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## Millimeterwave and Submillimeterwave Laboratory Spectroscopy in Support of Observational Astronomy

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### Keywords

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### Abstract

The recent advancements in far-infrared (far-IR) astronomy brought about by the *Herschel*, SOFIA, and ALMA observatories have led to technological advancements in millimeterwave and submillimeterwave laboratory spectroscopy that is used to support molecular observations. This review gives an overview of rotational spectroscopy and its relationship with observational astronomy, as well as an overview of laboratory spectroscopic techniques focusing on both historical approaches and new advancements. Additional topics discussed include production and detection techniques for unstable molecular species of astrochemical interest, data analysis approaches that address spectral complexity and line confusion, and the current state of and limitations to spectral line databases. Potential areas for new developments in this field are also reviewed. To advance the field, the following challenges must be addressed:

- Data acquisition speed, spectral sensitivity, and analysis approaches for complex mixtures and broadband spectra are the greatest limitations—and hold the greatest promise for advancement—in this field of research.
- Full science return from far-IR observatories cannot be realized until laboratory spectroscopy catches up with the data rate for observations.
- New techniques building on those used in the microwave and IR regimes are required to fill the terahertz gap.

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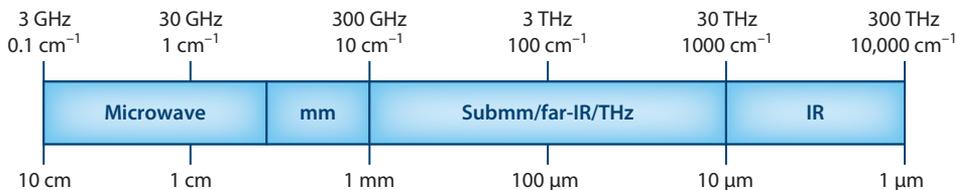
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## 1. INTRODUCTION

Molecular spectroscopy and observational astronomy have long been complementary fields, extending back to the detection of CH, the first molecule identified in space, by Swings & Rosenfeld (1937). The field was advanced by the pioneering work of Gerhard Herzberg, beginning in 1941 with the laboratory and observational investigation of CH<sup>+</sup> (Douglas & Herzberg 1941). This interdependence continues into modern research, as the construction of far-infrared (far-IR) observatories has provided much of the motivation for the development of radiation sources, detectors, and optics that are now routinely used in millimeter and submillimeter laboratory spectroscopy. This push forward in technology has led to a heyday of molecular astronomy, with an explosion of new capabilities in both observations and laboratory techniques over the past decade. This review provides an overview of the interplay between observational capabilities in the far-IR and the accompanying advancements in laboratory spectroscopy that cover this range of the electromagnetic spectrum.

As shown in **Figure 1**, the far-IR spectral region encompasses the wavelength range of 15  $\mu\text{m}$ –1 mm; hence, it is often referred to as the submillimeter range. This corresponds to frequencies of 300 GHz–20 THz, or in units commonly used in experimental IR studies, 10–667 wavenumbers ( $\text{cm}^{-1}$ ). It is in this range that small molecules display spectral signatures of pure rotation, large molecules display spectral signatures of low-frequency vibration (i.e., torsion), and molecules with low barriers to internal movement display spectral signatures of “fluxional” behavior (i.e., inversion or rotation of functional groups, scrambling of protons, etc.). As such, the submillimeter range offers a plethora of spectral fingerprint information that can be used to uniquely identify a given molecule. The bulk of the work in molecular astrophysics has focused on the pure



**Figure 1**

Graphical representation of the microwave, millimeter (mm), submillimeter (Submm), and infrared (IR) ranges of the electromagnetic spectrum.

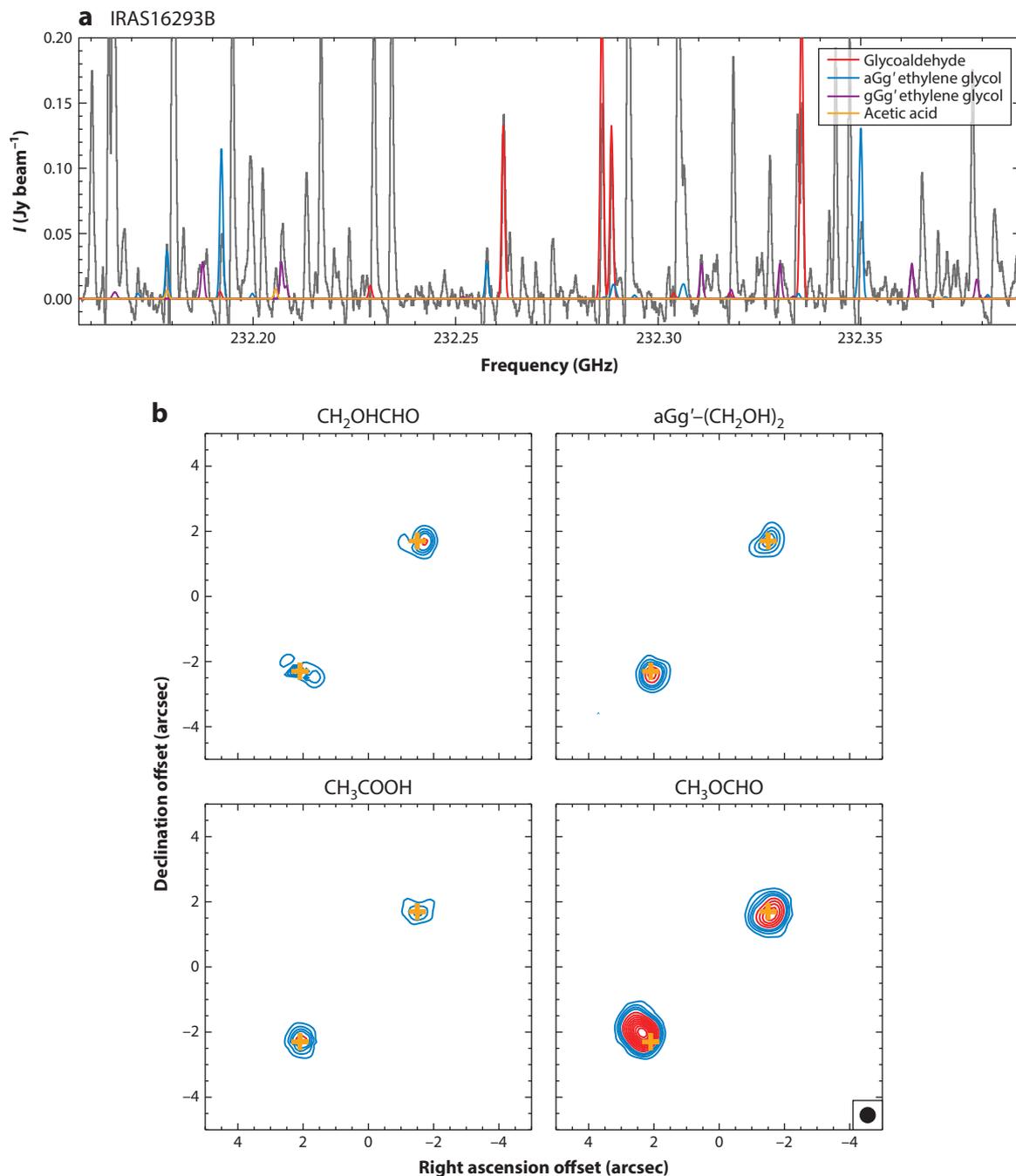
rotational signatures of small molecules, because those are the transitions that can be used to perform a Boltzmann analysis to quantitatively determine density and temperature. Only gas-phase molecules that are free to rotate and those that are polar, or possess a permanent electric dipole moment, have a pure rotational spectrum; as such, observations in this wavelength region are limited to polar gas-phase species that are linear, symmetric tops, or asymmetric tops (i.e., those molecules for which at least one principal moment of inertia is unequal to the other two). IR observations can be used to detect vibrational bands of symmetric molecules that do not possess a dipole moment, as well as molecules trapped in ices on grain surfaces in cold regions. But these spectra are typically not of sufficient resolution to uniquely identify individual rovibrational lines and therefore cannot be used to identify a specific molecule in most cases. This is particularly true for the IR spectra of ices, where molecules that contain similar functional groups (i.e., structural subcomponents of a molecule like a  $-\text{CH}_3$  group or an  $-\text{OH}$  group) have overlapping spectral features. Pure rotational spectroscopy therefore offers the most straightforward path to identification and quantification of molecules in astronomical sources because the spectral signatures are unique and structure specific.

Rotational spectroscopy, and hence molecular astronomy, began at much longer wavelengths in the radio and microwave regimes, primarily because this was the region where spectroscopic equipment was historically available. The first molecular spectrum measured in this range was the inversion spectrum of ammonia ( $\text{NH}_3$ ) at 1.1 cm (Cleeton & Williams 1934). The development of radar for World War II led to a surplus of equipment that spawned the development of radio and microwave spectroscopic techniques, culminating with the MASER experiments conducted by Townes and coworkers that directly led to lasers (Gordon et al. 1955). The techniques typically used in laboratory rotational spectroscopic investigations have therefore been gradually built to access the submillimeter region based on technology from the original radio or microwave experiments that rely on the electronic generation of light. Although far-IR radiation can be generated through difference frequency techniques using IR or optical lasers, most of those experimental approaches result in broadband, low-resolution spectra and do not provide the high-resolution spectra needed to guide observational astronomy; the exceptions to this are the tunable far-IR approaches developed by Evenson and coworkers (Odashima et al. 1999) and Blake and coworkers (Farhoomand et al. 1985, Blake et al. 1991). Up until a decade ago, there were significant limitations in power and frequency coverage offered by all far-IR sources regardless of the method for light generation. Therefore, spectral applications in the submillimeter range were limited to astronomical techniques and a handful of simple spectroscopic experiments. However, these historical challenges have recently been overcome with the next generation of far-IR astronomy ushered in with the launch of the *Herschel Space Observatory* in 2009 and the commissioning of the Atacama Large Millimeter/submillimeter Array (ALMA) in 2011 coupled with the new technology developments tied to the communications and security sectors. Because of these technology developments, the submillimeter regime has been opened for routine investigation. Most millimeter

and submillimeter laboratory spectrometers focus on the range of 100 GHz–1 THz, but new spectrometers are starting to push to frequencies above 1 THz. This region, called the terahertz gap (THz-gap), is the final wavelength region to be accessed by commercial spectrometers.

Far-IR observations have moved from a data-poor field to a data-rich explosion of information over the past decade. *Herschel* launched in 2009, providing a wealth of high-sensitivity, high-resolution, broadband spectral information on a range of sources. Before *Herschel*, single-dish ground-based observatories, such as the NRAO (National Radio Astronomy Observatory) 12-m telescope (currently managed by the University of Arizona), the Caltech Submillimeter Observatory (CSO), the James Clerk Maxwell Telescope (JCMT), the Institut de Radioastronomie Millimétrique (IRAM) 30-m telescope, and the Atacama Pathfinder Experiment (APEX), led the field in terms of spectroscopic observations of molecules in interstellar clouds and star-forming regions. Limited by the bandwidth of the receivers and spectrometers ( $\sim 10$ –500 MHz), the observing strategy was primarily one molecule at a time, one line at a time, one source at a time. There was some pioneering work collecting unbiased spectral line surveys of a few key sources, the most comprehensive of which were the surveys of the Orion-KL (Sutton et al. 1985; Blake et al. 1986, 1996; Schilke et al. 1997) and Sgr B2 (Nummelin et al. 1998, 2000) star-forming regions. These surveys set the standard for molecular identification in interstellar sources and revealed the potential complexity of molecular identification arising from the inhomogeneity of the sources and the potential for spectral line confusion. To address the issue of inhomogeneity, interferometric observations were employed to map the spatial distributions of molecules in these sources. Interferometers such as the Plateau de Bure Interferometer (PdBI), the Smithsonian Millimeter Array (SMA), the Owen's Valley Radio Observatory (OVRO), the Berkeley-Illinois-Maryland Array (BIMA), and later the Combined Array for Millimeter/Submillimeter Astronomy (CARMA) were used for imaging molecular distributions in interstellar regions of star and planet formation. The spatial scales that can be probed by these arrays is on the order of a few arcseconds at best, limiting the types of sources that could be imaged to star-forming cores and the extended structure of an accretion disk. The recent implementation of ALMA has shifted the paradigm in the field, offering subarcsecond spatial resolutions and broadband spectral line observing capabilities such that now each observation produces a high spatial resolution image, where each pixel has its own broadband spectral information. An example from the ALMA Protostellar Interferometric Line Survey (PILS) of the low-mass protostar IRAS 16293–2422 is shown in **Figure 2**. For the first time, astrochemists can observe multiple spectral lines from multiple molecules in one observation while determining the spatial distributions at extraordinary resolution. Coupled with this is advancement in both sensitivity and bandwidth for receivers that has increased the data acquisition speed for single-dish telescopes by orders of magnitude over previous techniques. As such, broadband, high-resolution, high-sensitivity spectral information coupled with high-resolution images has become the standard of the field. The tools needed to analyze these complicated data sets, and the fundamental laboratory information required to do so, are in urgent need of advancement. Although the main goal of this review is to overview the current capabilities available for such studies, the limitations of the field and the needs for new developments are also addressed.

