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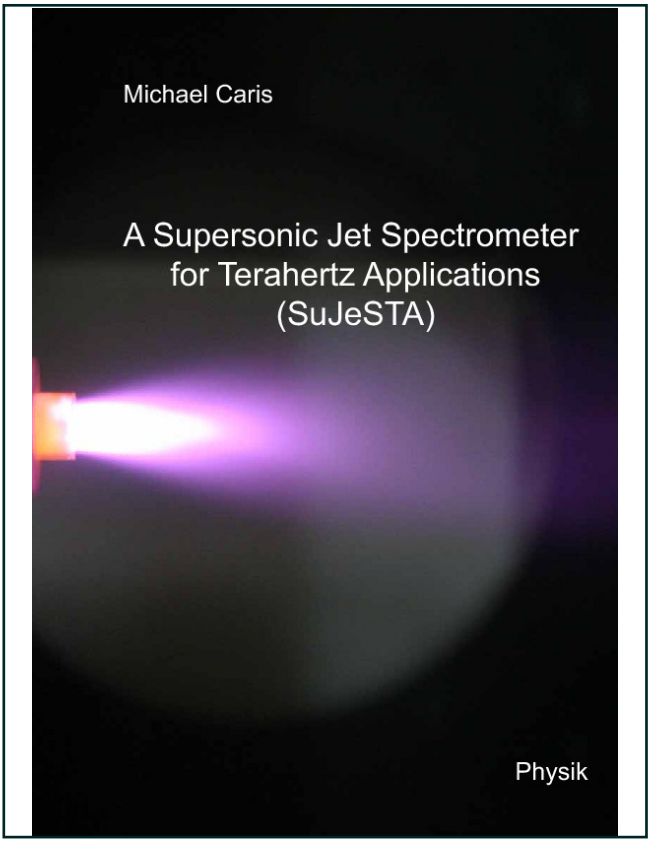
A Supersonic Jet Spectrometer for Terahertz Applications (SuJeSTA)



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Introduction

The interstellar medium (ISM) contains a rich variety of molecular species of which more than 130 have been identified beyond doubt by means of their characteristic spectra. Organic and inorganic species with up to 13 atoms have been found in interstellar molecular clouds, circumstellar regions, gas outflows, and planetary atmospheres (see Tab. 2.1). So far, the heaviest element in any detected interstellar compound is iron which is the ninth abundant atom. The elements with masses up to that of ***Fe*** are produced in nuclear synthesis of active stars and amount almost 100 % of the cosmic mass. The heavier, less abundant (0.0005 %) elements are generated in super novae by proton- or neutron-accretion. The 22 most abundant elements are listed in Tab. 2.2.

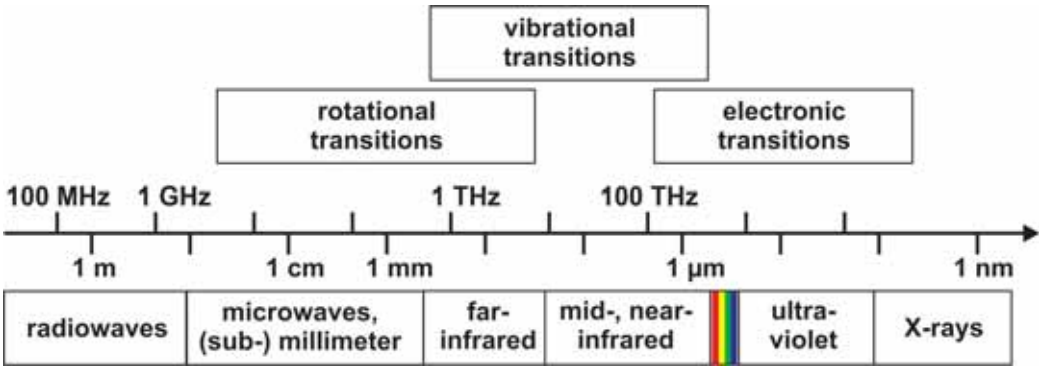

Figure 2.1: Schematic diagram of the electromagnetic spectrum and corresponding interactions of radiation with molecules.

