

Chapter 2

Molecules Detected in Interstellar Space

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In this section, an overview is given of molecules detected in the interstellar medium and circumstellar envelopes. Given that so far more than 150 species have been observed in interstellar space, this overview can by no means be complete. Therefore, we focus on the detections of the first molecules and then give examples of prototypical molecules and recent new detections. This section is based on the Menten (2003) article presented in the proceedings of the 2003 Zermatt conference [1].

2.1 Detection of the First Interstellar Molecules

The first optical detections of the diatomic radicals CH and CN and the CH⁺ ion were already described in Sect. 1.3.1. Here, the first *radio* detections are discussed.

The late 1960s and early 1970s were an era of great excitement in all branches of radio astronomy. In spectral line research, 12 years after the detection of the first line, the 21 cm HI hyperfine structure (hfs) transition [2], finally, the first molecule was found: the hydroxyl (OH) radical [3].

The OH Λ -doublet transitions, as well as many other lines at m-, cm- and mm-wavelengths from a variety of molecules, had been identified as possible astronomical targets in a visionary article by Charles Townes [4].¹

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¹ see also Shklovsky [5].

Shortly after the detection of OH, Hoglund and Mezger [6] discovered the first radio recombination line, H109 α at 5009 MHz. *Molecular* radio astronomy started in earnest in 1968/1969, with the discoveries of ammonia (NH₃; Cheung et al. [7]) and water vapor (H₂O; Cheung et al. [8]) by a group around Townes,² as well as the first complex organic species, formaldehyde (H₂CO; Snyder et al. [9]), breaking loose a real gold rush that has yet to stop. Even today, approximately 2–4 “new” interstellar or circumstellar³ molecules are found each year, totaling to more than 150 species (not counting isotopomers).⁴

The early history of “molecule-hunting” is well documented in the review by Snyder (1972; “Molecules in Space” [10]), which gives a very useful introduction to molecular radio astronomy, that is still very much readable today. In the same volume, the review, following Snyder’s by Winnewisser et al. and presents an equally excellent overview of the laboratory side of “Millimetre Wave Spectroscopy” [11]

As shown in Table 2.1,⁵ many of the early molecular detections were made at low radio frequencies (and toward Sagittarius B2). For a full list of interstellar molecules detected in space, see Chap. 5.

Almost concurrently with cm-wavelength molecular radio astronomy, shorter wavelength exploration started. Driven by new high-frequency receiver technology and, generally, higher line intensities and a much higher “line density” (i.e., lines per GHz) the “millimeter explosion” started with the discoveries of CO by Wilson et al. [35] and HCO⁺ (“X-ogen”) by Buhl and Snyder [36] both in 1970 (the latter published in 1971), and continues through today, having reached the submillimeter range in the 1980s.

After the millimeter window was opened, (most) people spontaneously lost interest in the cm-range because

- Most molecules have the bulk or the entirety of their rotational spectrum at (sub)millimeter wavelengths.
- Almost all “simple” (di- or triatomic), light molecules have (sub)mm or far-IR (FIR) rotational spectra.
- Many of the complex molecules were (for a long time) *only* found in Sgr B2.

Interest remained high in special cm-wavelength lines, including the NH₃ inversion transitions near 24 GHz, a number of prominent maser lines from OH (hfs, 1.7 GHz and higher frequencies), H₂O (22.2 GHz), CH₃OH (25, 12.2, and

² Both lines were on Townes’ (1957) list [4]!

³ Circumstellar molecules exist in the envelopes of evolved giant stars. Many species are detected there which are also found in interstellar clouds, whereas some others, have so far *only* been detected in a circumstellar environment.

⁴ See http://www.ph1.uni-koeln.de/vorhersagen/molecules/main_molecules.html.

⁵ The frequencies are taken from the JPL catalog [33]; see <http://spec.jpl.nasa.gov/> or the Cologne Database for Molecular Spectroscopy (CDMS) [34]; see http://www.ph1.uni-koeln.de/vorhersagen/molecules/main_molecules.html. Numbers in parentheses are uncertainties in the last significant digit(s).

