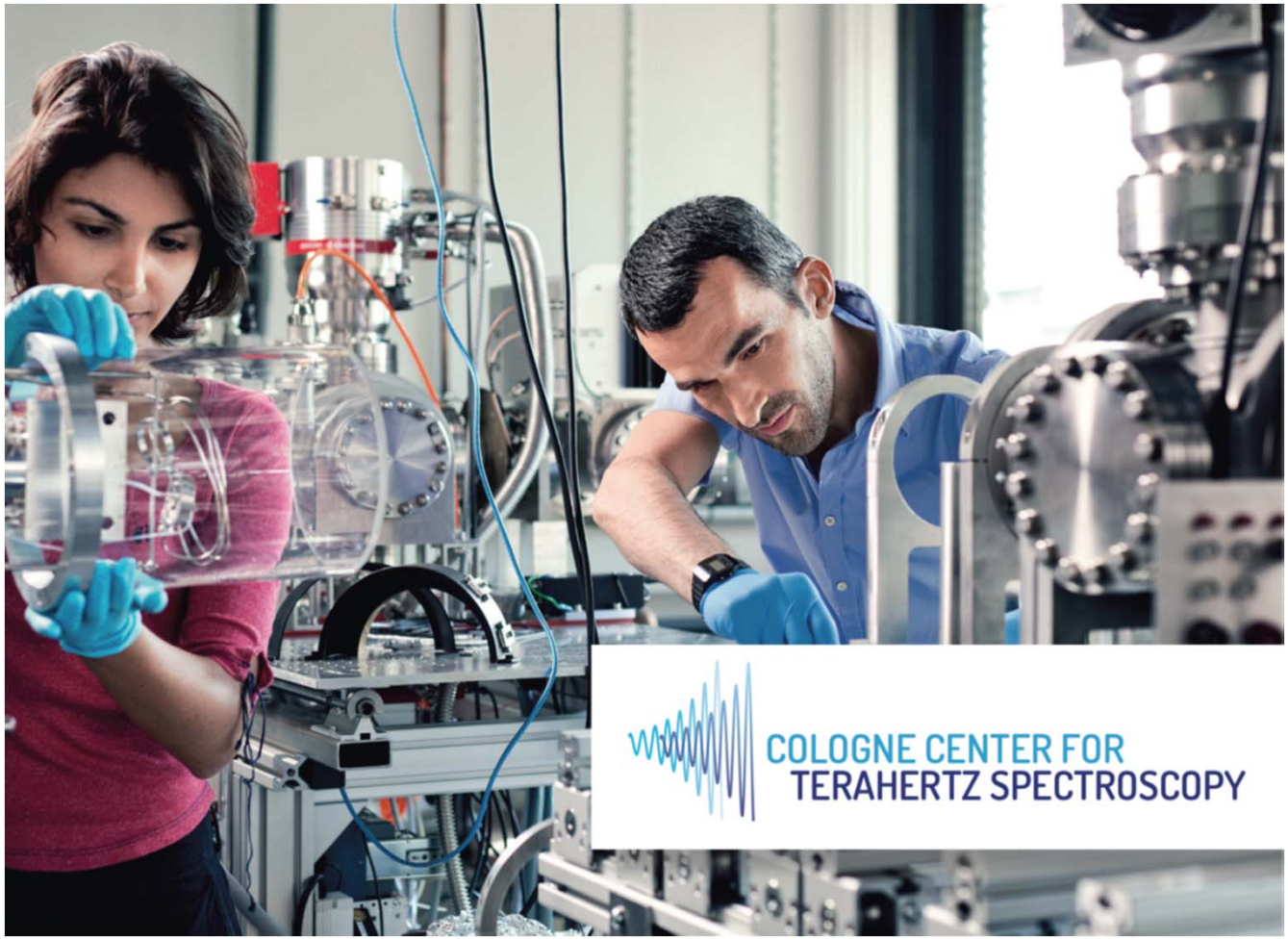

Molecular Astrophysics

Schlemmer Group

SFB 956
Cologne | Bonn

DFG

erc

Beyond the publications found on our web-page (see below) the work of our group has been summarized in the following monographic works and recent review articles:

S. Schlemmer, T. Giesen, F. Lewen, and G. Winnewisser, *High-Resolution Laboratory Terahertz-Spectroscopy and Applications to Astrophysics*, in: *Frontiers of Molecular Spectroscopy*, J. Laane (ed.), Elsevier 2008, ISBN-10: 0-444-53175-0.

S. Schlemmer, *Gas Phase Chemistry*, in: *Laboratory Astrochemistry - From Molecules through Nanoparticles to Grains,* S. Schlemmer, T. Giesen, and H. Mutschke (Eds.), 1st edition 2015, Wiley-VCH, Berlin, ISBN 978-3-527-40889-4

S. Schlemmer, *High-Resolution Laboratory Terahertz-Spectroscopy and Applications to Astrophysics*, in: *Frontiers and Advances in Molecular Spectroscopy*, J. Laane(ed.), Elsevier 2018, ISBN: 978-0-12-811220-5.

S. Schlemmer, *Molecular Spectroscopy of Astrophysical Molecules*, in: *Gas-Phase Chemistry in Space*, F. Lique and A. Faure (eds.), IOP Publishing Ltd, 2019, ISBN: 978-0-7503-1426-8

B.A. McGuire, O. Asvany, S. Brünken, S. Schlemmer, *Laboratory spectroscopy techniques to enable observations of interstellar ion chemistry*, Nature Review Physics (2020) **2**, 402–410

O. Asvany and S. Schlemmer, *Rotational action spectroscopy of trapped molecular ions*, Phys. Chem. Chem. Phys., 23, 26602–26622 (2021)

Contact: Prof. Stephan Schlemmer
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I. Physikalisches Institut, Universität zu Köln
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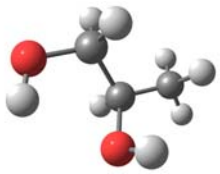
http://www.astro.uni-koeln.de/labastro

We acknowledge continuous funding through German Science Foundation, DFG. Many thanks go to all current and former group members who made and make this work possible.

Molecular Astrophysics

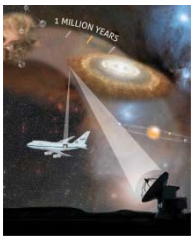
Schlemmer Group



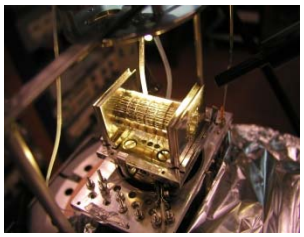
Molecules

Physical Parameters & Abundances

Synthesis & Methods

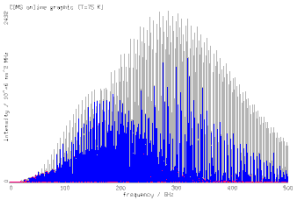


Observation & Modelling



Experiments & Theory

Analysis



Data Bases

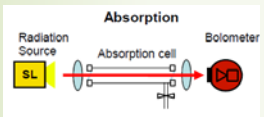
Line Positions
Intensities
Rate Coefficients

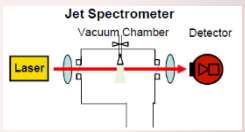
Spectroscopy
Collisions
Reactivity

Models

In the Molecular Astrophysics Group we investigate the quantum physics of interstellar molecules. We develop special techniques to hunt for new molecules in the laboratory and in space. We provide molecular parameters and spectral information to help astrophysicists predict their observations. To do this we follow the scientific approaches outlined below:

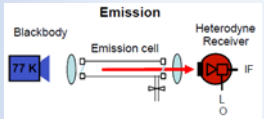
THz Absorption Spectroscopy

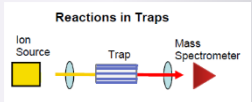




Jet Spectroscopy

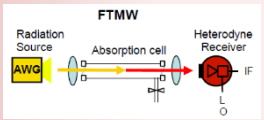
THz Emission Spectroscopy

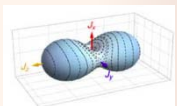




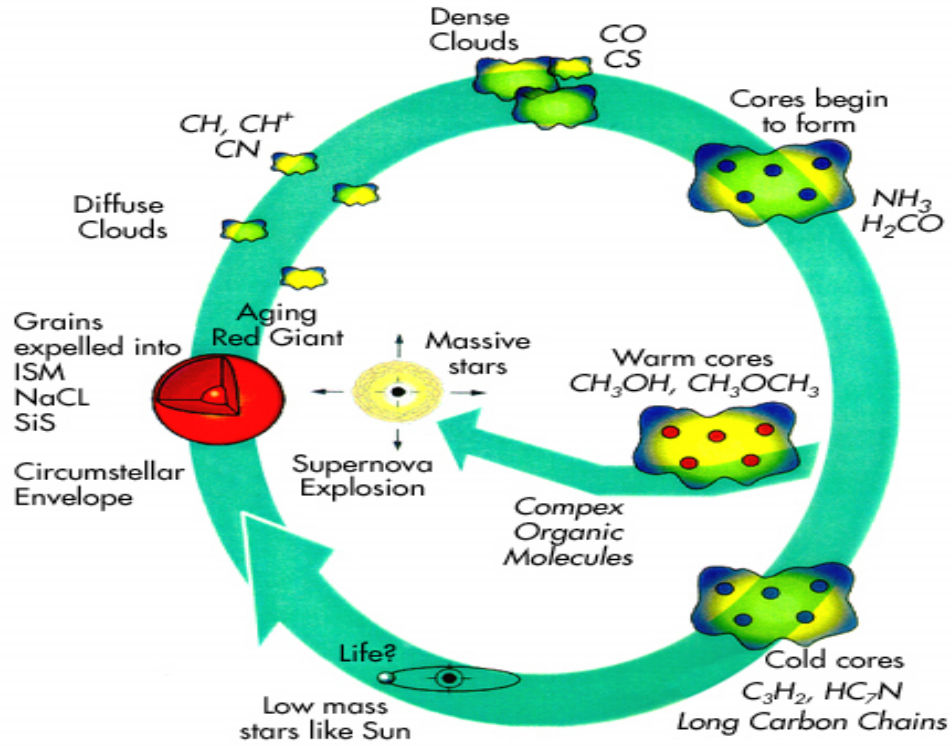
Spectroscopy & Reactions in Traps

Chirped Pulse Spectroscopy





Theory, Modelling & Data Base (CDMS)



Scientific motivation: The life cycle of stars and planetary systems like our own solar system is accompanied by the presence of a large variety of molecules. Their observed spectra teach us about the physical conditions (pressure, temperature) in space. The presence of small molecules, radicals or ions or complex organic molecules provides information on the evolutionary stage of the interstellar medium. Our group measures and calculates fundamental data on the spectroscopy of these molecules and investigates how they are formed and destroyed.

(Figure courtesy: http://herschel.jpl.nasa.gov)

<u>For Students:</u>

We offer projects at all levels of knowledge, lab courses for students and pupils, thesis projects at the Bachelor and Master level. Students are thoroughly guided by team members throughout their work.

Doctoral students from our group enjoy the competitive science projects, the international recognition of their work and the multinational environment of the *Cologne Center for THz Spectroscopy (CCTS)*.

The scientific education in our group prepares our graduates for challenging future careers in research, academic and commercial areas.

Molecular Astrophysics

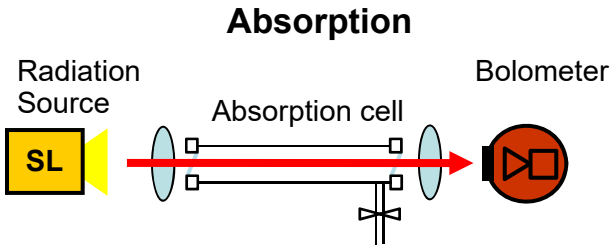
Schlemmer Group

In this brochure we briefly introduce our scientific approaches.
Laboratory instruments are shown in their principle and in pictures.
Experimental methods are described in example measurements.
Molecules of current interest are listed graphically.
Recent results are presented and references to publications are given.
Below current group members carrying out the research are listed together with our scientific methods.

THz Absorption Spectroscopy	Sven Thorwirth, Frank Lewen, Holger Müller, Luis Bonah, Mariyam Fatima
THz Emission Spectroscopy	Ernest Michael, Mariyam Fatima, Bettina Heyne
Chirped Pulse Spectroscopy	Mariyam Fatima, Bettina Heyne, Luis Bonah
Spectroscopy & Reactions in Traps	Oskar Asvany, Philipp Schmid, Sven Thorwirth, Weslley Silva, Divita Gupta, Thomas Salomon, Marcel Bast, Ernest Michael
Jet Spectroscopy	Sven Thorwirth, Thomas Salomon
Theory, Modelling & CDMS	Sven Thorwirth, Holger Müller, Stefan Brackertz, Luis Bonah

More detailed information can be found on our webpage or just contact us.
The people listed above are associated with the specific methods used.

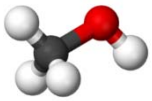
THz Absorption Spectroscopy



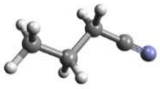
Many molecules have their fingerprint-like spectra in the sub-millimeter wavelength region, where many radio telescopes such as ALMA are operated and are hunting for them.

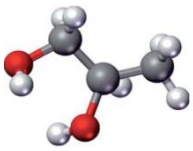
Our absorption experiments cover the range from 0.030 – 2 THz. Such a wide range is mandatory to generate complete line predictions for complex molecules. Current research includes the spectroscopy of isotopically substituted or hot molecules.

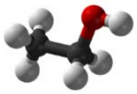
Molecules of Interest

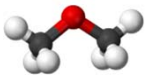

Methanol

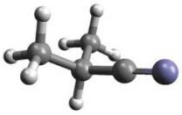

Acetone

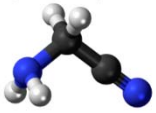

n-propyl cyanide

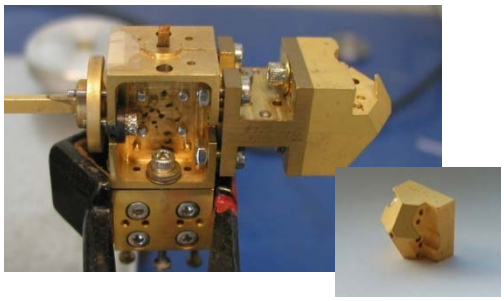

1,2 Propanediol


Ethanol

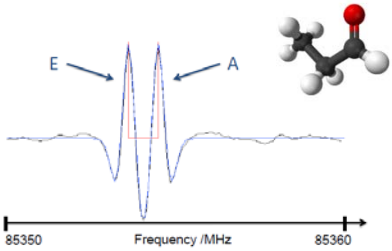

Dimethylether


Isopropylcyanide

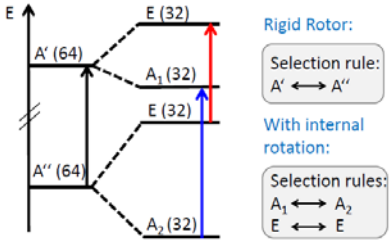

Aminoacetonitril
e


Superlattice (SL) Device generating radiation at high harmonics

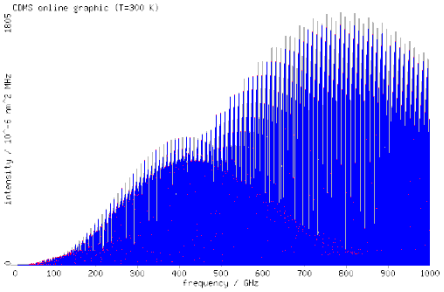

Very long absorption cell for high sensitivity measurements.