This review is structured as follows. First, a basic overview of rotational spectroscopy and molecular observational astronomy is given, including a discussion of limitations and data needs. Then laboratory spectroscopic techniques are reviewed, focusing first on the historical approaches to spectroscopy in the millimeter and submillimeter regime, followed by new advancements made possible by technological developments in recent years. Various approaches for production of unstable molecular species that are the linchpins of astrochemistry are then discussed. The issues faced by both laboratory and observational investigations concerning spectral complexity and line confusion, and approaches being developed to address these issues, are presented. The current



**Figure 2**

(a) A section of the Atacama Large Millimeter/submillimeter Array (ALMA) Protostellar Interferometric Line Survey (PILS) of IRAS 16293B. (b) Images of the emission of several complex organic molecules identified in the spectrum in panel (a). Figure adapted from Jørgensen et al. (2016, their figure 7 and appendix B) with permission from *Astronomy & Astrophysics*, ©ESO.

state of spectral databases is reviewed, and the associated limitations are discussed. And finally, the potential areas for new developments in this field are reviewed.

## 2. ROTATIONAL SPECTROSCOPY AND MOLECULAR OBSERVATIONS

Before the applications of spectroscopy to astrochemistry can be discussed, a general overview of rotational spectroscopy and its application to observational astronomy is required. For a detailed and comprehensive treatment of the topic, the reader is referred to related textbooks, including (but not limited to) those written by Townes & Schawlow (1975), Gordy & Cook (1984), and Bernath (2005). A basic overview of the general principles is given here.

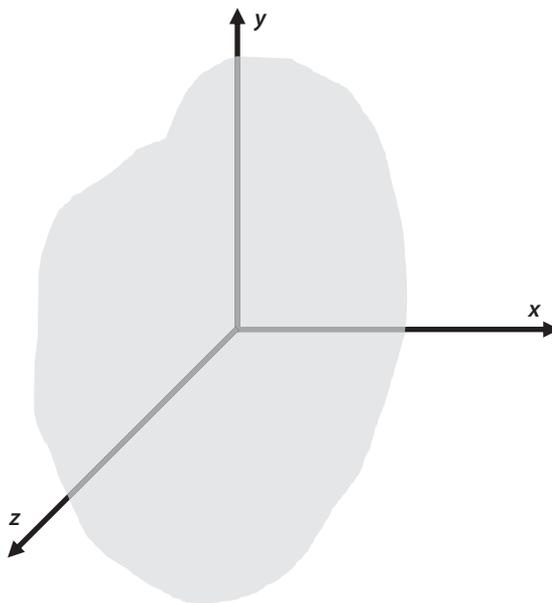
### 2.1. Rotational Spectroscopy

Rotational spectroscopy is inherently linked to molecular structure. As shown in **Figure 3**, all three-dimensional objects, including molecules, have unique structures that give rise to three perpendicular principal axes and three moments of inertia about these axes. For a molecule, the moment of inertia,  $I$ , is related to the atomic masses ( $m_i$ ) and their radii from the center of mass ( $r_i$ ) given by

$$I = \sum_i m_i r_i^2. \quad 1.$$

The rotational energy levels of a molecule can be expressed in terms of the moments of inertia and the angular momentum ( $L$ ) of the molecule about each axis by the relationship

$$E = \frac{L_x^2}{2I_x} + \frac{L_y^2}{2I_y} + \frac{L_z^2}{2I_z}. \quad 2.$$



**Figure 3**

Three-dimensional objects have three perpendicular axes with unique moments of inertia about each axis.

These energy levels can be found by solving the Schrödinger equation using the corresponding angular momentum operators via the relationship

$$\hat{H}\Psi = E\Psi = \frac{\hat{L}_x^2}{2I_x} + \frac{\hat{L}_y^2}{2I_y} + \frac{\hat{L}_z^2}{2I_z}. \quad 3.$$

The Hamiltonian operator  $\hat{H}$  can be written in terms of body-fixed coordinates such that

$$\hat{H} = \frac{\hat{J}_a^2}{2I_a} + \frac{\hat{J}_b^2}{2I_b} + \frac{\hat{J}_c^2}{2I_c}, \quad 4.$$

where  $J_i$  is the angular momentum quantum number about the body-fixed axis  $i$ , and  $I_i$  is the moment of inertia about axis  $i$ . The three primary axes defined in body-fixed coordinates  $a$ ,  $b$ , and  $c$  and their corresponding moments of inertia  $I_i$  are found by diagonalizing the three-dimensional moment of inertia tensor. The rotational constants  $A$ ,  $B$ , and  $C$  are defined in terms of these  $I_i$  values as

$$A = \frac{b}{8\pi^2 I_a}, B = \frac{b}{8\pi^2 I_b}, \quad \text{and} \quad C = \frac{b}{8\pi^2 I_c} \quad 5.$$

in units of Hz, where  $b$  is Planck's constant, and each rotational constant,  $A$ ,  $B$ , and  $C$ , corresponds to a particular primary axis ( $a$ ,  $b$ , and  $c$ , respectively).

Spherical tops have three equivalent moments of inertia, and as such have full symmetry and do not display rotational spectra. For the other classifications of rigid rotors, expressions for the rotational energy levels can be found. The energy levels of a linear molecule (where  $I_b = I_c$  and  $I_a = 0$ ) are given by

$$E_J = \frac{\hbar^2}{2I} J(J+1) = BJ(J+1). \quad 6.$$

The energy levels for symmetric tops in the prolate (i.e.,  $I_a < I_b = I_c$ ) or oblate (i.e.,  $I_a = I_b < I_c$ ) limits, respectively, are given by

$$E_{JK} = BJ(J+1) + (A-B)K^2 \quad \text{and} \quad E_{JK} = BJ(J+1) + (C-B)K^2, \quad 7.$$

where  $K$  is the projection of  $J$  onto the axis of the molecule having the unique moment of inertia. The case of asymmetric tops, in which three unique moments of inertia are found, is much more difficult because general analytical solutions to the Schrödinger equation are not possible. The energies of the first few rotational levels for a rigid asymmetric top are given in the textbooks listed above. Computer programs such as Pickett's SPCAT program (Pickett et al. 1998) can also be used to tabulate rotational energies for asymmetric tops.

For linear molecules in which only one moment of inertia is defined, the energy levels are labeled simply with  $J$  quantum numbers. For symmetric top molecules, the energy levels are labeled by both values of  $J$  and  $K$  and are denoted as  $J_K$ . For asymmetric top molecules,  $K$  is not a good quantum number because  $J$  can be projected onto any axis. Nonetheless,  $K$  can still be used to specify energy levels, and a set of  $K$  values labeled according to the corresponding principal axis are used. These asymmetric top energy levels are typically denoted  $J_{K_a, K_c}$ , though in some older literature  $J_{K_p, K_o}$  or  $J_{K_{-1}, K_{+1}}$  are used to designate the near-prolate and near-oblate limits. Other variations of asymmetric top energy level labels can be found in the literature, but the standard in the field is now  $J_{K_a, K_c}$ . This is based on the formalism set forth by Watson (1968) when solving the Hamiltonian for an asymmetric top with centrifugal distortion effects. The Watson A

and S reductions of the nonrigid asymmetric top Hamiltonian are used in all modern rotational spectroscopy.

The matter of centrifugal distortion leads to complicated additions to the equations presented here, and the specific mathematical formulations to account for its effects are beyond the scope of this review. Nonetheless, this is an important consideration when using laboratory spectral information for observational astronomy, and it must be mentioned. Molecules are typically not rigid rotors, especially at higher rotational energies where vibration–rotation coupling can become important and centrifugal distortion becomes significant. Centrifugal distortion constants must be used to alter the equations given above to account for these effects. Watson’s A and S reductions (Watson 1968) give rise to the Hamiltonians used for near-prolate and near-oblate asymmetric tops, respectively, where expansions are used to extend the energy-level expressions and account for the centrifugal distortion effects. Centrifugal distortion constants are particularly important when examining spectra in the far-IR regime, where high values of  $J$  and  $K$  must often be considered. As such, quartic, sextic, and in many cases octic centrifugal distortion constants (or higher) must be included in the Hamiltonian. Care must be taken to include the appropriate centrifugal distortion constants when extrapolating a spectral prediction to submillimeter wavelengths based on microwave spectroscopic studies.

Selection rules for rotational transitions are important considerations in observational astronomy. For allowed rotational transitions, the transition dipole moment must be nonzero; in all cases here, that means a nonzero dipole moment along the primary axis involved in the transition. The basic set of selection rules, rather than their detailed mathematical derivation, is given here; the  $M$  quantum number is not discussed here because it is not involved in state labels. Transitions with  $\Delta J = \pm 1$  are allowed for all types of molecules;  $\Delta J = +1$  are R-type transitions, whereas  $\Delta J = -1$  are P-type transitions. Therefore, based on the energy expressions given above, sets of rotational transitions involving  $J$  values that differ by 1 are separated by  $\sim 2B$  in frequency space. Asymmetric top molecules, as well as some cases of linear or symmetric top molecules with other contributions to the angular momentum besides  $J$ , also have transitions allowed for  $\Delta J = 0$ ; these are Q-type transitions. In the case of linear molecules,  $\Delta K = 0$  is required, whereas  $\Delta K = \pm 1$  transitions are also possible for symmetric and asymmetric tops. For asymmetric tops,  $a$ -type transitions, i.e.,  $\Delta K_a = 0 (\pm 2, \pm 4\dots)$  and  $\Delta K_c = 1 (\pm 3, \pm 5\dots)$ , are allowed when the dipole moment along the  $a$  axis is nonzero. Likewise,  $b$ -type transitions, i.e.,  $\Delta K_a = 1 (\pm 3, \pm 5\dots)$  and  $\Delta K_c = 1 (\pm 3, \pm 5\dots)$ , are allowed when the dipole moment along the  $b$  axis is nonzero; and  $c$ -type transitions, i.e.,  $\Delta K_a = 1 (\pm 3, \pm 5\dots)$  and  $\Delta K_c = 0 (\pm 2, \pm 4\dots)$ , are allowed when the dipole moment along the  $c$  axis is nonzero.

Most of the transitions observed in observational astrochemistry are pure rotational transitions, in which the rotational states change but the vibrational and electronic states for the molecule do not. There are cases, however, where rovibrational or vibronic transitions can be observed. In those cases, the selection rules become more complicated and depend on the type of transition involved. More commonly there are cases in which a molecule is detected through pure rotational transitions within an excited vibrational state. In those cases the rotational selection rules described above still apply.

There are many caveats to the very general overview of rotational spectroscopy given here, and special cases arise that lead to deviations from the standard models. Most notably for astrochemistry, the influence of fluxional behavior can have significant effects on the rotational spectrum. When a molecular functional group can rotate or invert with a low barrier hindering the internal motion, this motion couples with the rotation of the molecule and leads to splitting of the rotational energy levels. This gives rise to splitting of the rotational lines that complicates the spectrum and its assignment. Additional complicating factors include, but are not limited to,

hyperfine splitting arising from angular momentum coupling with the nuclear spin of atoms in the molecule and Coriolis coupling arising from vibration–rotation interaction. For these cases, the reader is referred to the spectroscopy textbooks listed above as well as the extensive molecular spectroscopy literature related to each of these effects.

## 2.2. Rotational Spectroscopy as Applied to Observational Astronomy

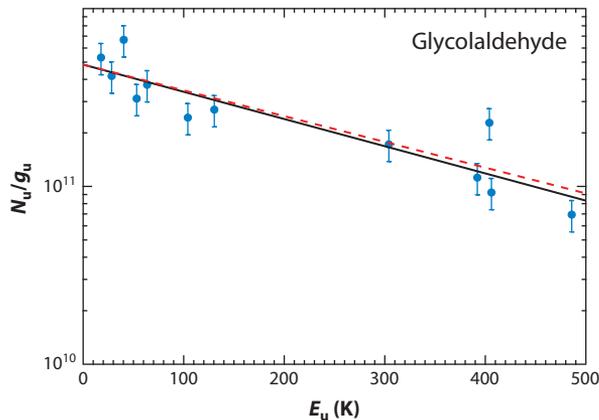
Rotational spectroscopy is a useful tool in observational astronomy because it directly probes the physical properties of molecular gas in interstellar clouds. Dense clouds are the birthplaces of stars and young solar systems, which are the most chemically rich sources in the ISM. But the high densities of these sightlines make IR and optical investigations difficult, because the clouds are opaque to this radiation. However, far-IR light can penetrate even the densest regions of interstellar space and as such offers a means to remotely investigate the molecules composing these objects. It is the emission of rotational energy from molecular gas that leads to the cooling of molecular clouds during star formation; otherwise gravitational collapse would lead to an increased kinetic temperature that would detrimentally impact the star-formation process. Although there are a few sightlines with a background source that allow for absorption spectroscopy to be conducted (Lucas & Liszt 1993), emitted radiation is most commonly observed during far-IR observations of interstellar clouds.

The basic relationships for the interaction between light and matter govern the spectroscopic signals that are observed through molecular line observations of the ISM. For a review, the reader is referred to the introductory chapter of Bernath's textbook (Bernath 2005), or for a more in-depth analysis of interstellar radiation fields and their interactions with atoms and molecules, the textbook by Rybicki & Lightman (1986). For the specific case of molecular emission in the limit of local thermodynamic equilibrium (LTE), Goldsmith & Langer (1999) provide a detailed derivation of the rotation diagram approach, which is the focus of the material presented here.

