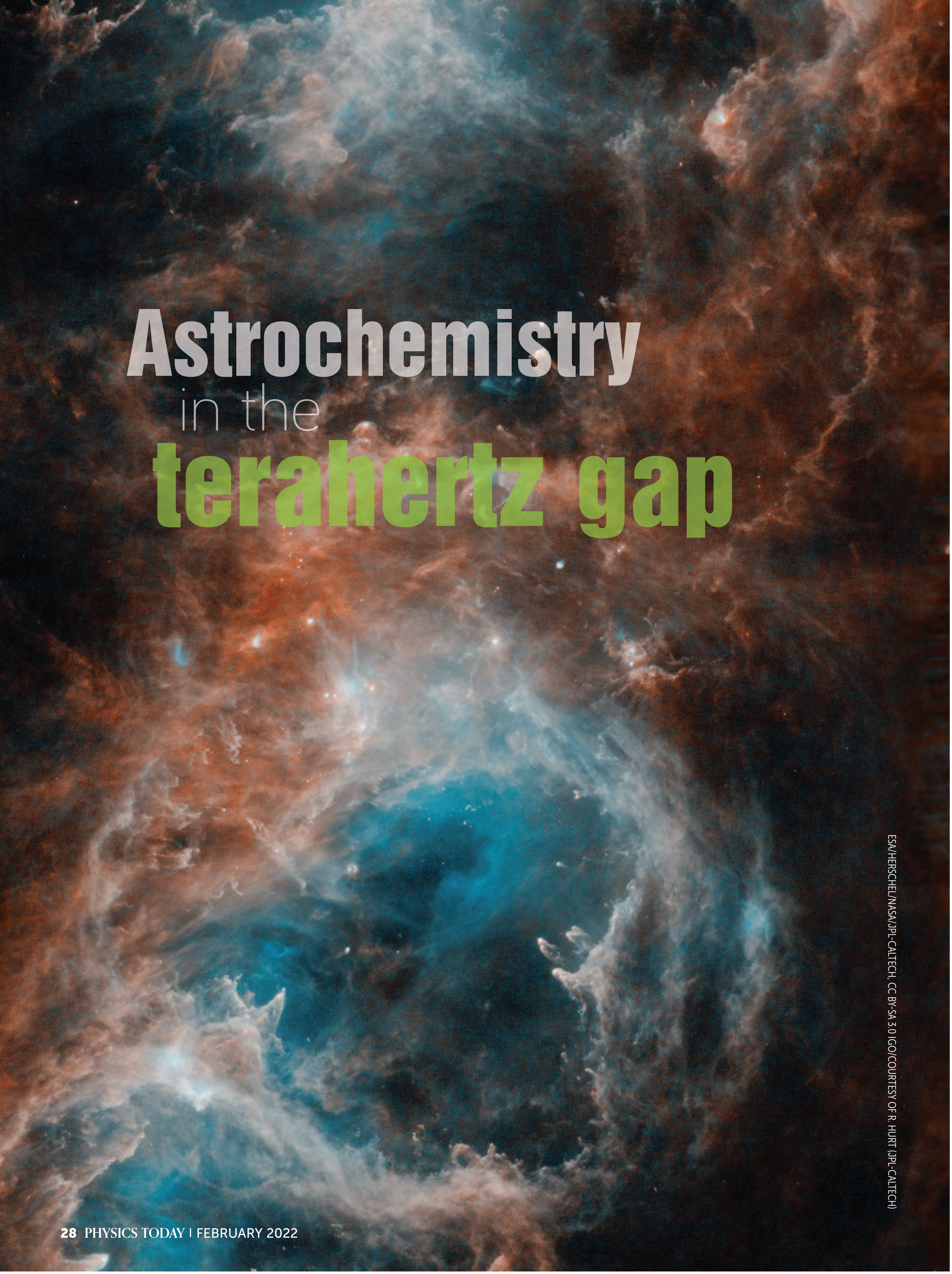
Astrochemistry in the terahertz gap

Susanna L. Widicus Weaver

Citation: Physics Today **75**, 2, 28 (2022); doi: 10.1063/PT.3.4939
View online: https://doi.org/10.1063/PT.3.4939
View Table of Contents: https://physicstoday.scitation.org/toc/pto/75/2
Published by the American Institute of Physics

