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Instrumentation for THz Spectroscopy in the Laboratory and in Space

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ABSTRACT Spectroscopic measurements in the millimeter, submillimeter, or THz range, with resolutions exceeding a MHz, provide for highly specific detections of gas-phase absorption and emission by atoms and molecules. Due to relatively low excitation energies involved in the transitions, multiple features are observable in most physical systems, and thus such observations dominate the scientific discovery of molecules in space and contribute significantly to remote sensing of the Earth and planetary bodies. The methods and techniques of THz spectroscopy continue to evolve as capabilities and technologies expand. In this article, we review the genesis of THz spectroscopy in both the laboratory and in space, and follow its development to date, providing background on the challenges, and context for the current developments that promise to extend both remote and *in-situ* gas composition sensing.

INDEX TERMS Spectroscopy, millimeter, submillimeter, absorption, emission, space, laboratory.

I. INTRODUCTION

The THz region, between 0.5 and 10 THz (600-30 μ m or 16.7-333.5 cm⁻¹), is one of the few remaining regions of the electromagnetic spectrum where the generation, control, and to a lesser extent, detection, of coherent radiation remains far from routine. As a direct result, the development of Doppler limited or velocity resolved THz spectroscopy has been completely tied to the available sources of radiation and how well these sources are controlled.

The 0.5 to 10 THz region has often been dubbed the "THz gap" due to difficulties in achieving the small scales necessary to minimize the parasitic capacitance and line inductance in conventional electronics or the large uniform layer size needed in quantum electronic devices. As a result, there have been numerous strategies involved in attempts to cover the THz region, including just about every imaginable approach involving diffractive spectrometers, up-conversion, novel fundamental oscillators, sum and difference frequency generation and numerous combinations of the various methods. Because of dispersion it is very difficult to achieve Doppler limited resolution, which we will focus on, with incoherent detection methods. Here we examine in depth the coherent techniques generally applied below 3 THz and defer

discussion of competitive incoherent techniques at the upper edge of the THz gap [1]. Almost all the techniques have found their way into some sort of laboratory system, but no technique has enabled the entire region to be completely exploited in either the laboratory or in the space environment. Now, more than ever, there is hope that generation and control of coherent THz radiation will become routine in the not so distant future, but similar statements have been made by many authors since the discovery of laser action in water, the first THz laser [2].

The development of molecular spectroscopy and its application in understanding molecular processes has been both a reason to perform THz spectroscopy and a driving force for the development of THz technology. The application of molecular spectroscopic techniques to astrophysics was also essential in the development of radio astronomy. Subsequently, access to fundamental molecular processes and the information these processes provide has driven laboratory spectroscopy and radio astronomy into the THz frequency region. However, to understand the present state-of-the-art, and what must be done to further advance the field of THz spectroscopy, requires an inventory of the technology and governing physical principles of THz spectroscopy.

Initial forays into microwave molecular spectroscopy were a direct result of the development of electron beam tube microwave oscillators (e.g., magnetrons, klystrons, BWOs) for use in radar in the 1930's and 1940's. Application of this technology to gas phase molecules led directly to the field of rotational spectroscopy. The details of these early developments are nicely tracked by a number of review articles [3]-[8] and books [9], [10]. A major limitation of early microwave spectroscopic measurements was the relatively small frequency window that could be used. This prevented many molecules from being studied and resulted in attempts to increase the operating frequency of beam tubes [11] and promoted the idea of electronic up-conversion to millimeter and ultimately submillimeter wavelengths [12]. The two ideas were not decoupled, since the frequency of the tube had to be compared to a known reference through some kind of electronic upconversion. While the details have evolved significantly, the basic approaches and challenges remain central to THz instrumentation today. Today the story of THz instrumentation is still one of searching for better fundamental oscillators or improving the efficiency of electronic up-conversion techniques. The two remain inextricably tied to the need to know the radiation frequency to better than a Doppler limited line width of ~ 1 part in 10^6 .

The discovery of the maser [13] and water laser [2] produced new sources of THz radiation and the possibility for THz generation through a difference frequency. However, the problem of knowing the frequency with sufficient precision remained. Direct THz generation was first realized with the discovery of the discharge laser action in H₂O [2] and HCN [14]. Subsequently, the CO_2 laser pumped far infrared laser [15] was discovered in CH₃F and numerous lasing transitions were quickly discovered in a variety of gases [16]. Lasers also offered the prospect of generating coherent signals through mixing. For the THz region, this involved optical difference frequency generation [17]. Proof of concept was first realized in the microwave with ruby lasers [18] and with Neon lasers [19]. Initially all the THz lasers featured little or no frequency tuning ability making the prospect of a coincidence with molecular transition quite low. As a result, useful THz laboratory spectrometers required either a means to shift the transition into resonance with the fixed laser or a way to make the radiation tunable.

A number of spectroscopic techniques were developed to shift the molecular transition frequency into resonance with a laser including Doppler shifting [20], Zeeman shifting (Laser Magnetic Resonance or LMR)[21], and Stark shifting (Laser Stark)[22]. A number of methods to generate tunable radiation were developed including laser sideband [23], tunable klystrons [24], tunable backward-wave oscillators (BWOs) [25], tunable far-infrared (TuFIR)[26], and optical difference frequency generation (photomixing)[27]. These techniques are discussed in more detail in the section on THz laboratory spectroscopy. Lastly the continued prospects for novel sources like quantum cascade lasers [28] and improved electronic up-conversion (multiplication)[29] are presented.

