1

Introduction

Electromagnetic radiation is the main carrier of information about space. Its generation by and interaction with cosmic matter is used to gain insights into the formation and evolution of stars and galaxies. Both the birthplaces and graveyards of stars are populated by a plethora of interstellar molecules. To date approximately 140 molecular species have been detected in the interstellar medium (ISM) and circumstellar shells. The temperatures found in these objects are typically ranging from below 10 to 200 K for dense molecular clouds and star-forming regions up to a few hundred K for circumstellar shells. Consequently, radiation from the low energy part of the electromagnetic spectrum, i.e. from the microwave to far infrared region, where most molecules interact via rotational transitions, is best suited for diagnostics of these sources (see Figure 1.1). The accurate knowledge of laboratory transition frequencies of the molecules used as diagnostic tools is the prerequisite for the analysis of astronomical observations, and ever since the first detection of an interstellar molecule by radio waves [2], laboratory spectroscopy and radio astronomy have worked hand in hand.

The submillimeter wavelength and terahertz frequency regime has been opened up by extensive technical developments both for laboratory spectroscopy and for radio astronomy during the last decade.

Among the submillimeter wavelength telescopes that have been or are operated are high-altitude observatories like the Kölner Observatorium für SubMillimeter Astronomie (KOSMA), the Caltech Submillimeter Observatory (CSO), the James Clark Maxwell Telescope (JCMT), the SubMillimeter Array (SMA) and satellite based facilities like the Submillimeter-Wave Astronomy Satellite (SWAS) and the Infrared Space Observatory (ISO). Further improvements in receiver technology will enable future projects such as the Atacama Large Millimeter Array (ALMA) and its pathfinder experiment APEX, the Herschel Space Telescope, and the airborne Stratospheric Observatory for Infrared Astronomy (SOFIA) to extend the accessible frequency range further into the terahertz region.

This progress is accompanied in the field of laboratory spectroscopy by the development of very accurate and sensitive spectrometers. The experiments carried out in

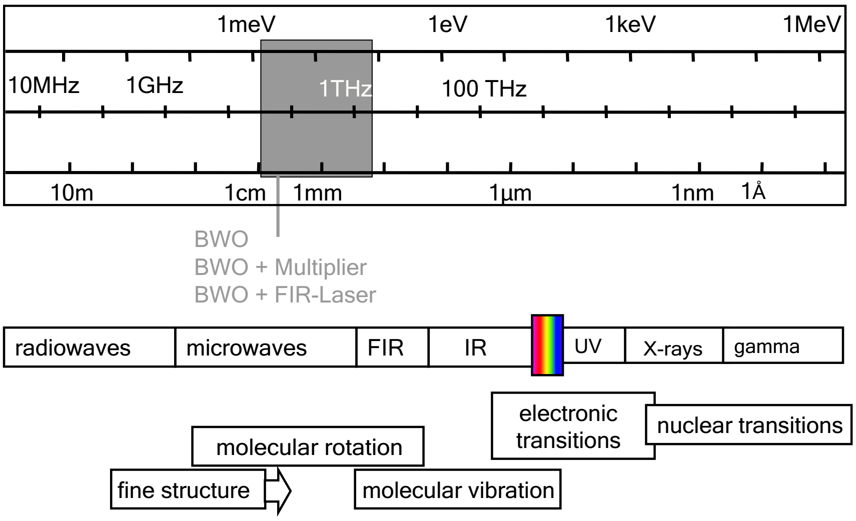

Figure 1.1: The electromagnetic spectrum and the main interaction processes of radiation with matter.

the course of this work employed spectrometers with phase-stabilised backward wave oscillators (BWOs) as key element. These radiation generators can be used either as direct sources as in the Cologne Terahertz Spectrometer [3, 4], as fundamental sources in combination with harmonic mixers operating as frequency multipliers [5], or as sideband sources in combination with a fixed frequency far infrared laser as in the Cologne Sideband Spectrometer for Terahertz Applications (COSSTA) [6, 7]. The frequency coverage of the Cologne spectrometers is summarised in Figure 1.2 and compared to that of major future radio telescopes.