Table 2.1 The first interstellar “Radio” molecules

Name	Species	Transition	Frequency (MHz)	Reference
Hydroxyl	OH	$^2\Pi_{3/2}, J = \frac{3}{2}$	1665.4018(2) ^a	[3]
Ammonia	NH ₃	(1, 1)	23694.4955(1) ^b	[7]
Formaldehyde	H ₂ CO	1 ₁₁ – 1 ₁₀	4829.660(1) ^b	[9]
Water	H ₂ O	6 ₁₆ – 5 ₂₃	22235.08(2) ^b	[8]
Methyl alcohol	CH ₃ OH	1 ⁺ – 1 [–]	834.267(2)	[12]
Formic acid	HCOOH	1 ₁₁ – 1 ₁₀	1638.804(1)	[13]
		2 ₁₁ – 2 ₁₂	4916.319(3)	[14]
Formamide	NH ₂ CHO	1 ₁₁ – 1 ₁₁	1539.58(2) ^c	[15]
		2 ₁₁ – 2 ₁₂	4618.55(2) ^c	[16]
Cyanoacetylene	HC ₃ N	1 – 0	9098.6537(3) ^c	[17]
	H ¹³ C ₃ N	1 – 0	~ 9060 ^d	[18]
	H ¹²⁺¹³ C ₃ N	1 – 0	~ 9000 ^d	[19]
Acetaldehyde	CH ₃ CHO	1 ₁₀ – 1 ₁₁	1065.075(5)	[20]
Methylidine	CH	$^2\Pi_{1/2}, J = \frac{1}{2}$	3263.788(10) ^c	[21]
Thioformaldehyde	H ₂ CS	2 ₁₁ – 2 ₁₂	3139.38(3)	[22]
Methanimine	CH ₂ NH	1 ₁₀ – 1 ₁₁	5290.31(4)	[23]
Methylamine	CH ₂ NH ₂	2 ₀₂ – 1 ₁₀	8776.2(1) ^f	[24]
Vinyl cyanide	H ₂ CCHCN	2 ₁₁ – 2 ₁₂	1371.8262(1)	[25]
Methyl formate	HCOOCH ₃ -A	1 ₁₀ – 1 ₁₁	1610.2445(7)	[26]
	HCOOCH ₃ -E	1 ₁₀ – 1 ₁₁	1610.91(10)	[27]
Dimethyl ether	(CH ₃) ₂ O	2 ₀₂ – 1 ₁₁	9119.668(15) ^c	[28]
Cyanodiacetylene	HC ₅ N	4 – 3	10650.650(4)	[29]
		2 – 1	5325.328(2)	[30]

Only those molecules first detected at cm-wavelengths are listed. For early detections in the mm-range, see Snyder [10]. All molecules were first detected in the transitions listed, except for dimethyl ether which was discovered in its 6₀₆ – 5₁₅ line at 90938.10(3) MHz by Snyder et al. [31]. No detections for isotopomers are listed, except for HC₃N

^aApart from the $F = 1 - 1$ line listed, also the $2 - 2$ line at 1667.3590(2) MHz was reported in the detection paper

^bLine with hfs, intensity-weighted frequency is given

^cLine with hfs, average of the lowest and the highest hfs line frequency, is given

^dVarious lines with differently placed ¹³C between 8815 and 9100 MHz

^eApart from the $F = 0 - 1$ line listed, also the $F = 1 - 1$ and $F = 1 - 0$ lines at 3335.475(10) and 3349.185(10) MHz, resp., were reported in the detection paper (frequencies from Rydbeck et al. [32])

^fFrequency from Fourikis et al. [24]

6.7 GHz), as well as the CH hfs lines (3.3 GHz). All of these, except for CH₃OH, have all or the bulk of their *rotational* spectra at submillimeter and far-infrared wavelengths.

Considering the mm-wavelength data coming in, soon after the radio observations, it became clear that the emission from many low-frequency, low- J lines of complex molecules toward Sgr B2 must be (weakly) inverted. Morris et al. [37] pointed out that this can be understood if the dipole collision is not the dominant factor of the collisional process; in such cases, population inversion for the $J = 0$

and 1 levels (at least for linear or near-linear species) may occur easily over a wide range of physical conditions (e.g., [38]). This is borne out by their statistical equilibrium calculations.

After the first complex molecules were found in Sgr B2, this source turned into a Bonanza: The described inversion mechanism together with a relatively strong, extended continuum background “boosted” many otherwise undetectable lines into “observability”. As a consequence, the vast majority of interstellar molecules was and still is found in Sgr B2, many of the most complex ones *only* there. All of the molecules listed in Table 2.1 are found in this source.