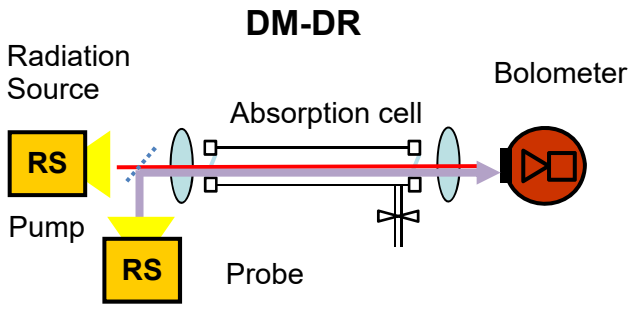
Observed splitting of the $12_{2\,11} - 12_{1\,12}$ transition of *syn*-propanal. ERHAM Predictions in red.



Schematic energy diagram for *syn*-propanal: rigid rotor with/without internal rotation.

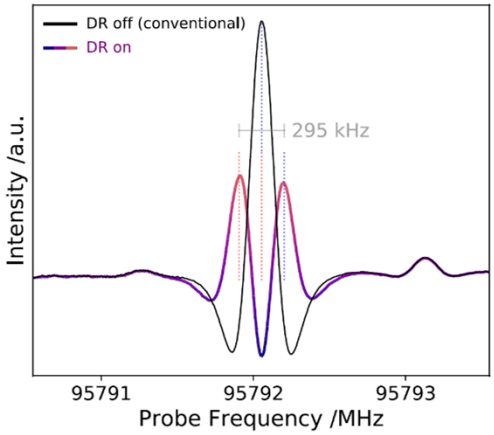

CDMS predicted THz spectrum of *syn*-propanal

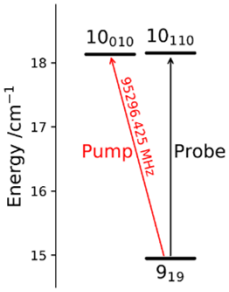
Advanced THz Techniques

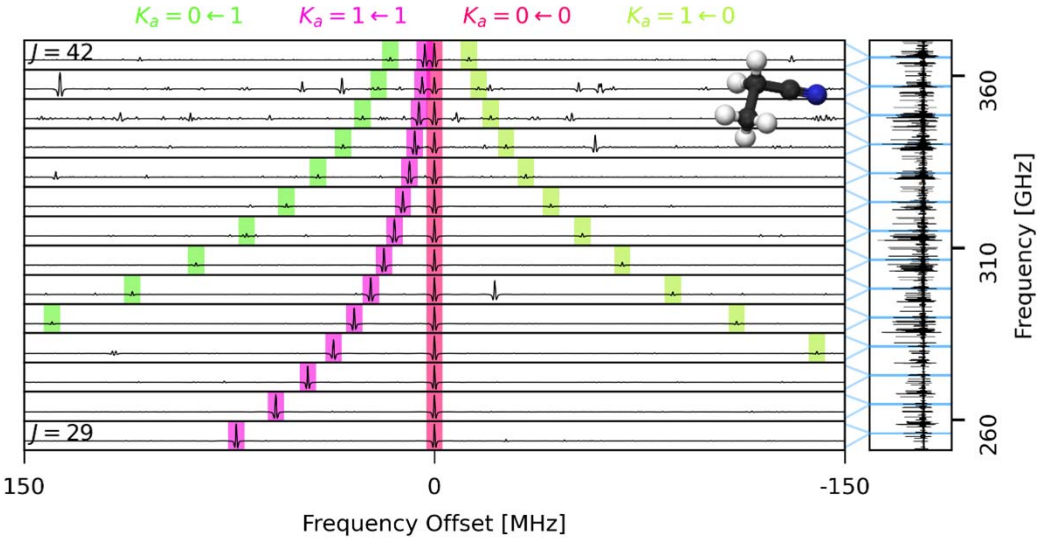


For double-modulation double-resonance we uses a second radiation source, the so-called pump source. Its frequency is set to a known transition which results in all transitions, that share an energy level with this pump transition, splitting into two less intense transitions. This massively simplifies finding related transitions and understanding the spectrum.

This massively simplifies finding related transitions and understanding the spectrum. The double-resonance double-modulation method immediately realizes the difference between the spectrum with and without pump source. The resulting spectrum shows only transitions that share an energy level with the pump transition.





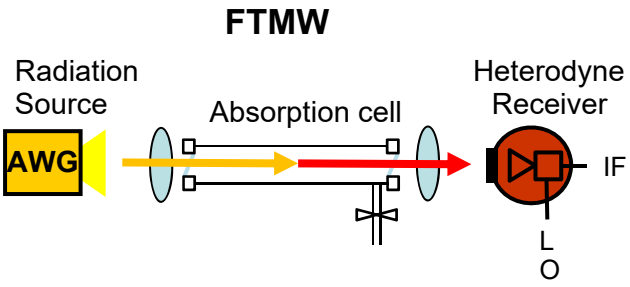


Loomis-Wood plots are a visual aid for assigning quantum numbers to lines in the spectrum. Adjacent transitions of a series are plotted above each other for reference.

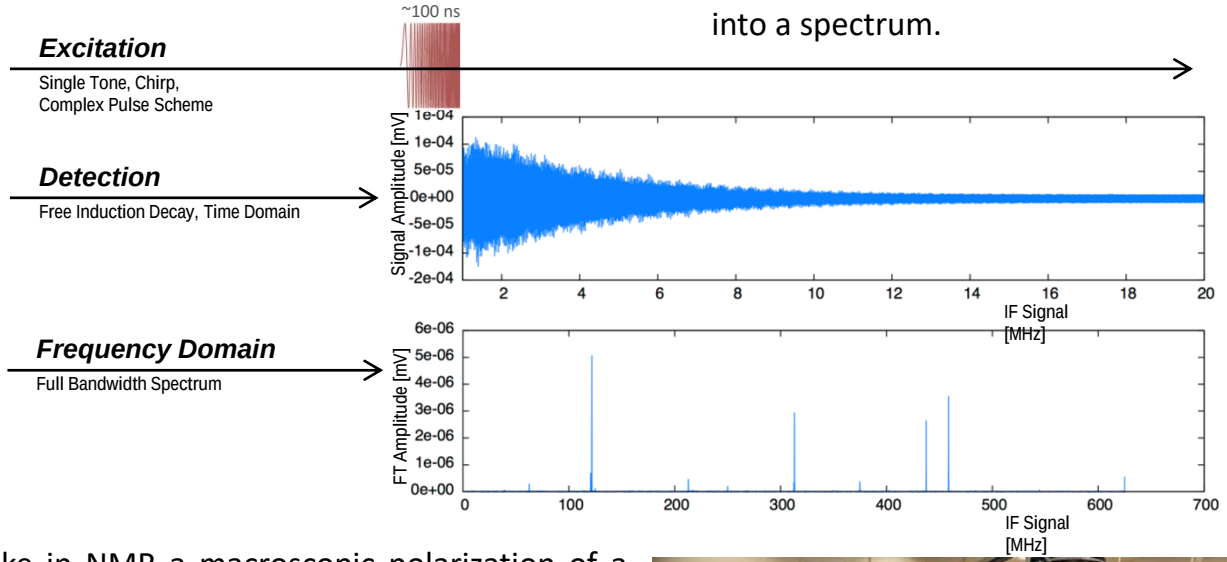
Transitions of one series appear as almost straight lines. This makes assignments faster and more confident. We are actively developing our own Loomis-Wood software called LLWP. More information can be found on its website

