DOI:10.1177/00037028221111174

Journal Title
XX(X):1–9
©The Author(s) 2022
Reprints and permission:
sagepub.co.uk/journalsPermissions.nav
DOI: 10.1177/ToBeAssigned
www.sagepub.com/
SAGE

Accurately Measuring Molecular Rotational Spectra in Excited Vibrational Modes

Paul Chevalier[1], Marco Piccardo[1,2], Arman Amirzhan[1], Federico Capasso[1] and Henry O. Everitt[3,4]

Abstract

Although gas phase rotational spectroscopy is a mature field for which millions of rotational spectral lines have been measured in hundreds of molecules with sub-MHz accuracy, it remains a challenge to measure these rotational spectra in excited vibrational modes with the same accuracy. Recently it was demonstrated that virtually any rotational transition in excited vibrational modes of most molecules may be made to lase when pumped by a continuously tunable quantum cascade laser (QCL). Here we demonstrate how an infrared QCL may be used to enhance absorption strength or induce lasing of terahertz rotational transitions in highly excited vibrational modes in order to measure their frequencies more accurately. To illustrate the concepts, we used a tunable QCL to excite v_3 R-branch transitions in N_2O and either enhanced absorption or induced lasing on 20 v_3 rotational transitions, whose frequencies between 299-772 GHz were then measured using either heterodyne or modulation spectroscopy. The spectra were fitted to obtain the rotational constants B_3 and D_3, which reproduce the measured spectra to within the experimental uncertainty of $\pm$ 5 kHz. We then show how this technique may be generalized by estimating the threshold power to make any rotational transition lase in any N_2O vibrational mode.

Keywords

rotational spectroscopy, excited vibrational modes, quantum cascade lasers

Introduction

The venerable field of gas phase molecular rotational spectroscopy has for decades provided an unparalleled ability to identify and discriminate species, even for subtly different isomers, and reconstruct molecular structures and their dependence on rotational state[1,2]. However, the vast majority of these measurements have been performed in the ground vibrational mode of the molecule because the thermal population of excited vibrational modes drops exponentially with vibrational energy. Because rotational spectra in these excited vibrational modes are often profoundly altered by the associated vibrational motions and coupling among neighboring ro-vibrational energy levels, measuring these spectra is essential for reconstructing the complex rotational-vibrational motion of and intramolecular energy transfer pathways within these molecules.

Heating the gas produces little benefit for measuring these spectra, as the number of available rotational levels grows rapidly as $T^{3/2}$, non-selectively redistributing population among an increasing number of thermally accessible rotational states and vibrational modes. Consequently, clever strategies for circumventing this limitation have been developed, most notably through infrared difference frequency measurements or frequency combs[3–7] However, these techniques typically suffer from complexity or reduced precision (> 1 MHz) compared to that routinely achieved for rotational spectra in the ground vibrational mode (< 10 kHz).

The invention of the frequency-tunable quantum cascade lasers (QCLs) has created the opportunity for measuring and even pumping ro-vibrational transitions of highly excited vibrational modes[8,9]. In a recent modification of the original concept for optically pumped far infrared lasers (OPFIRs), we and others have demonstrated lasing of rotational states in excited vibrational levels pumped by QCLs precisely tuned to a specific ro-vibrational transition[10–15]. In our previous work with nitrous oxide (N_2O), we were able to pump the v_3 (00^01) R-branch transitions from J = 9 to 31 with a tunable QCL spanning the range 2231-2247 cm^{-1}, producing lasing on all 29 v_3 rotational transitions between 251 and 955 GHz[13]. This QCL-pumped molecular laser (QPML) is a universal concept: virtually any rotational transition in an excited vibrational mode of virtually any molecule with a permanent electric dipole moment may be made to lase.

Building on this concept, we report here a new technique for accurately measuring the rotational spectra of vibrationally excited molecules. Instead of traditional techniques that depend on measuring the weak ambient absorption spectra, we introduce two complementary techniques to enhance the strength of that spectra. In the first “lasing technique,” specific rotational transitions of those

---

[1] Harvard John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, MA, 02138, USA
[2] Center for Nano Science and Technology, Fondazione Istituto Italiano di Tecnologia, Milan, Italy
[3] DEVCOM Army Research Laboratory, Houston, TX 77005, USA
[4] Department of Physics, Duke University, Durham, NC 27708, USA