Astrochemistry in the terahertz gap



ESA/HERSCHEL/NASA/JPL-CALTECH, CC BY-SA 3.0 IGO/COURTESY OF R. HURT (JPL-CALTECH)

Susanna Widicus Weaver is a professor of chemistry and astronomy at the University of Wisconsin–Madison.

Susanna L. Widicus Weaver

New capabilities are enabling laboratory spectroscopists to acquire more molecular spectra that advance our chemical understanding of the universe.

Studies of the atomic and molecular universes rely heavily on various spectra recorded in the long-wavelength range of the electromagnetic spectrum. At those wavelengths, astronomers identify the fingerprints of organic molecules, determine the conditions inside stellar nurseries, and detect redshifted transitions of atoms in distant galaxies. The false-color image on the opposite page, for example, shows the W3-W4-W5 complex of molecular clouds and star-forming regions in the Milky Way.

Much of the previous work has been conducted in the microwave regime, which covers 300 MHz to 300 GHz in frequency, or 1 m to 1 mm in wavelength. But recent insights into the molecular universe have come from far-IR (FIR) observations in the range of 300 GHz to 20 THz in frequency, or 1 mm to 15 μm in wavelength. The era of FIR astronomy brought about by the *Herschel Space Observatory*, the Atacama Large Millimeter/Submillimeter Array (ALMA), and the Stratospheric Observatory for Infrared Astronomy (SOFIA) has led to a recent heyday of molecular astronomy.

In the past, advancements in this field have been held back by the "gap" in the terahertz regime arising from the relative lack of molecular spectroscopic information in this range as compared with other regions of the electromagnetic spectrum.[1] The gap, illustrated in figure 1, had arisen because of historical limitations in the technology available for laboratory and observational studies. Because of advances in telecommunications, security, and astronomical instrumentation design in the past 20 years, however, astronomers are now making rapid improvements.[2] New tunable terahertz light sources, higher-power terahertz amplifiers, more sensitive detectors, and rapid and broadband data-acquisition capabilities have revolutionized the field. Researchers are starting to fill the terahertz gap.

Terahertz spectroscopy

Atomic and molecular spectra in the FIR range are the tools that astronomers and planetary scientists most commonly use to study chemistry in space. Important features found in the regime include the electron spin flip of the hydrogen atom at a wavelength of 21 cm; the ammonia structural inversion transitions at a frequency of 23 GHz; the pure rotational lines of carbon monoxide, which are the signposts of telescope receiver bands; and the rotational and rovibrational lines of organic molecules that have been seen in comets and the interstellar medium and may be the precursors to life throughout the universe.

But what is a spectral line? Atoms and molecules absorb only at certain wavelengths that correspond to specific energy transitions. For molecules, that can be energy changes associated with rotation, vibration, or electronic energy. Molecular transitions are quantized, which simply means that the transitions occur only at particular amounts, or quanta, of energy. The transitions are sharp, meaning that they happen over a narrow range of frequencies. If you shine a particular wavelength of light through a sample and watch the response with a detector, you can determine how the molecules interact with the light. Repeating that process over a range of wavelengths allows you to construct a spectrum.

If a molecule responds to light through either absorbing or emitting it, the signal at the detector changes abruptly. Spectral transitions appear as narrow spikes (hence the use of the word "line" to describe them). Each line in a spectrum corresponds to a specific transition of the molecule. Figure 2 shows an example spectrum.