Information about interstellar objects is mainly obtained via detecting electromagnetic radiation which is either emitted or absorbed by gas phase molecules, atoms, and ions. Due to the large temperature scale, ranging from a few Kelvin, in dense molecular clouds and star forming regions, to several hundred Kelvin, in circumstellar shells, a great part of the electromagnetic spectrum is appropriate for analyzing interstellar objects. It is the submilli-

meter and millimeter wavelength region (far-infrared), where molecular rotation transitions dominate, adjacent the near- and mid-infrared regime, with vibrations, followed by the optical and ultraviolet part of the spectrum which is caused by electronic transitions (see Fig. 2.1). The unambiguous identification of an interstellar molecular species strongly depends on the precise knowledge of its spectrum which is obtained by measuring transition frequencies in the laboratory and by deriving molecular parameters for further line predictions. Powerful tunable radiation sources, for instance synthesizers and Backward Wave Oscillators (BWOs), are used in laboratory spectrometers to generate radiation in the frequency region up to 1 THz. Especially the spectra of the centimeter and millimeter wavelength region are of great importance, since most of the molecules have been detected in the frequency region between 10 and 300 GHz (see Tab. 2.1).
At frequencies above 500 GHz the earth's atmosphere starts getting opaque for electromagnetic radiation and radioastronomic observations are hampered mainly due to atmospheric water. In near future, telescopes based on new receiver techniques, such as APEX[1], the airborne observatory SOFIA[2], and the HIFI[3] instrument aboard the Herschel satellite, will extend the observable spectral range towards shorter wavelengths, opening the terahertz domain for radioastronomy. In return, new techniques, such as superlattice devices combined with BWOs [24] or laser sideband generation [25], provide electromagnetic radiation sources above 1 THz for laboratory applications (see Fig. 2.2).

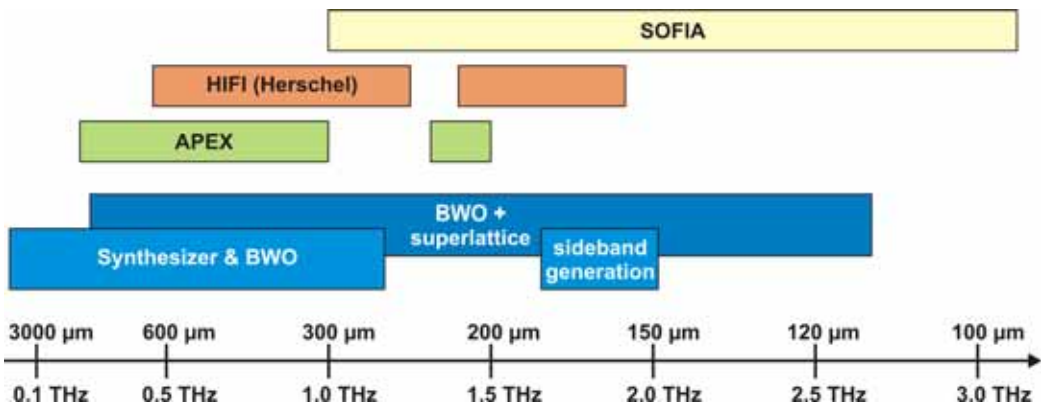

Figure 2.2: Schematic diagram of the frequency coverage of the Cologne terahertz radiation sources (two lower rows) compared to the frequency range of some telescopes (top rows).

In general, molecules split into two groups: Molecules which have a permanent dipole moment and those which do have not. The nonpolar species, for instance C_n, CO_2, C_2H_2, or CH_4, have no pure rotational spectrum. They

[1] Atacama Pathfinder Experiment, 200 μm – 230 μm and 300 μm – 1500 μm
[2] Stratospheric Observatory For Infrared Astronomy, 5 μm – 300 μm
[3] Heterodyne Instrument for the Far Infrared, 156 μm – 212 μm and 240 μm – 624 μm

Table 2.1: List of interstellar molecules detected by means of their rotational spectra in the radio to far-infrared frequency region.