2.2 The Habitat of Interstellar Molecules

The by-far most abundant interstellar molecule is molecular hydrogen, H_2 . Since H_2 , because of its symmetry, does not have an electric dipole moment, only weak electric quadrupole transitions between rotational or ro-vibrational levels can be observed. Therefore, low rotational transitions of the CO molecule, although about by 10^{-4} less abundant than H_2 , have become the most important tool to study the large scale distribution of the molecular gas in the interstellar medium. Most of the molecular gas can be found in giant molecular clouds such as the region shown in Fig. 2.1. These clouds have diameters of 10–100 pc, masses of $\sim 10^{5-6.5} M_\odot$, and mean densities of several 100 cm^{-3} , but they are strongly clumped (e.g., [39]). The higher density clumps are probed in Fig. 2.1 by submillimeter dust continuum emission and are most closely associated with star formation. Giant molecular clouds are distributed along the Galactic plane with a small scale height of only $\sim 100 \text{ pc}$. Although they occupy only a relatively small volume of the interstellar medium, they contain a large fraction of its mass.

In addition, molecules can also be found in the so-called diffuse clouds, which are more tenuous and fully exposed to UV radiation from stars (see the review by Snow and McCall [41]). In fact, the first detections of molecules in space have been done by the observations of sharp optical absorption lines in diffuse clouds.

Molecules can even be found in circumstellar envelopes which are due to strong mass loss of stars in their late stages of evolution. The central stars in this stage have a low temperature so that molecules and dust can be formed and fueled into the interstellar medium.

2.3 Metal-Bearing Molecules in the Interstellar Medium

Observations of species containing metals, as well as other refractory species such as SiO , deliver important information on depletion into dust grains. Moreover, when released either from sputtering of the grains or their mantles by violent

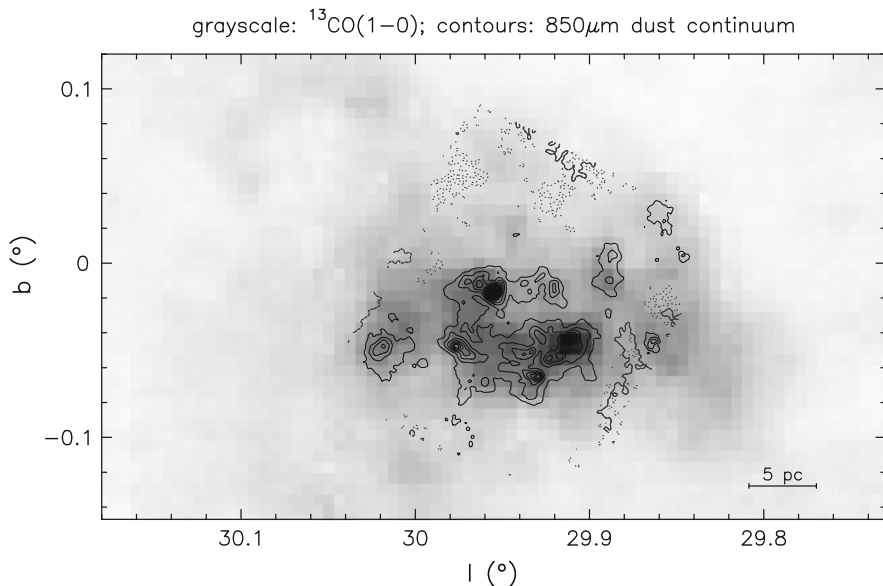


Fig. 2.1 The giant molecular cloud G29.9 seen in $^{13}\text{CO}(1-0)$ emission (grayscale) from the Galactic ring survey by Jackson et al. [40] overlaid with archival dust continuum observations from SCUBA at the JCMT

dynamics, such as protostellar outflows, they can be used as probes of these phenomena (see, e.g., Bachiller [42]).

To date, four diatomic, non-H-bearing metal compounds (NaCl , KCl , AlCl , and AlF and three triatomic ones (MgNC , MgCN , NaCN , and AlNC) have been detected in the dense envelope of the carbon star IRC+10216 [43–49]. MgNC , NaCN , AlF , and NaCl were also found, recently, toward the proto-planetary nebula (PN) CRL 2688 ([49–51]; see Petrie [52] for a discussion of other candidate species for detection). Still, only one metal-containing molecule, FeO , has been detected in the interstellar medium, toward Sgr B2 [53].

