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Introduction

Terahertz (THz) radiation is located in the electromagnetic spectrum between the microwave and the far infrared region at wavelengths between 1 mm and 0.1 mm. Just like other spectral regions, the complementary properties of THz radiation enable a large field of unique applications. A wide variety of non-conducting materials, such as paper, wood, plastic, ceramics and clothing are transparent at THz frequencies. As the photon energy is far below the ionization limit, THz radiation, unlike X-rays, is non-destructive, yet well-suited for imaging as the wavelength is small enough to provide spatial resolutions below 1 mm. These properties make THz frequencies attractive for use in the field of material testing, security applications, medical and biological imaging. In particular, scientific applications are of inestimable value, because this frequency domain is best suited to study a variety of physical processes. Astronomers, chemists as well as earth, planetary and space scientists have been applying THz technology for over 25 years to measure, catalog, and map thermal emission lines for a variety of light-weight molecules. In this part of the spectral region, chemical species provide an exceptional amount of information. The wavelength range corresponds to an equivalent black body temperature between 14-140 K. Thus, the radiated power of cold interstellar dust (<100 K) is largest at these frequencies. Thousands of individual spectral lines can be distinguished and provide deep insights into the composition of dark clouds, which are opaque at higher frequencies.

Despite the great opportunities provided in this field, the THz frequency region is still one of the most unexplored regions in the electromagnetic spectrum. Powerful radiation sources have been practically non-obtainable, and only due to the tremendous efforts during the last years, more and more monochromatic, tunable and compact radiation sources have become available. THz radiation, often also referred to as sub-mm-waves, is at the interface between electronics and photonics. The attempt to apply techniques, known from the bordering frequency regions of the microwave and the infrared, is still accompanied by a drastic drop of output power, which is often called the “THz-gap”. Nevertheless, a number of radiation sources are now available, which has made a variety of applications feasible and has triggered numerous commercial activities in this field. Besides the limited output power of radiation sources, most applications are hampered by the strong absorption features of water all over the THz range. The transmission is already drastically reduced by air humidity. That is why extremely dry environments are a prerequisite for most applications. Since the beginning of radio-astronomy, enormous efforts have been made to steadily increase the frequency region of telescopes, and nowadays a growing number of telescopes is ready to explore the THz frequency region. Telescopes, such as 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) as well as the Infrared Space Observatory (ISO), are operating successfully and have been important milestones on the way to accessing even higher THz frequencies. The enormous activities are also reflected by the number of next generation telescopes. APEX (Atacama Pathfinder Experiment) has recently started its scientific operation. Built as a pathfinder experiment for the large interferometer ALMA (Atacama Large Millimeter Array), it enables measurements in the atmospheric window at around 1.3 THz. Just like ALMA, it is located in the Atacama dessert in Chile, in large heights and an extremely dry environment - perfect conditions for THz measurements. With an array of about 66 antennas, ALMA will set new standards in spatial resolution, frequency coverage and sensitivity. To access frequencies, which are not accessible from ground based observations, the observatories SOFIA (Stratospheric Observatory for Infrared Astronomy) and the space observatory Herschel have been developed. The Hifi receiver on board of Herschel, which has recently been successfully launched, covers frequencies up to almost 2 THz. In addition the airborne observatory SOFIA will start its operation within the next years, granting observations at high THz frequencies in heights where atmospheric absorption is largely reduced.

As indicated in Fig. 1.1, rotational transitions and low lying vibrational transitions of molecules are located at THz frequencies. The uniqueness of rotational spectra of molecules plays an essential role in the identification of molecules in interstellar objects. Therefore, rotational spectra are often designated as “fingerprints” of molecules. This frequency region is hence particularly suited to study cold interstellar objects, where usually only rotational levels of molecules are populated. Objects such as dark clouds, prestellar cores and protostars play an important role in the evolution of stars. Studying the interstellar spectra of molecules does not only provide information about the chemical composition of astronomical objects, it also provides important clues about the physical condition and its environment. These analysis require a comprehensive understanding of the spectra of the involved molecules. Accurate rest frequencies and line intensities are essential prerequisites for the detection of molecules and the interpretation of astronomical spectra. An understanding of line profiles provides direct information about the physical properties of the investigated object, such as molecular abundances, temperatures, and velocity structure.