Transitions between energetically low lying rotational levels of very light molecules, e.g. mono- and dihydrides, and between higher excited rotational states of medium-sized molecules, e.g. CH_3OH or SO_2, fall predominantly in the terahertz region. In other words, terahertz transitions of the first class of molecules can be used to probe the cold interstellar medium like dark molecular clouds, whereas the latter probe the denser, warmer regimes like hot cores in star-forming regions or excited gas in the vicinity of old stars. Especially these comparatively small molecules up to 4-5 atoms are found with high abundances in the interstellar medium. Most of them, such as water, OH^+, CH, CH_2, NH_3, HCO^+, H_3^+, HCN, H_2CO etc., are important reagents in interstellar chemistry reactions and thought to be the building blocks of larger molecules. Relative abundances and physical parameters obtained from the astronomical observation of these species give valuable information about the underlying chemical pathways for molecule formation as well as the physical and chemical evolution of the sources.

In the course of this work a large variety of molecular species have been investigated by means of rotational spectroscopy in the terahertz region. Among these are fully deuter-

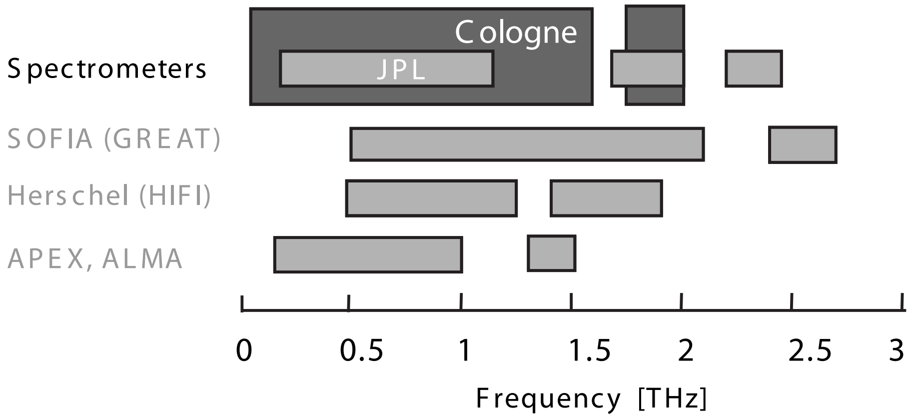

Figure 1.2: Frequency coverage of the terahertz spectrometers in Cologne compared to the operation range of future major telescope projects.

ated phosphine (PD_3), formaldehyde (H_2CO), oxadisulfane (HSOH, DSOD), molecular oxygen (O_2), sulphur dioxide (SO_2), deuterium isocyanide (DNC), hydrogen cyanide (HCN) and its isotopomers, methylene (CH_2) and water (H_2O) and its isotopomers. This thesis will concentrate on the three latter molecular species in detail, since their measurement and analysis account for the most extensive studies. They serve the astrophysical and spectroscopic community in different ways.

Deuterium Cyanide and its Isotopomers

Hydrogen cyanide (HCN) was one of the first molecules detected in the interstellar medium [8]. It is very abundant in a variety of interstellar environments and commonly used as a high density gas tracer. Moreover, it has been observed in very highly excited rotational and vibrational states [9]. Since the main isotopomer often exhibits opacity effects, the less abundant isotopically substituted species are frequently used as an alternative to obtain information on the physical conditions in an interstellar source. Furthermore, isotopic enrichment in the interstellar medium is subject of prevailing scientific discussion. In particular in the cold interstellar medium, deuterated species are found to be much more abundant than expected from the cosmic D/H ratio. Molecular isotopic ratios, deduced from chemical calculations, have been shown to be highly dependent upon the underlying chemical reaction network (e.g. [10] for deuterated species). Therefore, observationally deduced ratios are a test of the chemical models employed, for example gas-phase or grain-surface reaction pathways. Moreover, there is a need for highly accurate laboratory data for the analysis of the extremely narrow molecular lines observed in quiescent dark clouds, where hyperfine components of cyanide species can be used to gain insight into cloud dynamics [11].

In order to provide accurate laboratory data for these investigations, the rotational spectra of the deuterated cyanide species DCN, $D^{13}CN$, $DC^{15}N$, and $D^{13}C^{15}N$ in their vibrational ground and first excited bending state have been recorded up to 2 THz. The technique of sub-Doppler spectroscopy has been applied to be able to resolve the underlying hyperfine structure due to the nitrogen nucleus. The subsequent analysis yielded considerably improved spectroscopic parameters, which in turn are used to obtain highly accurate transition frequency predictions up to 2.5 THz.

