Chapter 1

Molecular Spectroscopy: a Tool to Unveil the Universe

1.1 Spectroscopy and radioastronomy: symbiotic sciences

Most of the mass that composes the Universe is not molecular. Actually most of the mass that composes the Universe is not even baryonic material: dark matter counts for 90% of the mass of the Universe. Most of the remaining 10% is locked in stars, and just 1% of the total mass is gas distributed around the stars, the so-called Interstellar Medium (ISM), and half of it is molecular. The reason why studying the molecular composition of the Universe is important, is that astrophysical events such as galaxy, star, and planetary system formation happen in the dense parts of the Universe, which can be traced by molecules. The gas composing the ISM is at the same time the "exhaust" from old stars and galaxies, and the material that "feeds" the birth and growth of new galaxies, new stars, and eventually new planets. Understanding the chemistry that drives these phenomena is crucial to understand the phenomena themselves. The chemical inventory of a source, or of a source prototype, can unveil the evolution of the source itself. Furthermore molecules are tracers of physical properties such as temperature, density and the kinematics of astrophysical sources. For example, although it was quite disputed at the beginning of the 1970s [1, 2], the gravitational collapse that occurs prior to the formation of a star is traceable by the line profile of molecular transitions [3].

In order to interpret the steadily increasing amount of high resolution astronomical data, high resolution laboratory spectroscopy data are necessary. It is thanks to accurate spectroscopic data that in the last 50 years just few misidentification happened. In order to firmly detect a new molecule in space, prior (or subsequent) laboratory identification is mandatory. Furthermore, precise rest frequencies allow the spatial correlation of different species, which is very important for the consistency of astrochemical models.

1.1.1 Interstellar molecules

CH, CH^+ and CN have been the first molecules observed in space in 1937. The identification happened a little later [4]. It was not understood at that time that the very low rotational temperature inferred from the intensity ratio of the $N = 0$ and $N = 1$ CN lines had indeed a physical meaning. The measured rotational temperature of 2.7 K was in fact due to the cosmic microwave background radiation [5]. The cyanide radical, CN, was acting as a molecular thermometer by measuring the blackbody temperature of the Universe. The study of interstellar molecules has flourished in the 1980s, and it developed in parallel with the millimeter receiver technology. Up to date, around 180 different interstellar molecules have been detected, ranging from simple diatomic to complex organic molecules. The molecules detected in the ISM so far are listed in Table 1.1. One of the most interesting open questions in astrochemistry at the moment is how far the molecular complexity can go in space, and what is the link between the prebiotic molecules detected in space and the life on our planet, and eventually other planets. Molecular spectroscopy and radioastronomy are symbiotic sciences concerning the effort to answer these, and other questions.

TABLE 1.1: Molecules detected in the interstellar medium and circumstellar shells up to July 2013 (CDMS: http://www.astro.uni-koeln.de/cdms/molecules)