Space-based astronomy, or generally THz remote sensing, is, in many regards, similar to laboratory spectroscopy with the fundamental difference that mass, electrical power and complexity can be prohibitively expensive. As such, it is unrealistic to consider many of the previously mentioned sources of THz radiation. Additionally, the signals emitted by the interstellar medium are tiny, requiring that such detections be highly sensitive. In the THz region, Doppler limited (velocity resolved) astronomical spectroscopy is only practical with heterodyne techniques due to the enormous size needed for dispersive elements or the large path differences required for interferometers. To date there have been only six space-based systems that have operated in the 0.5-10 THz region with velocity resolved capability. Four of these (SWAS [30], Odin [31], MIRO on Rosetta [32], and SMILES [33]) operated below 0.65 THz. Only the EOS-MLS on Aura [34] and HIFI on Herschel [35] have operated heterodyne spectrometers in space at frequencies above 1THz. In addition to these systems, the heritage of Kuiper Airborne Observatory [36] was critical in the development of THz space-based systems and will be discussed in the context of the technology used in THz astronomy. At the moment the only operational (airborne and space) >1 THz system is the German Receiver for Astronomy at Terahertz frequencies, known as upGREAT [37]. upGREAT currently includes a 14 pixel array (7 in each polarization) operating between 1.835 and 2.065 THz. It also employs single pixel bands covering 914-635 GHz, 890-1092 GHz, 1240-1525 GHz, and 2490-2590 GHz using solid state local oscillators. Another band at 4.7 THz uses a quantum cascade laser local oscillator [38]. The other space-based THz system under development is for the European Space Agency's Jupiter Icy Moons Explorer. The Submillimeter Wave Instrument will have two all solid-state channels covering 530-625 GHz and 1080-1275 GHz [39].

Available technology has dictated which atoms and molecules have been studied in the laboratory and the interstellar medium. Development of subsequent generations of THz system can be greatly aided by remembering solutions to a number of technical challenges documented in this review.

II. THZ LABORATORY SPECTROSCOPY TECHNIQUES A. THZ LASER SOURCES

The discovery of single frequency HCN [14] and H_2O [2] lasers in THz produced the first strong coherent sources of radiation in this frequency regime, making it possible to consider Doppler limited spectroscopy in this wavelength range. The first step towards using far infrared molecular lasers was the measurement of their frequencies. The first two molecular lasers, HCN [14] and water [2], were frequency measured [40]–[44] with heterodyne techniques. In the course of such measurements, it became apparent that laser action could be supported anywhere within the Doppler line profile. Unlike carbon dioxide lasers, where the emission is on the fundamental vibrational band, the emission in THz discharge lasers originated from highly excited states, making Lamb-dip



stabilization of the laser to the transition frequency extremely difficult. As such, the best approach was to perform a heterodyne measurement of the laser emission as precisely as possible while averaging over the drifts. The actual laboratory frequency of these lasers drifts a couple MHz on modest time scales. The ultimate solution is to treat the laser like any other free running microwave oscillator and phase-lock it to some up-converted reference. Unfortunately, up-converting a reference frequency to the laser frequency can be non-trivial. Conversely, the frequency measurements [40]–[44] required some sort of down-conversion scheme that could have been used in a phase-lock (essentially the same issue). The frequency measurements are an existence proof that powerful CW lasers can be locked anywhere in the THz region. The first such example of a phased locked laser was an HCN laser that was locked to a harmonic of a klystron source [45]. However, many laser transitions were too high in frequency and to low in power to be easily locked to microwave sources. This made contending with the uncertainty in the absolute laser frequency a significant source of error in spectroscopic measurements.

The second source of molecular lasers is through optical pumping of various molecular gases. Optically pumped lasers use a high efficiency mid-infrared laser, such as a CO₂ laser, to illuminate a molecular gas. If the CO₂ laser frequency overlaps with a vibrational transition in the molecular gas, the gas is strongly pumped into a rotational level of the excited state, creating a population inversion in the rotational manifold of the excited vibrational state. The inversion results in emission from transitions where the pumped state is the upper state, facilitating laser action in a suitable resonator. The first optically pumped far-infrared laser was discovered in 1970[15] and the field developed very rapidly, finding many suitable molecular gases and laser frequencies [16]. Optically pumped lasers are still being identified today in the laboratory [52] and in space [53]. Tunable high-power solid-state pump lasers will ultimately make it possible to design the optically pumped lasers in the future. It is interesting to note that the spectroscopy of many optically pumped far-infrared lasers remains unknown. Only half of the lasing transitions in methanol can be assigned after decades of very high quality spectroscopy [51].