In the FIR, researchers observe rotational lines from small molecules, which contain about 2–10 "heavy" atoms, primarily

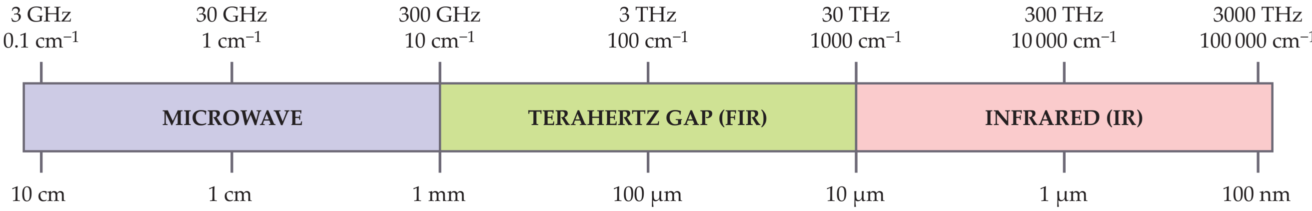


FIGURE 1. A GAP in the collection of molecular spectroscopic data has long existed between the microwave and IR wavelength ranges of the electromagnetic spectrum. Now technological advances are equipping far-IR (FIR) astronomers with the instrumentation they need to fill the terahertz gap.

carbon, nitrogen, oxygen, and associated hydrogens. For larger molecules, they observe rovibrational lines, which arise from changes in both rotational and vibrational energies. The specific energies of rotational transitions are related to a molecule's structure. As such, each rotational spectrum is molecule specific. If several lines for a given molecule are observed, the temperature and density in a sample of gas can be quantified by comparing the lines' relative intensities.[3] Molecules, therefore, are routinely used as probes of the physical properties of objects in space. For astrochemists, the molecular information gained through such measurements improves their understanding of how chemistry evolves as stars and planets form.

To study a particular molecule in space, one must first obtain a laboratory spectrum and assign the lines therein. Spectral lines are measured across a given frequency range and matched to a spectral prediction based on a quantum mechanical model of the molecule's energy levels. Usually not all of a molecule's spectral lines are measured. Frequency coverage, spectral sensitivity, and sample conditions all influence what lines can be observed in the lab and in space. But even with only partial spectral information from the laboratory, one can assign the spectrum and predict the rest of the lines. That's because the lines in a rotational spectrum follow a regular pattern that is linked to the molecular structure. With that information, spectroscopists can identify the molecule's transitions and determine its physical parameters.

Simple molecules require only a few parameters for a full spectral assignment. Complex molecules, however, demand dozens of parameters to achieve a level of assignment that leads to reliable predictions. If researchers collect sufficient information in the lab, they can determine the parameters with a high degree of precision. They can then use the information to extrapolate the spectrum to other frequency ranges at any temperature. Astronomers use this lab information to analyze observational spectra.

The spectrum that is collected during telescope observations contains all the lines from every molecule in the source. When a molecule is identified, its spectral features are matched to those predicted from the laboratory spectral assignment. Matching requires knowledge of not only the spectrum for the molecule of interest but also the spectra for all the molecules in the source. Astrochemists can then connect each line to a molecule and sort out any ambiguities by recognizing the patterns from known laboratory measurements. If enough spectral lines are observed that can be uniquely assigned to a given molecule and if their relative intensities match the expected physical parameters of the source, the molecule is said to be detected in space.

Such a process relies on laboratory measurements of spectra across the terahertz range so that the laboratory's spectral assignment can be matched to observations. Unfortunately, laboratory studies have been limited because of the challenges of filling the terahertz gap. Historically, researchers have lacked stable, high-powered, tunable light sources in the FIR regime and sensitive detectors that cover that part of the electromagnetic spectrum. IR spectroscopy, which covers 20–430 THz in frequency, or 15 μm to 700 nm in wavelength, is well established, and commercial spectrometers are a standard characterization tool in nearly every chemistry laboratory. Microwave spectroscopy, covering 300 MHz to 300 GHz in frequency, or 1 m to 1 mm in wavelength, is not as widely used as an analytical tool. But it is just as powerful as IR spectroscopy and is a well-established field of research dating back to the development of radar during World War II.