A rotation diagram is a quantitative method for determining the density and rotational temperature of a molecular gas based on a Boltzmann analysis of the relative spectra line intensities for a set of molecular transitions. An example for glycolaldehyde from the ALMA PILS survey shown above is given in **Figure 4**. This treatment is limited to cases in which LTE conditions can be assumed. This approximation works remarkably well for most molecules in interstellar clouds and star-forming regions, where the overall kinetic temperature of the gas may not be uniform, but a given molecule can be described with a unique set of physical parameters and one well-defined temperature. For this analysis to be robust, the emission must also be optically thin, and the background radiation brightness must be negligible compared to the line strengths. The integrated intensity of a transition,  $\int_{-\infty}^{\infty} T_b dv$ , is

$$\int_{-\infty}^{\infty} T_b dv = \frac{hc^3}{8\pi kv^2} Ag_u \frac{N_T}{Q(T_{\text{rot}})} e^{-E_u/kT_{\text{rot}}}, \quad 8.$$

where  $\nu$  is the frequency of the rotational transition,  $N_T$  is the column density of the molecular gas,  $A$  is the Einstein  $A$  coefficient for the transition,  $g_u$  is the upper state degeneracy,  $Q(T_{\text{rot}})$  is the partition function,  $T_{\text{rot}}$  is the rotational temperature of the molecule, and  $E_u$  is the transition upper state energy. A rotation diagram is constructed by plotting  $\ln\{[(8\pi kv^2)/(bc^3 Ag_u)] \int_{-\infty}^{\infty} T_b dv\}$  versus  $E_u$ . If the molecular gas is in LTE and undergoing optically thin emission, the plot gives a line with slope inversely proportional to  $T_{\text{rot}}$  and with intercept equal to  $\ln[N_T/Q(T_{\text{rot}})]$ . Therefore, a rotation diagram can be used to directly extract quantitative information for both the column density and temperature of the molecule. For a source with multiple temperature components, multiple



**Figure 4**

Rotation diagram for glycolaldehyde from the Atacama Large Millimeter/submillimeter Array (ALMA) Protostellar Interferometric Line Survey (PILS) of IRAS 16293-2422. The solid line shows the least squares fit to the observational data, and the dashed red line gives the fit for a temperature of 300 K. Adapted from Jørgensen et al. (2016, their figure 9) with permission from *Astronomy & Astrophysics*, ©ESO.

lines can be fit to the rotation diagram, and the temperatures and densities can be extracted. For a case in which the emission is not optically thin, optical depth corrections must be applied to some or all the data points before the linear fit is performed (Goldsmith & Langer 1999).

The integrated intensity of a transition with a Gaussian line shape is given by

$$\int_{-\infty}^{\infty} T_b dv = 1.064 T_b \Delta v, \quad 9.$$

where  $T_b$  is the brightness temperature of the line and  $\Delta v$  is the full width at half maximum (FWHM) of the line. The brightness temperature  $T_b$  is approximated as  $T_{MB}$ , the antenna temperature of the line ( $T_A^*$ ) corrected to the main beam temperature scale by the relationship  $T_{MB} = T_A^*/\eta$ , where  $\eta$  is the aperture efficiency of the telescope. The main beam temperature must also be corrected for beam dilution in the case where the molecular emission and the beam size of the telescope do not match. For this,  $T_b = BT_{MB}$ , where  $B$  is the beam filling factor;  $B$  is calculated from the relationship between the source size,  $\theta_s$ , and the beam size,  $\theta_b$ , by

$$B = \frac{\theta_s^2}{\theta_s^2 + \theta_b^2}. \quad 10.$$

For interferometric observations,  $T_A^*$  (in K) can be determined by

$$T_A^* = \frac{1.22 \times 10^6 Int}{\theta_A \theta_B \nu^2}, \quad 11.$$

where  $\theta_A$  and  $\theta_B$  are the beam FWHMs,  $Int$  is the peak intensity in Janskys per beam, and  $\nu$  is the frequency of the transition in gigahertz.

The Einstein A coefficients of the molecular lines can be calculated from the information given in the catalog files associated with Pickett's CALPGM program suite and listed in the rotational spectral line databases maintained by NASA's Jet Propulsion Laboratory (JPL; <https://spec.jpl.nasa.gov/>) (Pickett et al. 1998), the Cologne Database for Molecular Spectroscopy (CDMS; <https://cdms.astro.uni-koeln.de/>) (Endres et al. 2016), and the Splatalogue Database

(<https://www.cv.nrao.edu/php/splat/>), which was developed in support of the ALMA observatory and combines information from the JPL and CDMS databases as well as several other sources of spectral information. The catalog files are generated by the SPCAT program within the CALPGM program suite. Such files are available in these public databases for a wide variety of species. In these catalog files, the line strengths are given as the log of the line intensity at 300 K. A given observed line may involve several degenerate transitions with different sets of quantum numbers occurring at the same frequency. In these cases, the catalog intensities for the degenerate transitions can be summed using the relationship

$$I = \sum_1^j 10^{\log I_j}. \quad 12.$$

The intensity of these transitions is given in the catalogs in units of  $\text{nm}^2 \text{ MHz}$ ; these units were chosen so that the catalog would follow the format of the HITRAN database. The  $A$  coefficient can then be calculated by the relationship

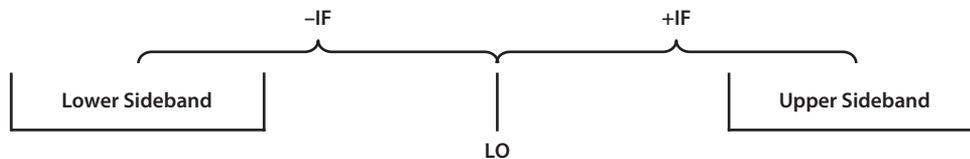
$$A = \frac{2.7964 \times 10^{-16} I \nu^2 Q(T)}{g_u (e^{-E_l/kT} - e^{-E_u/kT})} \quad 13.$$

when  $\nu$  is in MHz and  $I$  is in  $\text{nm}^2 \text{ MHz}$  (Pickett et al. 1998).

An important consideration when performing a rotation diagram analysis is the molecular partition function. When a molecule is included in one of the online databases, or a spectral catalog using Pickett's SPCAT is employed, it is critical that the partition function given as an output of the SPFIT program be used for analysis. This is because SPCAT uses internal partition function information to numerically tabulate the line intensities at the temperature specified for the catalog using the information contained in the fit for that particular molecule. Using another form of the partition function introduces error into the line strengths and, therefore, the rotation diagram analysis. One must use care when determining values of the partition function at temperatures other than those listed in the catalog information; appropriate expressions for extrapolation or interpolation of the partition function values must be used, especially at extremely high or low temperatures.

### 2.3. Observational Spectral Analysis

Putting together the basics of rotational spectroscopy and the basics of observational astronomy now gives rise to the question, How does one go about collecting and analyzing spectral information from a far-IR observatory? These observatories use high-resolution spectrometers coupled with heterodyne receivers to collect highly sensitive spectra. Heterodyne detection in radio astronomy has historically limited the bandwidth of observations to a few tens or hundreds of megahertz in spectral coverage. In a heterodyne detection scheme, overviewed in **Figure 5**, the local oscillator (LO) frequency, the intermediate frequency (IF), and the bandwidth values are chosen such that the molecular lines of interest are found within the frequency window of observation. Care must be taken to guarantee that the setup ensures the appropriate spectral coverage and frequency resolution such that the lines of interest can be fully characterized. Some observatories have sideband rejection systems, but most collect data in a double-sideband observing mode, meaning that the image and the frequency sidebands are superimposed onto one another. Spectral lines from both sidebands must be considered during analysis. If spectral complexity is a challenge, which is often the case with warm star-forming regions harboring dozens of molecules, multiple observations can be collected using slight frequency offsets in either the LO or IF values such



**Figure 5**

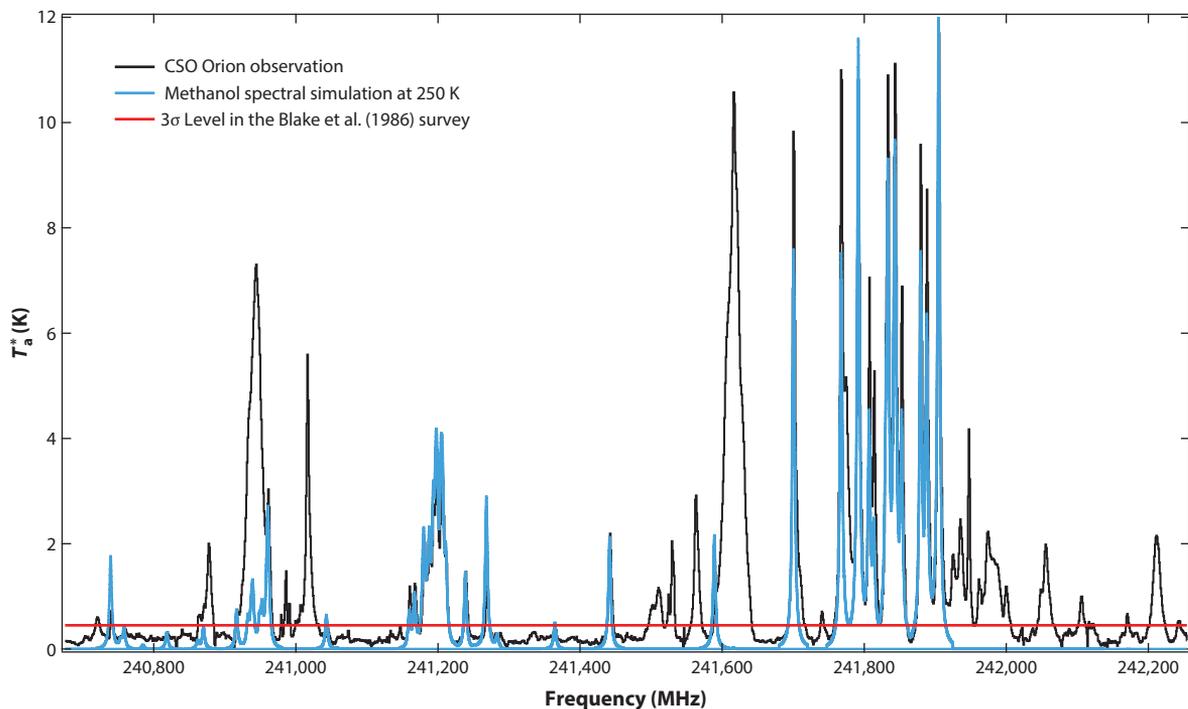
The frequency coverage of a heterodyne receiver, indicating the local oscillator frequency (LO) and intermediate frequency (IF) and the resultant sidebands.

that spectral lines are sampled many times with shifts in the sidebands. With sufficient sampling (typically using a redundancy of at least eight), the observer can deconvolve the double-sideband spectra into their single-sideband components. Double-sideband observations coupled with spectral deconvolution can therefore be used to rapidly cover a large swath of frequency coverage for a given source, revealing a broadband spectrum containing lines from multiple molecular components. With the implementation of the broadband spectral observing capabilities of *Herschel*, SOFIA (Stratospheric Observatory for Infrared Astronomy), and ALMA, this is now the standard in the field of far-IR astronomy. Analysis of such data sets is challenging, even for a single double-sideband observation, because the spectral lines are often blended, and line confusion can become a problem. Reliable rest frequencies for molecular lines and intensity information are needed for all molecules detected in a given source to be able to fully analyze such data sets. A concerted effort is therefore needed to supply both the laboratory molecular spectroscopic information and the spectral analysis tools to analyze these observational results.

Traditionally, observers approached spectral data analysis by fitting one line at a time for one molecule at a time in one source at a time. However, with the advent of broadband receivers and spectrometers in far-IR astronomy, such approaches are not reasonable because of the sheer number of lines that must be analyzed. Several software packages have been developed to aid astronomers in broadband spectral analysis; these include the XCLASS/MAGIX program suite (Möller et al. 2013), CASSIS (<http://cassis.irap.omp.eu>), WEEDS (Maret et al. 2011), and GOBASIC ([http://chemistry.emory.edu/faculty/widicusweaver/gobasic/GOBASIC\\_4.4.tar.gz](http://chemistry.emory.edu/faculty/widicusweaver/gobasic/GOBASIC_4.4.tar.gz); Rad et al. 2016). These programs differ in their respective approaches to spectral analysis—some focus on guiding fits for rotational diagram analysis, whereas others seek to completely automate the fitting process. Likewise, some of these programs offer fitting routines for one molecule at a time, whereas others provide iterative, multimolecule fitting. Regardless of the approach, all these programs take input spectral information in the SPCAT catalog format. The user must therefore be well versed in the details of the catalog format for each molecule under consideration and the proper use of the information contained therein.

Databases such as the JPL catalog (Pickett et al. 1998), CDMS (Endres et al. 2016), and Splatalogue contain spectral information in the SPCAT catalog format for hundreds of molecules that have either been detected in space or are suspected to be candidates for detection. Although the information contained in these catalogs is extensive, it is not comprehensive. Key molecules that were identified as “interstellar weeds” by the Workshop on Laboratory Spectroscopy in Support of *Herschel*, SOFIA, and ALMA<sup>1</sup> have been comprehensively characterized for all frequencies up to those accessed by the HIFI instrument on *Herschel*. These interstellar weeds are molecules with complicated and strong spectral signatures that cover the entire millimeter and submillimeter regime and are the major contributors to spectral line density in interstellar observations. Included on this list are methanol (CH<sub>3</sub>OH), methyl formate (CH<sub>3</sub>CHO), dimethyl ether

<sup>1</sup> See the report available at [http://www.submm.caltech.edu/labspec/Workshop\\_Report\\_Final.pdf](http://www.submm.caltech.edu/labspec/Workshop_Report_Final.pdf).



**Figure 6**

Spectrum of Orion-KL taken in a broadband line survey using the Caltech Submillimeter Observatory (CSO). This spectrum shows the spectral complexity arising from methanol, one of the dominant interstellar weeds, and the noise level of this survey as compared to that obtained by Blake et al. (1986). This figure was constructed from data available in Widicus Weaver et al. (2017).