Measurement of laser frequencies with heterodyne techniques was critical for spectroscopy since it was usually technically impossible to lock most far infrared lasers. Many of the laboratory spectroscopic measurements utilized in astrophysics (and a number Kuiper Airborne Observatory results) employed free running molecular lasers and assumed the measured frequency. Recently, a number of lasing transitions have been measured by Doppler limited laboratory spectroscopy [52]. A complete list of Doppler limited measurements of laser transitions would be a major undertaking, but a sense of the accuracy of the previous heterodyne measurements can be conveyed by comparison with HCN and selected transitions in H₂O and methanol. Table 1 lists the molecule, transition, and both the reported heterodyne frequency measurement and our Doppler limited laboratory result. Both water and HCN were



TABLE 1. Comparison of Heterodyne Laser Frequencies to Doppler Limited Absorption

Molecule	Transition		Laser Heterodyne	Traditional Absorption
HCN	9-8	04°0	804750.9 ^a	804751.188(30) ^b
HCN	10-9	$011-04^{0}0$	890760.7ª	890760.216(50) ^c
HCN	10-9	0400	894414.2ª	894413.436(30) ^b
HCN	11-10	011-0400	964313.4ª	964312.827(30) ^b
HCN	11-10	011	967965.8ª	967966.070(30) ^b
H_2O	6 _{4,2} -6 _{6,1}	001-020	2527952.8 ^d	2527953.387(200)°
CH ₃ OH	16_{8} -15 ₇	E Vco	2522782.464^{f}	$2522782.74(8)^{\rm f}$
			2522782.311 ^g	$2522782.759(100)^{h}$
CH ₃ OH	15_4-14_4	E*	2541485.6 ⁱ	2541485.359(300) ^h
CH ₃ OH	15_4-14_4	E*	1822367.2 ⁱ	1822362.07(15) ^c
CH ₃ OH	27 ₁₀ -27 ₉	E Vco	1819314i	1819313.479(100) ^c
HCN	9-8	0400	804750.9ª	804751.188(30) ^b

*Denotes a transition from the excited torsional state ($v_t=1$) of the CO stretch to the $v_t = 1$ state of the CH₃ in-plane rocking mode.

^aReference [44]. ^bReference [46]. ^cThis Work. ^dReference [40]. ^eReference [47]. ^fReference [48]. ^gReference [49]. ^hReference [50]. ⁱReference [51].



FIGURE 1. A composite of two HCN laser lines recorded in a 600 Watt RF discharge through a 50/50 mixture of N₂ and CH₄. The 890 GHz 110-04⁰0 J=10-9 transition of HCN shown in the first part of the panel is observed in emission and the 894 GHz 04⁰0 J=10-9 transition is a weak absorber due to contributions from the population inversion cancelling part of thermal population difference.

excited in a discharge so several of the laser transitions were observed in emission rather than absorption. Fig. 1 shows two of the HCN laser transitions recorded in an RF discharge through a 50/50 mixture of N_2 and CH₄. The 894 GHz transition is weak due to incomplete inversion while the 890 GHz transition is completely inverted in population.

An interesting case study is the 2522 GHz methanol laser transition which has been frequency measured numerous times. The best free running frequency measurement [48] and a Lamb-dip locked frequency measurement [49] agree within error bars but neither agree particularly well with the TuFIR [48] or the multiplier frequency measurement [47]. These sorts of shifts in optically pumped lasers are believed to be due to imperfect overlap of the pump laser with the pump transition. The important point is that use of a free running gas laser is not a completely adequate frequency standard if accuracy higher than 1 MHz is required.

B. FIXED FREQUENCY LASER SPECTROSCOPY

Spectroscopy with a fixed frequency laser requires a means to shift a molecular transition into resonance with the laser. Over the years, three methods have been developed to shift molecular absorptions into resonance with a fixed laser. The first technique is to use a molecular beam that can be Doppler shifted to coincide with the laser frequency. This has been used successfully with ions in the infrared [20] but has not been demonstrated at longer wavelength. The second technique is to Zeeman shift a transition into resonance with the laser [21]. This generally requires that the molecule be paramagnetic, which produces a significant interaction between magnetic field and the magnetic moment of the unpaired electron(s), allowing the magnetic field to alter the energy of the state. The third technique is to Stark shift a transition into resonance with the laser [22] with an external electric field. This generally requires a strong first or second order Stark shift in the molecule and relatively close proximity to the laser line.

1) LASER MAGNETIC RESONANCE

The technique of Zeeman shifting a molecular transition with a variable magnetic field into resonance with a laser is known as laser magnetic resonance (LMR). LMR remains a powerful spectroscopic tool and has been used to determine much of what is known about many open shell radicals and most atoms in the ISM. Equation 1 gives the general form of a molecular Hamiltonian for an open shell molecule in a magnetic field [48]. For simplicity this example is for a ${}^{3}\Sigma$ diatomic that does not include hyperfine structure.

$$H = \mu_b \lfloor g_\perp \vec{S} \cdot \vec{B} + (g_z - g_\perp) S_z B_z + g_n \vec{N} \cdot \vec{B} \rfloor$$
(1)

In this equation μ_b is the Bohr magneton, the vectors \vec{S} , N, and B are the electron spin, the end-over-end rotational angular momenta, and the magnetic field, respectively. The subscript 'z' denotes the component along the molecular axis. The three g factors are denoted with a perpendicular symbol, an 'n' and a 'z'. In LMR it is necessary to fit the molecular constants as well as the molecular g-factors, which may be highly correlated. The correlations may be constrained to some extent by calculation of the g-factors, but the best method of breaking the correlation is to make measurements of the same Zeeman components at multiple lasers frequencies. When multiple laser frequencies are employed and their frequencies are known very well, LMR results can be as precise as a frequency measurement, but the precision of LMR degrades quickly when there is only one laser frequency. The errors in LMR include the frequency precision of the laser, knowledge of the magnetic field strength, knowledge of the *g*-factors and the usual problem of picking line center (in this case as a function of magnetic field). A major advantage of LMR is that powerful lasers with high sensitivity are used to detect the absorption. As such the technique has been used to determine the transitions of a long list of atoms, radicals and ions. For velocity resolved astronomy, LMR is not accurate enough for molecules. As a result, zero field frequency measurements are certainly needed for molecules measured only by LMR and probably are required for some atoms as well. Some of the many contributions to THz spectroscopy by LMR are discussed in the subsequent section on atoms and molecules.