FIR spectroscopy, however, has not been widely pursued. Of all the high-resolution spectroscopy research laboratories in the world, around 10 have spectral access from 300 GHz to 1 THz. The number of labs with high-resolution spectral access above 1 THz can be counted on one hand. But with the development of new FIR observatories has come new technological capabilities, and many of the historical limitations in the FIR range have been overcome. A deluge of astronomical spectra is now arriving from FIR telescopes. My research group and the handful of others who work at the millimeter-to-micrometer wavelengths are striving to develop laboratory techniques to keep up with the quantity of data.

Laboratory challenges

The simplest and most straightforward way to obtain terahertz spectral data in the laboratory is to conduct what is called a direct-absorption experiment. When light is shone into a molecular sample, a detector records the amount that passes through it. Spectroscopists then reference the input light to the output light to determine how much the sample absorbed. By scanning the input light across frequency steps that are smaller than the width of a spectral line, they can piece together an absorption spectrum.

To extend measurements beyond the simple direct-absorption method requires borrowing techniques used to gather data in the IR and microwave regimes. In the IR, light sources that include lasers and optics based on ground glass with mirrored coatings are used. In the microwave, radiation is generated by crystal oscillators, like those used in a watch and car radio, and circuitry directs it to the sample. The FIR is often called the quasi-optical regime because it draws methods and equipment from both approaches. A FIR lab uses Teflon lenses, beamsplitters made of thin sheets of Mylar, mirrored focusing optics, and diodebased frequency multipliers. Combining the two types of experiments into one system that works for all wavelengths in the FIR is complicated and technologically challenging.

Unfortunately, the challenges of FIR experiments do not stop there. Once a system is established for generating light and directing it into the sample, a detector that is sensitive enough to measure the signals is required. Although some room-temperature devices cover the longer-wavelength end of the FIR regime, anything above roughly 300 GHz requires a custom-built detector cooled with liquid helium. Unless kept at extremely low temperatures, the detector elements that have the best response at FIR wavelengths are flooded with thermal background noise.

Helium boils at a temperature of 4.2 K, and keeping a detector at that temperature requires routine cryogen fills, which greatly complicates the logistics of experiments. In addition, the natural supply of helium on Earth is rapidly dwindling, and using helium-dependent devices is increasingly expensive (see PHYSICS TODAY, April 2019, page 26, and "Helium shortage has ended, at least for now," PHYSICS TODAY online, 5 June 2020). Detector manufacturers are now implementing closed-cycle cooling systems that use helium recirculation to better conserve the supply. But those detectors are not readily available to every spectroscopy laboratory.

Once a source and detector are set up, the next step is to deliver the molecular sample into the system. Rotational spectroscopy requires gas samples for analysis because the molecules have to be free to rotate and will not do so as a liquid or solid. For stable molecules, spectroscopists can fill a cell with gas and record the spectrum. For molecules that are highly reactive or unstable, however, they need to devise ways to produce the molecule and keep it sufficiently isolated to avoid its reaction or decomposition while recording spectra. Most options require sources that continually flow or pulse the gas mixture through the system. Those sources introduce complications for gas handling because they require large pumps and vacuum fittings, windows, and other hardware to couple the spectrometer to the gas cell.

Another challenge astrochemists face has to do with the nature of the molecules. In the low density of space, molecules react slowly because they take tens of thousands of years to collide. Their reaction rates speed up considerably when an ion is involved because its charge attracts molecules. But ions are difficult to produce in the lab at sufficient quantities to study their spectra. Plasmas are used to make the ions, and then the gas sample is expanded into a vacuum, which leads to cooling and stabilization of the products. But even with the most efficient ion sources, only 1 in every 10 000 molecules gets ionized, and once expanded into the vacuum, the gas sample is even further diluted.