2 atoms	3 atoms	4 atoms	5 atoms	6 atoms
H_2	$C_3{}^*$	$c-C_3H$	$C_5{}^*$	C_5H
AlF	C_2H	$l-C_3H$	C_4H	$l-C_2H_4$
$AlCl$	C_2O	C_3N	C_4Si	$C_2H_4{}^*$
$C_2{}^{**}$	C_2S	C_3O	$l-C_3H_2$	CH_3CN
CH	CH_2	C_3S	$c-C_3H_2$	CH_3NC
CH^+	HCN	$C_2H_2{}^*$	CH_2CN	CH_3OH
CN	HCO	NH_3	$CH_4{}^*$	CH_3SH
CO	HCO^+	$HCCN$	HC_3N	HC_3NH^+
CO^+	HCS^+	$HCNH^+$	HC_2NC	HC_2CHO
CP	OHC^+	$HNCO$	$HCOOH$	NH_2CHO
SiC	H_2O	$HNCS$	H_2CNH	C_5N
HCl	H_2S	$HOCO^+$	H_2C_2O	$l-HC_4H^*$ (?)
KCl	HNC	H_2CO	H_2NCN	$l-HC_4N$
NH	HNO	H_2CN	HNC_3	
NO	$MgCN$	H_2CS	$SiH_4{}^*$	
NS	$MgNC$	H_3O^+	H_2COH^+	
$NaCl$	N_2H^+	$c-SiC_3$		
OH	N_2O	$CH_3{}^*$		
PN	$NaCN$			
SO	OCS			
SO^+	SO_2			
SiN	$c-SiC_2$			
SiO	$CO_2{}^*$			
SiS	NH_2			
CS	H_3^{+*}			
HF	H_2D^+			
SH^*	HD_2^+			
HD	$SiCN$			
FeO (?)	$AlNC$			
O_2 ?	$SiNC$			
7 atoms	**8 atoms**	**9 atoms**	**10 atoms**	**11–13 atoms**
C_6H	CH_3C_3N	CH_3C_4H	CH_3C_5N	HC_9N
CH_2CHCN	$HCOOCH_3$	CH_3CH_2CN	$(CH_3)_2CO$	$C_6H_6{}^*$ (?)
CH_3C_2H	CH_3COOH	$(CH_3)_2O$	$(CH_2OH)_2$ (?)	$CH_3OC_2H_5$
HC_5N	C_7H	CH_3CH_2OH	H_2NCH_2COOH ?	$HC_{11}N$
CH_3CHO	H_2C_6	HC_7N	CH_3CH_2CHO	
CH_3NH_2	CH_2OHCHO	C_8H		
$c-C_2H_4O$	$l-HC_6H^*$ (?)			
H_2CCHOH	CH_2CHCHO (?)			

* indicates molecules that have been detected by ro-vibrational spectroscopy.

** indicates molecules that have been detected by electronic spectroscopy.

l indicates linear molecules.

c indicates cyclic molecules.

? indicates a questionable or (probable) tentative detection

can be identified by means of infrared active transitions in the near- and mid-infrared belonging to ro-vibrational modes. The molecules with a permanent dipole moment can be traced by means of pure rotational transitions in the millimeter and submillimeter wavelength region. Additionally, many chain molecules also have low energy bending vibrations in the terahertz region.

An important class of interstellar species are diatomic compounds. The list of diatomic molecules detected currently comprises of 30 entries two third of which are inorganic species. In 1987, Cernicharo and Guélin reported the detection of four metal halides, i.e. KCl, $NaCl$, AlF, and $AlCl$, towards the circumstellar envelope of late type star IRC+10216 [14]. The relative high cosmic abundance of aluminium, sodium, potassium, and chlorine, i.e. the 13th, 14th, 20th, and 19th most abundant element (see Tab. 2.2), lend encouraging motivation to continue searching for metal halides towards hotter and even denser core regions. The recently detected rotational lines of $NaCl$ on Jupiter's moon Io at frequencies of 143 and 234 GHz [15] demonstrate how special conditions, for instance continuous volcanic output, can produce spectroscopical measurable amounts of KCl, $NaCl$, etc.
Experimental studies on diatomic gas phase alkali halides in the laboratory are complicated due to the low vapor pressure of these molecules. Special vaporization conditions are necessary to provide them for gas phase spectroscopy. On the other hand, these species possess a very large dipole moment because of their highly ionic character. This means, they reveal a pure rotational spectrum with mainly large intensities. Reliable data on the alkali halides is rare. First spectroscopic data of $NaCl$, $RbCl$, and $CsCl$ in the millimeter wavelength range was published already in 1964 [3]. In 1997, the infrared emission spectra of KCl and $NaCl$ were published [16]. First high resolution measurements on sodium chloride in the THz region were performed with the Cologne terahertz spectrometer in 2001 (Caris *et al.* [26], [2]).