The Methylene Radical

The methylene radical (CH_2) is of high interest for both astrophysical and spectroscopic reasons. It is an important reactant in gas-phase chemical models of interstellar molecular clouds and has already been observed in the hot cores of star-forming regions [12]. Furthermore, combined gas-phase and grain-surface models predict it to have high abundances in the cold interstellar medium [13]. However, transitions involving the energetically lowest rotational levels of CH_2 are located in the terahertz domain due to the extreme lightness of the molecule, and are not accessible with ground-based telescopes. Moreover, the methylene radical is also challenging for laboratory spectroscopy, since it is, on the one hand, difficult to produce in sufficient amounts to perform absorption spectroscopy, and, on the other hand, it cannot be described easily by standard theoretical models. This is reflected in the very sparse experimental dataset on this molecule and large uncertainties for transition frequency predictions, respectively.

This work reports on highly accurate measurements of two energetically low-lying rotational transitions of methylene near 2 THz. Furthermore, a global analysis of all published data on this molecule with a non-standard approach is presented, which enables the prediction of further transition frequencies relevant for astrophysical searches. A successful search in the ISO database for terahertz methylene absorption lines in cold interstellar gas in the line of sight towards the galactic center source Sagittarius B2 was triggered by this new analysis [14].

Water and its Isotopomers

Water is the third most abundant molecule in the interstellar medium. It has been detected in a wide variety of galactic and even extragalactic sources. Whereas its observation from the ground is hampered by strong absorption of atmospheric water vapour, the search of rotational water lines, which are the major cooling lines of star-forming regions, is one of the main scientific projects of the future submillimeter wavelength and terahertz satellite and airborne missions Herschel and SOFIA [15]. Most of its energetically low lying transitions appear in the submillimeter wavelength and terahertz regimes. Moreover, in the warmer interstellar medium, particularly in shock regions or circumstellar shells of late type stars, higher rotational and vibrational levels of water are likely to be populated considerably [16, 17], giving rise to additional transitions in this frequency domain. The knowledge of accurate transition rest frequencies is, therefore, mandatory up to notable high energies. Also, the observation of deuterated water species is important to increase the knowledge about isotopic fractionation and, thereby, to gain insight into molecular

formation processes [10].
Furthermore, water is the main absorbant in the earth's atmosphere, and accurate transition frequencies and intensities of its abundant isotopomers are demanded for atmospheric modelling.

As in the case of methylene, there is also a great purely spectroscopic interest in water and its isotopomers. It is the prototypical asymmetric rotor molecule, exhibiting large centrifugal distortion interactions, and many theoretical investigations employing different models to describe its rotational and rovibrational energy level structure have been carried out (see a recent review by Bernath [18]). Highly accurate laboratory data is needed to test these models.

Whereas for the main isotopomer new far infrared measurements and a thorough analysis of the eight lowest vibrational states has been recently published [19], the dataset on the deuterated species HDO and D_2O is considerably smaller, in particular highly accurate rotational data on higher excited rotational levels and in vibrationally excited states was missing. During the course of this work, this dataset has been extended significantly on both isotopic species in the vibrational ground and first excited bending state by measurements performed in the terahertz domain. Furthermore, a global analysis with a non-standard model is described, capable of providing reliable rotational transition frequency predictions of HDO and D_2O up to the far-infrared region and also of their fundamental vibrational bending mode in the IR.

Outline of this thesis

The experimental measurements and spectroscopic analyses of three molecular species are reported in this thesis. Although each of these species requires the introduction of certain experimental methods and theoretical models to some extent, they have in common that their rotational spectra were recorded mainly in the terahertz domain and that their rovibrational spectra were analysed with the aid of an effective Hamiltonian. Both the description of the experimental setup used for the measurements and the available theoretical armamentarium is, therefore, summarised for all three classes of molecules in Chapter 2 and 3, respectively. In Chapter 2, the sub-Doppler technique employed for the DCN isotopomers and the implementation of a Zeeman modulation at the laser sideband spectrometer necessary for the methylene measurements, are elucidated to some extent. A more thorough introduction of the Euler expansion of the Hamiltonian, applied for the analysis of water and methylene, is given in Chapter 3, together with a compilation of standard theoretical approaches for the class of linear and asymmetric rotor molecules with varying interactions. The following chapters deal with the spectroscopic investigations in detail. Chapter 4 contains information on the measurement and analysis of the deuterium cyanide isotopomers DCN, $D^{13}CN$, $DC^{15}N$, and $D^{13}C^{15}N$. The investigation of the methylene radical is described in Chapter 5, together with a discussion of the applicability of standard models for its analysis and a report of the detection of cold interstellar CH_2. In the last chapter (Chapter 6), new measurements on the two water isotopomers

D_2O and HDO are presented, in combination with the results of a thorough literature research on available published data and a global analysis of the extensive purely rotational and rovibrational dataset.