Remarkably, detecting some ions in the lab is more difficult than in space. Fortunately, now that the technology is available to ease the design problems associated with FIR spectrometer instruments, several creative production techniques for producing molecular ions have been implemented and are leading to great advances in their study.

Once all those challenges are overcome and a spectrometer is constructed and signals are optimized, it may take anywhere from a few days to many months to record the spectrum of interest. Traditional techniques scan step-by-step at small frequency increments to capture all the molecular lines. Some techniques are designed to increase data-acquisition speed, but most are limited to the microwave regime. Fortunately, the development of more advanced telecommunications devices is now enabling complementary techniques for the FIR. But such extensions are limited by the available technology, and many techniques used in other frequency ranges that involve more sophisticated detection schemes are not yet applicable in the FIR. Most FIR instruments in the laboratory, therefore, are still focused on simple direct-absorption techniques.

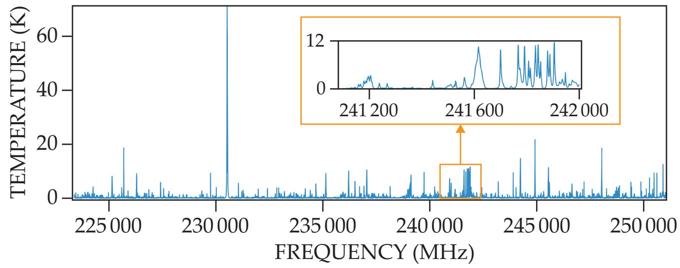


FIGURE 2. THIS SPECTRUM of the Orion molecular cloud was measured using the Caltech Submillimeter Observatory. The inset features spectral lines from methanol.[12] (Courtesy of Caltech/NSF, AST-0838261.)

Collecting astrochemistry data

Much of the equipment used in telescope observatories is similar, if not identical, to the equipment used in spectroscopy laboratories. Signal collection with a radio telescope, however, is more complicated than it is with a spectrometer in the lab because of heterodyne receivers used to detect the weak signals from space. Those receivers mix the observed light from space with a well-known local-oscillator frequency. The slight offset of the signal frequency from the local-oscillator frequency results in a beat frequency, which corresponds to the difference between the two. ALMA uses a collection of antennas, some seen in figure 3, to capture signals.

Telescope receivers are designed such that the beat frequency falls within standard radio bands. Researchers can then use powerful signal amplifiers commonly found in radar, cellular phones, televisions, radio transmitters, and other RF devices. The radio signal can be rescaled to the correct frequency range after all the signal-processing steps are completed at the higher signal power. Heterodyne techniques are thus incredibly sensitive and enable researchers to detect weak signals from space that would otherwise be indistinguishable from background noise.

Unlike the absorption spectra collected in the lab, observations typically consist of emission spectra. Molecules in space absorb light from nearby stars and then emit light at FIR wavelengths as they cool to their lowest energy states. That molecular emission thermally stabilizes an interstellar cloud during star formation. To observe the emission, astronomers tune their telescope receivers to the wavelength of a particular molecular transition previously measured in the lab and collect a signal to see whether any sign of emitted light rises above the background. Figure 4 shows some of the pieces of an ALMA telescope receiver that are used to collect molecular-emission measurements.

In the past, the bandwidth of heterodyne detections was so

FIGURE 3. THESE ANTENNAS are part of the Atacama Large Millimeter/Submillimeter Array, a radio telescope located in Chile and used for far-IR observations. (Courtesy of ESO/S. Guisard, www.eso.org/~sguisard.)

small that astrochemists had to target narrow frequency windows and match spectral signatures to molecules one line at a time, one molecule at a time, and one source at a time. But the new generation of FIR observatories employs novel broadband receiver technology to rapidly collect broad swaths of spectral information. The advances have prompted researchers to change their approach to data acquisition and allowed them to observe a wealth of molecular information. For perspective, the spectrum shown in figure 2 was collected in blocks of spectral data 4 GHz wide. The generation of receivers that were in use just a few years ago offered a maximum spectral bandwidth of 500 MHz. Receivers now offer bandwidths of up to 12 GHz.

