



# A Terahertz VRT spectrometer employing quantum cascade lasers



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## ABSTRACT

The first application of a commercial Terahertz quantum cascade laser (QCL) system for high resolution spectroscopy of supersonic beams is presented. The QCLs exhibited continuous linear voltage tuning over a 2 GHz range about a center frequency of 3.762 THz with ~1 ppm resolution. A sensitivity of ~1 ppm fractional absorption was measured with a single pass optical system. Multipass operation at the quantum noise limit of the stressed photoconductor detector would produce a 100-fold improvement.

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## 1. Introduction

The use of high resolution Terahertz spectroscopy radiation sources for spectroscopy of jet cooled expansions of ions, clusters, and molecules has engendered important advances in the understanding of intermolecular forces and molecular structure. Of particular interest to our group is the study of water clusters, as these are a route to a more detailed understanding of bulk water [1–4]. However, the paucity of Terahertz sources operating above 3 THz, and increasing constraints on laser safety have stifled progress in this field [5]. Recently emerging frontiers in space, atmospheric, and defense-related research have driven the development of new Terahertz laser source technologies that are having a broad impact on the Terahertz region in general [6–9]. One notable advance has been the development of Quantum Cascade Lasers (QCLs) that function in the low Terahertz regime (1.2–5 THz). These devices offer many attractive features for spectroscopy, such as high power, narrow bandwidth, and continuous tunability over a broad spectral range [10–13]. While the advent of QCLs has greatly impacted infrared spectroscopy [14], only recently have commercial Terahertz QCLs become available to the general scientific community, and these have primarily been employed for imaging technologies [15–18].

The principal motivations for using a Terahertz QCL as the laser source for high resolution VRT spectroscopy include the desire to simplify the experimental design and to increase the sensitivity

and the operating frequency. Prior to the Terahertz QCL, uW power levels were generated with microwave sidebands on Schottky diode mixers pumped with high-power CO<sub>2</sub> laser-pumped gas lasers. These systems are difficult to operate, unstable, have diminishing amounts of power at frequencies > 3 THz, and are constrained in operating frequency to regions around the discrete gas lines of the gas laser. The new QCL source offers much higher powers than previous solid state sources (mWs compared to 10s of μWs). QCLs are available in a continuous range of frequencies, where the emission can be engineered coarsely by adjusting the band structure, and finely by design of the optical cavity. Additionally, the operation of this commercial device is safe and relatively simple, allowing facile integration into an experimental setup and straightforward operation. As a field test of these performance features, the EASY-QCL was integrated into the Berkeley Terahertz VRT spectroscopy setup and used to measure absorptions in a supersonic expansion of methanol/Ar.

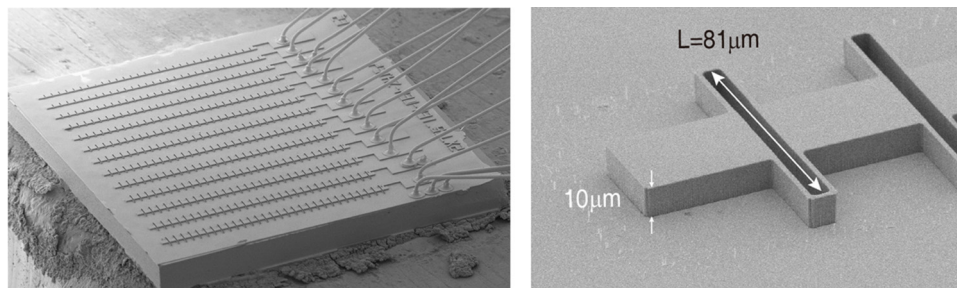
## 2. Experimental

### 2.1. Terahertz VRT spectrometer design

The EASY-QCL system provided by longwave photonics comprises two main components: the Stirling cycle He cryocooler and the fabricated QCL semiconductor chip based on MIT group's design, mounted inside a vacuum cell mounted on the cooler. The chip itself consists of distributed feedback (DFB) laser array using a metal–metal waveguide and has been described in detail in [17,19] to achieve better efficiency and beam divergence. The fabricated QCL chip contains 20 independent devices, each capable of lasing

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**Figure 1.** A portion of the DFB QCL chip; the individual devices can be seen on the left hand side of the figure. The right hand side shows the design of the antenna-coupled DFB laser and dimensions of the multiple quantum well (MQW) stack.

at center frequencies separated by a few GHz. The emitting power is around 1–1.5 mW depends on the laser frequency. A chip similar to that used in this study is shown in Figure 1.