( $\text{CH}_3\text{OCH}_3$ ), ethyl cyanide ( $\text{CH}_3\text{CH}_2\text{CN}$ ), vinyl cyanide ( $\text{C}_2\text{H}_3\text{CN}$ ), sulfur dioxide ( $\text{SO}_2$ ), methyl cyanide ( $\text{CH}_3\text{CN}$ ), cyanoacetylene ( $\text{HC}_3\text{N}$ ), acetaldehyde ( $\text{CH}_3\text{CHO}$ ), and their isotopologs. An example of the spectral complexity arising from methanol is shown for the Orion-KL region in **Figure 6**. For other molecules included in the catalogs, spectral information may be limited to certain frequency ranges, depending on the information available in the literature. Likewise, not all interstellar molecules are included in the catalogs, as the catalog entries are based on the information provided by the authors of the laboratory investigations. In addition, information for excited vibrational states and isotopologs may not be available in the catalogs or the literature. The JPL Catalog and CDMS often have complimentary rather than overlapping information, where a given molecule is listed in only one catalog. Splatalogue seeks to resolve this issue and pulls information from both databases, as well as other sources of information including private spectral catalogs that were historically maintained by members of the molecular spectroscopy community. Care should be taken to use the most recent information available for a given molecule by comparing the documentation provided by the catalogs.

Because these databases have gaps in coverage for some species and are also lacking information for some species, analyzing a complicated observational data set can be challenging. Most of the known interstellar molecules are included in the catalogs with coverage up to  $\sim 300$  GHz. Fortunately, this covers the 3 mm and 1 mm receiver bands most frequently used at single-dish observatories for ground-based observations of molecular spectra. But for ALMA, *Herschel*, and SOFIA observations, this information is inadequate. Although a concerted effort to complete analysis for

the interstellar weeds was undertaken before *Herschel* launched, ALMA's routine observations at frequencies above 300 GHz show that key spectral information is still lacking for many known interstellar molecules. Most notably, excited vibrational states and isotopologs have not been comprehensively characterized for most molecules. As observational astronomy advances to higher and higher frequencies, laboratory efforts to provide the critical spectroscopic data must also advance.

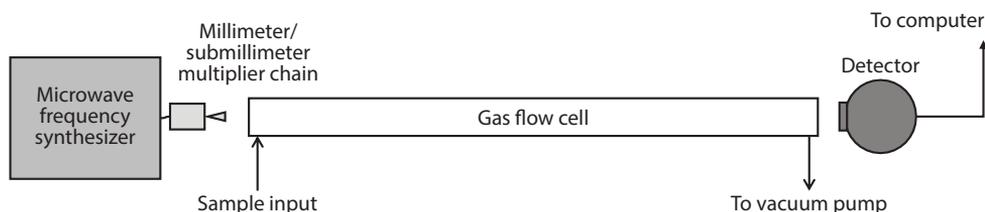
### 3. LABORATORY MILLIMETER AND SUBMILLIMETER SPECTROSCOPIC TECHNIQUES

Advancement of laboratory spectral capabilities to support observational astronomy in the far-IR relies on an increase in frequency coverage, spectral sensitivity, and spectral acquisition speed compared to current techniques. The current state of the art in millimeter and submillimeter spectroscopic techniques and the limitations on pushing forward in each of these aspects are discussed below.

#### 3.1. Frequency-Domain Absorption Spectrometers

Direct absorption spectrometers such as the one shown in **Figure 7** dominate millimeter and submillimeter spectroscopy. In this type of experiment, a long-pathlength cell contains the gaseous molecular sample, and the input signal passing through this cell is detected after only a few passes. The spectra generally have Doppler-limited linewidths, and the dynamic range of the setup is limited by the type of detector used. In this simple Beer–Lambert law experiment, the signal-to-noise ratio (SNR) of the spectrum is ideally limited by the pathlength that the radiation travels through the sample. However, there are losses at the cell walls if a waveguide cell is not used; such a setup is not realistic due to the small waveguide size in this wavelength regime. The attenuation of the radiation power during propagation through the cell limits the possible number of passes and, hence, the overall SNR that can be achieved. Lock-in detection is used to further enhance the SNR, resulting in second-derivative lineshapes. The minimum detectable absorption coefficient is  $\alpha_{\min} \geq 10^{-7} \text{ cm}^{-1}$ , depending on the pathlength of the spectrometer. Typical spectrometers cover the frequency range from 50 GHz to 1 THz, with scanning speeds of  $\sim 10$  GHz per hour.

Historically, such systems used klystron or backward wave oscillator (BWO) technology as the source for submillimeter radiation. Examples include, but are not limited to, those employed in the De Lucia lab at The Ohio State University, the University of Cologne spectroscopy group led first by Winnewisser and later by Schlemmer, and the Kisiel lab at the University of Warsaw. Although this technology had been used for submillimeter spectroscopy for decades, the phase stability and tuning reproducibility of such sources was not as reliable as diode-based frequency multipliers. The tunable far-IR sources developed by Evenson and coworkers (Odashima et al. 1999)



**Figure 7**

Schematic of a direct absorption millimeter/submillimeter spectrometer.

using difference frequency generation from photomixing CO<sub>2</sub> lasers, and those developed by Blake and Pickett and their coworkers (Farhoomand et al. 1985, Blake et al. 1991) that employed photomixing of microwave light with a fixed far-IR laser output that was pumped by a CO<sub>2</sub> laser, offered alternative submillimeter light sources. However, these systems were only employed by a handful of labs because of the cost and complexity of the equipment involved. The development of millimeter and submillimeter diode-based frequency multipliers dramatically impacted the field in the 1990s and early 2000s, when the push to higher frequencies for observational astronomy driven by the development of the ALMA, *Herschel*, and SOFIA observatories led to the development of off-the-shelf components for submillimeter light generation. Now diode-based sources are commercially available that cover frequencies up to 3.3 THz.

Despite this great push forward in frequency coverage over the past few decades, there is still a limitation in the power levels that can be achieved at higher frequencies. This is because the most efficient power amplifiers are limited to the microwave and millimeter regimes. Nonetheless, the field is marching forward in technological advancements, and significant progress has been made in recent years in terms of both frequency coverage and power output. A few labs now have frequency multipliers that extend to frequencies above 1 THz, but most of these setups are limited in coverage to a spectral band centered on a particular molecular or atomic line of interest, such as the OH pure rotational lines at 1.9 and 2.5 THz, the O<sub>I</sub> lines at 2 THz and 4.7 THz, the C<sub>II</sub> line at 1.9 THz, or the N<sub>II</sub> lines at 1.5 and 2.5 THz.

Other technological advancements show great promise for opening up the far-IR spectral regime for routine study. Far-IR quantum cascade lasers based on phase-locked technology (Betz et al. 2005) are now commercially available. Although these devices have limited tuning ranges, they do offer significantly more power than multiplier technology at frequencies above 1 THz. Quantum cascade lasers have been used not only for direct spectroscopic studies but also as sources for far-IR frequency combs, which are devices that output a set of discrete frequencies at regularly spaced intervals. Frequency combs are routinely used in optical spectroscopy to perform multi-color experiments. Applications of frequency combs are just starting to be explored as a means for broadband spectroscopic investigations in the far-IR (Cossel et al. 2017).

The handful of laboratories that have millimeter or submillimeter direct absorption spectrometers tend to focus on stable molecules, because most of these spectrometers are flow or static cells with no capabilities for producing ions or radicals. Laboratories that have capabilities to study stable molecules in a static or a flow cell experiment include the JPL Molecular Spectroscopy Group, the Blake group at The California Institute of Technology, the De Lucia group, the McCarthy group at the Harvard-Smithsonian Center for Astrophysics, the spectroscopy groups at the University of Lille, the Alonso group at University of Valladolid, the Caselli group at the Max Planck Institute for Extraterrestrial Physics, the Kisiel group, the spectroscopy group at the University of Cologne, the Ilyushin group at Kharkiv National University, and the Widicus Weaver group at Emory University. The Ziurys group at the University of Arizona employs such a spectrometer coupled with a Broida oven to study metal-containing species and radicals relevant to circumstellar shells (Ziurys et al. 1992). Several groups have also used long-pathlength discharge spectrometers to study molecular ions through submillimeter spectroscopy (see below for more details).

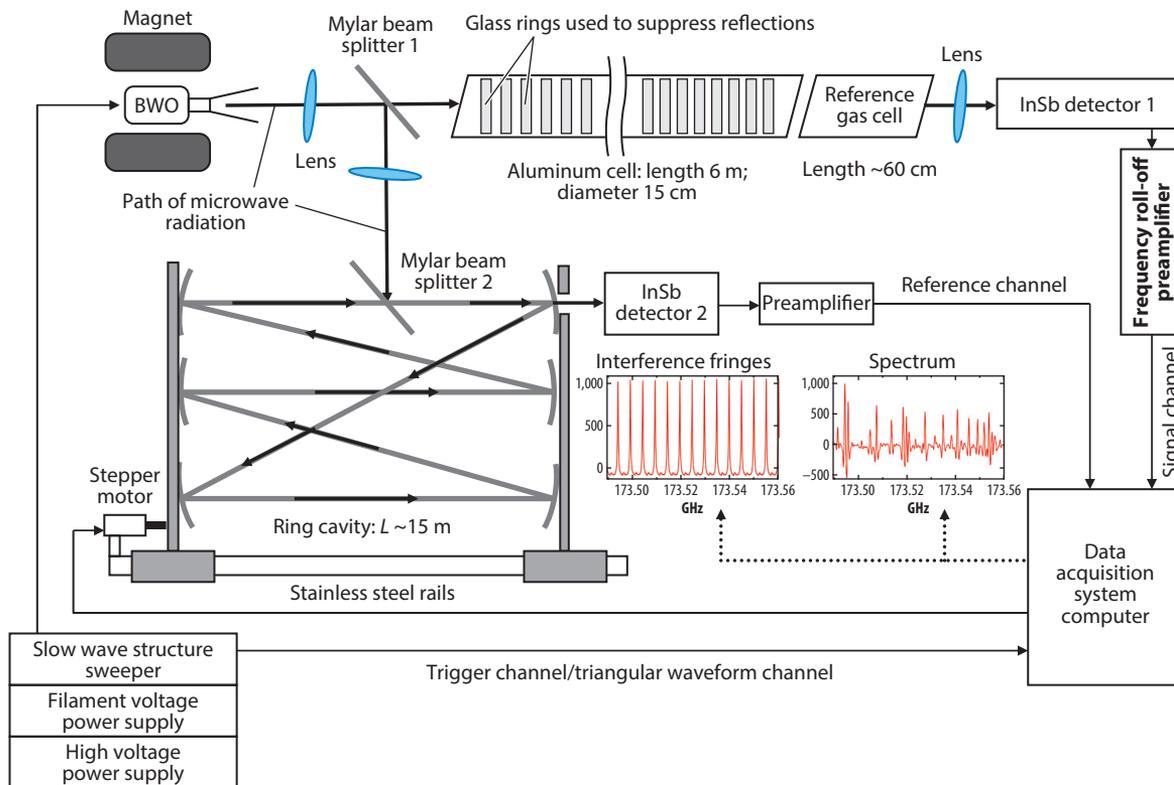
There are two major limitations to these standard direct absorption spectrometers. The first limitation is data acquisition speed. The submillimeter regime is broad, and to cover the whole range at the 10–100 kHz resolution required for rotational spectroscopic investigations takes immense amounts of scanning time; at the 10 GHz per hour scanning rate quoted above, complete spectral coverage from 100 GHz–1 THz would take 90 h of scanning time with no averaging! The second limitation is sensitivity. At the low power outputs of submillimeter multipliers, the study of stable molecules is straightforward, but molecules with weak signals such as radicals and

ions challenge the current level of detection limits. Long-pathlength techniques do work well for simple molecules, but discharge cells are not feasible options for larger organic species in which the chemistry becomes complicated in the plasma and the precursors and products can condense onto the cryogenically cooled cell. As such, supersonic expansion discharge sources such as those developed by Thaddeus & McCarthy (2001), Duncan and coworkers (Douberly et al. 2007, Duncan 2012), and Nesbitt and coworkers (Davis et al. 1997) must be used for unstable molecule production, in which the reactions are quenched and the products are cooled. This reduces the sample pathlength down to a few centimeters, greatly decreasing the magnitude of the absorption signal compared to the meters-long spectrometers used to study stable species. Techniques that increase sensitivity are therefore essential to the study of larger radicals and ions of relevance to astrochemistry. New spectroscopic techniques are being developed that address each of these limitations; these specialized spectrometers are discussed below.

### 3.2. Techniques for Rapid Spectral Acquisition in the Millimeter/Submillimeter Regime

As the frequency range accessible by direct absorption spectrometers continues to increase, new methods must be developed that increase spectral acquisition speed so that data collection is efficient. De Lucia and coworkers laid the foundation for such advancements with implementation of the FAsT Scan Submillimeter Spectroscopic Technique (FASSST) spectrometer (Petkie et al. 1997), a schematic of which is shown in **Figure 8**. In this setup, a tunable frequency source is rapidly swept across a broad frequency swath, and the spectrum is collected using a highly sensitive hot electron bolometer (HEB) detector. A reference gas cell is used to frequency-calibrate the resultant spectrum. When coupled with a long-pathlength sample cell, this technique has comparable sensitivity with traditional direct absorption techniques but offers a three-orders-of-magnitude improvement in the data acquisition rate. This improvement can be used to either increase scanning speed or allow more averaging, which in turn increases the detection sensitivity. This approach was first implemented with BWOs but was more recently upgraded to use more stable frequency multiplier chains as the radiation source.