Corresponding author:
Henry O. Everitt
Email: everitt@phy.duke.edu

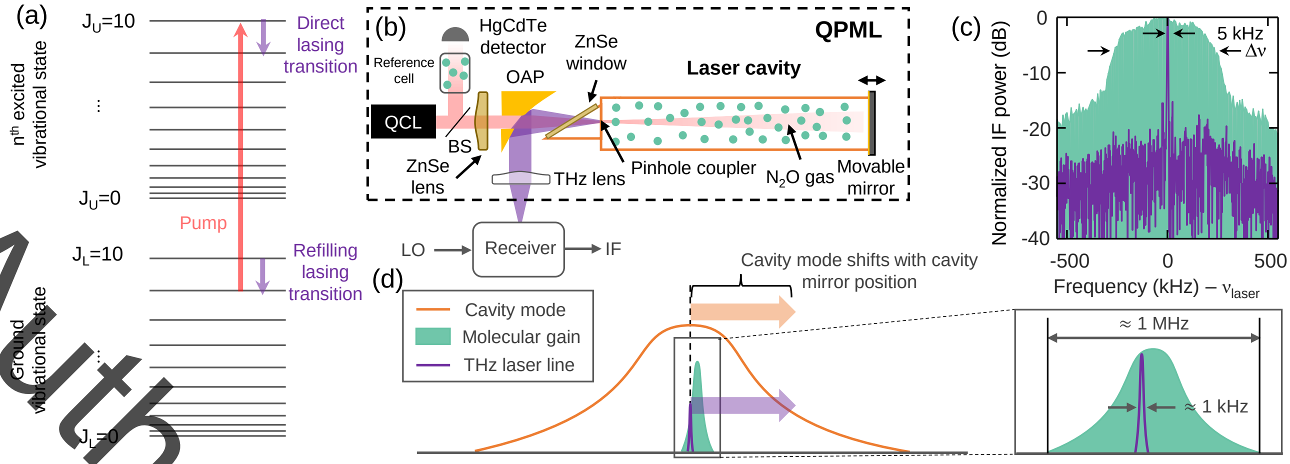

Figure 1. (a) A Quantum cascade laser Pumped Molecular Laser (QPML) consists of a widely tunable QCL pumping a specific ro-vibrational transition of a gas to induce rotational population inversions in the ground (refilling lasing transition) and excited (direct lasing transition) vibrational modes. (b) Schematic diagram of the "lasing technique" using a QPML. It consists of a pump laser (QCL), a molecular laser cavity, collection optics: off-axis parabolic mirror (OAP) and Teflon lens, and a heterodyne receiver. Part of the beam is sent to a reference gas cell containing 50 mTorr of N_2O using a beam splitter (BS), and the transmitted light is monitored with an HgCdTe detector. (c) Sample spectral measurement of the intermediate frequency (IF) output of the receiver (blue) over its measured tuning range $\Delta\nu$ (gray) for the transition at 373.6 GHz (J = 15 → 14). (d) Schematic of the laser line within the molecular laser gain bandwidth, and the cavity mode bandwidth, showing that the spectral accuracy of the technique is limited by cavity frequency pulling of the laser frequency.

spectra are made to lase by QCL pumping of N_2O in a laser cavity, and the laser frequency is measured using heterodyne spectroscopy. Although these lasing spectra are strong and easily measured, the frequency accuracy is only on the order of ±100 kHz because of the tuning range of the QPML and the uncertainty of where line center is located.

To improve the accuracy of this method, a second "enhancement technique" avoids lasing by replacing the laser cavity with a long, mirror-less gas cell that is pumped with the same QCL to enhance the absorption or induce amplification of N_2O rotational spectra. Using traditional modulation spectroscopy to measure these stronger line shapes, this technique was shown to improve the accuracy significantly, on the order of ±5 kHz.

We demonstrated both concepts by first measuring the laser frequency for 20 rotational transitions (J_L = 11 - 30) in the v_3 (00^01) vibrational band of N_2O, then measuring the frequency of 15 QCL-enhanced rotational transitions using the second technique. The measured frequencies were used to deduce the rotational constants B_3 and D_3. After confirming that these measurements are consistent with, if not superior to, previous measurements, we discuss the universality of this technique. The lessons learned from N_2O indicate that as long as a sufficiently tunable and powerful QCL is available, the frequency of any rotational transition in any excited vibrational mode accessible by a QCL may be accurately measured.

Methods

Nitrous oxide (N_2O), a well-known anesthetic, is a linear tri-atomic molecule often used as a reference gas for rotational spectroscopy because of its simple spectra, strong lines, and non-toxicity. Its rotational spectrum in the ground vibrational state was among the first measured following the advent of microwave spectroscopy[16]. However, the rotational spectra of only a few of its excited vibrational modes have been measured accurately (with uncertainty < 1 MHz)[4,17–20]. For example, only 4 rotational transition frequencies have been directly measured in the v_3 mode at $\nu_3 = 2224$ cm^{-1} (recently renamed as the v_1 mode by some authors[20]), whose room temperature population is down by a factor of 2×10^{-5} ($h\nu_3 \approx 10.7$ kT) from the corresponding ground state populations[19,20].

Both techniques introduced here require a tunable QCL pump to span a given vibrational mode. The "lasing" technique requires (1) a QPML in which the QCL pump creates a rotational population inversion within a laser cavity, (2) a tunable high resolution terahertz source as a local oscillator (LO) near the frequency of the QPML emission, and (3) a mixer to generate an intermediate frequency (IF) from the QPML emission and the LO. The energy levels and the lasing transitions of a QPML are illustrated in Fig. 1a for the linear molecule N_2O. Frequencies were measured by inducing the rotational transition to lase, then beating the laser output against the LO (spanning either 350-500 or 500-750 GHz) in the sub-harmonic mixer of a frequency-stabilized heterodyne receiver so that the IF could be measured with a spectrum analyzer (see Fig. 1b for the experimental schematic). We measured the IF twice, once for the LO red-detuned approximately 1 GHz from the laser line and once with it blue-detuned a similar amount, each measured with a precision of ~25 kHz (Fig. 1c). The frequency we report in Table 1 was taken from the average of these two measured IFs.

For these measurements, we used the same QPML cavity used in[13]: a cylindrical copper tube of 5 mm diameter and 15 cm length, into which was inserted an adjustable copper plunger to act as a highly reflecting back mirror to tune cavity length into resonance. The front mirror contained a 1