The QCL system is integrated into the Berkeley VRT spectrometer as shown in Figure 2.

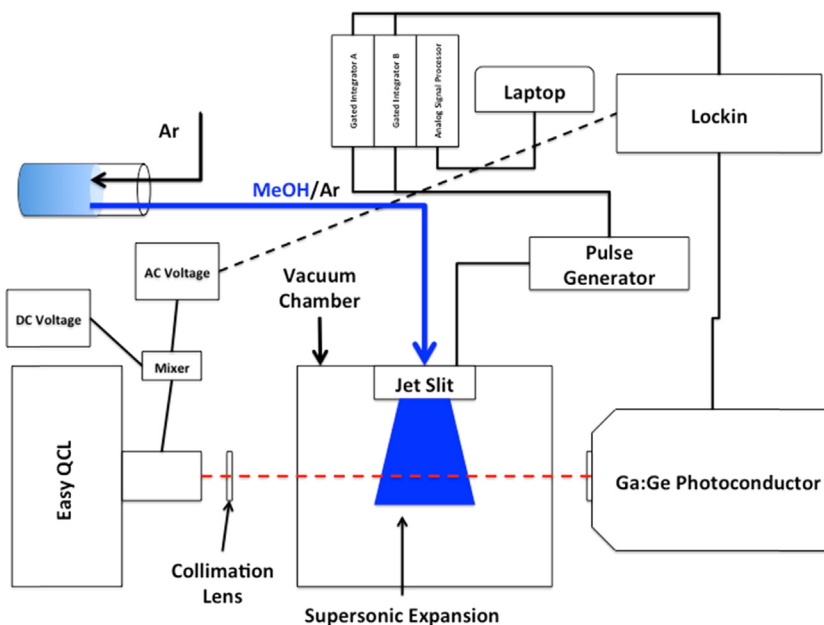
Briefly, a DC power source (Keithley, Model 2230-30-1) provides a DC voltage which is mixed with a 0.5 mV, 50 kHz sine wave AC voltage, provided by the lockin (Stanford Research Systems, Model 830), in a bias tee (ThorLabs, Model T1G), the resultant of which is then applied to the QCL device. The laser output is collimated by a concave-hemispherical HRFZ-Si lens treated with an anti-reflectivity coating (Tydex, St. Petersburg, RN) and directed through a Zenor window to a vacuum chamber maintained at 70 mTorr by a Roots blower (Edwards EH4200) backed by two rotary pumps (Edwards E2M275). The laser beam passes through the chamber and a second window to the detector, a stressed Ge:Ga photoconductor mounted in a side-looking IR Labs dewar which is cooled to 4K with LHe. Signal from the detector is amplified by a transimpedance preamplifier (IRLabs, LN-8) before being sent to the lockin and detected at twice the modulation frequency ( $2f$ ). For scans of ambient pressure methanol, the signal was digitized and sent directly to the computer. For scans of the pulsed supersonic jet, the signal was routed to two boxcar integrators (Stanford Research Systems, Model SR250) operating with delays of 300  $\mu\text{s}$  and 1.3 ms with respect to the supersonic pulse trigger. The gate width on both integrators was set at 150  $\mu\text{s}$ ;

a 100-point running average was sent to an analog processor (Stanford Research Systems, Model SR 235) where the signals were subtracted from each other before being digitized and sent to the computer. The entire system was controlled by an in-house Lab-view program.

The demodulated signal from the scan has a second derivative shape with respect to a traditional absorbance feature. The reason that  $2f$  detection is so useful for this type of spectroscopy is that it effects both high (ca. 1 ppm) absorption sensitivity and suppression of baseline due to systematic power variation of the source with a relatively simple and convenient configuration. In combination with a lockin at kilohertz frequencies drastic noise reduction further increases the sensitivity [20].