In the course of this work, high resolution measurements on five isotopomers of potassium chloride, i.e. $^{39}K^{35}Cl$, $^{39}K^{37}Cl$, $^{41}K^{35}Cl$, $^{41}K^{37}Cl$ and $^{40}K^{35}Cl$, have been performed up to 930 GHz with the Cologne terahertz spectrometer. A special evaporation cell has been used. The obtained data has been analyzed in an isotopically invariant form and a new set of invariant Dunham parameters has been derived including the first order Born-Oppenheimer breakdown corrections. With these molecular constants, reliable frequency predictions for the spectra of all six isotopomers are available which open the field for further astronomical detections.

A plethora of detected interstellar molecules contains one or more carbon atoms (75 %). Carbon is the fourth abundant element, after hydrogen, helium, and oxygen, and reveals a wealth of possible chemical bondings. One characteristic feature of the carbon atom is the tendency to build chain molecules, such as the stable cyano-polyynes, HC_nN (with $n = 1, 3, 5, ...$). This type of molecules has been detected in many astronomical sources, for instance towards the circumstellar envelope IRC+10216 (e.g. HCN [28], [29]; HC_3N

Table 2.2: Cosmic abundance of the elements normalized to $Si = 10^6$. Values taken from the publication of A. G. W. Cameron [27].

Element	Symbol	Abundance
Hydrogen	H	$3.18 \cdot 10^{10}$
Helium	He	$2.21 \cdot 10^{9}$
Oxygen	O	$2.15 \cdot 10^{7}$
Carbon	C	$1.18 \cdot 10^{7}$
Nitrogen	N	$3.74 \cdot 10^{6}$
Neon	Ne	$3.44 \cdot 10^{6}$
Magnesium	Mg	$1.061 \cdot 10^{6}$
Silicon	Si	$1.00 \cdot 10^{6}$
Iron	Fe	$8.3 \cdot 10^{5}$
Sulfur	S	$5.0 \cdot 10^{5}$
Argon	Ar	$1.172 \cdot 10^{5}$
Calcium	Ca	$7.21 \cdot 10^{4}$
Aluminium	Al	$8.5 \cdot 10^{4}$
Sodium	Na	$6.0 \cdot 10^{4}$
Nickel	Ni	$4.80 \cdot 10^{4}$
Chromium	Cr	$1.27 \cdot 10^{4}$
Phosphorus	P	9600
Manganese	Mn	9300
Chlorine	Cl	5700
Potassium	K	4200
Titanium	Ti	2775
Fluorine	F	2450
All other elements		5069

[30]; HC_5N, HC_7N [31]).
Besides the persistent carbon chains, there are numerous unsaturated and reactive molecules, for instance C_nH, C_nN, pure carbon chains C_n (with $n = 1,2,3,...$), and those cyano-polyynes with even numbers of carbon atoms. They are of significant astrophysical relevance and have been observed, for instance towards cold molecular clouds, such as TMC-1 and L183 (e.g. $l-C_3H$, C_4H, C_5H, C_6H [5]). Unlike the laboratory, the interstellar medium with ultralow pressure, density, and temperature conditions is a repository for this class of molecules. Thus, many radicals have been detected first by radio astronomers rather than in the laboratories, for example C_3N [32] and C_4H ([33], [34], and [35]) which were first observed in 1977 and 1978, respectively. The frequency predictions for theses detections had to be taken from ab inito calculations, since laboratory spectroscopy could not catch up with the interstellar detections for a long time until sophisticated production methods were developed. Nowadays, laboratory spectrometers for the investigation of radicals are available mainly in the infrared region, while the terahertz range is barely involved in the investigation of reactive species.