As regards metal hydrides, radio and (sub)millimeter wavelength searches for interstellar NaH [54] and LiH ⁶ have so far been unsuccessful, as was a search for MgH in IRC+10216’s envelope [56]. Optical wavelength absorption from CaH , AlH , FeH , and MgH has been found in cool stars and the Sun: MgH even in the integrated light of external galaxies (see, e.g., [57]).

⁶ The ground state $J = 1 - 0$ transition of LiH is near 444 GHz, an atmospherically very unfavorable frequency. A tentative detection of this line was made in the redshifted ($z = 0.68$) dense absorbing cloud toward the B0218+357 gravitational lens system [55].

2.4 Light Hydrides

The history of interstellar hydrides begins with the detection by Dunhum [58] of three optical absorption lines at 3957.7, 4232.6, and 4300.3 Å from diffuse interstellar clouds [58], which subsequently were found to arise from CH (4300.3 Å; McKellar [59]; suggested by Swings and Rosenfeld [60]) and CH⁺ (the former two; [61]).

It has been thought for a long time that hydrides might play an important rôle in cooling the highest density regions of interstellar clouds. Hydrides have, first, large level spacings, allowing them to emit relatively a large amount of energy per quantum. Second, their large dipole moments require high critical densities for their excitation. Thus, their rotational levels are only excited in high-density regions with $n > 10^6 \text{ cm}^{-3}$, making them effective coolants in this regime, where even rare CO isotopes are so optically thick that CO cooling becomes negligible compared to that of (the hydride) H₂O.

This regime was excluded in the classical study by Goldsmith and Langer [62] on “Molecular Cooling and Thermal Balance in Dense Molecular Clouds”, but was re-addressed by Neufeld et al. [63], who found that for elevated temperatures, $T = 100 \text{ K}$, H₂O cooling dominates, and the hydrides’ contribution is comparable to that of *all other molecules combined*, i.e., $\approx 30\%$ of the former.

Recent detections of hydride rotational transitions were made by the Caltech Submillimeter Observatory (CSO), namely H₃O⁺ ($J_K = 1_1^- - 2_1^+, 3_2^+ - 2_2^-, 3_0^+ - 2_0^-$ /307, 365, 396 GHz, [64, 65]), SiH ($^2\Pi_{1/2}, J = \frac{3}{2} - \frac{1}{2}$ /625, 628 GHz; [66]),⁷ HCl ($J = 1 - 0$ /626 GHz; [67]), H₂O, H₂¹⁸O ($1_{10} - 1_{01}$ /557, 548 GHz; [68]), HDO (the $1_{01} - 0_{00}$ /465 GHz and $1_{11} - 0_{00}$ /894 GHz ground-state transitions; [69, 70]),⁸ and NH₂ ($J = \frac{3}{2} - \frac{3}{2}, \frac{1}{2} - \frac{1}{2}, \frac{3}{2} - \frac{1}{2}$ /462, 459, 461 GHz; [71]). H₂D⁺ ($1_{10} - 1_{11}$ /372 GHz), the deuterated isotope of the key H₃⁺ molecule was discovered with the James–Clerck–Maxwell telescope [72].⁹ Observations using the Long Wavelength Spectrometer aboard the Infrared Space Observatory led to the discoveries of HF ($J = 2 - 1$ /2.47 THz; [74]), HD ($J = 1 - 0$ /2.68 THz and $2 - 1$ /5.36 THz; [75]), plus various H₂O, OH, and CH rotational and some H₃O⁺ inversion transitions (many toward Sgr B2; [76] and in the proceedings [1]).