Number of atoms	**Molecules**
2	H_2, AlF, AlCl, C_2, CH, CH^+, CN, CO, CP, SiC, HCl, KCl, NH NO, NS, NaCl, OH, PN, SO, SO^+, SiN, SiO, SiS, CS, HF, HD FeO, O_2, CF^+, SiH, PO, AlO, OH^+, CN^-, SH^+, SH, HCl^+, TiO
3	C_3, C_2H, C_2O, C_2S, CH_2, HCN, HCO, HCO^+, HCS^+, HOC^+, H_2O, H_2S HCN, HNO, MgCN, MgNC, N_2H^+, N_2O, NaCN, OCS, SO_2, c-SiC_2, CO_2, NH_2, H_3^+ SiCN, AlCN, SiNC, HCP, CCP, AlOH, H_2O^+, H_2Cl^+, KCN, FeCN, HO_2, TiO_2
4	c-C_3H, l-C_3H, C_3N, C_3O, C_3S, C_2H_2, NH_3, HCCN, $HCNC^+$, HNCO HNCS, $HOCO^+$, H_2CO, H_2CN, H_2CS, H_3O^+, c-SiC_3, CH_3, C_3N^-, PH_3 HCNO, HOCN, HSCN, H_2O_2, C_3H^+
5	C_5, C_4H, C_4Si, l-C_3H_2, c-C_3H_2, H_2CCN, CH_4, HC_3N, HC_2NC, H_2C_2O H_2NCN, HNC_3, SiH_4, H_2COH, C_4H^-, HC(O)CN, HNCNH, CH_3O, NH_4^+
6	C_5H, l-H_2C_4, C_2H_4, CH_3CN, CH_3NC, CH_3OH, CH_3SH, HC_3N^+, HC_2CHO, NH_2CHO C_5N, l-HC_4H, l-HC_4N, c-H_2C_3O, H_2CCNH, C_5N^-, HNCHCN
7	C_6H, CH_2CHCN, CH_3C_2H, HC_5N, CH_3CHO, CH_3NH_2, c-C_2H_4O, H_2CCHOH, C_6H^-
8	CH_3C_3N, $HC(O)OCH_3$, CH_3COOH, C_7H, C_6H_2, CH_2OHCHO l-HC_6H, CH_2CHCHO, CH_2CCHCN, H_2NCH_2CN, CH_3CHNH
9	CH_3C_4H, CH_3CH_2CN, $(CH_2)_2O$, CH_3CH_2OH, HC_7N, C_8H, $CH_3C(O)NH_2$, C_8H^-, C_3H_6
10	CH_3C_5N, $(CH_3)_2CO$, $(CH_2OH)_2$, CH_3CH_2CHO
11	HC_9N, CH_3C_6H, C_2H_5OCHO, $CH_3OC(O)CH_3$
12	c-C_6H_6, $C_2H_5OCH_3$, n-C_3H_7CN
more than 12	$HC_{11}N$, C_{60}, C_{70}

1.2 New radio and far-infrared observatories

The upcoming radio and far-infrared observatories will challenge the work of spectroscopists. Laboratory data is urgently needed in order to interpret the astronomical spectra that have been taken with instruments such as HIFI on the Herschel satellite, and that will be taken at new and upcoming observatories such as ALMA, SOFIA and CCAT.

The Atacama Large Millimeter/submillimeter Array (ALMA), see Figure 1.1, is an interferometric array, composed initially of 66 antennas located at 5000 meters altitude on the Chajnantor Plateau, in northern Chile. ALMA provides an unprecedented sensitivity, angular resolution, spectral resolution and imaging fidelity in the frequency range between 84 and 950 GHz. ALMA is a giant array of 12-m antennas, with baselines up to 16 km, and an additional compact array of 7-m and 12-m antennas to image extended targets. Rare isotopologues and vibrationally excited states of known astronomical species, as well as new interstellar molecules will be detected by ALMA in the upcoming years. For the proper identification of these species, laboratory data is necessary.

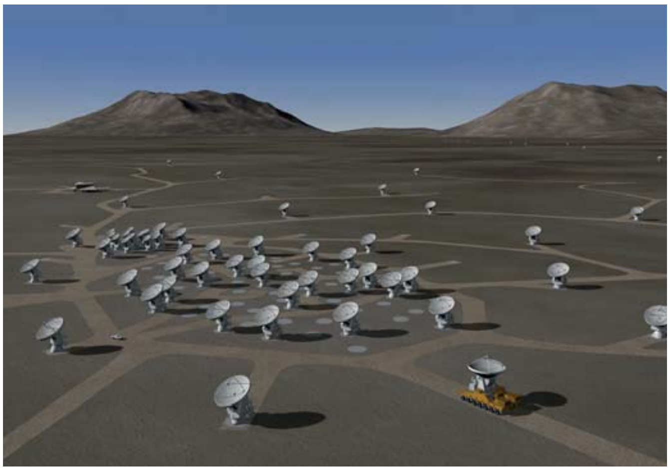

FIGURE 1.1: The Atacama Large Millimeter/submillimeter Array.
Credits: www.eso.com