2) LASER STARK

A less utilized technique in the THz is to Stark shift transitions into resonance with a molecular laser by applying an electric field. In Stark spectroscopy the electric field exerts a torque on the rotating dipole of the molecule breaking the degeneracy in the energy levels of the different M components. If the Stark shift is linear in the dipole times the electric field it is a first order Stark effect and if it is proportional to the dipole times the electric field squared it is a second order stark effect. Molecules without a projection of the overall rotation (e.g., linear) show only second order stark effects. Like in LMR, multiple frequencies of lasers or precise knowledge of the dipole are required to extract highly reliable frequencies from laser Stark data. Additionally, there must be enough information to solve for all the components simultaneously. The primary disadvantage is the Stark shifts are generally much smaller that Zeeman shifts requiring the probing laser be very close to the transition frequency.

The application of laser Stark spectroscopy to rotational spectroscopy of methanol has been discussed in detail [54]. Equations 2 and 3 give the form of the first and second order Stark shifts, respectively. In methanol, there are components of the dipole along both the a and b molecular axes so the Stark shift constants A, B, and C are linear combinations of the dipole matrix elements [54]. A and B involve the dipole matrix elements squared while C involves the dipole matrix element.

$$H_{St1} = -\frac{\mu \varepsilon KM}{J \left(J+1\right)} = -CM\varepsilon \tag{2}$$

$$H_{St2} = \left(A + BM^2\right)\varepsilon^2 \tag{3}$$

Here *M* represents the decoupling of the rotational degeneracy and ε is the electric field. In the generic molecule, both first and second order Stark effects contribute, such that all the combinations for *A*, *B* and *C* must be determined along with the dipole moment. A microwave measurement of the dipole moment often greatly simplifies the process, but distortion corrections to the dipole often become important in analyzing the Stark data and these are rarely determined in microwave Stark measurements.



C. TUNABLE LASER TECHNIQUES

1) LASER SIDEBAND

LMR and Laser Stark spectroscopy cannot access all of the interesting molecules in the THz region. Additionally, the challenges associated with extracting reliable frequencies from these two techniques made it highly desirable to have sources of THz radiation where the radiation could be tuned through the resonance of the desired transition. The first approach was to mix a known frequency molecular laser with a microwave source to generate tunable sidebands. The first demonstration of laser sideband spectroscopy [23] proved that Schottky barrier diodes could work as mixers in the THz. In addition to the drift of a free running molecular laser, laser sideband suffers from the challenges of relatively low power in the sideband relative to the carrier and the presence of a second sideband that moves oppositely in frequency relative to the first. The technical challenge, in a practical system, is to reject the carrier and the unwanted sideband so that the remaining signal power could be more unambiguously detected. Like LMR, a number of laser sideband systems were produced [55]-[58] and used to measure everything from water clusters to open shell ions. The historical precision of free-running laser sideband measurements is about 0.5 MHz, however where the laser has been locked the measurement precision is entirely dependent on the accuracy of determining the center of the observed transition [58]. Laser sideband is still utilized in a few laboratories around the world.

2) TUNABLE FAR INFRARED

The challenge of not being able to lock all molecular lasers and thus retrieve precise frequencies remains a problem in many optical frequency standard measurements [59]. As such, it remains highly desirable to have a THz frequency standard that does not have to be phase locked and counted. The precision measurement of CO₂ laser frequencies and the possibility of Lamb-dip stabilizing the laser to an external CO₂ gas cell made absolute knowledge of most CO₂ laser frequencies to 10 to 20 kHz possible [26]. The beat between different CO₂ lasers allowed a comb covering about 6 THz to be produced. It was known that metal insulator metal (MIM) diodes would mix CO₂ lasers and generate a beat note or generate a sideband on a CO₂ laser [60]. After some RF engineering was applied to the MIM diode, the amount of radiation that was coupled out was greatly increased [61]. By combining two Lamb-dip locked CO₂ lasers and a microwave source in a MIM diode, a tunable THz beam could be generated [14]. Like laser sideband, the THz beam does feature both lower and upper sidebands, but unlike laser sideband the frequencies of the CO₂ lasers are known and Lamb-dip stabilized to a few 10's of kHz. As a result, frequencies to over 6 THz could be synthesized. The technique has been extended to nearly 10 THz by using NH₃ lasers [62], [63]. This technique is still utilized in the laboratory of Prof. Matsushima in Toyama, Japan and remains a unique way to make precision measurements in the region above 3 THz. The major challenge is



the complexity of the system and the low, and often, variable output power from the MIM diode.