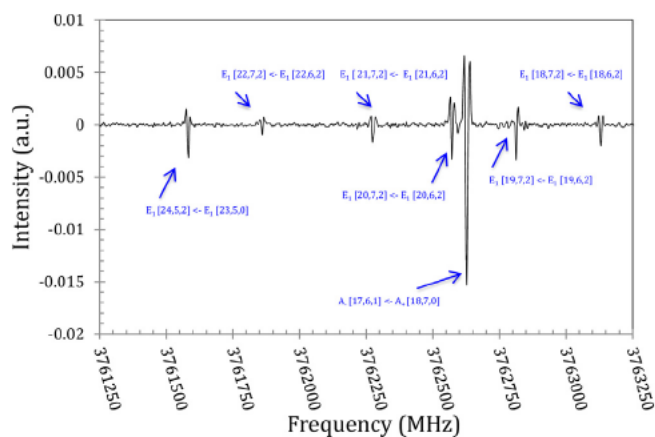
## 2.2. Ambient methanol measurements

Spectroscopic grade methanol (Sigma–Aldrich) vapor was introduced into the chamber at a pressure of ca. 400 mTorr and then the chamber was sealed. Laser scan conditions were as follows: voltage swept from 16.3 to 17.8 V in 1 mV steps, time between steps was 0.5 s, sine wave modulation at 50 kHz with 0.5 mV amplitude. The stressed photoconductor detector was biased at 40 mV via the preamplifier and the resulting signal was amplified  $10\times$ . The signal was detected by the lockin at 100 kHz with a time constant of 300 ms and the output was sent directly to the computer for analysis.



**Figure 2.** Diagram of the apparatus for Terahertz VRT spectroscopy of supersonic jets using the EASY-QCL system.





**Figure 3.** 2f absorption spectrum of methanol at a pressure of 400 mTorr. All transitions are assigned to the JPL methanol line catalog. The format for the assignments is (Symmetry of upper state)  $(J'',K',v'') \leftarrow (J'',K',v'')$ . FWHM linewidths range from 8 to 13 MHz. Calibration of the initial QCL voltage to the frequency domain was accomplished by a linear fit to the JPL methanol line catalog (a cubic fit was also performed but did not yield significantly different results).

Several pressures were tested in the range 100–2000 mTorr. The reported pressure was chosen empirically as a compromise between good signal to noise ratio and insuring that pressure broadening was not causing consecutive peaks to overlap.

### 2.3. Supersonic methanol/Ar jet measurements

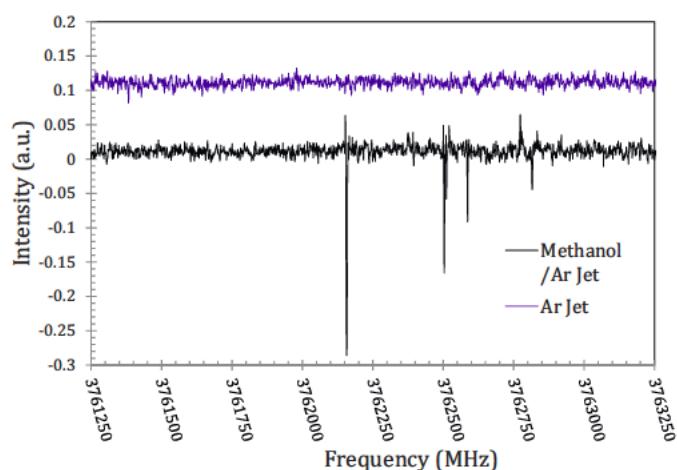
Planar supersonic beams of Ar and methanol/Ar were produced as follows. For the Ar jet, pure Ar gas was fed directly to the jet input at a backing pressure of 1–2 atm. The methanol/Ar jet was created by bubbling Ar gas through a flask containing spectroscopy grade methanol at a backing pressure of 1–2 atm. The jet operation has been described in detail elsewhere [21]. In brief, the gas is expanded through a  $4'' \times 0.005''$  slit nozzle pulsed at a rate of 40 Hz, as controlled by a pulse generator (Stanford Research Systems, Model DG535). The planar supersonic beam was overlapped with the laser beam at a distance of  $1''$  below the slit and parallel to the slit direction to maximize signal and minimize residual Doppler broadening; rotational temperature are expected to be  $\sim 4$  K in the jet [21]. Laser scan conditions were as follows: the laser DC voltage was swept from 16.3 to 17.8 V in 1 mV steps, time between steps was 1 s, modulation was at 50 kHz with an amplitude of 0.5 mV. The detector was biased with 40 mV supplied by the preamplifier and the signal was amplified  $10\times$ . The lockin demodulated the signal at 100 kHz with a time constant of 100  $\mu$ s. Observed peaks were optimized by fixing the laser frequency on the peak and adjusting the lockin phase until the peak completely disappeared, and then switching the phase by  $90^\circ$ .

## 3. Results

### 3.1. Ambient pressure methanol

A 2f absorption spectrum of a gas cell containing methanol at a pressure of approximately 400 mTorr was taken as an initial test of the setup. The spectrum is shown in Figure 3, the frequency of the laser was determined as described in the following section.