SOFIA, the Stratospheric Observatory For Infrared Astronomy, see Figure 1.2, is the largest airborne observatory in the world, working at far-infrared and submillimeter wavelengths. SOFIA performs observations at wavelengths that are impossible to observe also for the largest and highest ground-based telescopes. A 2.5-meter telescope is housed in a Boeing 747-SP aircraft in order to make sensitive infrared measurements at an altitude 12.5 km, where the pw, precipitable water vapor level, is less than 7 micron. The telescope has a pointing accuracy better than 1 arcsec. GREAT (German REceiver for Astronomy at TeraHertz frequencies) is an infrared heterodyne spectrometer working in the frequency range of (1.25 - 1.5) THz and (1.82 - 1.92) THz, and allowing a maximum resolution of 47 kHz. This combination of frequency coverage and resolution has never been reached before. GREAT will allow to study, among other, small light molecules that could not be studied before.

FIGURE 1.2: SOFIA, the Stratospheric Observatory For Infrared Astronomy. Credits: www.dlr.de

CCAT will be a 25-meter telescope for astronomy in the submillimeter-wave range, see Figure 1.3. It will be located at 5600 m altitude on Cerro Chajnantor in northern Chile. CCAT will combine high sensitivity, a wide field of view, and a broad wavelength range to provide an unprecedented capability for deep, large-area, multicolor submillimeter surveys. First light for CCAT is planned for 2017. Given its high angular resolution, 3.5 arcsec at 350 micron, CCAT maps will resolve structural features and allow to study processes that are crucial for star formation.

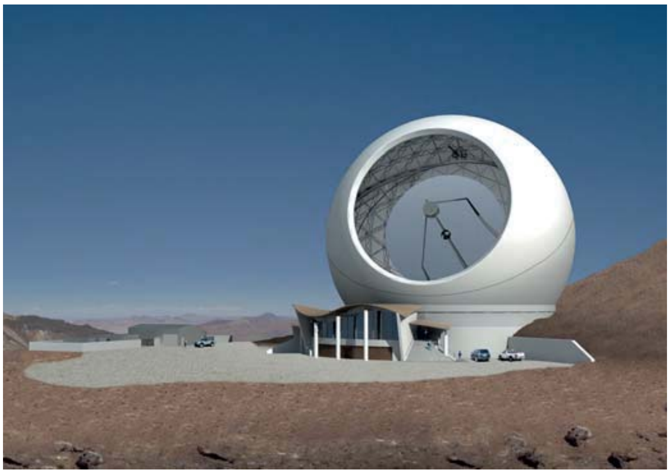

FIGURE 1.3: Concept View of the CCAT on Cerro Chajnantor, Chile.
Credits: www.ccatobservatory.org

In the course of this thesis I have performed observations with the IRAM 30 m telescope located at almost 3000 m altitude on Pico Veleta in Sierra Nevada (Spain), see Figure 1.4. It is a sensitive single dish telescope with a 30 m antenna, operating at 3, 2, 1, and 0.9 mm. In particular, for my observations I used the EMIR receiver in the 3 mm band (E090 band) with the Fourier Transform Spectrometer (FTS) backend at high spectral resolution (50 kHz). The total instantaneous bandwidth at a resolution of 50 kHz is 7.2 GHz, while at 200 kHz is 16 GHz.

FIGURE 1.4: The IRAM 30 m telescope, located in Pico Veleta in Sierra Nevada (Spain).