https://llwp.astro.uni-koeln.de/

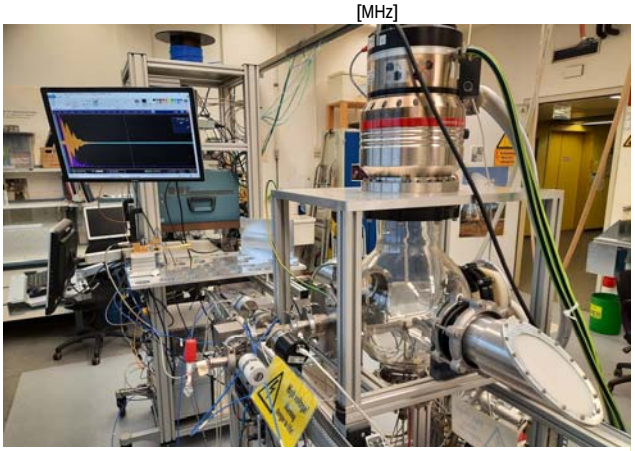
Chirped Pulse Spectroscopy



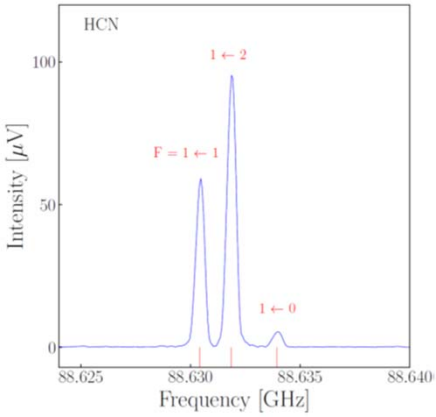
A short chirped pulse or a single tone is generated by an arbitrary waveform generator (AWG) and, after amplification, coupled into a molecular sample cell. The molecules are coherently excited and polarized. The free induction decay (FID) of this signal is recorded with a heterodyne detector and Fourier transformed into a spectrum.



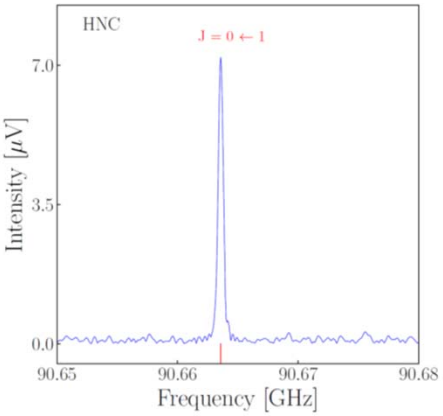
Like in NMR a macroscopic polarization of a molecular ensemble is created, resulting in a free induction decay (FID). As a result, broad band spectra as well as the temporal behavior, e.g. due to collisions, can be determined with µs resolution. The spectra of complex molecules of astrophysical interest are recorded in several experimental setups operating in the 12-26 and 75 -100 GHz range.



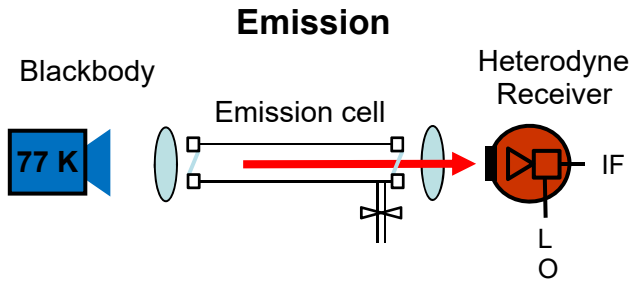
W-band CPFTS instrument



Spectra of transient species: Example spectra of HCN and HNC, both produced in DC discharge of CH_3CN in a pulsed jet. The nozzle can be spotted in the center of the glass cell above.



Emission Spectroscopy

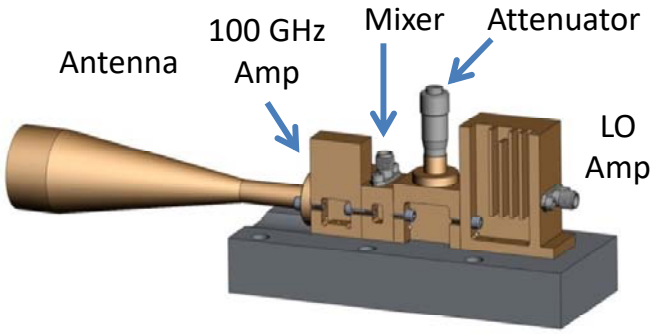


Emission Spectrometer

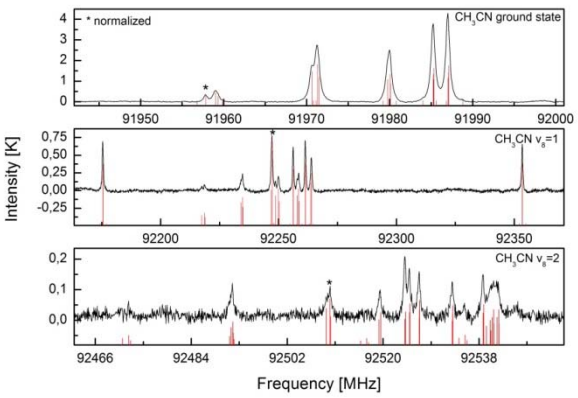
Liquid N_2 is used to detect the warm molecular emission in front of a cold (77 K) blackbody background. For absolute intensity calibration a room-temperature emitter is used. Both receivers, at 100 and 300 GHz, send an intermediate frequency (IF) into an IF-processor electronics. The IF signal is amplified and subsequently recorded by an extended FFT-spectrometer.

Our laboratory emission spectrometers employ heterodyne detection which is commonly used as front ends of radio telescopes. These instruments record molecular line emission over a wide frequency range. Spectra with highly reliable intensity information result from these experiments.

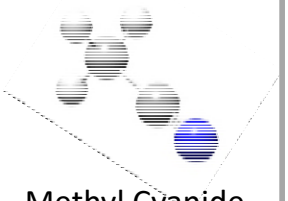
3 mm Room Temperature Receiver



FIRST LIGHT @ 100 GHz



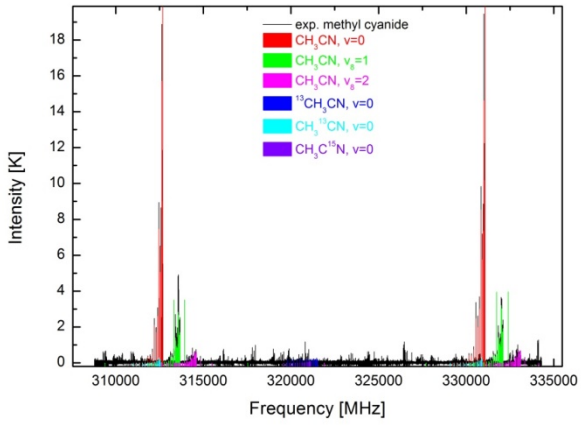
Left: Emission spectrum of methyl cyanide, detected at 92 GHz using the room-temperature receiver. Rotational spectra of the ground vibrational state (top panel), first vibrationally excited state (middle panel), and second vibrationally excited state (lower panel).