The Cologne Supersonic Jet Spectrometer for Terahertz Applications (SuJeSTA) has been developed within the scope of this thesis to overcome this lack of terahertz data for radicals. The new instrument combines an efficient source for radicals and a powerful terahertz radiation source to obtain high resolution spectra of the instable species and to provide the necessary laboratory data for future search for reactive, interstellar species. The molecules are formed by means of a pulsed discharge in the throat of a slit nozzle. The subsequent adiabatic, supersonic expansion into the vacuum chamber is almost collision-free and cools the rotational degree of freedom of the gas molecules to a few Kelvin. SuJeSTA is embedded in the international network of the Laboratoire Europeén Associé (LEA *HiRes*) which aims at developing a regional structure promoting the applications of high resolution spectroscopy in the field of molecular physics. Applications concern planetary science, atmospheric studies, astrophysics of the interstellar medium, time dependent chemistry, analytical chemistry, and process analysis.

The first application of SuJeSTA has been an investigation of the linear $X^2\Pi$ propynylidyne radical, $l-C_3H$. This chain molecule has been subject of many astronomical observations, since it is supposed to play a major role in the carbon chain growth in the interstellar medium. The linear C_3H radical in its vibrational ground state was first detected by Thaddeus *et al.* [4] towards IRC+10216 and the cold dark cloud TMC-1 in 1985. In 2000, Turner *et al.* [5] reported cyclic and linear C_3H in three small translucent molecular clouds (CB 17, CB 24, and CB 228), in TMC-1, and L183. The most recent detection of C_3H stems from an extensive spectral line survey towards TMC-1 (Kaifu *et al.* in 2004 [6]).
The C_3H radical is not only of astrophysical interest, but also a challenging molecule for spectroscopists. First information on C_3H came from theoretical studies. *Ab initio* calculations revealed the equilibrium geometric structure and provided vibrational frequencies ([17], [18], [19]). Effects, such as

spin-orbit coupling due to the $^2\Pi$ electronic ground state, and the hyperfine structure due to the nuclear spin of the hydrogen, were treated in many publications (e.g. [36], [37], [20]). Recently Perić *et al.* [21] investigated the Renner-Teller effect of C_3H, resulting from a coupling of the electronic angular momentum and the bending vibrational motion. Due to this strong coupling, the lower $^2\Sigma^\mu$-state of the ν_4 CCH bending mode is shifted towards lower energies and into the submillimeter region. This effect is typical for carbon chains and the understanding of its nature will support *ab initio* calculations of other chain molecules.
SuJeSTA has facilitated the first experimental study of this Renner-Teller shift due to the precise data of ro-vibrational transitions of the $^2\Sigma^\mu$-$^2\Pi_{3/2}$ band system, which is described in this work. A reasonable value for the Renner-Teller constant ε of C_3H has been evaluated, based on these measurements. Furthermore, the value of the excitation energy E_{ν_4} of the ν_4 ($^2\Sigma^\mu$) state has been strongly improved.
Another interesting feature of C_3H is a Coriolis coupling which causes perturbations of the rotational levels in the ground and the vibrationally excited states. First accurate values for the Coriolis interaction constant will be presented in this work. The pure rotational transitions in both $^2\Pi$ ground states and in the first excited vibrational state $v_4 = 1$ ($^2\Sigma^\mu$) have been recorded up to 600 GHz and the earlier measurements by Gottlieb *et al.* (1985 [7] and 1986 [8]) and Yamamoto *et al.* (1990 [9]) below 360 GHz have been substantially extended. From a least squares fit to a standard Hamiltonian a new set of molecular parameters has been obtained which is most reliable to predict transition frequencies up to 1 THz.