3) QUANTUM CASCADE LASERS

THz quantum cascade lasers can be designed and fabricated to produce frequencies below the phonon band in the GaAs material used in the active region. The radiation is produced in a small frequency window around the center frequency. Tuning is achieved with temperature and current. QCLs have proven spectrally pure enough to be used as local oscillators for cryogenic mixers. There direct use in spectroscopy has been limited and there will be more discussion pertaining to LO generation for remote sensing.

4) OPTICAL DIFFERENCE FREQUENCY GENERATION

A similar technique to Tunable Far Infrared radiation is laser difference frequency generation or photomixing. Here two lasers are beaten together in a non-linear material that has been carefully designed to radiate the difference frequency. The first technical challenge is obtaining a suitable material to generate and efficiently radiate the difference frequency. The second challenge is to obtain sufficiently precise knowledge of the two laser frequencies since the sum of the two laser accuracies is the accuracy of the generated frequency. Many types of photomixing devices have been constructed, with varying degrees of success. Presently the most promising are low temperature grown GaAs [64], GaP [65], and uni-travellingcarrier photodiodes [66]. Unfortunately, none have proven effective above 3 THz in a continuous wave system. Frequency precision has been obtained with two different techniques. The first approach was to lock two lasers to different modes of a high Q optical cavity with a precisely calibrated free spectral range combined with a third laser that is microwave offset locked to one of the cavity locked lasers [27]. The accuracy of the synthesized THz frequency is proportional to the knowledge of the cavity free spectral range. A more elegant approach is now possible by locking only two lasers to different teeth of a frequency comb. The comb spacing is then locked to a microwave standard and tuned, precisely synthesizing the THz frequency to the same accuracy as the reference as demonstrated in the THz difference frequency generation system currently in use in Dunkerque, France [67]. The primary challenge of this technique is generation of sufficient power. An obvious future direction for this technique is exploitation of the broad frequency coverage at the upper end of the THz frequency range using more conventional non-linear difference frequency material, but this has not been realized yet. Heterodyne systems exploiting photomixing devices are now available commercially as THz Time Domain Spectrometers (THz-TDS, e.g., [68]), these systems routinely provide spectral coverage from 0.1 to 1.0 THz, and when used in dry environments, up to 3 THz, however practical limitations for timedelay lines and time resolution have limited high resolution efforts.

D. ELECTRONIC UP-CONVERSION

Another approach to generation of THz radiation is electronic up-conversion. In this case a microwave oscillator or arbitrary waveform generator is locked to a frequency standard and may be multiplied further. Regardless, the baseband source must be locked to a counted reference which must be up-converted to the oscillator frequency. Three general variations have been employed. The first is to up-convert the tunable reference signal to lock a higher frequency oscillator, the second is to multiply a tunable lower frequency oscillator up to higher frequency, the third is to directly multiply a chirped pulse. Just about all electronic up-conversion systems constructed to date use one of these approaches to synthesize a precise tunable THz frequency. Improvements in solid state amplifiers and improvements in multiplier efficiency and power handling are rapidly occurring, such that the achievable frequency range now extents to nearly 3 THz [29]. An enormous advantage of direct multiplication is that the signal processing can be performed at frequencies where components are plentiful and inexpensive and multiplied up for spectroscopy [69]. As long as the signal has low phase noise and does not include tones other than the carrier and desired modulation, it can be multiplied with only a 20Log(N) (where N is the number of multiples) growth in phase noise [70]. Most modern high-quality commercial microwave synthesizers easily achieve the necessary spectral purity and facilitate a number of modulation types. The simplicity of multiplying such a signal has made direct multiplication to THz frequencies the generally preferred approach for THz generation [70], [71], [72]. Microwave backward wave oscillators (BWOs) of Russian design are also widely utilized as sources up to 1.5 THz [73]. BWOs can be used as precision frequency sources once they are phase locked to some sort of electronic up-conversion scheme that often resembles the direct multiplication approach, but with relaxed harmonic purity requirements. Locked BWO sources have been used effectively for high precision spectroscopy using resonators [74], [75] and photo-acoustic sensing [76]. Alternatively, a free running BWO system, which must be calibrated with an external etalon, and a known calibration gas, has been proved useful [77]. However, the calibration approach makes signal averaging substantially more complicated than in a phase locked system.

The major advantage of the direct multiplication approaches (fix-tuned and chirped pulse) are that no high voltage or precisely aligned magnetic field is required to operate the fundamental oscillator. Initially, BWO tubes had a distinct advantage in power and bandwidth, but modern multipliers have nearly eliminated this advantage. The success of THz multipliers is the direct result of the development of planar Schottky diode circuits where the idler circuitry is placed very close to the diode (designed with modern electromagnetic modeling software). The other technology that has allowed the rapid increase in up-converted frequency coverage is the ability to use active multiplication where MMIC power amplifiers are used to enormously increase the power levels at frequencies up to 115 GHz [78]. Regular amplifier developments ensure the available power to continually improve higher frequency generation, with 1 mW now demonstrated at 1 THz [79]. Direct multiplication techniques covering 0.1-2.7 THz (e.g., References [70], [71]) were exploited for development of gasphase databases [80], [81] for a multitude of remotely sensed species and their isotopologues, however the custom parts for these high-performance systems are cost prohibitive in many research laboratories. An economy of scale may yet be proven in the market for chirped pulse systems. The development of chirped pulse techniques, with significantly less expensive fundamental microwave baseband hardware [82], multiplied up to millimeter [83] and submillimeter [84] wavelengths may open up general research efforts significantly, and have been shown to be useful for medical [85] and defense applications [86]. Meanwhile, advances in the submillimeter wavelengths continue to be led by detector developments which can spur also laboratory systems that utilize ambient emission [87], [88]. Finally, developments associated with synchrotron sources of THz radiation are pushing to Doppler limited resolutions [89].