Although FASSST provides a great improvement in data acquisition rates for submillimeter spectroscopy, other approaches utilizing cutting-edge technology developments have offered even greater improvement. Arguably the greatest advancement in rotational spectroscopy in the past 30 years has been the development of the chirped-pulse Fourier transform microwave (CP-FTMW) spectrometer by Pate and coworkers (Brown et al. 2008). This technique has some parallels with the traditional Fourier transform microwave (FTMW) experiments that have historically been the workhorses of microwave spectroscopy (Balle & Flygare 1981). A comparison of the spectrometer setups for FTMW and CP-FTMW is shown in **Figures 9** and **10**. Both techniques rely on a high-power pulse of radiation that polarizes a molecular sample. In the case of traditional FTMW, this pulse is tuned to be resonant with a high-finesse cavity, and the free-induction decay of the molecules emitting in the cavity is recorded by a heterodyne detection scheme. A Fourier transform (FT) gives the frequency domain emission spectrum. The cavity quality leads to incredible sensitivity, but spectra can only be collected in narrow bands of a few hundred MHz in bandwidth that are resonant with the cavity tuning. In the CP-FTMW experiment, no cavity is used, eliminating the need to couple the signal into and out of a narrow band optical system. Instead, a short time pulse of radiation, i.e., the chirped pulse (CP), is injected into the system using a microwave feed horn; high-power amplifiers are used to drive the signal input. The molecular sample is subjected to a broad range of frequencies at high power, the sample is polarized, and during relaxation the free induction decay of the sample is recorded using a heterodyne detection

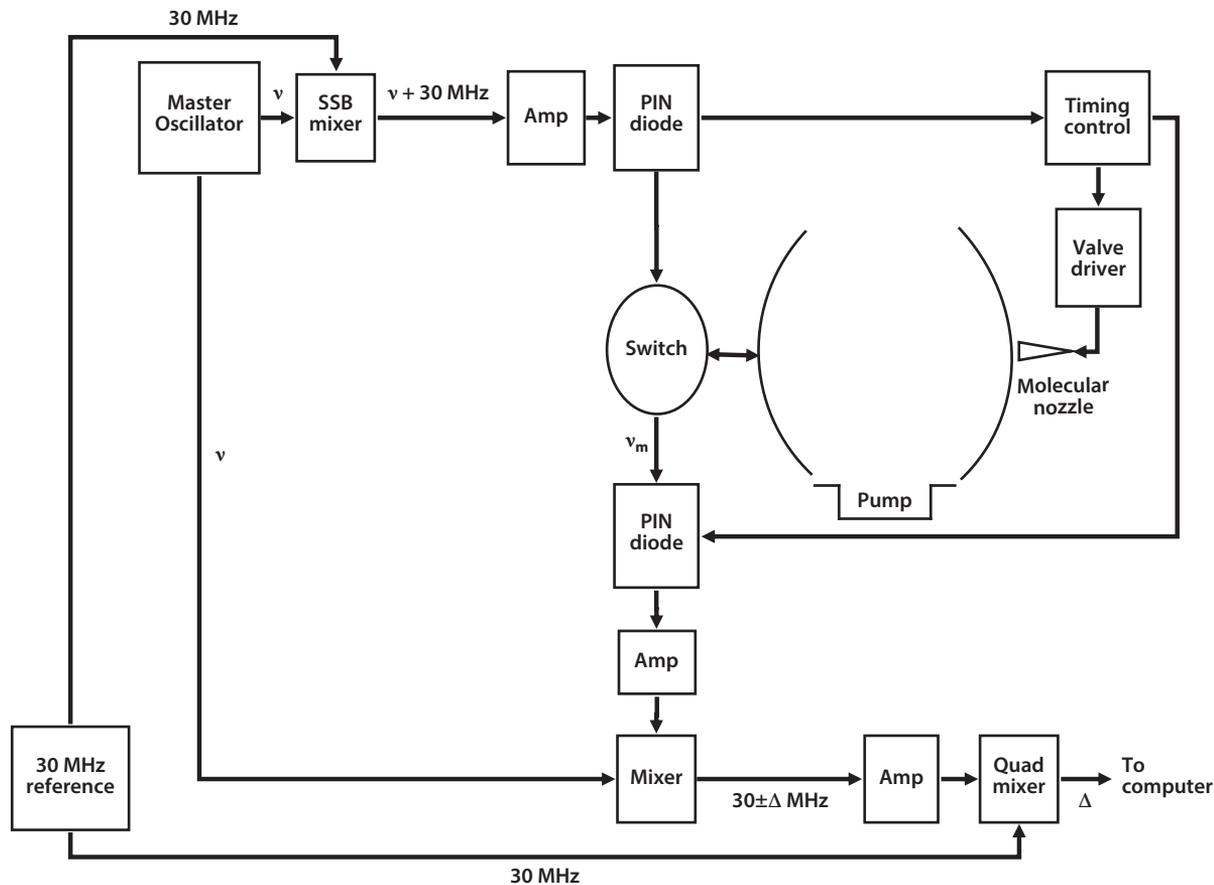


**Figure 8**

Schematic of the FASST Scan Submillimeter Spectroscopic Technique (FASST) spectrometer. Adapted from De Lucia (2010, their figure 8) with permission from *The Journal of Molecular Spectroscopy*, ©Elsevier. Abbreviation: BWO, backward wave oscillator.

scheme. An FT gives the frequency domain emission spectrum. The chirp is broadband, covering tens of GHz in frequency space, which means that the data acquisition time of a microwave CP experiment is a factor of 40 less than that of a traditional FTMW experiment (Brown et al. 2008). Although CP-FT techniques are primarily used in microwave spectroscopy, some groups use frequency multipliers to access the millimeter range with these experiments. By segmenting the CP, Pate, Plusquellic, and coworkers (Neill et al. 2013) have now extended these techniques to the submillimeter range. This spectrometer gives a four-orders-of-magnitude improvement over the FASST spectrometer in terms of data acquisition speed, giving a seven-orders-of-magnitude improvement over traditional direct absorption experiments. However, the proprietary nature of some of the hardware used in the segmented CP-FT submillimeter experiments limits their widespread use. As the technology sector continues to be driven toward higher-frequency components for the security and telecommunications markets, these approaches will become more widely applicable. In the meantime, other approaches must be considered that speed up acquisition time in the submillimeter regime without requiring a prohibitive investment in equipment.

Widicus Weaver, Shipman, and coworkers have developed two alternative signal modulation and detection schemes to circumvent the hardware requirements of both the FASST spectrometer and the CP-FT submillimeter approach. The first of these spectrometers (Hays et al. 2016) uses a CP as the input to a multiplier chain, in which the broadband submillimeter output is coupled with a traditional direct absorption spectrometer. Here, instead of detecting the free-induction

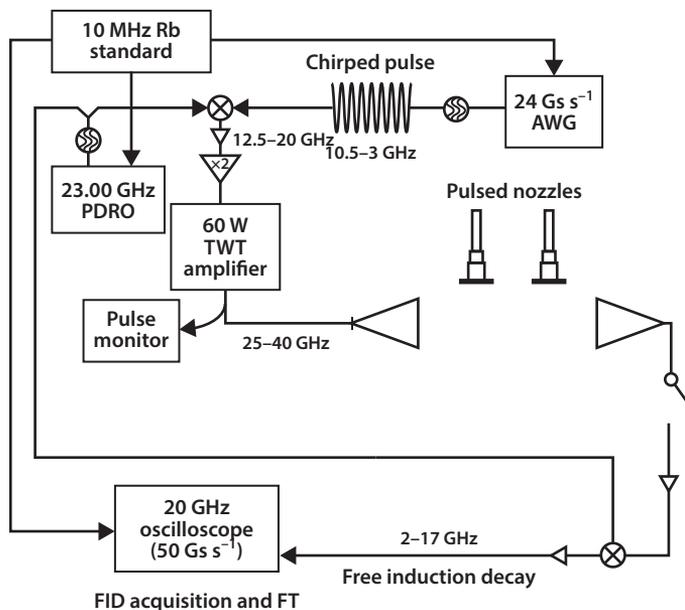


**Figure 9**

Schematic of a traditional Balle–Flygare Fourier transform microwave spectrometer. Reproduced from Widicus Weaver (2005, her figure 2.1) with permission. Abbreviation: SSB, single sideband.

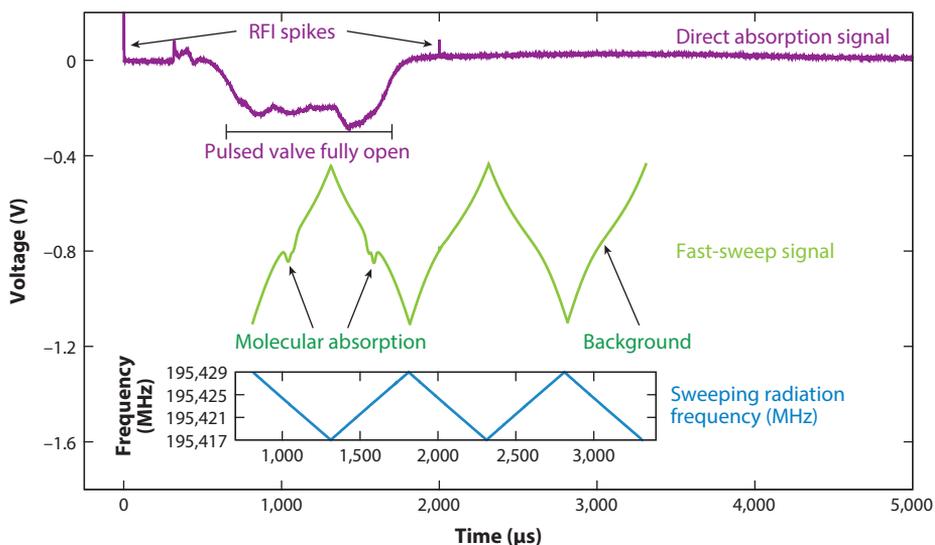
decay of the polarized sample that requires high power amplification of the input signal, the direct absorption signal is superimposed on the time response of a highly sensitive HEB detector. This combination of technology yields the broadband acquisition capabilities of CP techniques with the high-sensitivity detection capabilities of an HEB operating in the submillimeter regime. This yields a SNR and data acquisition speed comparable with that of both the FASSST and CP-FT submillimeter techniques. However, the applications of this technique are hampered owing to significant challenges with spectral processing because of difficulty in removing spectral baselines. Nonetheless, eliminating the need for higher powers or specialized equipment makes this approach a feasible option for many laboratories.

The other approach developed by Widicus Weaver and coworkers (Zou et al. 2016) is a fast-sweep technique employing the internal signal modulation options offered by a standard microwave signal generator. An overview of the data acquisition scheme for this technique is shown in **Figure 11**. Here the input signal for a direct absorption spectrometer is modulated using a triangle wave and multiplied to the submillimeter regime; the time response of the spectral signal is collected using an HEB. This enables an increase in spectral bandwidth while retaining the sensitivity of the HEB detection. Although traditional lock-in detection is still more sensitive than this



**Figure 10**

Schematic of a chirped-pulse Fourier transform microwave spectrometer. Adapted from Zaleski et al. (2012, their figure 1) with permission from *The Journal of Molecular Spectroscopy*, ©Elsevier. Abbreviations: AWG, arbitrary waveform generator; FID, free-induction decay; FT, Fourier transform; PDRO, phase dielectric resonator oscillator; Rb, rubidium; TWT, traveling-wave tube.



**Figure 11**

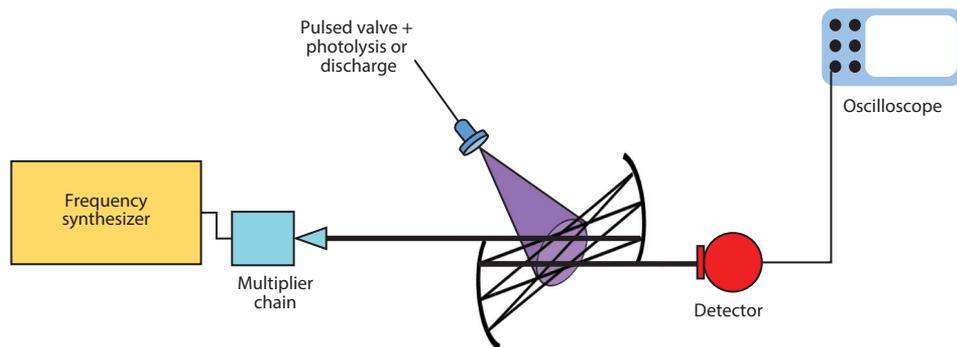
Overview of the data acquisition scheme for the fast-sweep technique. Adapted from Zou et al. (2016, their figure 2) with permission from *The Journal of Physical Chemistry A*, ©American Chemical Society. Abbreviation: RFI, radio frequency interference.

approach, the fast-sweep method gives an order-of-magnitude improvement in spectral acquisition time for spectra with the same SNR. When a new species is being investigated in the lab and the spectral search is dependent on a theoretical prediction that may be off by hundreds of MHz, this approach offers an affordable alternative to searching for new lines across a large frequency range.

### 3.3. Techniques for Increasing Spectral Sensitivity in the Millimeter/Submillimeter Regime

Despite the great advancements in spectral acquisition rates based on new technology development in the submillimeter regime, the limitation of sensitivity remains a challenge for studies relevant to astrochemistry. A straightforward way to increase sensitivity is to increase pathlength through the sample. Several spectrometer optical designs have therefore been explored that would provide this mechanism for sensitivity increase. The simplest way to do this is to increase the number of optical passes through the sample. Many long-pathlength direct absorption spectrometers use wire-grid polarizers to achieve a double-pass optical arrangement. In this approach, the input submillimeter radiation is passed through a polarizer that is aligned with the linear polarization of the radiation. Once the radiation reaches the other end of the absorption cell, a rooftop reflector is used to rotate the polarization by  $90^\circ$  and reflect the light back through the cell. Once that signal reaches the polarizer, it reflects off the wire grid because it is not aligned with the orientation of the wires. The signal can then be directed into the detector.