Besides uncharged molecules, ions represent another class of astrophysically important species. Like radicals, these molecules are usually instable under laboratory conditions and difficult to analyze by spectroscopical methods. However, they are abundant in the interstellar medium and play a major role in astrochemistry, since many chemical reactions involve ions.
Furthermore, ions, such as CO^+ and C^+, play a decisive role as PDR tracer (Photon Dominated Region). In the interstellar medium, the CO^+ ion is rare and normally optically thin due to its reactivity, for instance with H_2 to HCO^+. With knowledge of the column density of CO^+ chemical models of PDRs are verified [11]. The first detection of CO^+ towards OMC-1, a molecular cloud in the Orion nebula, was reported by Erickson *et al.* [12] in 1981. Twelve years later, Latter *et al.* [38] observed CO^+ in the planetary nebula NGC7027 and in the interstellar medium (M17SW).

SuJeSTA facilitates the analysis of adiabatically cooled ions in the terahertz region - in contrast to the production of ions in a DC glow discharge, where the ions usually have high rotational temperatures [10]. In this work, the carbon monoxide ion, CO^+, has been used as a test molecule. It turned out, that SuJeSTA is an expedient instrument for the spectroscopy of cold ions in the terahertz region and pure rotational transitions of CO^+ in the vibrational ground state have been observed.
CO^+, generated in glow discharges, was investigated in many laboratory mi-

crowave studies in the 1970s and 1980s ([39], [22], [40], and [23]). The latest set of isotopically invariant Dunham parameters was determined in the early 1980s. A very recent extensive investigation of the isotopomers $^{12}CO^+$ and $^{13}CO^+$ in the terahertz domain was carried out by Klapper [10] employing the Cologne Terahertz Spectrometer.
An updated isotopically invariant analysis of CO^+ including the Born-Oppenheimer breakdown corrections was not available, yet. Thus, the observed lines together with earlier data have been fitted in a mass independent least squares fit. The isotopically invariant mass-reduced Dunham parameters and the first order Born-Oppenheimer breakdown corrections for C and O have been determined. The resultant invariant parameter set of this work provides reliable frequency predictions for all isotopomers of CO^+ and encourages the astronomical search for those with low abundances.

Although the species which have been analyzed in this thesis require certain experimental setups and belong to different categories of molecules, they have all been investigated in the terahertz regime by means of laboratory spectroscopy. The rotational and, in case of C_3H, bending vibrational spectra have been analyzed with quantum mechanical methods to derive appropriate molecular parameters for their description. Upon these results the spectra are predictable in a wide range and the transition frequencies are available via the Cologne Database for Molecular Spectroscopy (CDMS) [41], [13].

3

Experimental Setup

The main aim of the present work is to combine a terahertz radiation source with a supersonic jet, to perform high resolution terahertz spectroscopy on molecular radicals and ions. For this purpose, the new Cologne Supersonic Jet Spectrometer for Terahertz Applications (SuJeSTA) has been setup which is described in Section 3.1. For the measurements on KCl the Cologne Terahertz Spectrometer has been used which has been described by Winnewisser *et al.* [1] in detail and in Section 3.2 of this work only briefly. Further details on the radiation sources are given in Section 3.3.

3.1 Supersonic Jet Spectrometer for Terahertz Applications

A main task in the course of this work was the construction and assembly of the new Cologne Supersonic Jet Spectrometer for Terahertz Applications (SuJeSTA). Extensive tests were performed to derive technical parameters, such as the amount of produced molecular transient species and lower limits for their detection. In a first scientific application SuJeSTA has been used to study pure rotational and ro-vibrational transitions of the linear C_3H radical (see Chapter 6). The new spectrometer has also been used to perform measurements on adiabatically cooled CO^+ ions (see Chapter 7).

The short absorption pathes and the low column densities of a jet spectrometer require a strong and stable radiation source besides a very sensitive detecting system. Backward wave oscillators provide enough power in the submillimeter and millimeter wavelength region to operate a terahertz jet spectrometer. SuJeSTA can be used in two different operational modes (see Section 3.3.2), either in a frequency stabilized mode or in a free-running mode: A highly precise mode for scans over small intervals, usually of 10–20 MHz width (see Fig. 3.1) and a fast scanning mode which covers a large frequency range of several hundred MHz (see Fig. 3.2). The less accurate