As rotational transition frequencies scale roughly with the inverse of the moment of inertia, rotational transitions of light hydrides and their deuterated isotopomers are located at high THz frequencies. They are highly abundant in very cold interstellar environments (<20 K) where only the lowest energy levels are populated. Often only few of their transitions are detectable, mainly located in the THz range, as it is the case for molecules, such as HD, H_3^+, CH_2. Some individual transition frequencies are of exceptional interest, such as the $J_{K_aK_c} = 1_{01} - 0_{00}$ transition of para-H_2D^+, which provides important information for understanding deuterium fractionation. Low lying vibrational transitions, which are usually large amplitude motions or bending motions, are also located in the THz region. Important examples are the bending modes of linear molecules, such as those of pure carbon chains (C_3, C_4, ...). Due to the lack of a permanent dipole moment, some linear molecules do not have a pure rotational spectrum. In these cases, their unambiguous detection is only feasible via rovibrational transitions. The frequency resolution provided within the THz range allows to obtain their rotationally resolved spectrum. Most molecules show rotational transitions within the whole microwave and THz region. In chemically rich interstellar environments, such as hot core regions, the rotational temperatures of molecules is usually between 100-200 K. At these temperatures, the most intense rotational transitions occur at around 1 THz. In order to study the chemical composition of interstellar objects, astronomers record spectra with very broad frequency ranges. These line surveys often show an immense density of spectral features, and in most cases molecular lines overlap and blend into each other. A large fraction of lines in surveys is caused by just a few molecules, which obey complex spectra.

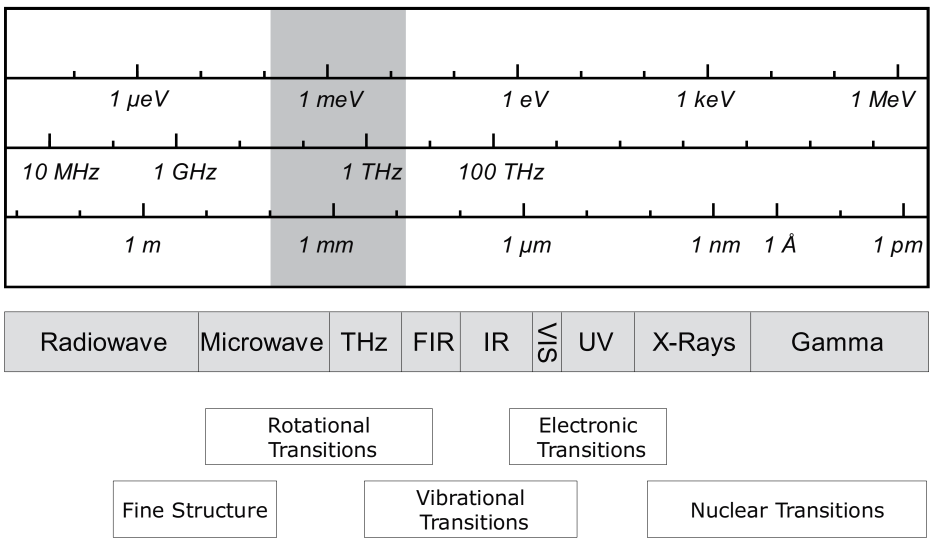

Figure 1.1: The electromagnetic spectrum and the molecular processes related to the different spectral regions.

As mentioned above, the knowledge of accurate rest frequencies is indispensable in order to decode astronomical spectra. This requires a comprehensive understanding of the rotational spectrum of each single molecule. The analysis of rotational spectra also provides important insights in the properties of molecules, such as structures, molecular bonds, inter-molecular forces, and processes. This is what laboratory spectroscopists aim to understand. Usually, quantum chemical models are applied to analyze experimental data and are an important tool to interpolate the experimental data to an extended frequency region. The quality of predicted transition frequencies strongly depends on the quality of the theoretical model and requires accurate experimental measurements. Usually, measurements within the entire frequency domain have to be carried out to access a sufficient number of energy levels to constrain the theoretical parameters to experimental values.

Many molecules, which obey complex spectra, have attracted the scientific interest for many decades, but a comprehensive analysis of their spectra still presents a challenge from the theoretical as well as the experimental point of view. In many of these molecules, atomic assembles undergo large amplitude motions by which the positions of the atoms vary according to the order of atomic distances. This complicates the quantum mechanical description considerably. In the astronomical context, molecules with complex spectra also pose an enormous challenge. Although many of them are unambiguously identified, the complexity of their spectrum and the spectral density of lines often hamper an accurate interpretation of the spectral features in astronomical spectra. In order to lift this line confusion, it is essential to know accurate rest frequencies over the entire spectral range.