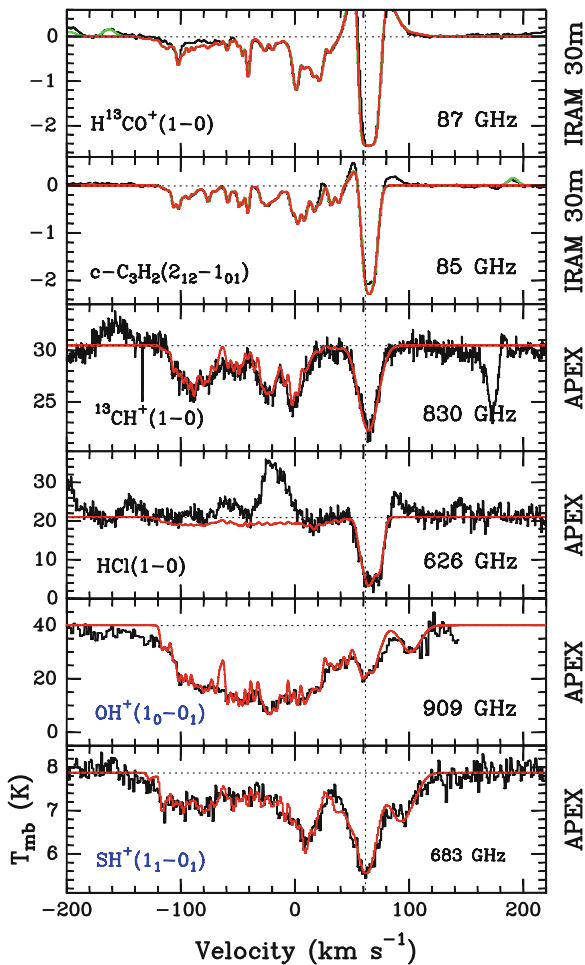
A preliminary conclusion is that (for the only two sources observed, Orion-KL and Sgr B2) the measured HCl and HF abundances indicate that only a low percentage of all chlorine is in these molecules, suggesting significant depletion. If this should hold true for other hydrides as well, then their cooling contribution

⁷ Tentative detection.

⁸ A number of higher excitation cm and mm-wavelength H₂O, H₂¹⁸O, and HDO transitions have also been found.

⁹ H₃⁺ itself was finally detected, after many arduous attempts, in absorption at near-infrared wavelengths by Geballe and Oka [73], benefitting from a monumental body of laboratory research, mainly gathered by Oka and collaborators (see the proceedings [1]).

Fig. 2.2 New hydrides, observations using APEX toward Sgr B2(M) (the upper two panels show IRAM 30-m detections for comparison. The gray lines show synthetic spectra based on the velocity components seen in the C_3H_2 spectrum



could be much smaller than that discussed above. More sensitive observations of more transitions toward more lines of sight are needed and are being observed now using the APEX telescope and at the Herschel Space Observatory.¹⁰

Using the APEX telescope in Chile on the 5000-m high Chajnantor plateau, several hydrides (SH^+ , $^{13}CH^+$, OH^+ , and HCl) have recently been studied from the ground by Menten et al. [77] and Wyrowski et al. [78] in the absorbing diffuse clouds towards Sgr B2(M). SH^+ and OH^+ were new interstellar detections, and the detected absorption of a continuous velocity range on the line-of-sight showed these molecules to be an abundant component of diffuse clouds (see Fig. 2.2).

¹⁰ <http://astro.estec.esa.nl/SA-general/Projects/First/first.html>.

With Herschel, also the HF ground-state transition has been detected in absorption (Neufeld et al., [79]), which shows that HF will be the dominant reservoir of interstellar flourine. From Herschel observations also, many detections of H_2O^+ are reported, which, compared to previous model predictions, turned out to have higher abundances in the low-density gas of diffuse clouds. Another new detection by Herschel is interstellar chloronium (H_2Cl^+ , Lis et al., [80]), again with surprisingly high abundances.

2.5 Ions

2.5.1 Cation

In 1970, Buhl & Snyder found an unidentified interstellar line during their search for the HCN (1–0) line at 86.3 GHz and labeled it “X-ogen” [81]. Even before this article was published in *Nature*, Klemperer [82] proposed HCO^+ as the carrier of the X-ogen line, but only several years later, this claim could be confirmed by laboratory measurements and interstellar observations of H^{13}CO^+ . This first detection of an interstellar ion, triggered studies on ion–molecule chemistry as the basis for the formation of interstellar molecules in the gas phase (e.g., [83]). In dense molecular clouds, the degree of ionization is determined by cosmic ray ionization of molecular hydrogen which further reacts with H_2 to form H_3^+ . The H_3^+ ion, which plays a key role in driving the chemistry in molecular clouds, was only detected in 1996 by Geballe and Oka by infrared absorption of three rotation–vibration transitions [73]. About a dozen cations have so far been detected and, only recently, several anions as well.

