Abstract

Molecules are important tools to unveil the history, the structure and the evolution of the Universe.
In this thesis I underline the importance of high resolution spectroscopy in the laboratory and in space, and the symbiotic bond between laboratory spectroscopy and radioastronomy.
My work is divided in two parts. The first part concerns high resolution spectroscopy of unstable molecules in the laboratory. The second part deals with radioastronomical observations of deuterated molecules in dense cores.

CO^+ is the cation of the second most abundant molecule in space, carbon monoxide, and it is a good tracer of Photon-Dominated Regions (PDRs).
In this work the rotational spectra of CO^+, $^{13}CO^+$ and $C^{18}O^+$ in the v = 0 and 1 vibrational states have been measured in the submillimeter-wave range. Furthermore, the first THz spectra of the main isotopic species have been measured in the course of this thesis. An isotopically invariant fit has been performed, and a set of independent molecular parameters has been derived. The measured and predicted high frequency transitions of CO^+ will guide new astronomical observations.
Performing high resolution spectroscopy on ions is not trivial. The ions are unstable molecules and have to be produced in situ, at cryogenic temperatures by using a DC electrical discharge.
An experimental setup to produce and probe ions in the laboratory, based on a new cryogenic discharge cell, has been developed and tested. The new experiment is reliable, the discharge cell is vacuum tighter and it has a better control of the temperature with respect to the one previously used for the production of CO^+.
The new experiment is presented, and some possible implementations for the future are discussed.

The doubly deuterated cyclopropenylidene, *c*-C_3D_2, has been detected for the first time in space toward the starless cores TMC-1C and L1544. The chemistry of deuterated molecules in space is connected to the early stages of star formation. Having more probes to study these processes is therefore crucial.
Lines of the main species, *c*-C_3H_2, the singly deuterated *c*-C_3HD, and the species with one ^{13}C off of the principal axis of the molecule, *c*-$H^{13}CC_2H$, have also been detected. The lines of *c*-C_3D_2 have been observed with high signal-to-noise ratio, better than 7.5 sigma in TMC-1C and 9 sigma in L1544. The *c*-C_3D_2/*c*-C_3H_2 ratio is found to be around 1% in both sources.
The chemistry that leads to the formation of *c*-C_3D_2 has been studied and is discussed in this thesis.
The observed abundances of *c*-C_3D_2 can be explained solely by gas-phase processes, supporting the idea that *c*-C_3H_2 is an excellent probe of gas-phase deuteration.
l-C_3HD is the monodeuterated isotopologue of the linear isomer of cyclopropenylidene, propadienylidene. *l*-C_3HD has been tentatively detected towards TMC-1C and L1544.
One line of *l*-C_3HD has been observed both in TMC-1C and L1544. In order to confirm this detection, a proposal has been submitted to the IRAM 30 m telescope to observe one additional line.
If this detection will be confirmed, this would be the first interstellar detection of this molecule.
Furthermore, the observed ratio *l*-C_3HD/*l*-C_3H_2 is around 50%in TMC-1C and 30% in L1544. This deuteration ratio is the highest detected in space so far.
If confirmed, it will put stringent constraints on the chemistry regulating deuterium fractionation.