This double-pass approach works well for experiments in which the gas sample fills the entire vacuum chamber but is not particularly helpful for experiments using a supersonic expansion with sample pathlengths of a few centimeters. The standard approach in laser spectroscopy is to use a multipass optical arrangement like a Herriott cell (Herriott & Schulte 1965) or a White cell (White 1942). This is challenging for millimeter and submillimeter radiation, in which the beam sizes are of the same size order as that of standard optics and diffraction losses are large. Both spectrometer designs also require the input radiation to pass through a small aperture that would greatly attenuate the beam. One way around this is to use a multipass arrangement based on the design of Perry and coworkers (Kaur et al. 1990); a schematic diagram is shown in **Figure 12**. Here, rather than passing through an aperture, the radiation is introduced into the optical cavity at a steep angle at the edge of one of the mirrors. Widicus Weaver and coworkers found that a seven-pass optical setup of this kind using large metal mirrors as the reflectors increases the sensitivity of the



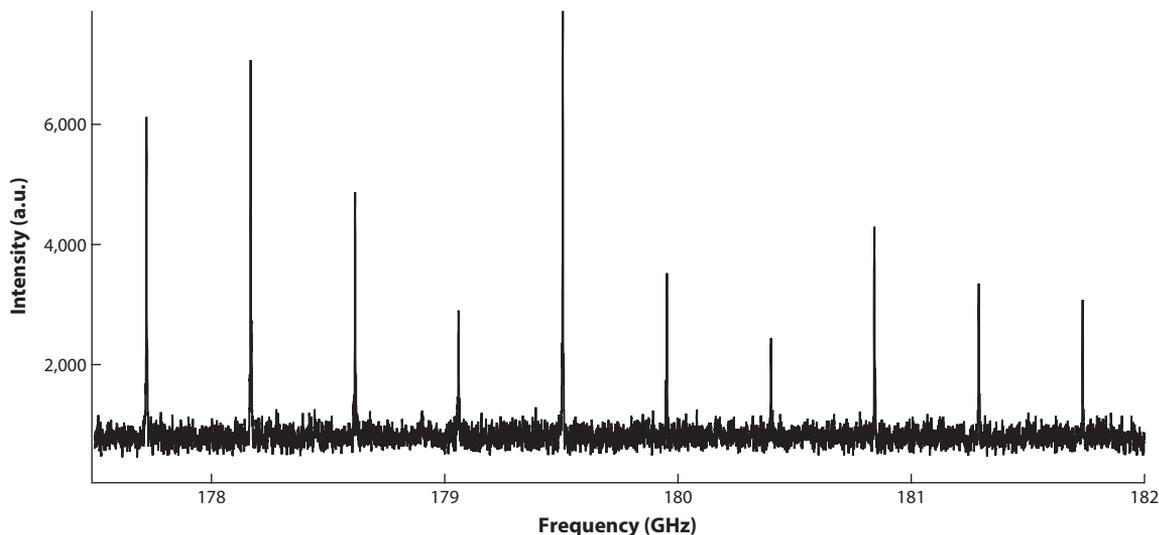
**Figure 12**

Schematic of a multipass millimeter/submillimeter spectrometer.

direct absorption spectrometer by a factor of five compared to a single-pass optical configuration; a value of  $\alpha_{\min} \geq 10^{-9} \text{ cm}^{-1}$  is obtained in their studies of the methoxy radical using a discharge supersonic expansion source (Laas et al. 2013).

Going beyond these direct absorption approaches, several groups have attempted to develop either FT-THz spectroscopy or THz cavity ringdown spectroscopy (CRDS). The FTMW technique developed by Balle and Flygare was discussed above; this technique uses a high-finesse cavity to greatly enhance the pathlength through the sample and, therefore, the sensitivity of the resultant spectra. Similarly, CRDS, developed by O’Keefe & Deacon (1988), is used in IR and optical spectroscopy to enhance spectral sensitivity. Akin to the FTMW technique, CRDS utilizes an extremely high-finesse cavity to enhance the pathlength through the sample by orders of magnitude. In the CRDS approach, the ringdown of the signal in the cavity owing to absorption or cavity losses is recorded, rather than the free-induction decay as is the case for FTMW instruments. The ringdown time for radiation tuned to be resonant with the cavity can be used to calculate the absorption coefficient of the sample at each frequency point, giving a highly sensitive spectral response that is independent of the intensity of the input radiation. The detector hardware and data acquisition system are much simpler for CRDS than those required for FT-THz studies, focusing instrumentation development in this area on THz-CRDS. The challenge with both techniques is coupling radiation into and out of the cavity. In FTMW approaches, a small aperture is machined in the middle of a very large metal mirror, allowing radiation to be coupled into and out of the cavity. This works well at long wavelengths, where the losses due to the aperture are minimal. But submillimeter radiation has much smaller wavelengths, and the mirror surface quality must be pristine for high reflectivity to be achieved; an appropriately small aperture cannot be machined to suit this purpose. One recent advancement may circumvent this challenge. Drouin and coworkers (Drouin et al. 2016, Nemchick et al. 2018) have developed a complementary metal-oxide semiconductor (CMOS)-based FT spectrometer, in which the cavity is part of an integrated circuit that is incorporated directly into the reflective surface of the cavity mirror. This solves the radiation coupling problem and provides the first step toward a higher-frequency instrument that can cover the entire submillimeter regime. Cavity quality is only 2,800 in this instrument, as compared to typical values of  $10^5$  for the original FTMW instrument (Nemchick et al. 2018). Nonetheless, this level of  $Q$  value leads to spectral detection limits that are better than those of the multipass system described above.

In contrast to the FTMW technique, IR-CRDS couples the light into and out of the cavity by passing the laser beam through the surface of the high-reflectivity mirrors. Although the reflectivity for CRDS mirrors is often 0.9999 or better, the small amount of light that can pass through the dielectric mirror coating gets trapped in the very high-quality cavity, providing thousands of passes through the sample and leading to highly sensitive molecular spectroscopy. Appropriate high-reflectivity optics for CRDS have been considered (Baker & Walker 1982, Clarke & Rosenberg 1982, Schiwon et al. 2002, Du Bosq et al. 2004, Truitt et al. 2018), and two millimeter-CRDS instruments were tested (Gopalsami et al. 2002, Meshkov & De Lucia 2005). Yet, no higher-frequency CRDS experiments have been reported in the literature. The design challenge has been the lack of suitable high-reflectivity mirrors to form the cavity. Blake and Braakman recognized that wire-grid polarizers can be used to circumvent this problem (Braakman & Blake 2011). Drawing from the approach used in long-pathlength absorption spectrometers, polarizers can be rotated  $90^\circ$  to serve as high-quality THz reflectors. The Widicus Weaver group tested several cavity designs based on wire-grid polarizers (Alligood DePrince et al. 2013) and found excellent cavity performance. Despite the sharp cavity modes corresponding to a cavity quality of  $10^5$  shown in **Figure 13**, technological limitations have hampered full development of CRDS using this design. The cavity is of sufficient quality to enable CRDS, but the detectors

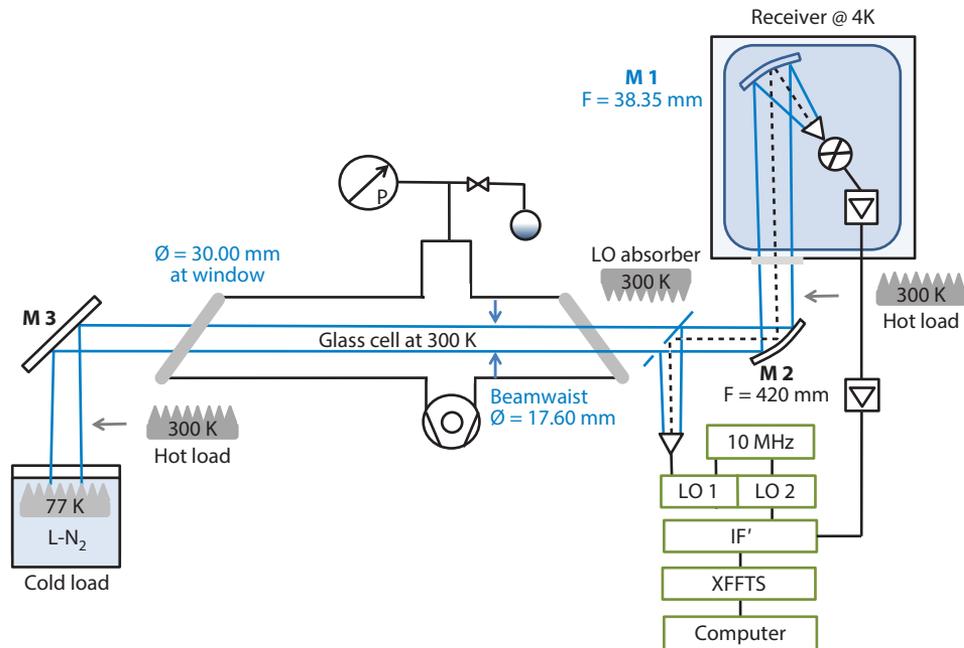


**Figure 13**

Cavity mode spectrum at 180 GHz detected using the cavity design of Widicus Weaver and coworkers presented by Alligood DePrince et al. (2013).

that are commercially available in this frequency range have response times that are too long to detect the CRDS signal. This could be overcome if the cavity was lengthened, but diffractive losses would dominate. There are faster prototype detectors under development, but at this time THz-CRDS is not technologically feasible. Nonetheless, a cavity of this quality can be used with a heterodyne detection scheme to reach sensitivity levels of  $\alpha_{\min} \leq 10^{-11} \text{ cm}^{-1}$ .

Heterodyne detection is another approach that might be used to increase sensitivity for millimeter and submillimeter spectroscopy as well as increase the data acquisition rate. Here, a heterodyne detector that operates in the same manner as a radio telescope receiver could be used to acquire double-sideband spectra. Increasing the instantaneous frequency coverage to the broadband capabilities and achieving the sensitivity levels of current telescope receivers would dramatically improve the capabilities of laboratory spectrometers. However, to realize the full potential of such a setup, a cryogenically cooled detector with a custom-designed mixer would need to be used, and those are typically custom built for observatories and, as such, are quite cost prohibitive. Nonetheless, both the University of Cologne spectroscopy group led by Schlemmer (Wehres et al. 2017, 2018) and the Consejo Superior de Investigaciones Científicas astrochemistry group led by Cernicharo (Tanarro et al. 2018) have recently tested emission spectrometers based on this design. The schematic of the spectrometer designed in Cologne is shown in **Figure 14**. The first Cologne instrument operates at millimeter wavelengths and uses a room temperature heterodyne receiver, and it achieves sensitivity levels that are only one order of magnitude less than those found with a cryogenically cooled receiver at a radio telescope (Wehres et al. 2017). The most recent advancement from this group employs a submillimeter heterodyne receiver with an SIS (superconductor-insulator-superconductor) mixer cooled with liquid helium (Wehres et al. 2018); they found that with similar integration times, direct absorption methods still outperformed the spectrometer by a factor of 8.5. Nonetheless, the broadband detection scheme enables them to dramatically increase the signal averaging time because scanning is not required, which would rapidly favor the receiver technology in terms of the ultimate SNR that can be achieved. They then go on to discuss the advantages of using this type of a detector in a CP experiment, which



**Figure 14**

Schematic for the submillimeter heterodyne emission spectrometer developed by the University of Cologne molecular spectroscopy group. Adapted from Wehres et al. (2018, their figure 1) with permission from *Physical Chemistry and Chemical Physics*, ©The Royal Society of Chemistry. Abbreviations: IF, intermediate frequency; LO, local oscillator frequency; XFFTS, eXtended bandwidth Fast Fourier Transform Spectrometer.

would lead to a dramatic improvement in sensitivity. Cernicharo and coworkers obtained similar results in terms of performance of a heterodyne emission spectrometer, as compared to direct absorption techniques (Tanarro et al. 2018), and applied this instrument to a series of experiments exploring reaction kinetics. The field can therefore look to expand in this direction if a means for transferring radio observatory equipment to spectroscopy labs can be found.

#### 4. TECHNOLOGICAL ADVANCEMENTS FOR STUDYING UNSTABLE SPECIES

All of the advancements outlined above for increasing data acquisition speed and sensitivity in the millimeter and submillimeter regimes are motivated by the desire to study unstable or reactive molecules that are key species in interstellar chemistry. Radical–radical reactions on ice surfaces dominate the condensed-phase chemistry of cold interstellar regions. Ion–molecule reactions dominate the chemistry in warm regions of star and planet formation, where molecules have been liberated from dust grains and the attraction between the ion and dipole speed up the reaction rates in the gas phase. Additionally, given the long timescales for collisions in even the densest interstellar clouds, higher-energy structural isomers and highly reactive species can be found at high densities. As such, to advance the field of astrochemistry and elucidate the full range of chemical mechanisms possible in space, laboratory studies must include methods that enable spectroscopic characterization of ions, radicals, and unstable species. Several methods are

routinely used to address such problems, and recent technological advancements are now pushing this area of research in new directions.