The spectrum shows well-defined absorptions of methanol in the roughly 2 GHz operating window of the specific QCL device. FWHM linewidths are measured to be 8–13 MHz, in reasonable agreement with the linewidths predicted by the methanol self-broadening coefficient of 30.5 MHz/Torr [11]. Doppler broadening



**Figure 4.** Comparison of 2f absorption spectra of Ar and methanol/Ar supersonic jets. Supersonic jet produced by bubbling Ar, at a pressure of 1–2 atm, through methanol into a chamber maintained at 70 mTorr by a roots blower through a  $4'' \times 0.005''$  slit nozzle at a pulse rate of 40 Hz. The 50 kHz FM modulated laser beam was passed once through the sample and collected by a stressed Ge:Ga photodetector. Detector output was demodulated, averaged, and background subtracted using a lockin and boxcar integrators. Significant peaks in the methanol spectrum do not belong to the methanol monomer transitions in the JPL catalog. Linewidths are between 2 and 3 MHz with the exception of the most intense line, which has a linewidth of 5.5 MHz, which could be explained by multiple transitions overlapping.

for the ambient methanol scans are expected to be negligible ( $<1$  MHz) compared to pressure broadening ( $\sim 10$  MHz).

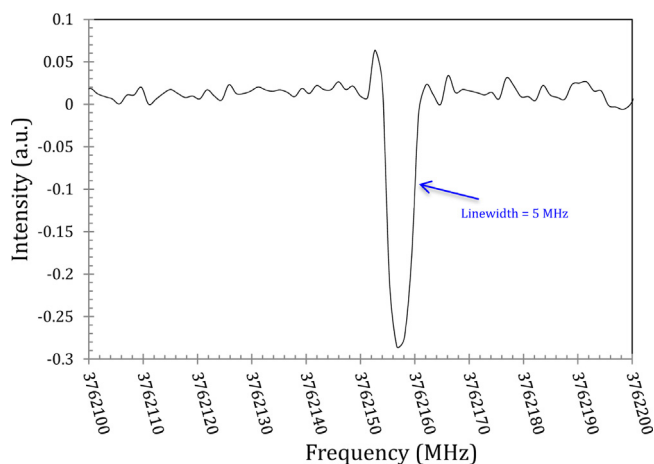
### 3.2. Calibration of QCL frequency

The observed peaks in the ambient methanol spectrum were used to calibrate the frequency tuning of the QCL by fitting to the JPL catalog frequencies of methanol lines, using the spectral assignment shown in Figure 3. This resulted in a linear fit with a start frequency of 3 761 245 MHz and a voltage tuning of 1321.4080 MHz/V. Other functions (e.g. cubic) were used to calibrate the data, but showed no significant improvement over the linear calibration. This result is encouraging as it demonstrates that the frequency tuning of the laser based on voltage alone for a single device is significant (a ca. 2 GHz total range) and quite linear over this range. Although the effect of operating temperature on the frequency tuning was not investigated here due to time constraints, the total (temperature and frequency) tuning for similar devices have been shown to be several times what we have measured [17]. The minimum estimate then for total frequency coverage provided by the 20 devices on the chip would be 40 GHz (electrical tuning only), but given the above, it is likely that the actual tuning of the QCL array is closer to 160 GHz, if thermal tuning were included. It should be noted that while this calibration procedure gives a relative constraint on the frequency of the laser, improvements must be made in order to achieve suitable frequency accuracy better than 1 MHz for high resolution spectroscopy applications.

### 3.3. VRT spectroscopy of supersonic expansions

Application of the QCL system to a supersonic expansion of methanol/Ar was accomplished and the results are presented in Figure 4. A scan of the same frequency region in an expansion of pure argon showed no spectra.

The spectrum was obtained from the same device used to capture the ambient methanol data and thus represents the same frequency window. When attempting to assign the measured



**Figure 5.** Expanded spectrum of the most intense methanol/Ar supersonic jet peak at 3762156.8 MHz. The peak shape is not a perfect 2nd derivative shape, but the laser may have been undermodulated, which could explain the irregularity.

transitions to the JPL catalog it was determined that the lines do not correspond to any known or predicted methanol monomer lines. From results obtained with the pure Ar expansion, it is clear the lines originate from a methanol-containing cluster, most likely  $\text{CH}_3\text{OH}-\text{Ar}$  or  $(\text{CH}_3\text{OH})_2$ . Definitive assignment of the cluster cannot be accomplished with the current limited frequency window. However, the spectrum clearly illustrates the exciting potential of the QCL device for VRT spectroscopy of supersonic expansions, which will soon permit access to a frequency domain that has never been explored previously by a high-resolution spectroscopy technique.