With THz time-domain spectrometers (TDS), chirpedpulse methods, and the ability to pulse modulate base-band [90], [91] and CMOS [91] sources, more and more THz spectroscopic techniques are operating with fast, coherent, detections in the time domain, even including dual frequency comb THz generation [92]. With this trend, applications for detections of transient species [93]–[95] are expected to proliferate. Additional applications in the medical and commercial sectors are even plausible with the miniaturization and power efficiencies of CMOS based systems [96]. Many of these systems' viabilities are reliant on system engineering considerations for efficiently handling THz radiation in the gas environment using either a corrugated waveguide [80], or cavities [91], [97], [98].

E. PRACTICAL THZ LABORATORY CONSIDERATIONS

One important aspect of laboratory THz spectroscopy for astronomy is how to best simulate the interstellar medium. Much of the chemistry in the interstellar medium occurs at low temperatures and densities too low for spectroscopy in finite path lengths. Further complicating the problem is the fact that much of the ISM chemistry is initiated by high energy cosmic rays. Neither the low density nor the ionizing radiation is well reproduced for laboratory experiments. As a result, the general approach of simulating the interstellar medium is to use energetic electrons in a plasma discharge. The typical configuration for a plasma discharge is a long tube with a cathode and anode at opposite ends. Maintaining the discharge requires that enough ionized particles slam into the negative electrode liberating enough electrons to sustain the reaction [93]. In the long tube configuration the energetic electrons quickly scatter to the cell walls losing most of their energy. A magnetic field along the cell extends the negative glow region by preventing the electrons from hitting the walls, but





FIGURE 2. The power spectrum of a 1.9 THz source recorded with (red) and without purge (black) of the air paths showing the effects of atmospheric water vapor absorption. The inclusion of the purge bags does result in a measurable loss at good frequencies and some small amount of residual water remains visible.

the magnetic field precludes studying species that are paramagnetic [94]. RF discharges have been used with some success in observing some paramagnetic radicals [95], but the electron energy in RF discharges is generally low due to the limited time acceleration time in the field. As such, RF discharges are often excellent in creating highly excited molecules but have mixed results in producing cold ions. As a result, producing a number of interstellar species in the laboratory will remain a black art until better laboratory techniques for simulating the ISM are invented.

THz laboratory spectroscopy also poses a number of practical challenges even after the radiation and transient analyte are generated. The atmosphere in the laboratory can be highly absorptive in the vicinity of atmospheric water lines. As such, it is often necessary to purge any air path between source and detector. Fig. 2 shows a power spectrum of a 1.9 THz multiplier with and without purge. The purge was accomplished by filling a very thin polyethylene trash bag with the boiled off effluent of liquid nitrogen. A second problem is that many materials that are transparent at microwave frequencies can greatly attenuate THz signals. For example, fused quartz makes good window material below 1 THz but the loss increases dramatically above 1 THz. The use of z-cut crystalline quartz solves this problem. Good window material can be made out of ultra-high resistivity silicon, sapphire, high density polyethylene, and z-cut quartz. In general, better performance is achieved with lower refractive index material.

III. AIRBORNE AND SPACE-BASED THZ SYSTEMS

The development of THz receivers for astrophysics is tied directly to the development of sources of THz radiation and suitable mixers to utilize the THz radiation. Until the extension of SIS mixers beyond the Nb superconducting band gap [99]



and the invention of superconducting hot electron bolometers [100], the only practical THz mixer was a Schottky diode. Despite low power consumption demonstrations of THz oscillators with Silicon (CMOS) and Silicon:Germanium (SiGE) electronics, progress in high-frequency mixing has been limited to millimeter wavelengths [101]. At room temperature, the Schottky and Silicon devices require local oscillator power levels on the order of 1 mW to promote efficient mixing, or approximately three orders of magnitude more local oscillator power than superconducting mixers. As a result, it remains only practical to drive THz mixers with an efficient gas laser, or at low frequencies (millimeter wavelengths), where enough electronically synthesized power be generated. Space-based systems have to carefully consider the power required for a THz laser local oscillator and the cooling necessary for superconducting mixers. As a result, the approach of many of the early space-based systems was to limit the frequency and not employ cryogenic mixers. In this case, a conventional lower frequency microwave source drives a Schottky diode mixer. This system design is used in SWAS [30], MIRO [32] and the 640 GHz channel of EOS-MLS [34] where all employ a Gunn oscillator driven multiplier and Schottky diode subharmonic mixer. The Odin [31] satellite was able to generate enough power at 560 GHz to use a fundamental mixer. The SMILES [33] instrument used a 640 GHz SIS mixer with fixed tuned, multiplied Gunn oscillator operating at the fundamental frequency. Of these systems only Odin [31] can tune the frequency of the local oscillator and the tuning range is limited to approximately 30 GHz.