2

Experimental Setup - Spectroscopy in the Terahertz Domain

Performing spectroscopy in the terahertz domain is still a technically challenging task. Whereas commercially available microwave synthesizers based on field-effect transistors have a maximum output frequency of only 60 GHz, another solid-state source, the Gunn oscillator, reaches frequencies of up to 150 GHz. It is a common approach to use frequency-multiplier devices, such as Schottky diodes, to extent the frequency range, but the conversion efficiency decreases fast for higher harmonics. Even with cascaded multiplier chains much effort has to be made to reach frequencies higher than 1 THz with sufficient output power. Moreover, contributions from lower harmonics have to be carefully filtered to obtain monochromatic radiation.

Backward wave oscillators, belonging to the group of vacuum tube generators, can produce monochromatic radiation up to 1200 GHz, with typical levels of output power of several tens of mW to a few mW for the highest frequencies. This is sufficient to measure even extremely weak absorption lines. These sources have been successfully used for laboratory spectroscopy in Cologne for several years now and are the principal elements of the Cologne Terahertz Spectrometer, which will be described in more detail in Section 2.1. Successful attempts have been undertaken in the past and at present to use frequency multiplier devices in combination with BWOs as pumping sources.

In the frequency range between $\sim 1-5$ THz, no tunable solid-state or vacuum tube sources are available. Therefore, this domain is often called the terahertz gap. Quantum cascade lasers (QCLs) are promising candidates for closing this gap in the future, since fast developments are underway at the moment to tune their output frequency [20] towards terahertz frequencies. However, no cw-devices below 5 THz are commercially available at the moment, and the problem of frequency stabilisation and tunability of these sources in the terahertz region has not been addressed properly. Several alternative methods have been used to explore the terahertz or far infrared region. The method of Fourier transform spectroscopy, very successful in the IR region, can also be applied to the FIR, but the transition frequency accuracy achievable is around a few MHz only. Another approach is frequency mixing, either of the output of two optical diode lasers on a nonlinear optical crystal (photonic mixing) or of that of two IR gas lasers on a metal-insulator-metal (MIM) diode (Tunable Far Infrared spectroscopy - TuFIR). In both cases a difference frequency in the THz region is generated. Whereas the first method is limited by usually very small output powers, the second one is technically very elaborate.

The Cologne Terahertz Spectrometer is a typical absorption spectrometer with a tunable frequency source, an absorption cell, and a broadband detector. A schematical drawing of the spectrometer is presented in Figure 2.1. The Cologne Terahertz Spectrometer will be described in Section 2.1; details on this spectrometer can also be found in [3, 4].

The technique of sideband mixing has been successfully implemented in Cologne and will be described in more detail in Section 2.2. With this method, two radiation sources, in the FIR and millimeter-wavelength region, are mixed on a non-linear device to produce radiation at the sum frequency. Conversion losses are considerably smaller than in the case of photonic mixing and TuFIR, and a broadband tunability can be reached by using backward wave oscillators as sideband sources.

2.1 The Cologne Terahertz Spectrometer

As radiation sources, frequency stabilised backward wave oscillators (ISTOK RPC, Fryazino, Moscow Region, Russia) are used. Each of these vacuum tube devices is tunable by about 30 % of its nominal frequency. In Cologne BWOs ranging from $130-1200$ GHz are available with variable output power between 0.5 and 100 mW. A sketch of a BWO is shown in Figure 2.2. In these sources, an electron beam, emitted from a cathode (1) and accelerated by a high voltage ($1-6$ kV) to non-relativistic velocities, is de- and accelerated by a periodic slow-wave structure (2), thereby emitting coherent terahertz radiation in direction opposite to its flight direction. The electrons are focussed by a strong magnetic field (3), generated by an electromagnet. The radiation is coupled out by a small monomode aperture. In most cases, a conical horn antenna is directly mounted on the output flange of the BWO (4). The output frequency is dependent upon the accelerating voltage applied, which allows for pure electronic tuning of the device.