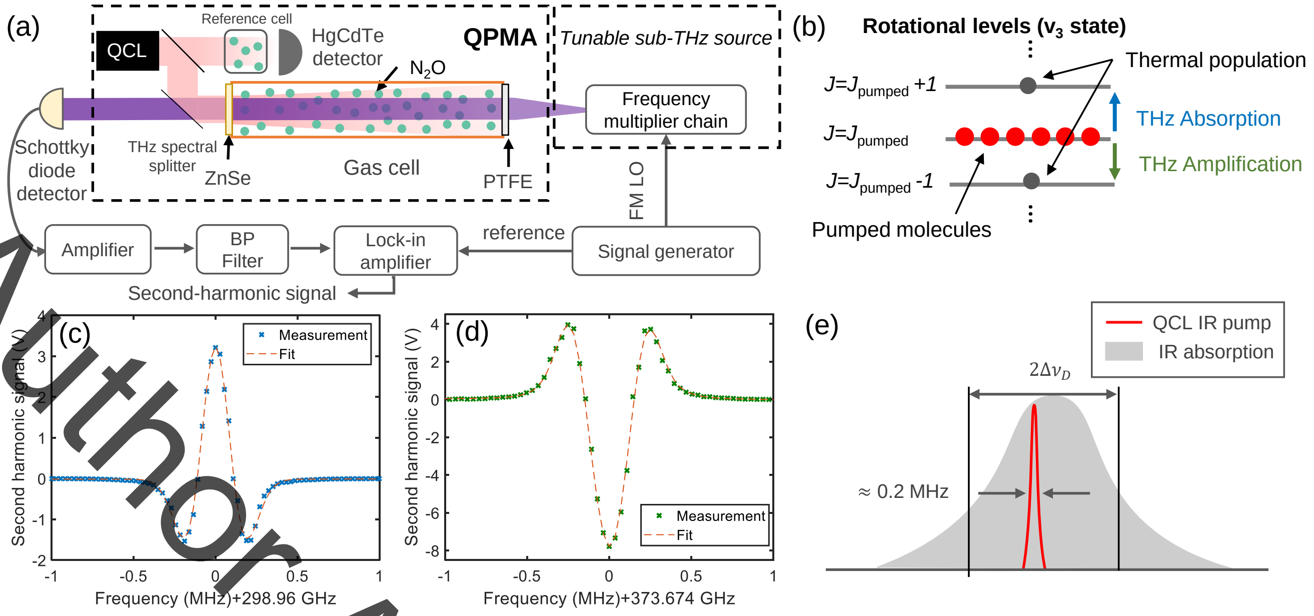

Figure 2. (a) Schematic diagram of the "enhancement technique" using Quantum cascade laser Pumped Molecular Amplifier, (QPMA). It consists of a pump laser (QCL), an absorption cell, and a frequency multiplier-based THz source driven by a frequency modulated local oscillator that uses modulation spectroscopy by demodulating the amplified THz signal with a lock-in amplifier at twice the modulation frequency. Part of the QCL beam is directed to a reference gas cell containing 50 mTorr of N_2O using a beam splitter (BS) for which the transmission is monitored using an HgCdTe photodetector. (b) Schematic energy level diagram showing the pumped rotational energy level and two comparatively empty adjacent levels, yielding an enhanced absorption line and an amplification line. Typical modulation spectra plotted as a function of the sub-THz frequency for transitions measured with (c) enhanced absorption (J = 11 → 12) or (d) amplification (J = 14 → 15). **E** Schematic of the QCL IR pump frequency lying within the IR absorption bandwidth. The uncertainty of the QCL IR pump frequency within the IR absorption bandwidth ultimately limits the resolution of this technique.

mm-diameter pinhole which acted as an input/output coupler through which the QCL pump was focused after passing through a ZnSe window mounted at Brewster's angle to maximize throughput. The terahertz beam diverging through the pinhole was captured by an off-axis parabolic mirror and focused into a Virginia Diodes, Inc. zero-bias Schottky diode detector. To ensure the proper ro-vibrational transition is being pumped by the QCL, it is necessary to have some way of confirming the QCL frequency, either by using an infrared spectrometer or a well calibrated QCL source. A frequency stabilized QCL is desirable to minimize laser drift during the spectroscopic measurement[9].

Detection of the IF by a microwave spectrum analyzer allows one to monitor how the QPML frequency depends on QCL frequency and cavity length. For these measurements, the QCL was tuned to coincide with the peak absorption of the ro-vibrational transition, monitored by an external reference cell as shown in Fig. 1b. By adjusting the cavity length, the laser frequency was then tuned toward the center frequency of the rotational transition. For N_2O transitions of frequency ν (THz), the lines were Doppler-broadened at low pressures with a full width at half maximum (FWHM) of $2\Delta\nu_D = 1870\,\nu$ (kHz). Most measurements were performed at higher pressures, between 40-60 mTorr, corresponding to a pressure broadened gain profile of 250-400 kHz FWHM, assuming an N_2O pressure broadening parameter of 6.3 MHz/Torr FWHM[21].

The precision of the measurements was strongly affected by cavity frequency pulling in the laser cavity (Fig. 1c), where the wide cavity mode ($\Delta\nu_{cavity} \approx 25$ MHz) dictates the laser emission frequency, as represented in Fig. 1d. We were able to tune the laser frequency over the width of the gain profile $\Delta\nu$ (~500 kHz) by adjusting the laser cavity length, so we measured the frequency as close as possible to the center of this tuning range where maximal power was produced (Fig. 1c). The frequency was measured with an accuracy limited by the laser bandwidth measured in the spectrum analyzer (<10 kHz), but we conservatively claim a precision of ±100 kHz to account for the uncertainty about whether our measurement occurred at line center. Note that this technique required no modulation of the LO, no large reference cavity, and no pulse-induced free induction decay, thus simplifying this technique relative to more traditional modulation spectroscopic methods[1,22,23].

The "enhancement" technique was used to improve the accuracy of our measurements. The QPML mirrors were removed and the laser was effectively turned into a single-pass QCL-pumped molecular amplifier (QPMA). As shown in the schematic in Fig. 2a, light from a QCL was coupled into an absorption cell (length 1 m, diameter 10 mm) through an anti-reflection coated zinc selenide window. Radiation from a modular and tunable sub-THz source using a chain of frequency multipliers (Virginia Diodes, Inc.) was coupled through a polytetrafluorethylene (PTFE) window on the other side and measured using the same Schottky diode detectors as for the laser method.

Pumping the gas with a QCL tuned to an IR absorption frequency (either a P, Q, or R branch transition) with final quantum number J_{Pumped} enhances two transitions between adjacent rotational levels (see Fig. 2b): a lower frequency "amplifying" transition (between J_{Pumped} and J_{Pumped} - 1), and a higher frequency "enhanced" absorbing transition (between J_{Pumped} and J_{Pumped} + 1). We have additionally observed weakly enhanced absorption and amplification signals from rotational transitions respectively farther above and below the pumped transitions, obtained by a mechanism similar to the recently observed cascaded lasing in the ammonia QPML[15].

Once the QCL is tuned into coincidence, both enhanced rotational transitions are strong enough to be measured by scanning the sub-THz source across their line shape. In order to measure each transition frequency with the highest accuracy, we used modulation spectroscopy in which the probe was modulated at frequency f and detected with a lock-in amplifier at frequency $2f$[24]. Specifically, the LO used a 10 MHz - 20 GHz microwave synthesizer (Wiltron 68347B) locked to a 10 MHz GPS reference (Stanford Research FS752) and was modulated with a triangular wave at a rate of $f = 20$ kHz with a depth of 5 kHz. Depending on the measured frequency and required multiplier chain (with multiplication factor 18, 27, 36, or 54 depending on the targeted frequency range), the modulation depth in the THz domain was between 100 and 250 kHz, comparable to the HWHM of the measured transition's Doppler width.