The history of THz astronomical receiver systems starts with Kuiper Airborne Observatory (KAO), which supported 0.6 THz [102] and 0.8 THz [103] receivers with enough electrical power available to support CO₂ lasers to drive the optically pumped far infrared lasers. The KAO routinely performed THz spectroscopy using a variety of fixed tuned optically pumped far-infrared lasers [36] that drove fundamental Schottky diode mixers. This basic design was used in the first space system operating at over a THz. The EOS-MLS 2.5 THz channel uses a CO₂ laser to pump a methanol laser that drives a 2.5 THz fundamental Schottky diode mixer [104], [105]. The primary challenges for the MLS system are supplying the 125 Watts required for the local oscillator and dissipating the heat generated. The solid-state local oscillators used in space systems generally required much lower DC power levels. In SMILES [33] the space platform was the international space station so there was enough power available to support a cryocooler to achieve the temperature necessary for the SIS mixer. Cryogenic mixers almost always have better sensitivity and reduced local oscillator power requirements but the demands upon spacecraft resources, of mass for a cryostat, or power for a cooler, are major design considerations.

A. HERSCHEL HIFI

The Heterodyne Instrument for Far Infrared (HIFI) on the Herschel Space Observatory was the only THz system to operate at over 1 THz with both a solid-state local oscillator and superconducting mixers. The local oscillator of HIFI featured a synthesizer driving active multiplier chains to 1.9 THz [35]. The local oscillators in HIFI employed exactly the same sort of technology as most laboratory electronic up-conversion systems [106]. All employed a synthesizer with a fundamental oscillator frequency below 20 GHz and actively multiplied the signal up to 1.9 THz.

The main feature of the Herschel Space Observatory was a 2500 liter tank of superfluid helium for cooling. The cost of this cooling was the relatively large 3300 kg launch mass of the observatory. Besides the local oscillator, the HIFI development had to overcome a variety of problems in the mixer design. Foremost was the limited bandwidth ($\sim 100 \text{ GHz}$) of a single tunnel junction SIS mixer. This was overcome through the uses of multiple junction designs allowing the 160 GHz required for HIFI bands. The second significant problem was the limitation imposed by the Nb superconducting band gap which limits superconducting response to frequencies below 750 GHz. This was overcome by the development of NbTiN, a larger band-gap superconductor. Finally, the NbN hot electron bolometer mixers are limited by phonon interaction times to a 3dB intermediate frequency bandwidth of approximately 4.8 GHz. As a result of all the challenges, HIFI employed 5 different mixer technologies in its 7 receiver bands and only produced 2.4 GHz of useful IF in the two highest frequency bands.

The primary advantage of HIFI was its ability to observe at a number of frequencies that were impossible from the ground and in the case of molecules like H₂O and CH⁺ aircraft as well. The primary motivation for the frequency range of HIFI was to observe the fine structure lines of N_{II} and C_{II} and a wide range of both ortho and para water lines. Water and C_{II} have been observed extensively while N_{II} remains an observational challenge. The major success of HIFI was access to the fundamental $\Delta J = 1$ transitions of the hydrides and hydride ions of C, N, O, F, S, and Cl. HIFI's access to the transitions of these molecules had a revolutionary impact on our understanding of the diffuse ISM, the importance of radiation by UV, X-ray and cosmic rays. Additionally, THz spectroscopy was beginning to revolutionize our understanding of the importance of shorter wavelength radiation in exciting many molecular species. The primary limitation of HIFI was the highest frequencies are not particularly stable or sensitive so it is difficult to perform deep searches or observe very broad features.

In spite of the capabilities in HIFI, the Photodetector Array Camera and Spectrometer on Herschel, the Spitzer space observatory and the Infrared Space Observatory detected a large number of THz features of both atoms and molecules that remain to be observed either in the laboratory or in space with velocity resolved line shapes. These astronomical lines are often very strong, and if the conditions determined from other tracers are a guide, they are likely to have complex velocity profiles. It will be the task of subsequent generations of astronomical systems to observe these lines using technology that still requires a significant amount of development or simply does not exist yet. Additionally, fundamental spectroscopy to determine line strengths and accurate rest frequencies is required in many cases.

B. UPGREAT DEVELOPMENTS

Most of the upGREAT [37] capabilities are comparable technologies to those developed and implemented for Herschel-HIFI, albeit with expanded bandwidth and novel array formats. Of particular note is the development of a viable Quantum Cascade Laser local oscillator [38] to allow capture of the 4.7 THz O-atom transition of fundamental importance to astronomy. This QCL provides 150 μ W power when cooled to 50K while dissipating minimal source power. The low power consumption is critical for efficient cryogenic operations, which are limited to 250 W to allow the system to operate within the aircraft resources.