Methyl Cyanide

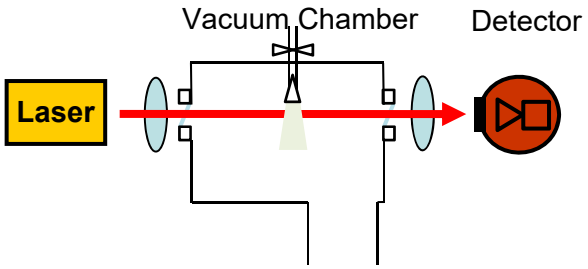
Unbiased Spectral Line Surveys of Complex Organic Molecules

First emission spectrum of methyl cyanide, detected at 315 GHz using the SIS receiver. Next to the rotational spectrum of the vibrational ground state also the spectra for the first and second vibrationally excited states are detected, as well as the spectra of ^{13}C and ^{15}N substituted isotopologs.

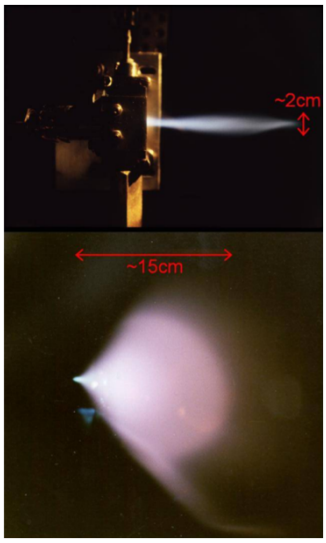


Infrared Jet Spectroscopy

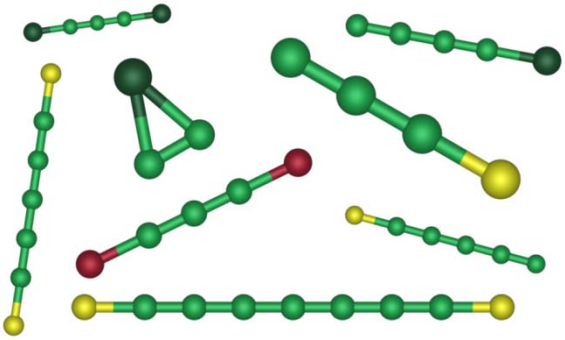
Jet Spectrometer

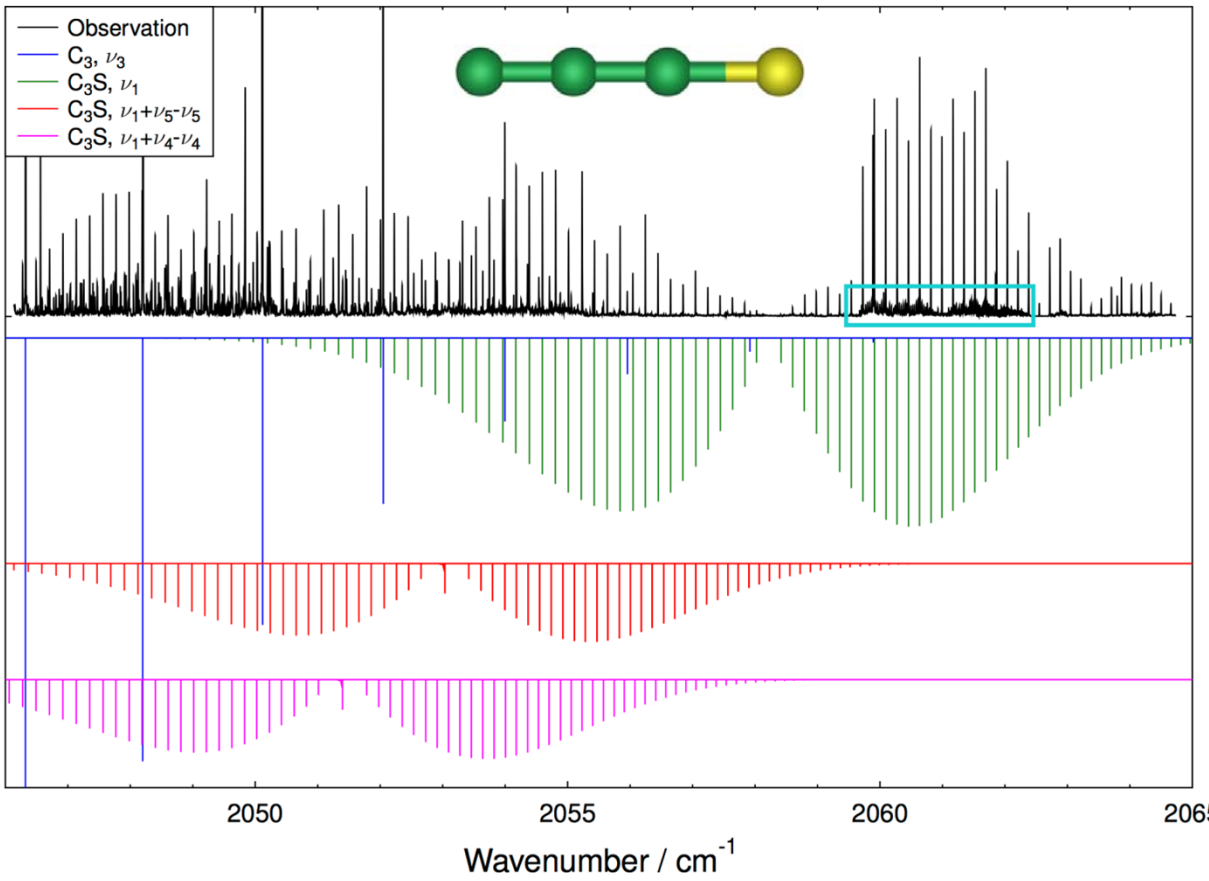


Carbon-rich chains exhibit intrinsically strong vibrational modes in the wavelength regime around 5 microns, corresponding to a photon energy near 2000 cm^{-1}. We are using laser ablation and high-resolution spectroscopic techniques to produce and characterize linear carbon-rich clusters that are of interest for both astrochemistry and molecular structure determination.



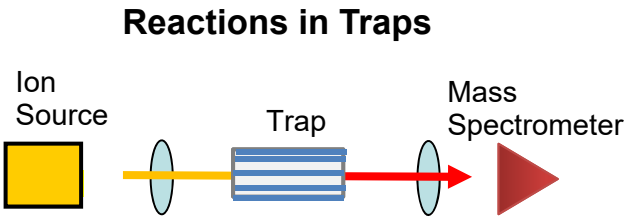
Left: Photographs from different directions of a jet of molecules expanding from a nozzle when carbon molecules are laser ablated.
Right: Typical carbon clusters with additional atoms indicated by different colors.