1.3 Necessity of laboratory data

The facilities described in the previous section promise to unveil the physics and chemistry of the interstellar and circumstellar medium. This will only be possible if the molecular databases used by radioastronomers will be fed with high quality new data. The most frequently used databases in the field of radioastronomy are the Cologne Database for Molecular Spectroscopy (CDMS) [6], and the JPL catalog, [7]. These catalogs are both intended to be a guide during the preparation of observations, and a reference for the identification of molecular species. In the CDMS and in the JPL catalog the same programs are used for fitting the spectra and generating the spectral catalog, SPFIT and SPCAT [8] respectively, so the output format is the same. The catalog lists frequencies with calculated uncertainties, intensities (300 K is used as a default temperature, but other temperatures may be requested in the catalog search form of the CDMS), the energies of the lower rotational levels, and the quantum numbers. The catalogs are generated by least-squares fitting of published spectral lines. The wider in frequency the set of measured lines is, the more accurate and reliable will be the generated catalog also at higher frequencies. Frequency accuracies well below the spectral resolution of the instrument are of crucial importance when analyzing an astronomical spectrum. Now that the far-infrared region of the electromagnetic spectrum is accessible, a big effort has to be made by the spectroscopic community in order to provide high quality data also at high frequencies.

Furthermore, with the high sensitivity of new facilities, new molecular species will be detected. Without high resolution spectroscopic studies, these molecular species will not be identified. Molecules with rare isotopes will finally come out of the noise where they were hidden in old surveys. Observations of all the isotopologues, or isomers, of a molecular species are important for astrochemical models in order to understand the path of formation of a molecule, or of a certain class of molecules.

Deuterium enrichment has been proven to be a good indicator of the early stages of star formation. With the upcoming observatories many more deuterated and multiple deuterated species will be observed.

The study of organic molecules such as methanol and dimethylether is also important, as they are widely distributed in space and have a dense spectrum. Sources such as Orion KL, an high-mass star-forming region, have a complicated spectrum to analyze. The spectrum is dominated by the features of complex molecules, such as methanol. Until the lines of methanol are not all assigned, it will be difficult to identify new species in such a spectrum. The only means to identify all the new features in the upcoming data (isotopologues, excited states, new molecular species) is to have very accurate rest frequencies, and this can only be accomplished with laboratory measurements.

1.4 This thesis

During my PhD thesis I have observed and analyzed spectra of elusive molecules in laboratory and in space.

The theory on which is based the analysis of the molecules object of my study, is introduced in Chapter 2.

I have developed a new discharge cell to produce and study unstable molecules such as molecular ions. The problems and challenges encountered during the development of the new discharge cell, as well as the first results, are described in Chapter 3.

I have also extended the frequency coverage on CO^+. The first THz spectra of this small cation have been measured in this work. All the available data for several isotopologues of CO^+ in the millimeter and submillimeter frequency range have been fitted together for the first time in an isotopically invariant fit. A much more accurate catalog at high frequencies is now available. This part of my work is described in Chapter 4. CO^+ is a good tracer of photon-dissociation regions (PDRs). PDRs are regions around massive young stars, in which far ultraviolet photons strongly influence the gas chemistry. So far CO^+ was detected just in the 2 lowest rotational transitions, and with very low rotational temperatures (around 10 K) compared to the surrounding medium (hundreds of Kelvin). Since few rotational levels have been probed, the processes responsible for its excitation cannot be fully understood. Recently the $N = 5$ - 4 at 500 GHz transition was detected toward Orion South [9]. This is the first high N detection of CO^+. We have performed observations with the APEX telescope* in order to map CO^+ in this source, and to observe also other transitions to better understand and model the excitation of this small cation.

*APEX, the Atacama Pathfinder Experiment, is a 12 m diameter antenna on the high altitude site of Llano Chajnantor in Chile.

Furthermore, I detected a new doubly deuterated molecule in space. *c*-C_3D_2 was observed toward two starless cores, TMC-1C and L1544, during a dedicated observing run at the IRAM 30 m telescope in the fall of 2012. The details and implications of this detection are discussed in Chapter 5.

In the data collected for the detection of *c*-C_3D_2, also *l*-C_3HD has been tentatively detected for the first time with a surprisingly high abundance in TMC-1C. The observed ratio between the fully hydrogenated and the monodeuterated linear C_3H_2 is around 50%. This is much more than the ratio observed for the cyclic isomer, around 10%, or for any other deuterated molecule observed so far. A new proposal has been submitted at the IRAM 30 m telescope in order to confirm this detection. The tentative detection of *l*-C_3HD is described in Chapter 6.