interaction path-lengths,” *Applied Sciences (Switzerland)* **11**, 1–13 (2021).
10. J. Qin, B. Zhu, Y. Du, *et al.*, “Terahertz detection of toxic gas using a photonic crystal fiber,” *Opt. Fiber Technol.* **52**, 101990 (2019).
11. F. Hindle, L. Kuuliala, M. Mouelhi, *et al.*, “Monitoring of food spoilage by high resolution THz analysis,” *Analyst* **143**(22), 5536–5544 (2018).
12. D. Stone, K. Au, S. Sime, *et al.*, “Unimolecular decomposition kinetics of the stabilised Criegee intermediates CH₂OO and CD₂OO,” *Phys. Chem. Chem. Phys.* **20**(38), 24940–24954 (2018).
13. N. C. K. Robertson, L. Onel, M. A. Blitz, *et al.*, “Temperature-Dependent, Site-Specific Rate Coefficients for the Reaction of OH (OD) with Methyl Formate Isotopologues via Experimental and Theoretical Studies,” *J. Phys. Chem. A* **128**(25), 5028–5040 (2024).
14. M. A. Blitz and P. W. Seakins, “Laboratory studies of photochemistry and gas phase radical reaction kinetics relevant to planetary atmospheres,” *Chem. Soc. Rev.* **41**(19), 6318–6347 (2012).
15. C. Zhang, X. Hu, Y. Yang, *et al.*, “Gas-phase Hydrogen/Deuterium Exchange on Large, Astronomically Relevant Cationic PAHs,” *The Astrophys. J.* **940**(1), 73 (2022).
16. S.-H. Yang and M. Jarrahi, “Navigating terahertz spectrum via photomixing,” *Opt. Photonics News* **31**(7), 36 (2020).
17. L. Zhang, G. Tian, J. Li, *et al.*, “Applications of absorption spectroscopy using quantum cascade lasers,” *Appl. Spectrosc.* **68**(10), 1095–1107 (2014).
18. J. R. Freeman, O. Marshall, H. E. Beere, *et al.*, “Improved wall plug efficiency of a 1.9 THz quantum cascade laser by an automated design approach,” *Appl. Phys. Lett.* **93**(19), 191119 (2008).
19. M. Shahili, S. J. Addamane, A. D. Kim, *et al.*, “Continuous-wave GaAs/AlGaAs quantum cascade laser at 5.7 THz,” *Nanophotonics* **13**(10), 1735–1743 (2024).
20. H. W. Hübers, S. G. Pavlov, H. Richter, *et al.*, “High-resolution gas phase spectroscopy with a distributed feedback terahertz quantum cascade laser,” *Appl. Phys. Lett.* **89**, 88–91 (2006).
21. B. Röben, X. Lü, M. Hempel, *et al.*, “Terahertz quantum-cascade lasers as high-power and wideband, gapless sources for spectroscopy,” *Opt. Express* **25**(14), 16282 (2017).
22. I. Kundu, J. R. Freeman, P. Dean, *et al.*, “Terahertz photonic integrated circuit for frequency tuning and power modulation,” *Opt. Express* **28**(4), 4374 (2020).

23. I. Kundu, P. Dean, A. Valavanis, *et al.*, "Continuous Frequency Tuning with near Constant Output Power in Coupled Y-Branched Terahertz Quantum Cascade Lasers with Photonic Lattice," *ACS Photonics* **5**(7), 2912–2920 (2018).
24. J. H. Krakofsky, M. Rieder, S. Stich, *et al.*, "Generation of continuous-wave 1–11 THz radiation with intersubband polaritonic metasurfaces," *Nat. Photonics* **20**(6), 699–704 (2026).
25. V. Ilyushin, H. Müller, M. Drozdovskaya, *et al.*, "Rotational spectroscopy of CH₃OD with a reanalysis of CH₃OD toward IRAS 16293-2422," *Astron. Astrophys.* **687**, A220 (2024).
26. I. E. Gordon, L. S. Rothman, R. J. Hargreaves, *et al.*, "The HITRAN2024 molecular spectroscopic database," *J. Quant. Spectrosc. Radiat. Transfer* **353**, 109807 (2026).
27. C. L. Chen, P. Bopp, and M. Wolfsberg, "Evaluation of the equilibrium constant for H₂O + D₂O = 2 HDO by direct summation over rotational-vibrational states," *J. Chem. Phys.* **77**(1), 579–580 (1982).
28. I. Mukhopadhyay and Y.-B. Duan, "Analysis of torsion-rotational transitions in the first three torsional states of CH₃OD," *Chem. Phys.* **257**(1), 91–101 (2000).
29. L. Schrottke, X. Lü, B. Röben, *et al.*, "High-Performance GaAs/AlAs Terahertz Quantum-Cascade Lasers For Spectroscopic Applications," *IEEE Trans. Terahertz Sci. Technol.* **10**(2), 133–140 (2020).
30. T. Hagelschuer, H. Richter, M. Wienold, *et al.*, "A Compact 4.75-THz Source Based on a Quantum-Cascade Laser With a Back-Facet Mirror," *IEEE Trans. Terahertz Sci. Technol.* **9**(6), 606–612 (2019).
31. J. Holstein, N. K. North, M. D. Horbury, *et al.*, "8×8 patch-antenna-coupled terafet detector array for terahertz quantum-cascade-laser applications," *IEEE Trans. Terahertz Sci. Technol.* **14**(6), 799–807 (2024).
32. H. Richter, N. Rothbart, M. Wienold, *et al.*, "Phase Locking of Quantum-Cascade Lasers Operating Around 3.5 and 4.7 THz With a Schottky-Diode Harmonic Mixer," *IEEE Trans. Terahertz Sci. Technol.* **14**(3), 346–353 (2024).
33. J. Holstein, N. K. North, A. Hof, *et al.*, "Improving terahertz-detection sensitivity of 8×8 FET arrays through liquid-nitrogen cooling in a compact low-noise cryostat," *IEEE Trans. Terahertz Sci. Technol.* **16**(4), 463–475 (2026).
34. N. North, J. H. Krakofsky, S. Appekey, *et al.*, "Dataset associated with "Terahertz gas-phase spectroscopy of water and methanol isotopologues through difference-frequency generation in an intersubband polaritonic metasurface"," Zenodo: Version 1, 14 Sept 2026, <https://doi.org/10.5281/zenodo.21279883>.