The detected signal was amplified and band-pass filtered between 30 kHz and 100 kHz (Stanford Research SR560), then demodulated by a lock-in amplifier (Signal Recovery 7265) at twice the reference frequency (40 kHz). The lock-in signal between -10V and +10V was acquired by a 12 bit data acquisition card (National Instruments DAQ) as a function of the LO frequency, which was stepped with a resolution of 1 kHz. Due to the weak signal strength from our multiplier-based THz source above 600 GHz, we could only perform measurements at lower frequencies.

Typical modulated enhanced absorption and amplification spectra are shown in Figs. 2c and 2d as a function of the sub-THz frequency, along with a fitted profile assuming a Voigt line-shape of the transition similar to[25]. Unlike the lasing technique, this method is immune to cavity frequency pulling effects, but it is not immune to pump pulling effects, as highlighted in Fig. 2e and discussed in the next section. The recovered frequencies for both the lasing method and the enhancement method are given in Table 1.

Discussion

Accuracy

To ascertain the precision of our lasing technique, we measured several "refilling" laser transitions connected to the rotational state in the ground vibrational level (see Fig. 1a) from which the molecules were pumped[13]. We then compared these measured frequencies (J_U = 12-18, between 301 – 452 GHz) with those available in the JPL molecular spectroscopy database (calculated using B_0 = 12561.6343439 MHz, D_0 = 5.279548 kHz)[26]. The root mean square (rms) for these eight measured transitions, calculated as the square root of the mean of the squared observed – calculated values, was 57 kHz, consistent with the precision of our v_0 and v_3 measurements. Note that we used the traditional definition for frequency $\nu = 2B_\nu(J_L+1) - 4D_\nu(J_L+1)^3$, with an implicit negative sign in the equation before D_ν, unlike SPFIT[27].

The laser measurement accuracy for rotational transitions in excited vibrational levels can be further improved by reducing the pump laser power closer to the lasing threshold. As shown in Fig. 3a, this will reduce the width of the gain profile and tuning range of the QPML so that power is only emitted near the center frequency. The figure shows how the measured QPML tuning range decreased with decreasing pump power. At a pump power of 140 mW, about twice the lasing threshold, the tuning range was reduced to about ±10 kHz. However, all measurements reported here used full QCL power in order to maximize signal strength and stability.

To ascertain the precision of our enhancement technique, we measured the frequencies of a few rotational absorption lines in the ground vibrational level in the absence of a laser pump and confirmed that the recovered values matched the known values to within the resolution of our modulation technique. Note that the enhancement technique would only weaken these ground state lines, but that reduction effectively tags those lines by connecting them to the enhanced line strengths in the excited vibrational level. This selection rule-determined tagging may prove helpful in assigning challenging excited state spectra of more complex molecules like methanol[28].

A striking difference in linewidths was observed between the enhancement spectra of excited state rotational transitions and their ground state counterparts. In Fig. 3b are plotted the normalized modulation spectra for the ground state (v_0) J = 7 → 8 transition near 200 GHz and the corresponding v_3 enhanced line near 199 GHz. These curves were obtained for the same modulation depth of the sub-THz signal (90 kHz) and same N_2O pressure (10mTorr). Notice, however, that the v_3 line appears significantly narrower than the v_0 line. The Voigt linewidth (FWHM) of the v_3 transition was extracted from the fitted modulation spectrum and plotted as a function of the gas pressure in Fig. 3c as blue crosses. On the same figure, the Voigt linewidths of the v_0 line is plotted with the red circles. The yellow line captures the predicted pressure-dependent Voigt linewidths at 200 GHz (with a ∼ 376 kHz Doppler broadened FWHM near 0 mTorr) for the N_2O pressure broadening coefficient of 6.3 MHz/Torr. The measured v_0 linewidths match the expected behavior in both the lower pressure, Doppler-broadened and higher pressure, pressure-broadened regimes.

Why is the v_3 line narrower? Consider that the IR ro-vibrational absorption line pumped by a QCL has much larger Dopper-broadened linewidth (∼ 63 MHz HWHM) than the QCL linewidth (< 1 MHz), as illustrated in Fig. 2e. The QCL therefore pumps a homogeneously pressure-broadened velocity subclass of that larger, inhomogeneously Doppler-broadened IR transition. If properly tuned to line center, the QCL pumps the velocity subclass centered at zero longitudinal velocity, so the molecules pumped are moving in the radial direction. Because the pressure-broadened linewidth is narrower than the Doppler widths for both the IR and terahertz transitions at the low pressures used here, the narrower linewidth for the v_3 transitions corresponds to this pumped velocity subclass. Notice that the linewidth