C. LIMB SOUNDING

Terrestrial limb sounders in the >0.5 THz range have not been further developed since the Japanese SMILES [33] use of SIS mixers. The focus in earth science on tropospheric composition has been a contributor to this trend since the cold, wet tropopause blinds limb sounders to the lower atmosphere at THz frequencies. Nevertheless, the 0.6 THz range has been widely acclaimed as a choice band (used by SMILES, EOS-MLS and Odin) for characterization of terrestrial stratospheric chemistry due to the confluence of gas emission features of radical and reactive species with HCl, the dominant chlorine reservoir. Unlike the targets in astronomy, there is little terrestrial stratospheric interest in additional diatomic hydrides that are only measurable at THz frequencies, with OH [107] shown by EOS-MLS to be fairly predictable based on photochemistry and kinetics rates. However, THz limb sounding may yet have an application at the intersection of Earth Science and Heliophysics where the mesosphere and ionosphere have open scientific questions regarding winds and gravity waves that may be traced by atomic and molecular emissions [108].

D. THZ BROADBAND RADIOMETRY

Developments of multiplier chains and Schottky detectors have enabled low cost radiometry that can be specific to gas features in atmospheres. Many radiometers have been built and operated at cm and mm wavelengths for use in weather sounding and science applications, however, very few instruments employing these techniques have featured THz channels. Demonstration of these techniques for the submillimeter has shown a sensitivity to cloud-ice features such as that exploited by the IceCube project [109] that created the first global map of earth's cloud ice features in the 883 GHz band through sub-harmonic mixing of an up-converted K-band local oscillator, all operating at ambient temperatures.

E. THZ RADAR

With the development of multiplier based electronic sources came also concurrent development of THz transceivers [110],



[111]. For application on earth, millimeter-wavelengths provide for significant propagation distances in the moist atmosphere. Non-spectroscopic methods focused on Cloud characterization [112] or hidden object detection [113]. Hybrid, radar spectrometry, systems, thus far designed for range sensitivity to atmospheric water vapor, feature frequency agility, and have been flown terrestrially to show simultaneous determination of cloud morphology and water vapor content, even in the presence of precipitation [114]. The technique can be applied short and long range, with bands and bandwidths chosen to extract specific information about a target including cloud morphology, cloud/haze particle size, surface altimetry and surface roughness; as well as information, separated by target(s), regarding atmospheric gas species. Extension of the water ranging technique to the submillimeter is emerging as a new method for water sounding in the Martian atmosphere [115].

IV. FUTURE THZ TECHNOLOGY

The region between 2.7 THz where multiplied local oscillators are feasible and 9 THz where tunable diode lasers can be operated remains the technological frontier for astronomical heterodyne receivers. Schemes like TuFIR, that have generated some radiation in this region, are too complex, and generally too low power, to serve as a local oscillator. It is more likely that this region can be filled in by two potential developments. First, the electronics industry has made enormous progress in developing fast electronics employing advanced e-beam lithography techniques. Amplifiers have now achieved nearly 1 THz operation [79] and the definable circuit feature sizes continue to shrink suggesting that active multiplier designs can be pushed to 5 THz in the near future. Combined with low power consumption CMOS millimeter-wave generators, practical system designs shrink dramatically.

Similar advances in emergent technology are seen with the THz quantum cascade lasers [28], [116]. QCLs still must overcome a number of practical challenges. First, THz QCLs require cryogenic cooling (to temperatures near liquid nitrogen) where they produce on the order of a Watt of heat that must be dissipated. The age-old problem of determining the frequency of the laser must also be solved. QCLs have been locked to gas lasers [117] and molecular lines [118] at frequencies in the range of modern THz frequency multipliers. Since it was possible to perform heterodyne measurements of optically pumped molecular lasers many years ago, it should be completely feasible to phase lock quantum cascade lasers to multiplied microwave sources over most if not all the THz region. A quantum cascade laser locked to an active multiplier currently appears to be the most likely path to space-based THz heterodyne receivers in the 3-9 THz range in the near future.

Optical difference frequency generation also remains a potentially interesting approach in generating THz radiation. In this case, the optical lasers can be locked to a frequency comb allowing for precise determination of the difference frequency [67]. However, the development of suitable mixing technology remains problematic due to difficulties in coupling the THz wave out of the device. The enormous advantage of optical difference frequency generation is in the wide tuning range available to many diode lasers, which would allow a single source to span much or all of the THz region. This area of research remains to be fully exploited.

Technology developments for laboratory efforts have opportunistically followed the drive for communications and remote sensing or both. The relatively stringent criteria for catalog quality, Doppler resolved, molecular spectra from the laboratory are relaxed somewhat for remote sensing needs. Coupled with the need to deploy remote sensing instruments in aircraft or space, the technologies of interest to the two communities may diverge based on stability, mass and power criteria. Nevertheless, the two efforts scientifically feed off each other and will continue to do so for the foreseeable future.

V. CONCLUSION

The field of Doppler limited THz spectroscopy has progressed from a technical impossibility to an important tool in both astronomy and physical chemistry. Technologies for remote sensing the upper atmosphere and the interstellar medium are mature and being miniaturized and multiplexed. Adaptations of radiometric and radar techniques to THz frequencies offer improved spatial resolutions and unique gas-phase specificities. The development of THz spectroscopy remains tied to continued development of source technology. THz spectroscopic technology will have to continue to develop if more of the atomic fine-structure lines are to be measured for associating velocity and ISM information with the filamentary dust structures that are ubiquitously observed. Additionally, there are basic questions on hydrogen, carbon, nitrogen, silicon, fluorine, and sulfur hydride chemistry that will require further astronomical and laboratory studies. These all require better THz technology.

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