Without a spectral assignment, no explicit determination of the rotational temperature can be made, but we expect it to be similar (4 K) to that observed in previous experiments using this same supersonic jet system [21]. The FWHM linewidths of peaks were measured to be 2–3 MHz with the exception of the most intense line, which had a linewidth of 5.5 MHz, as shown in Figure 5.

This larger linewidth is most likely explained by the presence of two unresolved lines separated by a frequency smaller than the experimental resolution. The other linewidths are slightly larger than the expected 4 K Doppler broadening of ca. 1 MHz. An explanation for this is that the voltage steps of the scans, 1 mV/step or 1.321 MHz/step, contributed an instrumental broadening to each peak. This could clearly be eliminated by using smaller frequency steps; however doing so greatly increased the scan time of the experiment, which was problematic due to the length of the current laser loan period. However, the currently employed experimental parameters clearly effect high-resolution scans.

Based on the measured spectra, we are able to determine the minimum fractional absorption sensitivity of the QCL spectrometer, defined as

$$\frac{\Delta P}{P} = \frac{N}{S/\sqrt{B}}$$

where  $N$  is the rms noise with the laser on and  $S$  is the maximum laser signal before amplification by the system with no methanol present in the spectrometer. Both quantities are adjusted for system amplification, and amplitude modulation/lockin detection.  $B$  is the detection bandwidths for the scan. The values we obtained from experiment were as follows: 115 mV laser signal, the detection bandwidth was 2.5 Hz, and the rms noise of the laser on the detector was  $0.293 \mu\text{V}/\sqrt{\text{Hz}}$ . The fractional sensitivity determined in this way is  $4.03 \times 10^{-6}$ , which is comparable to the far infrared laser sideband system, previously utilized for this experiment [22,23]. This is very promising, considering that the previous

designs utilized some form of multipass optics in the vacuum chamber [21–23], whereas the current setup employs only a single pass. Additionally, the stressed Ge:Ga photoconductor used for this experiment was likely to have been saturated by the high power (>1 mW) provided by the QCL; thus, it is likely that incorporation of multipass optics into the system will produce considerably higher signal to noise ratios that our previous designs. More evidence for the presence of saturation is the fact that the ultimate sensitivity limit of the detector, which can be regarded as the quantum, or ‘shot noise’ limit, is given by:

$$Q_L = 2.8 \times 10^{-10} \left( \frac{\nu}{\eta P \tau M^2} \right)$$

Here  $\nu$  is the laser frequency (in  $\text{cm}^{-1}$ ),  $\eta$  is the detector quantum efficiency,  $P$  is the laser incident power,  $\tau$  is the integration time, and  $M$  is the modulation index ( $0 < M < 1$ ). Using typical values of 1 s for the integration time, 0.3 for  $M$ , 1 mW for  $P$ , and 0.1 for quantum efficiency we get a shot noise limited fractional absorption sensitivity of  $3.51 \times 10^{-8}$  for light at a wavelength of  $125.4 \text{ cm}^{-1}$ ; this is fully 2 orders of magnitude better than our measured value.

#### 4. Conclusions

We have described the first results reported from integrating a commercial Terahertz QCL system into a supersonic beam VRT spectroscopy apparatus. Moreover, this result is the first known example of a laser source access this frequency range for high-resolution spectroscopy experiments of supersonic expansions. Given that progress in the field of high-resolution Terahertz spectroscopy has stalled in the past years due to lack of available sources, this advance represents a promising means of accessing the important but totally unexplored frequency domain above 5 THz.

Comparing this system to our previously used laser sideband spectrometer, the sensitivity of this technique (ca. 1 ppm fractional absorption) is comparable without using any multipassing optics, which considerably simplifies the operation. A hundred-fold improvement is likely to be realized with incorporation of a multipass cell [21]. The measured continuous tuning range is also encouraging, as it can be regarded as only a fraction of the possible tuning range for a single device when temperature tuning is included. The biggest hurdle that needs to be overcome before the device can be effectively used for routine high resolution VRT spectroscopy is that of establishing a convenient means to accurately determine the laser frequency. Efforts are underway to phase lock the laser to high harmonics of a microwave source, which would provide the requisite frequency accuracy [24].

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