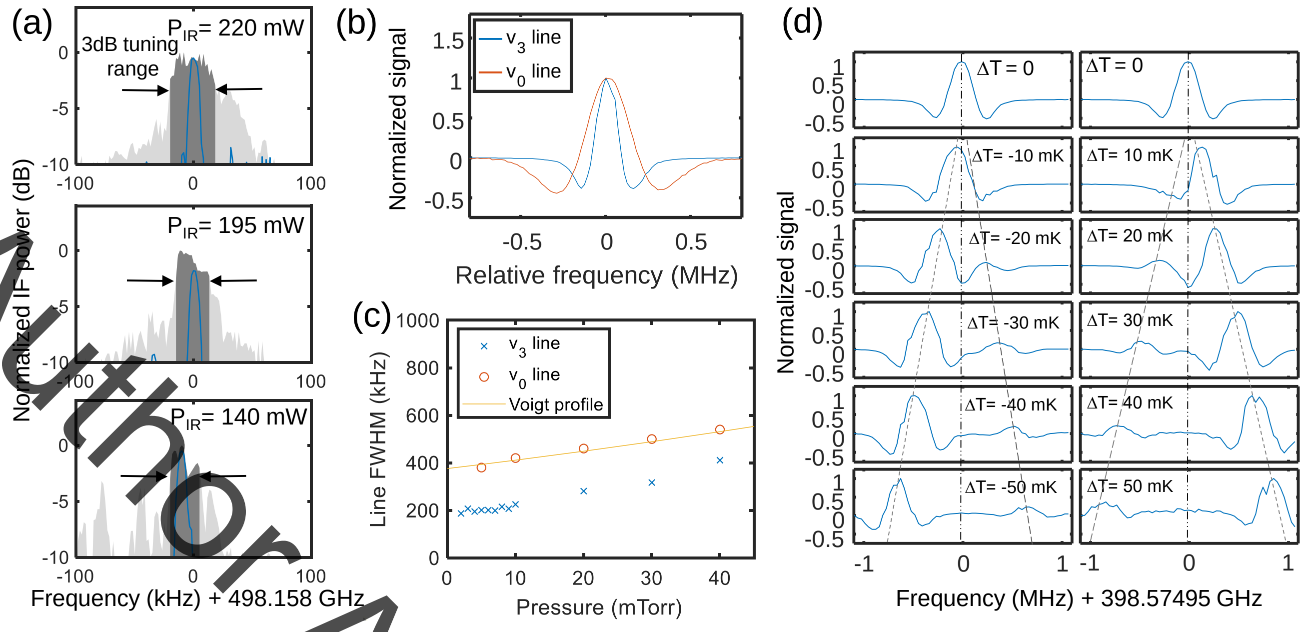

Figure 3. (a) The tuning range of the N_2O QPML around 498.158 GHz (J = 19 → 20) is plotted as a function of the relative laser frequency by tuning the cavity length. The gray areas represent the envelope of all the emitted lineshapes. The dark gray areas correspond to the 3 dB tuning range of the QPML. (b) The normalized modulation spectra (90 kHz modulation depth) of the J = 7 → 8 lines in v_0 (near 200 GHz) and v_3 (enhanced absorption near 199 GHz) measured at 10 mTorr. (c) The full-width half-maximum of these same v_3 and v_0 lines, plotted as a function of the gas pressure. The yellow line corresponds to the predicted width of the Voigt lineshape for these lines. (d) The modulation spectra for the J = 15 → 16 transition is plotted for different pump detunings (QCL temperature offset ΔT). The vertical line reflects the average frequency of the two observed lines.

plateaus near 200 kHz FWHM at the lowest pressures. Since the width of the velocity subclass should continue narrowing with decreasing pressure, this plateau corresponds to the linewidth of the QCL itself.

Because the ro-vibrational transition is inhomogeneously broadened, a small detuning of the QCL emission frequency from the peak IR absorption will shift the pumped population towards non-zero velocity subclasses, thereby shifting the rotational transition frequency measured by modulation spectroscopy. However, if this detuning, produced by small changes in QCL operating temperature ΔT, is greater than the pressure broadened linewidth of the pumped velocity subclass, two rotational transition peaks will be observed (see Fig. 3d): one pumped by the forward propagating IR beam, and one pumped by the weakly reflected beam within the absorption cell. Although observation of two peaks is a clear sign that the QCL detuning is too large, the average of these two frequencies must equal the actual center frequency of the rotational transition to a high degree of accuracy. Indeed, uncertainty about effect of QCL detuning can be removed in this way. Whether the QCL is perfectly tuned or somewhat detuned, the enhancement technique presented here provides a measure of rotational transition frequencies with an accuracy better than ±5 kHz. The only challenging technical requirement is the availability of a tunable terahertz source referenced to a frequency standard, which may limit this technique to frequencies below 1 THz for the near future.

Using the enhancement technique, all lines were measured twice, once through enhanced absorption and once through amplification, both of which are reported in Table 1. The difference between the two frequencies was always less than 11 kHz, usually less than 5 kHz. Through a nonlinear least squares analysis of these averaged enhancement spectra, we obtained values for the v_3 rotational constants B_3 = 12458.161(3) MHz, D_3 = 5.261(2) kHz and found they accurately predict these frequencies with a commensurate rms of 3.5 kHz (see Table 1). Refitting the spectra with three rotational constants only slightly improved the rms (3.4 kHz), indicating experimental uncertainty rather than imperfect fitting limits the accuracy.

For comparison, Toth used a high resolution Fourier transform spectrometer with frequency accuracy of $2 - 6 \times 10^{-5}$ cm^{-1} (0.6-1.8 MHz) to obtain three rotational constants (B_3, D_3, H_3) that reproduced our measurements with a slightly larger rms (9 kHz)[29]. Ting et al. used a tunable IR probe and high precision rotational spectroscopy to measure the rotational spectra and ascertain rotational constants for the v_3 band with 30 kHz accuracy[20]. Although they could only directly measure four pure rotation transitions below 1 THz, their five parameter fit reproduced our measured frequencies with an rms (4.2 kHz) comparable to the one we obtained using just two parameters. The JPL molecular spectroscopy database also lists predictions for these lines, which produce a rms comparable to the measurement uncertainty (16 kHz)[26]. Clearly our technique produces measurements with sufficient accuracy to provide trustworthy, even superior, rotational constants.

The frequencies measured using the lasing method, when compared to the calculated frequencies using the constants fitted for the enhancement data, yielded a rms of 91 kHz, commensurate with the measurement uncertainty. However, we discovered a non-zero average residual between the calculated frequency and the measured frequency, revealing a systematic error of about -20 kHz. This systematic error

Table 1. Measured rotational spectra of the N_2O v$_3$ vibrational mode for $J_L \to J_U$ transitions. The calculated values used the rotational constants (B_3 = 12458.161(3) MHz, D_3 = 5.261(2) kHz) obtained from the averaged enhanced transition frequencies.