A free running BWO will display frequency fluctuations of several MHz on a timescale of $\sim$1 minute, generally more than the Doppler linewidth of molecular transitions and much more than the desired precision of the spectrometer. Therefore, a phase-stabilisation of the BWO is realised in Cologne to improve the frequency stability of the system. For this purpose, a small part of the radiation (around 10%) is coupled via for example a polarisation selective beam splitter onto a harmonic mixer device, where it is mixed with the output of a commercial frequency synthesizer (KVARZ, Russia) operating between $78-118$ GHz. The harmonic mixer will generate harmonics (IF) of the two input frequencies

$$\nu_{\text{IF}} = \pm m \cdot \nu_{\text{BWO}} \pm n \cdot \nu_{\text{Synth.}}$$

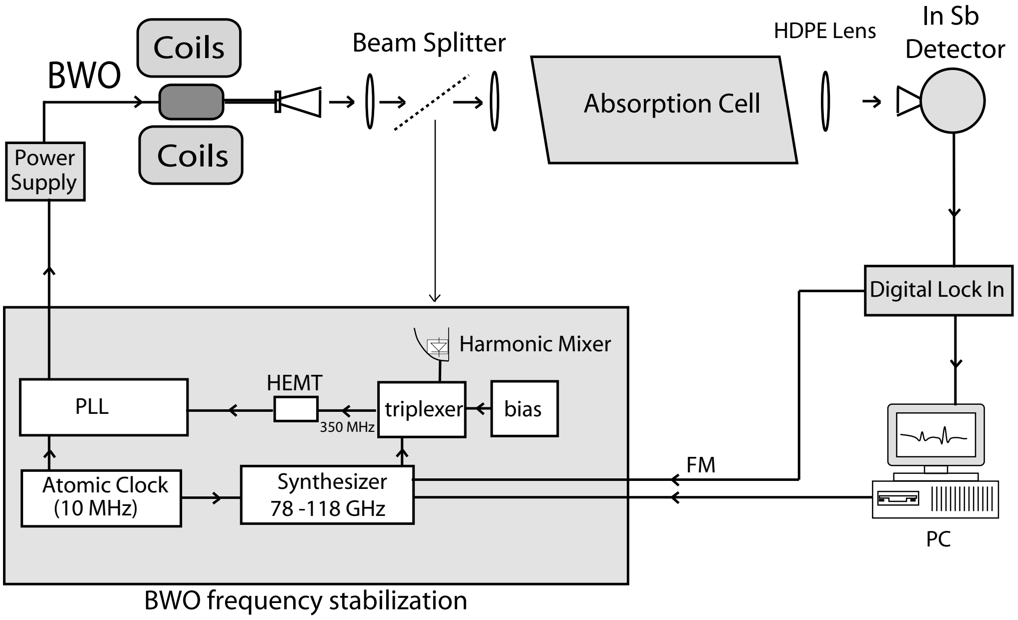

Figure 2.1: Schematical Drawing of the Cologne Terahertz Spectrometer.

For the stabilisation of the BWO, n and $\nu_{\text{Synth.}}$ are choosen in a way to obtain a ν_{IF} of 350 MHz for the desired BWO frequency ν_{BWO} ($m = +1$). This IF signal is compared in phase to a reference signal that is delivered by an atomic clock (rubidium reference, $\Delta\nu/\nu = 10^{-11}$). Any change in phase is converted into a voltage error signal applied to the BWO (see Figure 2.2 (5)) by the phase lock loop circuit (PLL). With this method, a frequency stability in the range of a few Hz can be achieved, reflecting the frequency accuracy of the atomic clock.

Pyrex glass tubes, typically between 1 and 3 m in length, are used as absorption cells. The radiation passes through Teflon or HDPE (high density polyethylene) windows which have low absorption coefficients in the terahertz region. The pumping system consists in general of a rotary vane pump followed by a turbo molecular pump and pressures of $8 \cdot 10^{-3}$ Pa can be reached.

A fast (relaxation time $\sim$1 μs) InSb hot electron Bolometer (QMC Instruments, Cardiff, UK) is used for the detection. This allows for a frequency-modulation of the BWO radiation up to 500 kHz, where $7 - 20$ kHz are typically used for the measurements. Measurements at the Cologne Terahertz Spectrometer are usually performed in 2f-modulation mode, resulting in recording of the second derivative of the absorption signal. A lock-in amplifier is used for demodulation of the signal. The amplitude of the frequency modulation can be optimised depending upon the expected linewidth and -strength.