In dimethyl ether (DME), which is the subject of the present thesis, the internal rotation of two methyl groups are large amplitude motions. DME is highly abundant in star forming regions and known to cause a large fraction of the observed lines in astronomical spectra. Although DME is one of the simplest molecules with two internal rotors, it has not yet been possible to accurately describe all spectral features. The analysis of its spectra is therefore well suited to develop new theoretical concepts and verify their quality for the class of molecules with internal rotors.

Laboratory observations in the THz frequency range are still a challenging task as powerful, monochromatic radiation sources are rare. Frequency stability and accuracy of the applied sources are essential for the measurements. Therefore, radiation sources used in the spectrometers are phase-stabilized to a frequency reference signal. More and more radiation sources have been available over the last years, realized by various technical approaches. Most commonly, frequency multiplication techniques are applied, which are well established in the mm-wave region for decades. They maintain the frequency accuracy of the input radiation. As will be discussed in the present thesis, frequencies up to almost 3.1 THz have been accessed. The limited output power of all radiation sources in the THz range requires the application of very sensitive detector systems. The signal to noise level is mainly determined by the interplay of radiation source and detector system.

Outline of the thesis

The present thesis is divided into two parts dealing with major questions which arise in the field of THz spectroscopy. The first part concerns the spectroscopic investigations of dimethyl ether. This molecule plays a key role when it comes to understanding the spectra of complex molecules, in which molecular subgroups perform large amplitude motions. For the reasons outlined above, a comprehensive and accurate description of the rotational spectrum is also of central importance for the interpretation of current and future astronomical spectra in the THz frequency region. Technical developments have been a prerequisite for the underlying comprehensive measurements particularly at highest frequencies. As more extensive and general technical studies of the spectrometer setups have been carried out, they are treated separately in part two.

This thesis aims to present a comprehensive analysis of the pure rotational spectrum in terms of astrophysical relevance. This includes the entire spectral range starting from mm-waves up to above 2 THz. The analysis focuses on the lowest vibrational levels, which are the vibrational ground state and the two lowest excited torsional states of the molecule. Particular attention is paid to the theoretical aspects including the applied model of the effective Hamiltonian, symmetries and the potential function of the torsional motion.

The introduction to the investigation of the torsion-rotational spectra of DME (chapter 2) gives the astrophysical context and motivation of this work, as well as a summary of previous laboratory works. As DME has been studied for many decades and under a variety of aspects, this summary focuses only on the major contributions directly concerning this work. Thereafter, the theoretical approach, which is applied in the analysis of the spectra, is discussed in detail (chapter 3). The effective Hamiltonian and its implementation in the applied fitting routines is described as well as other relevant properties, such as symmetry, spin statistics, and perturbations. The observed spectrum and the analysis of the rotational spectrum within the vibrational ground state and the two lowest excited torsional states are presented in chapter 4. The chapter comprises the description of recorded spectra and assigned transition frequencies. Sets of spectroscopic parameters are derived within the analysis and are used to predict transition frequencies and their line intensities as well as the potential function of the internal rotation. Finally, the huge dataset of transition frequencies has been used to obtain the first clear interstellar detection of DME in its excited torsional states. Part I ends with a conclusion of the obtained results.

The second part presents spectrometer setups which have been developed and realized within this work. The general introduction of spectrometer setups used in the THz frequency range (Chapter 6) is followed by an overview of these spectrometers which are well established in the Cologne laboratories and which have been applied in order to record spectra presented in part I

(Chapter 7). The extension of the spectral range, achieved by the application of a novel frequency multiplier, a so-called superlattice multiplier (SL), is one of the main technical results presented in this thesis (chapter 8). The construction of the SL spectrometers has been the prerequisite for measuring the spectrum of DME at highest frequencies and recording broad band spectra in the Cologne laboratories. Besides the properties of the SL devices, the design of the spectrometer is described in detail. Investigations have been carried out concerning frequency accuracy, tunability, and output power. At the end of part II, the application of heterodyne detection technique in laboratory spectrometer setups is presented (chapter 9). This extremely sensitive detection technique is well known in context with astronomical receiver systems and opens up new perspectives in the field of laboratory spectroscopy. In these preliminary studies, a variety of setups have been realized. The obtained results deliver important information to realize future spectrometers and outline applications of interest. The thesis concludes with a summary of the main results of both parts.