Infrared spectrum of C_3S in the 5 µm regime of the C-C stretch vibration

Reactions in Ion traps

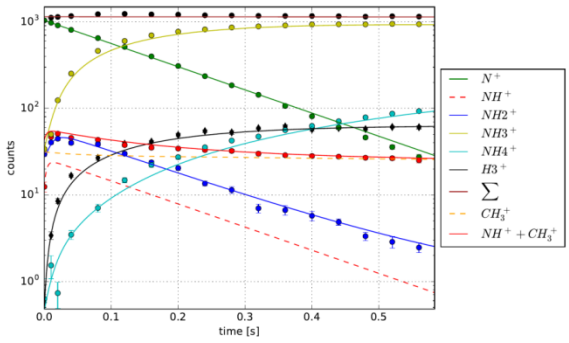


Cryogenic ion trap instruments allow to study the kinetics, i.e. temporal evolution, of ion-molecule reactions under controlled conditions and at low temperatures. The determined rate coefficients are important in reaction networks related to interstellar chemistry. Cold chemistry is also of fundamental interest in molecular physics.

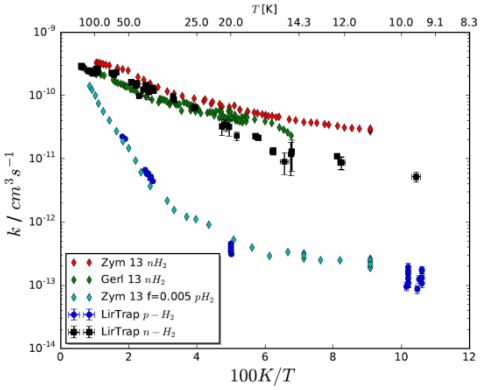
Ion-Molecule Reactions of Interest

Examples

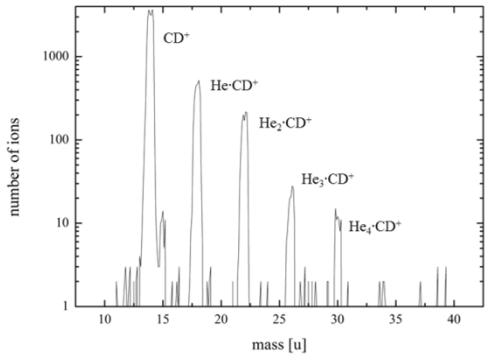
- Deuteration reactions: $H_3^+ + HD \leftrightarrow H_2D^+ + H_2$
- Nuclear spin effects: $o/p\text{-}H_3^+ + o/p\text{-}H_2 \leftrightarrow o/p\text{-}H_3^+ + o/p\text{-}H_2$
- Hydrogenation reactions: $N^+ + o/p\text{-}H_2 \rightarrow NH^+ + H$
- Proton transfer reactions: $H_3^+ + O_2 \leftrightarrow O_2H^+ + H_2$
- Ternary association reactions: $CD^+ + 2\,He \leftrightarrow He\text{-}CD^+ + He$



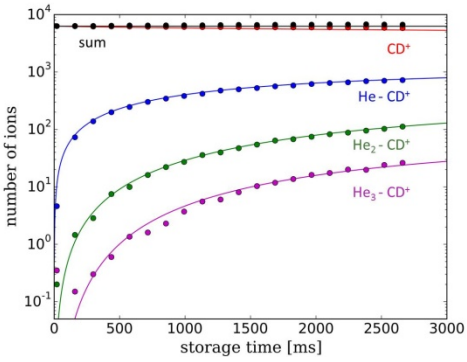
Measured time evolution of the $N^+ + H_2$ reaction system at 17.3 K. The number density is $[n\text{-}H_2] = 2.8 \times 10^{11}$ cm^{-3}.



Arrhenius-Plot of the reaction rate coefficient for $N^+ + H_2$ reaction for collisions with normal and para hydrogen



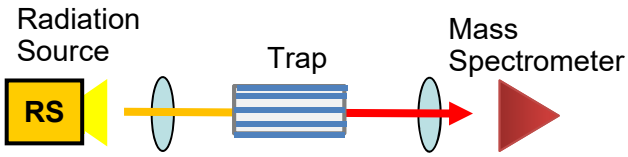
Mass spectrum after storing CD^+ for 600 ms at 4 K in a high density bath of He.



Kinetics measurement:
Consecutive ternary attachment of He to CD^+.

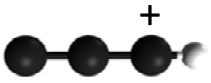
Infrared Action Spectroscopy

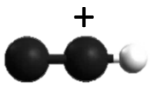
Action Spectroscopy

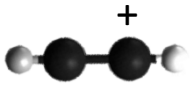


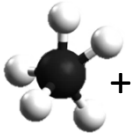
Spectroscopy in ion traps offers the advantage of cooling, mass selection and high sensitivity. With typically 10^4 trapped ions, the use of action spectroscopic schemes is mandatory. In recent years, new action spectroscopy schemes have been developed in Cologne, enabling broadband as well as high-resolution vibrational and ro-vibrational spectroscopy of any ion.

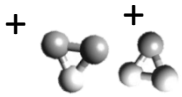
Molecules of Interest

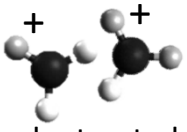

propynylidynium

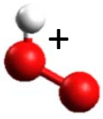

ethynyl cation

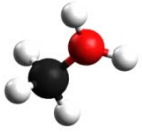

deuterated acetylene cation

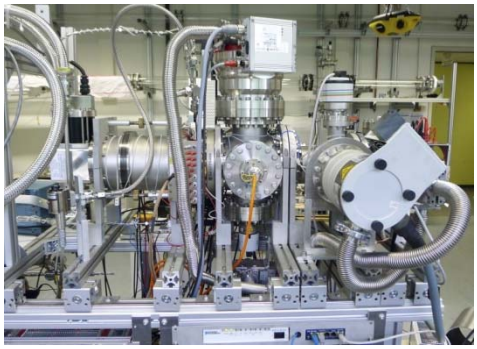

protonated methane


deuterated trihydrogen cation


deuterated methyl cation

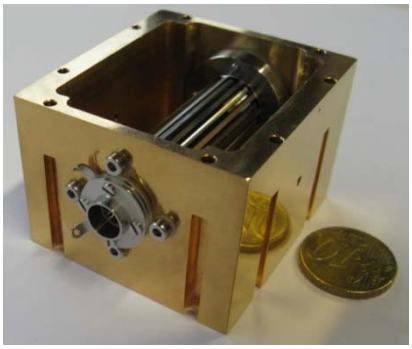

hydroperoxy cation

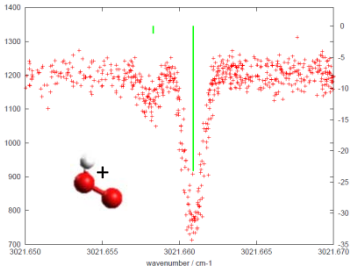

protonated methanol



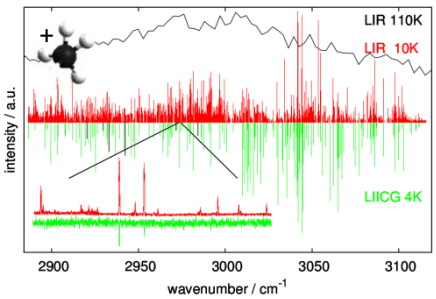
Left: FELion cryogenic ion trap instrument

Right: 22-pole ion trap, the *heart* of the trapping experiment.