In just the past few years, astronomical data sets have increased in size by a factor of 10–20, and the number of molecular lines in each spectrum has increased from a few to thousands, which has led to a wealth of new information. The *Herschel Space Observatory* had several key programs that were dedicated to broadband, high-resolution molecular-line surveys of clouds in various stages of star formation. The publicly available *Herschel* data archive is full of spectra from 600 GHz to 3 THz and contains thousands of unidentified spectral lines.[4] SOFIA routinely observes spectra at frequencies above 1 THz, where lab information is limited.[5] And the ALMA telescope has pushed data collection to the next level; for a week of observations, it can provide about 300 TB of terahertz-frequency spectral data.[6]

Few research laboratories have instruments that cover the entire terahertz gap, so only a few molecules have been fully characterized across that frequency range. That means that astronomers cannot analyze much of the spectral information gained from the new astronomical observations. Many astrochemists choose to focus on the molecules that have already been characterized, which are typically stable molecules that are good tracers of physical conditions in space. But what information could we glean from observations if we had the laboratory information with which to compare it?

Filling the terahertz gap

With the recent technology advances, laboratory spectroscopists are beginning to catch up with the influx of FIR observational spectra. Sources that offer enough power to drive absorption spectrometers in the FIR spectral regime are now available as off-the-shelf components that operate at frequencies of up to 3 THz. Detectors that provide the necessary sensitivity are now also commercially available. Increases in data-acquisition speed, driven by the telecommunications industry, are leading to the development of new broadband spectrometers. Based on those technology developments, research groups with spectrometers that cover the terahertz gap are now developing new techniques that offer increases in detection sensitivity, spectral acquisition speed, and spectral coverage. The improvements provide researchers with the means to study new molecules at an increased rate, make new identifications in space, and advance our chemical understanding of the universe.

Coupled with the advances in technology is a recent push to automate spectral assignments. Three main spectral catalogs are publicly available: the Jet Propulsion Laboratory Molecular Spectroscopy database,[7] the Cologne Database for Molecular Spectroscopy,[8] and the National Radio Astronomy Observatory's Splatalogue platform,[9] which combines information from the other two databases with information from several private catalogs maintained by laboratory groups. The databases maintain a list of molecules for which laboratory studies are available and provide catalogs that list all the assigned and predicted spectral lines and their associated frequencies and intensities. Such catalogs are incomplete for most molecules, but concerted efforts have been made to keep them up to date, at least for the most abundant molecules and for those that contribute the most lines to observational spectra.

The work is seemingly never-ending and, unfortunately, is not often supported by funding agencies. But fortunately, a few tireless heroes in the field have dedicated some of their time to maintaining those catalogs. The rest of us in the community are incredibly grateful for their work. Once a molecule has a catalog, either downloaded from a database or constructed by the group that does the laboratory analysis, the next step is to com-

FIGURE 4. ANTENNA COMPONENTS used in the Atacama Large Millimeter/Submillimeter Array (ALMA) telescope include **(a)** a cryostat, here being assembled by technician Patricio Escarate. It cools 10 receiver cartridges. The **(b)** cold receiver cartridges are paired with **(c)** warm receiver cartridges. Together, the assemblies are used to make observations in the 35–50 GHz frequency range. (Panel a courtesy of ESO/Max Alexander; panel b courtesy of ASIAA; and panel c courtesy of G. Siringo, ALMA, ESO/NAOJ/NRAO.)

pare the catalog entries with observations. A few software packages enable users to overlay on the spectra the information from the catalogs and perform a mathematical comparison. That analysis requires that one has mastered the nuances of laboratory spectroscopy and the technical details of observational astronomy.