2.5.2 Anions

In 1995, Kawaguchi et al. [84] reported in their centimeter spectral line survey of the circumstellar envelope of IRC+10216 the detection of a series of seven lines showing a spectral pattern of a linear molecule with a rotational constant of 1377 MHz. Only 11 years later, McCarthy et al. [85] could attribute with new laboratory measurements these lines to the first anion detected in interstellar space, C_6H^- . In addition, the lines from the ions C_4H^- , C_8H^- , and C_3N^- (and possibly C_5N^-) have been measured in the meantime as well, and these molecules are now also observed in dark clouds and star forming regions. Very recently, even CN^- was detected in the carbon star envelope IRC+10216 (Agundez et al., [86]). While based on ion-chemistry models, negative ions have been predicted many years ago, the new observations have now triggered a new set of chemical models with new mechanisms for anion formation. A nice review is given by Herbst [87].

2.6 Chain Molecules

Besides simple linear molecules, such as CO and HCN, much larger linear molecules, chain molecules, have been detected over the years mostly in cold dark clouds, but also in the envelopes of late-type stars and proto-planetary nebula. A considerable amount of carbon can be locked up in these chains, with the prime examples being chains such as HC_nN , C_nH , and C_nS . The recent detections of negatively charged chains have been discussed in the previous section. These carbon chain molecules are highly unsaturated. The current longest detected chain is HC_{11}N which was detected toward the cold Taurus Molecular Cloud 1 (TMC-1). Laboratory frequencies of even longer chains are available. The longest chain detected in circumstellar envelopes is HC_9N . Carbon chain molecules might be related to the formation and destruction of carbonaceous compounds such as polyaromatic hydrocarbons (PAHs, see also the section about cyclic molecules).

2.7 Symmetric and Asymmetric Top Molecules

Symmetric rotors are being used as interstellar thermometers. Two of their moments of inertia are equal; therefore, they can be described by only two rotational quantum numbers, the total angular momentum, J , and its component along the symmetry axis, K . Radiative transitions are only possible within the so-called K ladder. For symmetric tops, such as CH_3CN and CH_3CCH , the line frequencies of transitions with the same J but different K have only small separations, and lines from the complete K ladder can therefore be easily observed simultaneously. The level population within a given K ladder is mostly a function of the temperature of the emitting clouds—therefore, being in local thermodynamic equilibrium—Boltzmann plots can be used to estimate the temperature of the clouds as shown in Fig. 2.3.

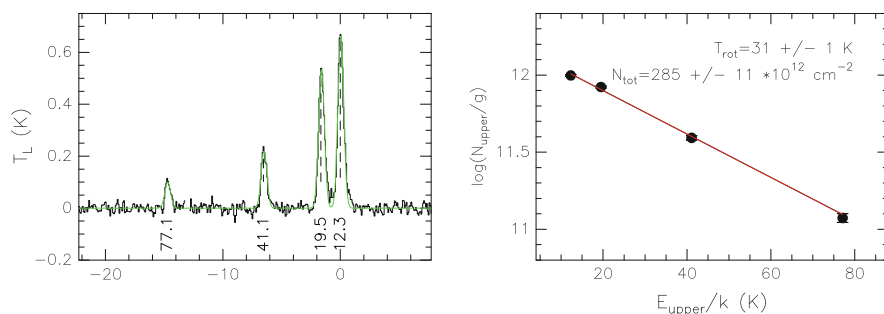


Fig. 2.3 IRAM 30-m telescope observations of the CH_3CCH $J = 5 - 4K$ ladder in a massive star forming clump. The temperature is estimated from the Boltzmann plot in the *right panel*

As already mentioned in Sect. 2.1, the first symmetric rotor detected in space was ammonia, NH_3 , since ammonia has observable lines in the centimeter wavelength range. These lines are due to the tunneling of the nitrogen through the plane of the hydrogen atoms and are called inversion lines. This effect causes a small splitting in energy of the rotational levels, and the so-called metastable inversion lines with $J = K$ can be observed in a relatively small frequency range around 24 GHz. An excellent review of ammonia is given in Ho and Townes [88]. Rotational transitions of ammonia were first observed in its lowest vibrationally excited state by Schilke et al. [89]. Rotational lines in the vibrational ground state cannot be observed from the ground. The first detection of the $(J, K) (1, 0) - (0, 0)$ line at 572 GHz was done with the Kuiper Airborne Observatory by Keene et al. [90].