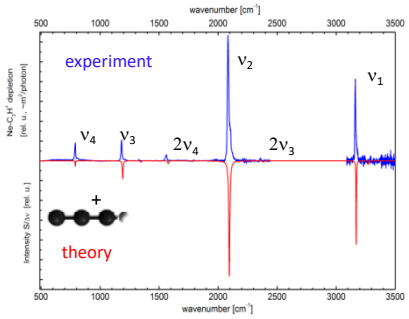




High-resolution ro-vibrational line of O_2H^+



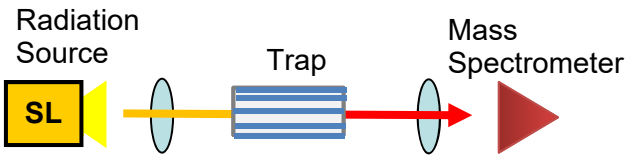
High-resolution ro-vibrational spectrum of CH_5^+



Broadband vibrational spectrum of C_3H^+ (experiment at FELIX and *ab-initio* calculations).

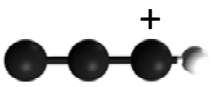
THz Action Spectroscopy

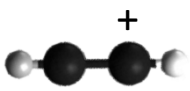
Action Spectroscopy

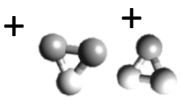


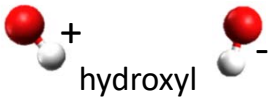
Molecular ions play an important role in interstellar chemistry. High-resolution rotational spectra are needed to identify them in the interstellar medium. We have developed and use sensitive action spectroscopic schemes to record the rotational fingerprint spectra of mass-selected, cold molecular ions stored in cryogenic ion traps.

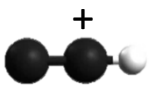
Molecules of Interest

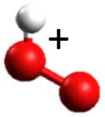

propynylidynium


deuterated acetylene cation


deuterated trihydrogen cation

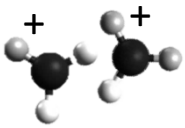

hydroxyl cation anion

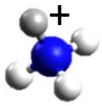

ethynyl cation

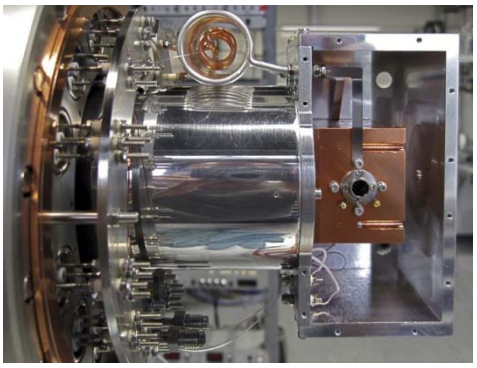

hydroperoxy cation

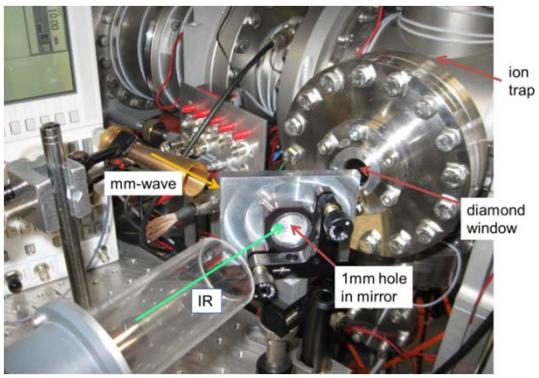

deuterated methylidyne cation


Fluoromethylidynium CF^+

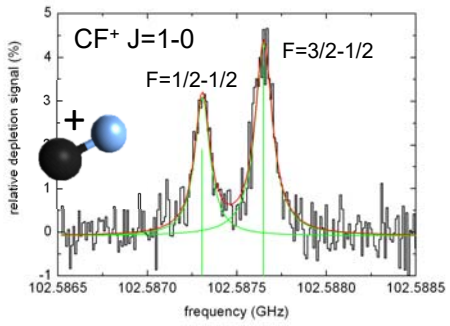

deuterated methyl cation


deuterated ammonium cation

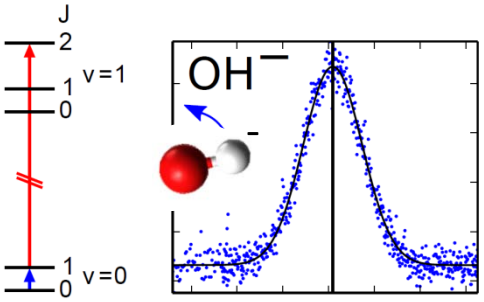

22-pole ion trap mounted on 4 K coldhead.



Optical setup for IR-THz double-resonance action spectroscopy on molecular ions.

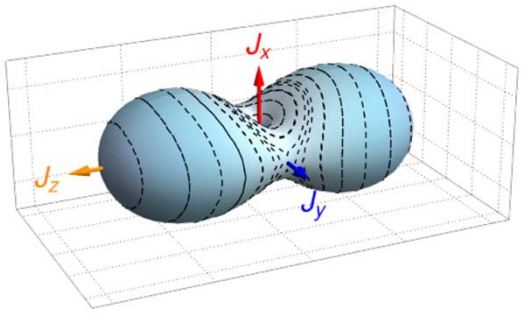


Direct rotational spectroscopy via state-dependent attachment of He atoms on the example of CF^+.



Rotational line of OH^- at 1 123 101.0410(14) MHz measured via Laser Induced Reactions (LIR) using a double-resonance scheme.

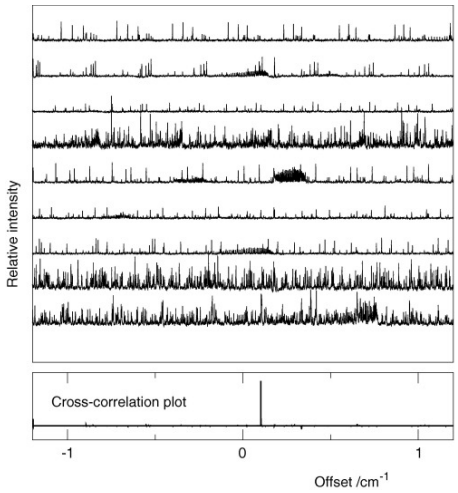
Theory of molecular dynamics



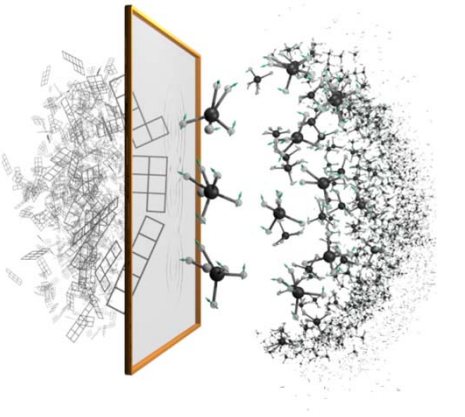
Semi-classical rotations

A theoretical understanding of the molecular dynamics helps to interpret experimental results. The topics in our group include:

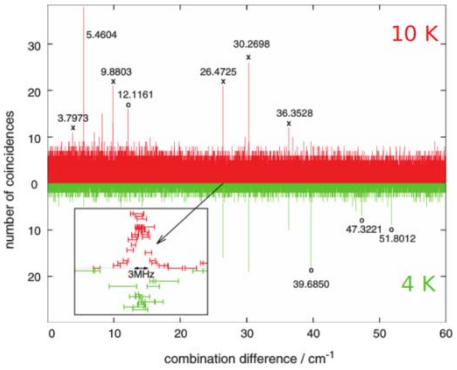
- Automated assignment of experimental spectra
- Numerical methods to reconstruct energy term diagrams from spectra
- Description of internal dynamics of extremely flexible molecules, the “superrotor”
- Semi-classical description of molecular states with high angular momenta
- Nuclear spin symmetry in molecular spectroscopy and molecular collisions