#### 4.1. Discharge Sources to Produce Radicals and Ions

Beginning with  $\text{CO}^+$  in 1975, Dixon & Woods (1975) pioneered the use of long-pathlength discharge spectrometers to study molecular ions using millimeter and submillimeter spectroscopy. Advanced by the techniques coupled with IR spectrometers pioneered by Oka (1980), these discharge cells included positive column discharges and negative glow discharges, depending on the ion of interest and the chemistry necessary for its formation. De Lucia and coworkers (De Lucia et al. 1983) pioneered the use of negative glow discharge sources for producing molecules of astrophysical interest; Caselli and coworkers are currently using a negative glow discharge to study sulfur-containing ionic species (Bizzocchi et al. 2017). Saykally and coworkers (Gudeman et al. 1983) adapted the velocity-modulation techniques used in the IR for use in submillimeter spectroscopy, where the polarity of the electrodes was alternated such that the ions were physically modulated and could be detected using a lock-in amplifier to eliminate background signal from neutrals. Additionally, Amano and coworkers (Gabrys et al. 1995) developed a long-pathlength hollow cathode spectrometer that greatly enhanced the production of protonated species based on the design of van den Heuvel & Dymanus (1982). The Widicus Weaver group is currently employing a spectrometer based on this design for the study of small ions at frequencies up to 1 THz (Wehres et al. 2014). These ion sources were used with standard direct absorption detection schemes to collect the millimeter and submillimeter spectra for comparison to observations. These spectrometers provided the wealth of data that is available in the spectroscopic databases for the small ionized species that drive interstellar gas-phase chemistry. However, these instruments are limited in their applicability to larger species because the chemistry becomes complex, and line confusion becomes a challenge. Spectral lines are also often quite weak, with overall ion densities being  $10^{-4}$  relative to the parent molecule, and any given ion density being  $\leq 10^{-6}$ . The challenge of weak spectral lines is also compounded by the temperature of the discharge, which is usually 300 K or higher. Additionally, for some discharge cells, cryogenic cooling is necessary for discharge operation. As such, the larger species tend to freeze out on the cell walls and cannot be studied using these methods.

To circumvent these challenges, Thaddeus & McCarthy (2001) developed discharge sources coupled with pinhole supersonic expansions so that the resultant ions are cooled to rotational temperatures  $\leq 20$  K. Such sources have been used to produce a variety of long-chain hydrocarbon ions that are prevalent in diffuse interstellar clouds. This group has also studied a variety of radicals and unstable isomers that are prolific in the ISM. Adaptation of this source design also led to McCarthy and coworkers characterizing and identifying the first molecular anions in space (McCarthy et al. 2006). Pinhole supersonic expansion sources are the most straightforward to implement, because only one pulsed valve is required and the discharge source can be mounted directly on the output of the valve. This dc discharge design, where two electrodes are separated by a spacer and the plasma is struck between them at the throat of the expansion, is the most commonly employed. Duncan and coworkers (Douberly et al. 2007, Duncan 2012) have developed discharge sources in which a needle in the throat of the expansion is used as the cathode; these sources are particularly good at producing protonated organic ions and have been used by this group to study a range of species in the IR. Amano and coworkers also developed a hollow cathode style expansion source (Fukushima et al. 1994) and a corona slit discharge source (Xu et al. 1995). The challenge with these designs is the small sample pathlength. Some laboratories do use the higher densities and longer pathlengths of slit discharge sources for high-resolution

spectroscopy of ions and radicals, as developed by Nesbitt (Davis et al. 1997) for IR and optical studies. These slit sources are difficult to employ because multiple pulsed valves must be synchronized and the o-ring seal must be maintained across the slit when the valves are closed. Much of the work of the Widicus Weaver group in recent years has been to develop higher-sensitivity spectroscopic methods so that discharge supersonic expansion sources can be used for the study of larger ions and radicals at millimeter and submillimeter wavelengths; this group successfully coupled a pinhole discharge source with a multipass direct absorption spectrometer to study the  $\text{CH}_3\text{O}$  (Laas & Widicus Weaver 2017) and  $\text{HO}_3$  (Zou et al. 2016) radicals. Coupling these types of sources with higher sensitivity cavity-based or CP instruments holds great promise for advancing the fields of molecular spectroscopy and astrochemistry.

Two other methods have recently been developed for the study of molecular ions. The first is a helium-cooled buffer gas cell based on the designs of De Lucia and coworkers (see Willey et al. 1988a,b) and applied to molecular ions by Gerlich and coworkers (Gerlich & Borodi 2009). In this setup, the discharge products are injected into a gas cell where helium gas is being held at cryogenic temperatures. The molecules collide with the cold helium atoms before they collide with the walls of the cell, cooling the sample to extremely low temperatures and enabling high-resolution spectroscopy. Another approach that has recently been employed by Schlemmer and coworkers (Asvany et al. 2008) for the study of molecular ions is to trap the ions in a 22-pole ion trap. This enables long integration times with a stabilized molecular sample, which leads to a better SNR for the resultant spectra; the detection level in this experiment was  $10^{11} \text{ cm}^{-3}$ .

## 4.2. Methods for Producing Unstable Molecules of Astrophysical Interest

In addition to discharge sources to produce radicals and ions, recent years have shown advancements in coupling sources that rely on laser-induced chemistry with rotational spectroscopic instrumentation. Only a handful of groups have coupled a microwave, millimeter, or submillimeter spectrometer with laser-induced chemistry to study products, reaction dynamics, or kinetics (Kolbe & Leskovar 1985, Schmuttenmaer et al. 1990, Duffy 2005, Prozument et al. 2013, Abeysekera et al. 2014, Hays et al. 2015). Of these, only one study specifically focused on molecules of astrophysical interest. Widicus Weaver and coworkers (Hays et al. 2015) produced the known interstellar molecules methanol and vinyl alcohol using insertion of electronically excited O atoms in the  $^1\text{D}$  state into C–H bonds of the precursor molecules methane and ethylene, respectively. In these experiments, measurements of the vinyl alcohol spectrum were extended well into the submillimeter regime using direct absorption spectroscopy. The source was a pinhole pulsed valve system with a fused silica tube affixed to the faceplate; UV light from an excimer laser was focused onto the tube to photolyze ozone, which then produced the  $\text{O}(^1\text{D})$  that reacted with the precursor molecule. This source design was based on that used by Lester and coworkers (Pollack et al. 2003, Konen et al. 2005) for IR action spectroscopic measurements of species that are important in atmospheric chemistry. As this technique and others that involve laser-induced chemistry expand into the millimeter and submillimeter regimes, new possibilities will open up in terms of the types of chemistry that can be studied.

## 5. STRATEGIES AND SOFTWARE TO AID IN SPECTRAL ASSIGNMENT

The laboratory astrochemistry field is on the brink of significant new breakthroughs because of the development of new spectrometers that are being combined with novel techniques for producing unstable species of astrophysical interest. The challenge that comes with this great progress is added complexity in terms of assigning molecular spectra. Paralleling the challenges faced by

observational far-IR astronomy, the broadband, high-resolution, high-sensitivity spectra produced by these new laboratory techniques are presenting great challenges to the traditional approach for assigning molecular spectra.

A comprehensive list of publicly available fitting programs and other software tools for rotational spectroscopy can be found at the Programs for ROTational SPEctroscopy (PROSPE) website (<http://www.ifpan.edu.pl/~kisiel/prospe.htm>) maintained by Kisiel. The most recent version of a given software package can be downloaded here, as well as crib sheets to help the user get started using these programs. Most rotational spectroscopic studies begin by using Pickett's CALPGM suite of programs, specifically SPFIT, to fit the spectra to a rotational Hamiltonian. Almost any combination of terms in the Hamiltonian can be included in a fit using this program, including the rotational constants, centrifugal distortion constants out to extremely high orders using either the Watson-A or Watson-S reduction, hyperfine effects, Coriolis terms, and excited vibrational states. This software was written in FORTRAN and therefore is not the most user-friendly software for the nonexpert. The reader is referred to the crib sheets on the PROSPE website as well as the recent review articles from Novick (2016) and Drouin (2017) about the use of these programs.

CALPGM was extended over a decade ago to include a spectral fitting and prediction package for internal rotors using Fourier series expansions in the internal axis system Hamiltonian as described by the Mathieu equation (Pickett 1997). However, the number of terms required in the Fourier series expansion can rapidly become large, making use of this software challenging for analysis of complicated internal rotor problems. Several other programs have been written to address various internal rotor problems, including Hartwig's XIAM for molecules with up to three symmetric internal rotors (Hartwig & Dreizler 1996), Groner's ERHAM for molecules that undergo two internal motions (Groner 1997), Kleiner and coworker's BELGI for molecules with a three-fold barrier (Kleiner & Hougen 2003, Lavrich et al. 2003), and Ilyushin's RAM36 (Ilyushin et al. 2010), which is an adaptation of BELGI offering increased speed and the possibility to analyze a molecule with a six-fold barrier. The reader is referred to the original authors of each of these programs for details in their use in analysis of spectra from molecules with complex internal motion.

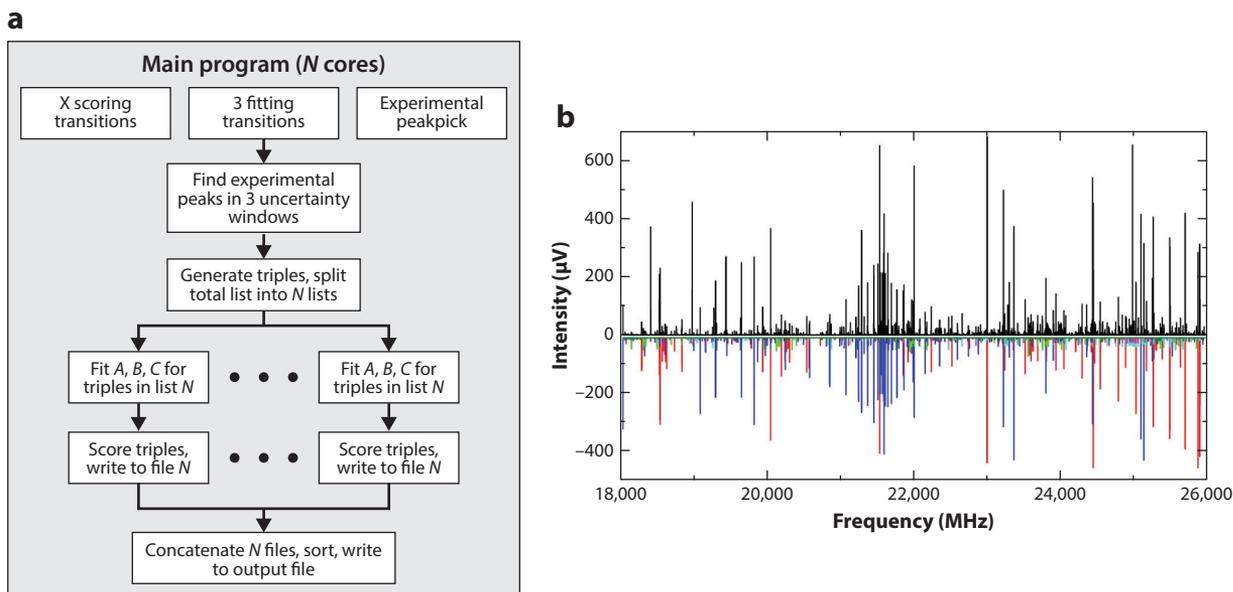
Working hand in hand with these fitting programs are a suite of analysis programs that have been developed to simplify the spectral assignment process by visualizing large spectral data sets overlaid with spectral predictions from Pickett's SPCAT, and work iteratively with SPFIT to refine the Hamiltonian as new line assignments are added to the fit. These programs include Kisiel's Assignment and Analysis of Broadband Spectra (AABS) package (Kisiel et al. 2005), Medvedev's Computer Aided Assignment of Asymmetric Rotor Spectra (CAAARS) package (Medvedev et al. 2005), Plusquellic's JB95 (<https://www.nist.gov/services-resources/software/jb95-spectral-fitting-program>) package developed for NIST, Drouin's Submillimeter Analysis Program (SMAP; <http://spec.jpl.nasa.gov/ftp/pub/calpgm/SMAP/>) developed for NASA, and Western's PGOPHER (<http://pgopher.chm.bris.ac.uk/>) program. There are also other analysis packages developed for specific applications in rotational spectroscopy that can be found at the PROSPE website.

Going beyond the basic spectral fitting routines and the software used to compare them to laboratory spectra, one must consider the analysis challenges that arise from the large size of the data sets that are now routinely produced by laboratory spectrometers. This challenge is coupled with the high sensitivity of these spectrometers, which are often used to analyze complex mixtures rather than one pure molecular sample. One illustration of the challenge in this field is the work by Pate and McCarthy and coworkers (Loomis et al. 2013, McGuire et al. 2016) to study the chemistry produced by a discharge supersonic expansion source with two simple astrochemical molecules being used as the starting material. Using a CP-FTMW instrument, they identified

27 known interstellar molecules as products of the chemistry resulting from a discharge of  $\text{CH}_3\text{CN}$  and  $\text{H}_2\text{S}$ ; new molecular identifications have also arisen out of this work (Loomis et al. 2013, McGuire et al. 2016). The products identified had already been previously characterized, and information was available in spectral line databases. It is unclear if such a feat would be possible with a millimeter/submillimeter spectrum. Would the databases be complete for all of the species that were produced? If not, could the information obtained from the associated microwave studies be used to reliably predict the higher-frequency spectra? What level of spectral confusion is observed? Can clear spectral patterns be picked out of the forest of weak lines? What tools could be used to automate such a process?

Several research groups have been working to address these questions. Motivated by this and other similar challenges, Pate and coworkers have developed a program called AUTOFIT (Seifert et al. 2015) that can be used to make catalog-free assignments for broadband rotational spectra. An overview of the basic operations of AUTOFIT and an example spectrum that was assigned using this program is given in **Figure 15**. AUTOFIT calculates the most probable matches in terms of rotational constants for all sets of three lines, or triples, in a spectrum. One can then use the AUTOFIT results to compare with a theoretical calculation of  $A$ ,  $B$ , and  $C$  rotational constants to identify possible molecular carriers in the spectrum. Thus far, AUTOFIT has been used exclusively for analysis of CP-FTMW spectra. However, one of the AUTOFIT developers has recently extended the program to work with millimeter and submillimeter spectra (S.T. Shipman, private communication).