J_L	J_U	Observed (lasing) (MHz)	Observed (absorption) (MHz)	Observed (amplification) (MHz)	Average observed (MHz)	Calculated (MHz)	Enhanced o - c (kHz)	Lasing o - c (kHz)
7	8	–	199319.810	199319.803	199319.807	199319.806	0.3	–
8	9	–	224231.567	224231.559	224231.563	224231.562	1.0	–
9	10	–	249142.186	249142.182	249142.184	249142.182	2.3	–
10	11	–	274051.539	274051.545	274051.542	274051.539	3.4	–
11	12	298959.37	298959.504	298959.512	298959.508	298959.507	1.3	-137
12	13	323865.95	323865.957	323865.968	323865.962	323865.959	3.0	-9
13	14	348770.63	348770.761	348770.766	348770.764	348770.770	-6.8	-140
14	15	373673.77	373673.810	373673.811	373673.810	373673.814	-3.3	-44
15	16	398574.95	398574.961	398574.959	398574.960	398574.963	-2.9	-13
16	17	423474.10	423474.097	423474.096	423474.097	423474.092	4.5	8
17	18	448371.04	448371.069	448371.068	448371.069	448371.075	-6	-35
18	19	473265.60	473265.790	473265.787	473265.789	473265.784	4.3	-184
19	20	498158.03	–	–	–	498158.095	–	-65
20	21	523047.81	–	–	–	523047.880	–	-70
21	22	547934.92	547935.011	547935.011	547935.011	547935.013	-2.7	-93
22	23	572819.43	572819.377	572819.366	572819.372	572819.369	2.6	61
23	24	597700.70	597700.820	597700.821	597700.820	597700.820	-1.6	-120
24	25	622579.31	–	–	–	622579.241	–	69
25	26	647454.63	–	–	–	647454.506	–	124
26	27	672326.35	–	–	–	672326.487	–	-137
27	28	697195.16	–	–	–	697195.059	–	101
28	29	722060.03	–	–	–	722060.095	–	-75
29	30	746921.24	–	–	–	746921.470	–	-230
30	31	771779.17	–	–	–	771779.056	–	104

occurred because the LO was not stabilized to an external reference during those measurements. Later measurements showed that the frequency error of the LO was on the order of -1.5 kHz at the typically used frequencies (9-13 GHz). Although the frequencies reported in Table 1 retain this systematic error, by taking this error into account and estimating corrected frequencies, the systematic error is virtually eliminated and a reduced rms of 77 kHz is obtained.

Lasing Threshold

To explore the universality of the lasing technique, consider its applicability to the other vibrational modes of N_2O. A rotational transition frequency in one of these modes may be measured if the QCL power is sufficient to make the gas lase on the pumped transition. In Refs. 13 and 30, an expression was derived for the threshold power P_{th} required for this to happen. Under the assumption of low pressure operation ($<$ 20 mTorr) in which ballistic molecular wall collisions dominate all other relaxation mechanisms, lasing may occur and the rotational transition frequency may be measured if the QCL power exceeds

$$P_{\text{th}} = \frac{h^2}{4\pi}\frac{\nu_{IR}}{\beta}\alpha_{cell}R_{cell}L\frac{u^2}{|\langle f|\mu|i\rangle|^2}, \qquad (1)$$

where ν_{IR} is the frequency of the pumped transition, α_{cell}, R_{cell}, and L are the loss (0.3 m^{-1}), radius (0.25 cm), and length (15 cm) of the QPML cavity, u is the absolute molecular velocity (379 m/s at 300 K for N_2O), and $|\langle f|\mu|i\rangle|^2 = \mu_0^2(J_L+1)/(2J_L+1)$ is the transition dipole matrix element for the N_2O lasing transition (μ_0 = 0.161 D for N_2O). The cavity loss used here corresponds to the estimated total losses of our laser cavity[13], whereas the calculated Ohmic losses give α_{cell} = 0.06 m^{-1}. Our lossier cavity raised the threshold by a commensurate amount.

The term

$$\beta = [1-\exp(-\alpha_0 L)]\left\{\frac{1+R_b e^{-\alpha_0 L}}{1-R_b R_f e^{-2\alpha_0 L}}\right\} \qquad (2)$$

represents the fraction of QCL power absorbed by the gas, where the term in large brackets estimates the number of round trips χ for the IR beam within the cavity, with back and front mirror reflectivities R_b (0.95) and R_f (0.912), respectively. β reduces toward $\approx \alpha_0 L\chi$ for weakly absorbing lines and ≈ 1 for strongly absorbing lines, where the infrared absorption coefficient α_0 is obtained from the HITRAN database[21].

Only at very low pressures when ballistic wall collisions dominate rotational relaxation does P_{th} decrease with increasing pressure (through the α_0 term). For higher pressures where dipole-dipole collisions dominate, a slightly modified version of Eq. 1 reveals that P_{th} grows quadratically with pressure[30]. From this, a molecule-dependent pressure for minimizing P_{th} may be found for each transition, which for N_2O generally occurs below 20 mTorr. The higher pressure regime is less desirable for spectroscopy because pressure broadening increases the linewidth, laser tuning range, and thus the uncertainty of the rotational transition's center frequency. Nevertheless, the measurements reported above were made in this higher pressure regime because the gain also increases with pressure, so that's where the peak QPML power occurred.

As noted above, operating with QCL power just above P_{th} yields the most accurate measure of the transition frequency for the laser technique. Using the cavity parameters provided earlier, Figure 4a plots P_{th} as a function of ν_{IR} at 20

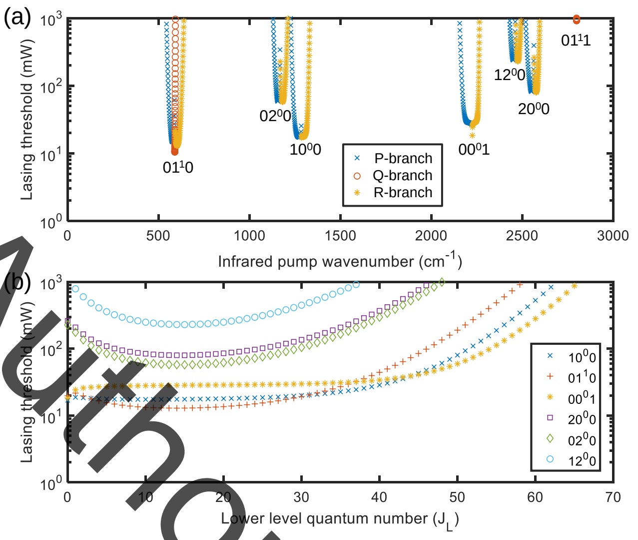

Figure 4. (a) Predicted P_{th} for every rotational transition in every N_2O vibrational mode below 3000 cm^{-1} whose P_{th} is less than 1 W at 20 mTorr. Blue, red, and yellow points represent rotational transitions pumped by P-, Q-, and R-branch transitions, respectively. (b) R-branch data from (a), labeled by vibrational mode, plotted as a function of J_L instead of ν_{IR}.