Ideally, an automated process would exist that could reliably compare the database information with the observations being produced. The greatest strides in the field over the past few years have focused on that goal. Automated spectral-assignment routines based on statistical analysis and in some cases machine learning are now being developed. It's an enormous step forward for the field and one that's still in its infancy. Several teams are working on various aspects of the huge undertaking, with goals of combining methods once each aspect has been developed. When fully optimized, researchers may finally be able to process all the information coming from FIR telescopes without assigning the individual spectral lines by hand.

Automated spectral analysis may be a promising horizon for the field of astrochemistry, but researchers will still rely on laboratory efforts to supply the spectral information to which such programs can be applied. Technology once again leads to a gap. The next step in filling the terahertz gap is to bring the advances of FIR observatories to the laboratory. Telescope receivers are intricate, custom-built, and expensive pieces of equipment. They are designed to sit at a particular wavelength and perform long integrations in search of weak spectral features from distant molecular clouds. Building one for laboratory studies is not financially feasible because a full implementation of one device requires both custom-built equipment and support for a PhD-level expert for at least a year or two. That expense stretches beyond the budget of a laboratory managed by one investigator who relies primarily on government funding to support their students and technical staff.

Observatory funding is a different story: All observatories have highly trained technical staff who spend their time developing such devices. The only spectroscopy groups that have access to them are the ones that have close ties to observatories. Typically, both observatory and laboratory staff work at the same institution or are affiliated with the same larger research infrastructure. Generally, such research groups purchase or borrow the used and out-of-date receivers after a major facility updates its equipment. Even in the best-case scenario, the equipment being used for laboratory spectroscopic studies is one generation behind the state-of-the-art technology. Of the small number of laboratory groups working in the field, only two thus far have developed laboratory instruments using telescope receivers. The tantalizing results from their first experiments show great promise for future developments.[10,11]

Despite all the challenges associated with working in the terahertz gap, astrochemists have made major strides over the past two decades to provide the laboratory information needed to guide FIR observations of molecules in space. With the new capabilities that are now available in terms of instrumentation and data analysis, the terahertz gap is being filled. Because of the explosion of FIR observational capabilities, we are now rapidly expanding our understanding of the molecular universe. It is an exciting time to be an astrochemist!

REFERENCES

1. G. A. Blake, in *Encyclopedia of Chemical Physics and Physical Chemistry*, vol. 2, J. H. Moore, N. D. Spencer, eds., IOP (2001), p. 1063.
2. S. L. Widicus Weaver, *Annu. Rev. Astron. Astrophys.* **57**, 79 (2019).
3. P. F. Goldsmith, W. D. Langer, *Astrophys. J.* **517**, 209 (1999).
4. For *Herschel Space Observatory* data, see http://archives.esac.esa.int/hsa/whsa.
5. For data from the Stratospheric Observatory for Infrared Astronomy, see www.sofia.usra.edu/data/science-archive.
6. For observation data from the Atacama Large Millimeter/Submillimeter Array, see https://almascience.nrao.edu/aq/?result_view=observation.
7. To view the Jet Propulsion Laboratory Molecular Spectroscopy database, see https://spec.jpl.nasa.gov.
8. To access the Cologne Database for Molecular Spectroscopy, see https://cdms.astro.uni-koeln.de.
9. To view data from the National Radio Astronomy Observatory's Splatalogue platform, see https://splatalogue.online/advanced1.php.
10. N. Wehres et al., *Phys. Chem. Chem. Phys.* **20**, 5530 (2018).
11. I. Tanarro et al., *Astron. Astrophys.* **609**, A15 (2018).
12. S. L. Widicus Weaver et al., *Astrophys J. Suppl. Ser.* **232**, 3 (2017). PT