Going beyond the basic premise of fitting triples to determine rotational constants, Zaleski & Prozument (2018) have recently developed an automated spectral fitting program that operates using neural networks. Here, the neural network “learns” the basic spectral patterns, starting with simple cases and building up in complexity using example molecules as test cases. The user enters



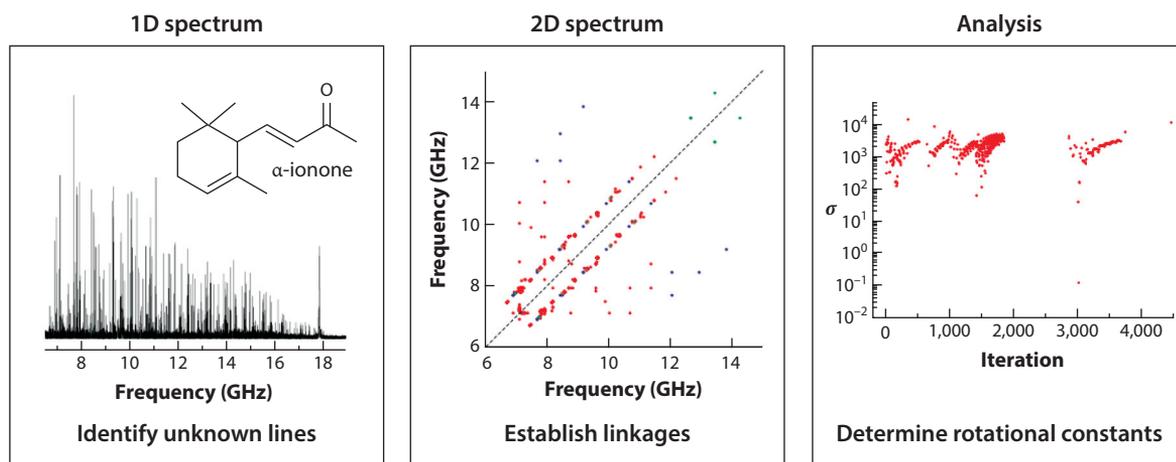
**Figure 15**

(a) An overview of the AUTOFIT approach and (b) the spectrum of hexanal assigned using this program. Adapted from Seifert et al. (2015) with permission, *Journal of Molecular Spectroscopy*, ©Elsevier.

a set of rules based on basic quantum mechanics and gives the program an example spectrum for a given type of molecule (i.e., a symmetric top). The program then learns the process for assigning that type of spectrum and can apply it to other molecules with similar spectral patterns. Thus far only a handful of applications have been tested, but this approach shows great promise in tackling the assignment of complex spectral patterns.

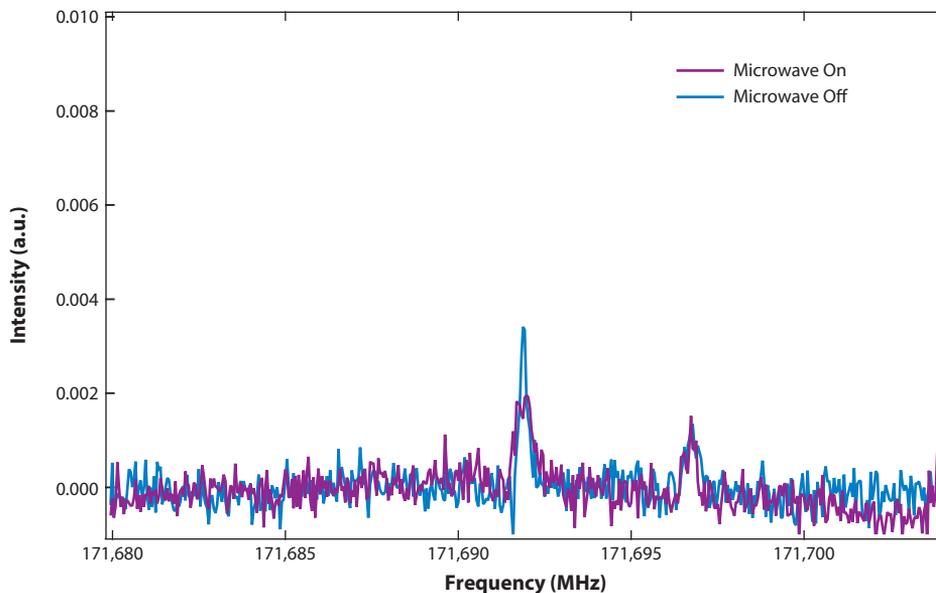
Although the automated spectral assignment approach works well for molecules with well-defined spectral patterns, challenges remain for molecules that suffer from spectral complexity arising from fluxional behavior, Coriolis coupling, or other perturbations to the basic rotational spectroscopic Hamiltonian. To deal with this, McCarthy, Martin-Drumel, Crabtree, and coworkers have developed a method for molecular taxonomy (Crabtree et al. 2016, Martin-Drumel et al. 2016) that uses double-resonance techniques to focus on connected transitions in a spectrum, simplifying the possible schemes for level connectivity and, therefore, aiding in spectral assignment of complex patterns. An overview is shown in **Figure 16**. Here, a given microwave transition is pumped with a high-power source, and the broadband spectrum is recorded both with and without the microwave signal being applied. Transitions that share an energy level with the pump transition are modulated in intensity, and unconnected transitions are not. By stepping across the spectrum with the pump, all possible connections can be observed. This group has developed software for visualizing the connections and aiding in spectral assignment.

Double-resonance approaches hold great promise for assigning complex spectra, because even in cases with high spectral density, only the connected transitions are modulated and can therefore be uniquely identified. Numerous groups have used microwave–microwave double resonance techniques to aid in spectral assignment; the taxonomy approach is the most advanced of the analysis techniques employed. Only two groups have focused on microwave–millimeterwave double-resonance techniques. Jäger and coworkers (Jäger & Gerry 1995, Markov et al. 1998) and Endo and coworkers (Suma et al. 2004, 2005; Sumiyoshi et al. 2005) separately developed microwave–millimeterwave schemes and applied them to a few molecular cases. Here, FTMW instruments were used to record the spectral response. Recently, Shipman, Widicus Weaver, and coworkers (Roenitz et al. 2018) developed microwave-millimeter and submillimeter double resonance using the broadband scanning capabilities of CP-FTMW and fast-sweep millimeter/submillimeter



**Figure 16**

Scheme for spectral taxonomy, based on the methods presented by Crabtree et al. (2016). Figure provided by M.A. Martin-Drumel and M.C. McCarthy based on Martin-Drumel et al. (2017).



**Figure 17**

Microwave–millimeterwave double-resonance response of 2-methylfuran, where one line from an A/E doublet is modulated by the presence of the microwave radiation, and the other line from the pair is not. Figure provided by S.L. Widicus Weaver and S.T. Shipman (unpublished results).

spectroscopy. An example is shown in **Figure 17**, where double resonance is shown to deplete the signal for one line of 2-methylfuran from an A/E doublet, whereas the other unconnected transition is not modulated. In these experiments, rather than observing full population transfer as is typical when a high-power amplifier is used to drive the pump radiation, they observed Autler–Townes doublets arising from the AC Stark effect. This is similar to the results obtained by Schnell and collaborators (Schmitz et al. 2015) in radio-microwave double-resonance experiments. This group also developed a method of three-wave mixing using CP-FTMW techniques to be able to uniquely identify separate enantiomers in a mixture (Patterson et al. 2013). Now that broadband approaches are being employed for these various techniques, they can be extended to higher frequencies, which will aid in assignment of complex spectra across the THz regime.

Medvedev & De Lucia (2007) approached the spectral assignment problem with a very different approach, removing the need for assigning quantum numbers to each observed transition and instead introducing an approach that allowed a spectrum to be simulated at any temperature with accurate intensity and frequency information. To do this, they used the FASSST spectrometer described above to take rapid, broadband scans of a given molecular sample over a range of frequencies at many different temperatures. They then used the relative intensities of the lines observed in these spectra to determine an intensity relationship that removed dependence on the quantum numbers of the transitions. By doing this, they could simulate an entire spectrum of a given molecule across a full telescope receiver band and could use that information to match the observations without ever having to make a specific set of line assignments or complete a full spectral analysis. Although this works well for comparison with observations (Fortman et al. 2012), its widespread use in both chemistry and astronomy applications requires an extensive database of information for all known and suspected interstellar molecules. Currently, such information exists only for a few species.

Inherent to all these approaches is a two-fold challenge: Broadband spectroscopic coverage must be achieved, and the appropriate Hamiltonian model must be used. As displayed by glycolaldehyde (Carroll et al. 2010), even the most rigid molecules that are well behaved in the  $\sim 300$  GHz regime deviate from predictions at frequencies above 1 THz. This becomes particularly challenging for fluxional species, for which there may not be an obvious spectral pattern and where large shifts from predictions may occur. As such, more tools need to be developed that take a spectral assignment from pure theory, through experiment, and then into predictions. One potential avenue is that used in the IR, where predictions-based high-level ab initio calculations are augmented with high-resolution spectral data and then extrapolated to other frequency ranges; J. Tennyson (Barber et al. 2006) and T.J. Lee (Fortenberry et al. 2014) are both leaders in this area, and applications to hot Jupiters and other exoplanet environments will become increasingly important in the era of the *James Webb Space Telescope* (JWST). If such an approach can be adapted for the even higher-resolution spectra measured in the far-IR, this would go a long way in easing the spectral analysis challenges faced where both laboratory measurements and observations are concerned.

## 6. RECENT DEVELOPMENTS AND FUTURE POSSIBILITIES FOR MILLIMETER AND SUBMILLIMETER SPECTROSCOPY

Far-IR spectroscopy has a rich history but has thus far been limited in application to smaller molecules in gas-phase experiments. The recent expansion of technical capabilities in this area is helping far-IR spectroscopy expand to other areas of spectral analysis. Three recently developed spectral techniques hold great promise for their impact on the field of astrochemistry.

In terms of the potential for extrapolating existing techniques to the far-IR, one major area of future expansion is to build on the CP-FTMW revolution in rotational spectroscopy. In one particular application, Schnell and coworkers developed a method of three-wave mixing using CP-FTMW techniques to uniquely identify separate enantiomers in a chiral sample (Patterson et al. 2013). This approach offers the first direct method for identifying the unique molecular components leading to enantiometric excess in a mixture. As CP techniques are expanded to include far-IR studies, the further development of this method will lead to new advancements that could open pathways for chirality studies using new techniques in remote observations or for application to sample return missions.

In the realm of new far-IR techniques, Blake and coworkers (Allodi et al. 2014) have generated far-IR light using an oscillating two-color plasma to produce broadband, high-power radiation in the time domain that can then be used to probe the low-resolution far-IR spectra of solids that are relevant for the ISM. Such measurements can be used to compare with far-IR observations, providing information needed to properly model the continuum observed in ISM observations.

Far-IR detection capabilities are also being applied to longstanding challenges in the field of laboratory astrochemistry. In particular, a new approach is being developed that couples gas-phase detection with experiments to study interstellar or cometary ice analogs. Here, the gas-phase products of thermal or photo processing of an ice sample can be detected using far-IR spectroscopy. Wadich Weaver, Milam, and coworkers have also developed a system for this type of spectral monitoring (Yocum et al. 2018). The greatest limitation in this approach is the sensitivity limits of the spectrometer, because the amount of sample released during ice processing is extraordinarily small; thus far, a detection limit of  $\sim 10^{11}$  cm $^{-3}$  has been achieved. As of now, mass spectrometric techniques are still much more sensitive but do not offer the isomer selectivity of rotational spectroscopy. The hope is that as high-sensitivity techniques such as THz-CRDS or FT-THz spectroscopy are developed, these approaches can be applied to the ice processing experiments already underway.

## 7. CONCLUSIONS

The far-IR–millimeter/submillimeter–THz regime is a wide and relatively unexplored spectral window that offers unique probes of the rich chemistry that is observed in astrophysical observations. Millimeter and submillimeter spectroscopic signatures are fingerprints of the pure rotational transitions of small molecules, rovibrational modes of large molecules, and internal motion signatures of fluxional molecules. Broadband, high-resolution spectra are now the standard output of nearly every astronomical observation conducted in this regime, offering both a great wealth of molecular information about the Universe and a great challenge in terms of spectral analysis and data interpretation. Although some molecules, especially the interstellar weeds, have been extensively characterized in the far-IR to support missions like *Herschel*, SOFIA, and ALMA, many other molecules are still lacking key spectral information needed to fully analyze observational spectra. Spectral catalogs are quite useful in interpreting observational results, but many catalogs are incomplete, and extrapolation to high or low temperature can result in inaccuracies. Laboratory efforts that directly probe the molecular information needed to extend these databases of spectral information and interpret the science return from astronomical missions in the far-IR are critical for advancing the field of molecular astrophysics. The recent explosion of technical innovation in this spectral regime, driven in part by the development of new far-IR observatories, offers new pathways forward in terms of molecular spectroscopic techniques that can be used to study molecules of astrophysical interest. The challenges of spectral acquisition rate, sensitivity, and analysis of complex mixtures in broadband spectra are pushing spectrometer development in new and exciting directions. This field is poised to fill the THz-Gap that has persisted in this region of the electromagnetic spectrum, offering analytical techniques that rival those used in the microwave and IR regions of the electromagnetic spectrum.

### SUMMARY POINTS

1. Millimeter and submillimeter spectroscopy support observational astronomy through spectral studies of molecules of astrophysical interest.
2. Full science return from far-IR observatories cannot be realized until laboratory spectroscopy catches up with the data rate for observations.
3. Data acquisition speed, sensitivity, and analysis approaches for complex mixtures and broadband spectra are the greatest challenges in this field of research.
4. New techniques building on those used in the microwave and IR regimes are required to fill the THz-Gap.

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