mTorr for all rotational transitions in the 15 N_2O vibrational modes available in the HITRAN database below 3000 cm^{-1}, excluding rotational transitions in the ground vibrational level v_0 and all hot bands originating above v_0. Because of the inverse dependence of P_{th} on α_0 and the enormous variation of α_0 values from mode to mode (almost ten orders of magnitude), the transitions show a wide variety of threshold powers, and only those with $P_{\mathrm{th}} < 1$ W are plotted here. Hundreds of rotational transition frequencies may be made to lase and therefore measured using the P, Q (for some v_2 modes), or R-branch pumped transition of choice, many of which have never been measured before.

The vibrational modes most amenable to this technique are the three principal modes of the molecule: $v_1 = 10^00$, $v_2 = 01^10$, and $v_3 = 00^01$ (recently relabeled by some[20]). All three have many rotational transitions with P_{th} below 100 mW, the minimum power available from currently available QCLs. With more powerful QCLs, a number of rotational transition frequencies may also be measured in the 02^00 and 20^00 overtone modes and the 12^00 and 01^11 combination modes. Notice that P_{th} is low even for the 01^10 bending mode, in spite of the effects of l-doubling and Fermi resonances which increase the number of rotational states, decrease α_0, and reduce the transition matrix element[18,19,29]. The other vibrational modes below 3000 cm^{-1} had very high values of P_{th}, including 02^20 ($P_{\mathrm{th}} > 11.7$ W), 03^10 (> 15.5 W), 11^10 (> 1.5 W), 04^00 (> 2.1 W), 04^20 (> 191 W), and 12^20 (> 74 W), all of which include bending modes as overtones or combinations. Measuring these modes with the lasing technique is not yet feasible with commercially available QCLs, but the enhancement technique will still work for them.

Figure 4b replots these same P_{th} data as a function of J_L rather than by ν_{IR}. Because of the multiple passes of the QCL pump beam within the QPML cavity, $\beta \approx 1$ for the three fundamental modes, so P_{th} is relatively insensitive to α_0 or J_L. Consequently, a large number of rotational transitions may be made to lase and their frequencies measured in our lossy cavity. Our ability to measure them is limited only by the availability of a heterodyne receiver at those frequencies. For the higher order vibrational modes, the rotational transitions most likely to lase and be measured are those associated with the largest values of α_0. Because there is greater variation of P_{th} with J_L, a more limited range of rotational transitions may be measured in them.

Interestingly, for transitions with large α_0 so that $\beta \approx 1$, equation (1) shows the lasing technique favors small cavities. Since P_{th} depends linearly on L, increasing the cell length to the more traditional $L = 100$ cm raises P_{th} a commensurate amount. Likewise, P_{th} depends linearly on cell diameter in this low pressure regime, so a smaller diameter cavity is favored over the more common $R_{\mathrm{cell}} = 1$ cm traditionally used for absorption spectroscopy. Ultimately, QCL power, as much as tunability, determines the number of transitions for which the lasing technique may work. By contrast, the enhancement technique is more amenable to QCL-pumping because the amplifying and absorbing transitions are only being strengthened, not made to lase.

Conclusions

We introduce techniques to measure the frequencies of rotational transitions in excited vibrational modes by using a QCL to pump the associated ro-vibrational transitions. The concepts of inducing lasing or enhancing rotational transition strength are universal, spanning all QCL-accessible transitions of all polar gas-phase molecules. If sufficient frequency tuning of the QCL is available, the entire rotational spectrum of any excited vibrational mode may be enhanced, and if sufficient QCL power is also available, these lines may be made to lase.

In order to demonstrate the lasing concept, we have induced lasing of rotational transitions in the v_3 vibrational mode of N_2O and measured their frequencies. By making those rotational transitions emit rather than absorb radiation, the lasing technique actually benefits from the sparsity of the population in such energetic modes at low pressures by minimizing the population that pumped molecules must overcome to achieve threshold. Thus, the primary hindrance to creating emission is producing sufficient gain to overcome cavity losses, not collisional quenching of the inversion. The compact cavity, whose volume is ~100 times smaller than most traditional absorption cells, requires much less gas to perform this measurement, an attractive feature when considering measurements of rare isotopes or expensive species. Frequency accuracy better than ±100 kHz was determined by the width of the gain profile of the QPML rotational inversion and cavity frequency pulling, but even greater precision could have been obtained at lower pump powers and lower pressures where P_{th} is minimized.

We also demonstrated an enhancement technique, which combines the benefits of QCL pumping of narrow velocity subclasses and modulation spectroscopy to measure center frequencies more accurately. This technique is not limited by the ability to tune the QCL frequency to coincide precisely with the corresponding infrared ro-vibrational transition, since detuned QCLs pump conjugate velocity subclasses whose frequencies may be separately measured and averaged. Accuracies better than ±5 kHz were demonstrated here, and even greater accuracies are possible with frequency stabilized QCLs.

With these techniques, a wealth of rotational spectra in excited vibrational modes of most polar molecules can now be easily measured, affording a tremendous opportunity to analyze anharmonicities and ro-vibrational and/or torsional couplings of rotational transitions in increasingly complex and energetic vibrational modes. It is well known that the number and complexity of vibrational modes increases with increasing frequency for every molecule, and commercial QCLs are already available to span the salient frequency range between 800-3300 cm^{-1} (3-13 μm) where these increasingly complex vibrational modes occur.

Acknowledgements

The authors thank Fan Wang for his early help with initial fits of the lasing spectra, Ivan Medvedev for suggestions regarding the modulation spectroscopy setup, and Minghe Lou for providing the code used to fit the modulated spectra.