Slightly asymmetric rotors offer, in addition to their dependence on the clouds' temperatures, the opportunity to probe the density of the molecular clouds. Important examples of this class of molecules that are often used in astronomical investigations are methanol (CH_3OH) and formaldehyde (H_2CO). To determine the physical parameters T and n of a molecular cloud, a range of transitions with different dependence on these parameters is observed.

The first asymmetric rotor detected in interstellar space was water, although it is very difficult to observe thermal water lines from the ground due to the large amount of water vapor in our atmosphere. Thermal lines of water have been studied with space observatories. The Infrared Space Observatory (ISO) made important detections of water. Its short-wavelength spectrometer (2–45 μm) covered mostly ro-vibrational lines, while its long-wavelength spectrometer (43–194 μm) covered pure rotational transitions, both with crude spectral resolution though. Velocity-resolved observations of the water ortho ground state line at 557 GHz have been conducted with the small space observatories, Odin and SWAS. A great progress in our understanding of interstellar water is currently being made with the Herschel Space Observatory, which allows to make velocity-resolved observations of many rotational lines of water with much higher spatial resolution than with the previous space observatories.

2.8 Cyclic Molecules

The first cyclic molecule detected in space was SiC_2 in the carbon star IRC+10216 observed by Thaddeus et al. [91] followed by the first truly hydrocarbon ring molecule C_3H_2 [92], which subsequently was extensively studied in many interstellar clouds. After these detections, only a few new ones joined the group of interstellar-detected cyclic molecules, namely, C_3H and $\text{C}_2\text{H}_4\text{O}$, and in 2001, Benzene (C_6H_6 ; Cernicharo et al. [93]) was detected in the infrared with ISO.

Polycyclic aromatic hydrocarbons (PAHs) can be considered as very big cyclic molecules, but their relation to their smaller siblings and the formation of PAHs are still not understood. For a recent review on PAHs, see Tielens [94].

2.9 Complex Molecules

A comprehensive review of complex organic interstellar molecules has recently been given by Herbst and van Dishoeck [95]. By interstellar standards, molecules containing six or more molecules are viewed as complex molecules. With this definition, about one third of the molecules detected in the interstellar medium or circumstellar shells are complex molecules. In the following, we give examples of the most complex molecules so far observed in interstellar space.

In 2003, Kuan et al. claimed to have detected the simplest amino acid, glycine ($\text{H}_2\text{NCH}_2\text{COOH}$) [96] in three warm, dense, interstellar clouds, including Sgr B2. If true, this would be the conclusion of a long quest (see, e.g., [97–100]).

Any such “identification” must rely on a large number of lines. Even so (or maybe *because of this*), the *confusion problem* is a formidable one. Inspecting any figure presented by Kuan *et al.*, one finds comparably many glycine lines as unidentified (“U”) lines. For a wider view, see the 218–263 GHz line survey by Nummelin et al. [101, 102], which, for Sgr B2(N), is at or near the confusion limit throughout that band, even at their relatively moderate sensitivity (compared to the interferometric data by Snyder and his collaborators).

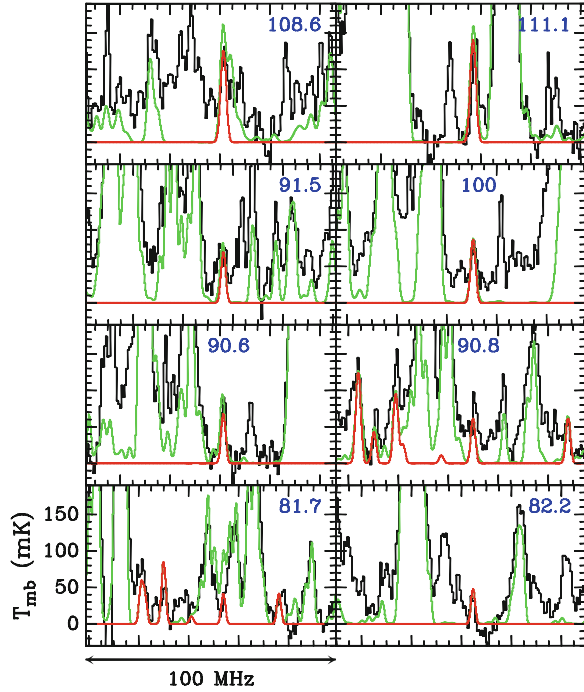
In the high-density ($n \sim 10^7 \text{ cm}^{-3}$) Sgr B2, “Large Molecule Heimat (LMH)” level populations are in Local Thermodynamic Equilibrium (LTE) characterized by rotation temperatures, T_{rot} , around 200 K [103]. At this temperature, the lower vibrationally excited states of a large number of complex molecules are populated, giving rise to a plethora of emission lines, probably with comparable intensities to the putative glycine lines. The width of the LMH’s lines, typically $\sim 6\text{--}10 \text{ km s}^{-1}$, adds additional complication. Given the gigantic partition functions, many of the lines are weak.

An instructive example of a well-founded detection of a large complex molecule is the amino acetonitrile’s (glycynonitrile) detection by Belloche et al. [104] in Sgr B2(N). This molecule is important since it is chemically related to the simplest amino acid, glycine. Many lines have been targeted (see Fig. 2.4). While many lines are blended, an important criterion is that all expected lines are actually seen. In addition, Belloche et al. performed interferometer follow ups, establishing that lines contributing to amino acetonitrile originate from the same positions in the cloud. In the future, the Atacama Large Millimeter Array (ALMA) will be an important instrument for the search for even more complex molecules, because the line-blending problem will be much smaller at high angular resolution.

2.10 Isotopologues and Deuterated Molecules

The observations of isotopologues of a given molecule has been important for several reasons: First of all, in many cases, the emission of the main isotopologue is optically thick (^{12}CO being the most prominent example), which leads to

Fig. 2.4 Spectra of amino acetonitrile lines at 3 mm obtained with the IRAM 30-m telescope [104]. A fit which includes all identified molecules at 3 mm in Sgr B2(N) is shown in *light gray*, whereas a fit of only amino acetonitrile lines is shown in *dark gray*



difficulties in the determination of column densities and the observations of the hidden, denser parts of the molecular clouds. Here, the rarer isotopologues come to help, in the case of CO, ^{13}CO , C^{18}O , and C^{17}O which are observed often to study the mass distribution in a cloud, while the optically thick main isotopologue is then used to derive the excitation temperature. Even detections of $^{13}\text{C}^{18}\text{O}$ have been made. Another important application is to use isotope abundance ratios as a tool for the understanding of stellar nucleosynthesis and to look for galactic gradients of these ratios (see, for example, [105]).

The large number of detected deuterated molecules came as a surprise, since the cosmic D/H ratio is only of order 10^{-5} , while new observations of deuterated molecules in cold molecular clouds find values of this ratio even above 0.1. The first radio detection of a deuterated molecule in the ISM was reported by Jefferts et al. [106] with the detection of the DCN (3–2) line in the Orion molecular cloud. In the same year, HD also was detected in the ISM with UV absorption measurements by Spitzer et al. [107]. The reason for the increased D/H ratio at low temperatures is that main reactions, such as $\text{H}_3^+ + \text{HD} \rightarrow \text{H}_2\text{D}^+ + \text{H}_2$, are exothermic. In addition, in cold environments, CO, the main reactant for H_2D^+ , is depleted further increasing the relative amount of deuterated molecules. This led in 2002 to record the detection of triple-deuterated molecules (ammonia and methanol).

2.11 Prospects for Future Detections

Science with the Herschel Space Observatory has just started in 2010 has just started, and the first results are encouraging (see the Astronomy & Astrophysics Herschel and Herschel/HIFI special issues of 2010). Unbiased line surveys from about 650 to 70 μm that are being performed toward the most fruitful astronomical objects in search of new detections of molecules in space have revealed already new species (e.g., H_2Cl^+). Many lines of these surveys will remain unidentified, and more laboratory spectroscopy and systematic computation and collections of frequencies, as provided by the JPL and CDMS catalogs, will be crucial. For the detections of more complex molecules, interferometers will be crucial. Besides ALMA, the Expanded Very Large Array (EVLA) also will play a major role at cm wavelengths, where, recently again, new heavy species are detected with the Greenbank telescope (e.g., the $\text{CH}_3\text{C}_6\text{H}$ detections by Remijan et al. [108] toward TMC-1).

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