Declaration of conflicting interests

The authors declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

Funding

This work was sponsored by the Army Research Office (W911NF-19-2-0168, W911NF-20-1-0157), by the Army DEVCOM Aviation & Missile Center and Army Research Laboratory, and the National Science Foundation (ECCS-1614631).

References

1. Townes CH and Schawlow AL. *Microwave spectroscopy*. Dover Publications, Inc., 1995.
2. Gordy W and Cook RL. *Microwave molecular spectra*. Wiley New York, 1984.
3. Liao CC, Lien YH, Wu KY et al. Widely tunable difference frequency generation source for high-precision mid-infrared spectroscopy. *Optics Express* 2013; 21(8): 9238–9246.
4. Knabe K, Williams PA, Giorgetta FR et al. Absolute spectroscopy of N_2O near 4.5 μm with a comb-calibrated, frequency-swept quantum cascade laser spectrometer. *Optics Express* 2013; 21(1): 1020–1029.
5. Mazzotti D, Cancio P, Giusfredi G et al. Frequency-comb-based absolute frequency measurements in the mid-infrared with a difference-frequency spectrometer. *Optics Letters* 2005; 30(9): 997–999.
6. Gatti D, Gambetta A, Castrillo A et al. High-precision molecular interrogation by direct referencing of a quantum-cascade-laser to a near-infrared frequency comb. *Optics Express* 2011; 19(18): 17520–17527.
7. Sterczewski LA, Westberg J, Yang Y et al. Terahertz spectroscopy of gas mixtures with dual quantum cascade laser frequency combs. *ACS Photonics* 2020; 7(5): 1082–1087.
8. Faist J, Capasso F, Sivco DL et al. Quantum cascade laser. *Science* 1994; 264(5158): 553–556.
9. Curl RF, Capasso F, Gmachl C et al. Quantum cascade lasers in chemical physics. *Chemical Physics Letters* 2010; 487(1-3): 1–18.
10. Pagies A, Ducournau G and Lampin JF. Low-threshold terahertz molecular laser optically pumped by a quantum cascade laser. *APL Photonics* 2016; 1(3): 031302.
11. Mičica M, Eliet S, Vanwolleghem M et al. High-resolution thz gain measurements in optically pumped ammonia. *Optics Express* 2018; 26(16): 21242–21248.
12. Lampin JF, Pagies A, Santarelli G et al. Quantum cascade laser-pumped terahertz molecular lasers: frequency noise and phase-locking using a 1560 nm frequency comb. *Optics Express* 2020; 28(2): 2091–2106.
13. Chevalier P, Amirzhan A, Wang F et al. Widely tunable compact terahertz gas lasers. *Science* 2019; 366(6467): 856–860.
14. Amirzhan A, Chevalier P, Rowlette J et al. A quantum cascade laser-pumped molecular laser tunable over 1 thz. *APL Photonics* 2022; 7(1): 016107.
15. Chevalier P, Amirzhan A, Rowlette J et al. Multi-line lasing in the broadly tunable ammonia quantum cascade laser pumped molecular laser. *Applied Physics Letters* 2022; 120(8): 081108.
16. Burrus CA and Gordy W. Millimeter and submillimeter wave spectroscopy. *Physical Review* 1956; 101(2): 599.
17. Everitt HO and De Lucia FC. Rotational energy transfer in small polyatomic molecules. *Advances in Atomic, Molecular, and Optical Physics* 1995; : 331–400.
18. Amiot C and Guelachvili G. Extension of the 106 samples fourier spectrometry to the indium antimonide region: vibration-rotation bands of $^{14}N_2^{16}O$: 3.3–5.5 μm region. *Journal of Molecular Spectroscopy* 1976; 59(2): 171–190.
19. Morino I, Yamada K and Maki A. Terahertz measurements of rotational transitions in vibrationally excited states of N_2O. *Journal of molecular spectroscopy* 1999; 196(1): 131–138.
20. Ting WJ, Chang CH, Chen SE et al. Precision frequency measurement of N_2O transitions near 4.5 μm and above 150 μm. *JOSA B* 2014; 31(8): 1954–1963.
21. Gordon IE, Rothman LS, Hargreaves RJ et al. The HITRAN2020 molecular spectroscopic database. *Journal of Quantitative Spectroscopy and Radiative Transfer* 2022; 277: 107949. DOI:10.1016/j.jqsrt.2021.107949.
22. Petkie DT, Goyette TM, Bettens RP et al. A fast scan submillimeter spectroscopic technique. *Review of Scientific Instruments* 1997; 68(4): 1675–1683.
23. Brown GG, Dian BC, Douglass KO et al. A broadband fourier transform microwave spectrometer based on chirped pulse excitation. *Review of Scientific Instruments* 2008; 79(5): 053103.
24. Silver JA. Frequency-modulation spectroscopy for trace species detection: theory and comparison among experimental methods. *Applied Optics* 1992; 31(6): 707–717.
25. Lou M, Swearer DF, Gottheim S et al. Quantitative analysis of gas phase molecular constituents using frequency-modulated rotational spectroscopy. *Review of Scientific Instruments* 2019; 90(5): 053110.
26. JPL. *JPL Molecular Spectroscopy Database*, https://spec.jpl.nasa.gov/ [accessed February 22nd 2022].
27. Pickett H, Poynter R, Cohen E et al. Submillimeter, millimeter, and microwave spectral line catalog. *Journal of Quantitative Spectroscopy and Radiative Transfer* 1998; 60(5): 883–890.
28. Lees RM. Far-infrared laser spectroscopy of methanol: A probe for vibrational mode coupling. In *Millimeter and Submillimeter Waves II*, volume 2558. SPIE, pp. 262–284.

29. Toth RA. N_2O vibration–rotation parameters derived from measurements in the 900–1090-and 1580–2380-cm^{-1} regions. *JOSA B* 1987; 4(3): 357–374.
30. Wang F, Johnson SG and Everitt HO. Maximizing performance of quantum cascade laser-pumped molecular lasers. *Physical Review Applied* 2021; 16(2): 024010.