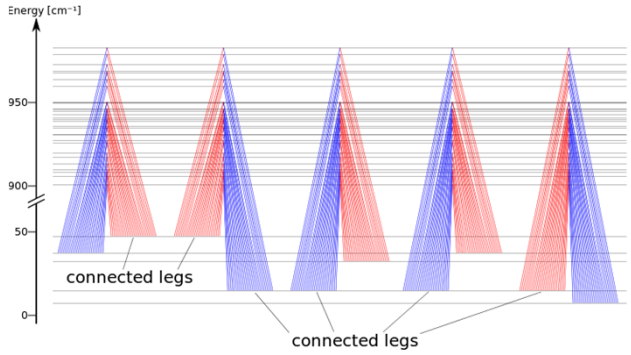
Spectral slices and cross-correlation for the fundamental bending mode of disulfur monoxide, S_2O.
An unconventional spectroscopic analysis: Cross-correlation plots as products of individual spectra and rapid automated level energy determination



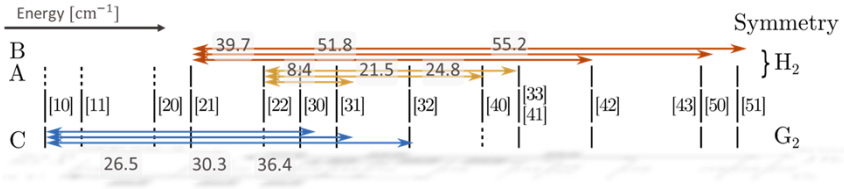
Nuclear spins as Young tableaus

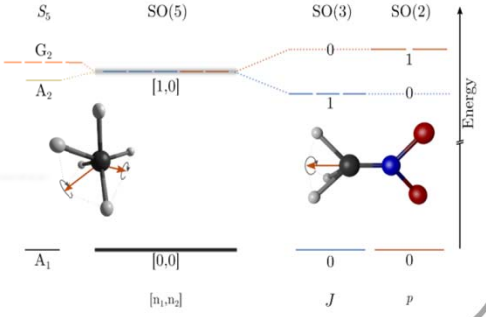


Combination difference spectrum of CH_5^+



Reconstruction of energy term diagrams





Molecular Superrotor states
and comparison to experiments

COLOGNE CENTER FOR TERAHERTZ SPECTROSCOPY

DFG

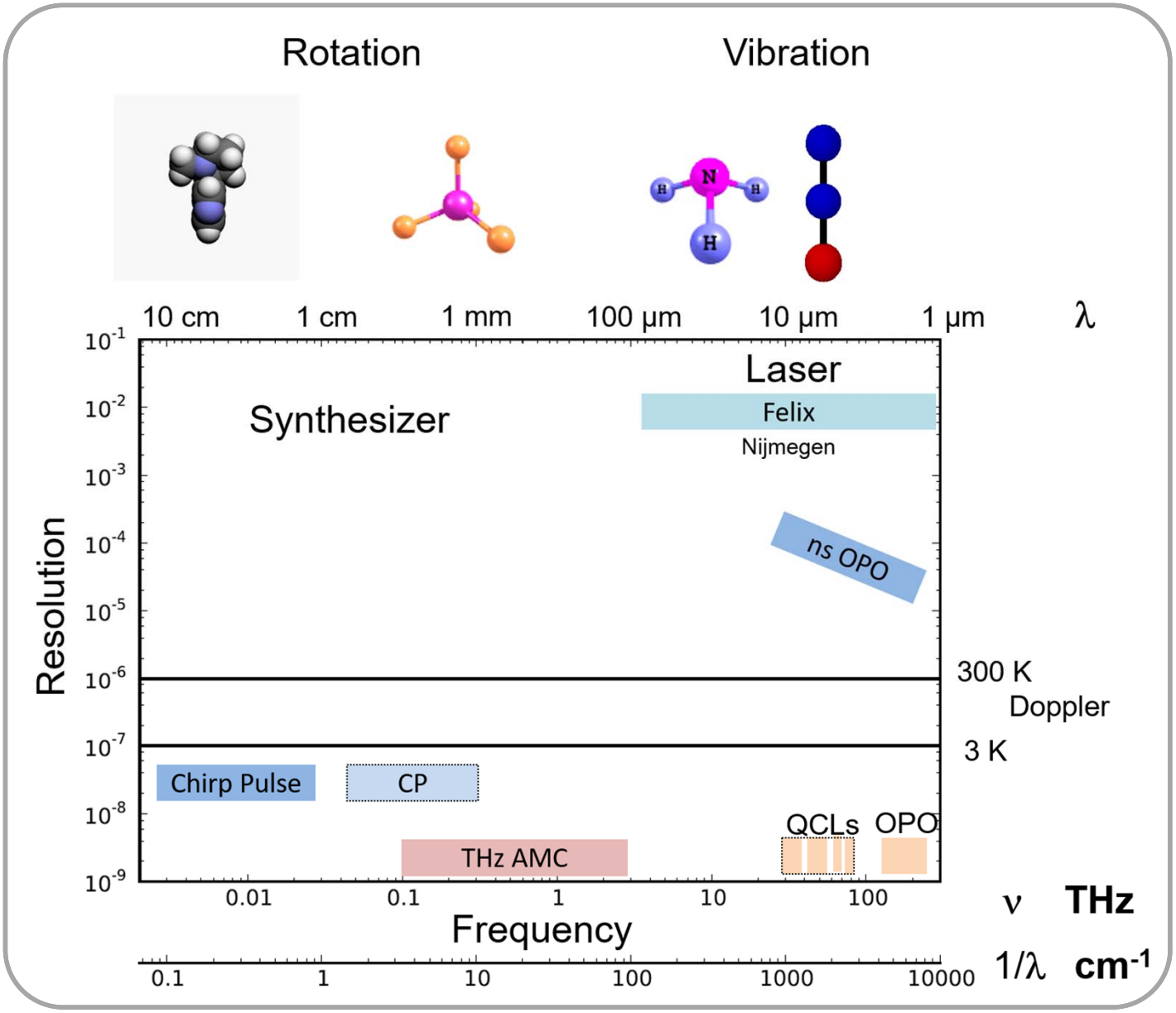
SFB 956 Cologne | Bonn

For other researchers:

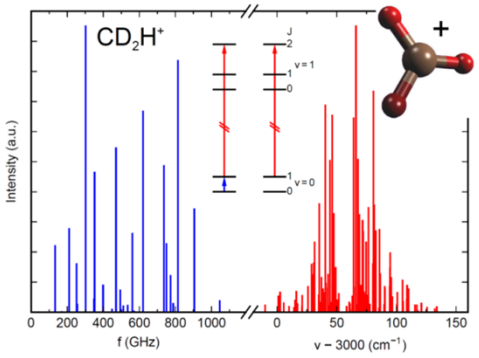
We make our unique instrumentation available to colleagues throughout the world, thanks to funding as a DFG core facility:

Cologne Center for THz Spectroscopy (CCTS)

You can conduct your research using our experiments. We are supplying assistance by well trained specialists for the experiments and for the analysis. Data recorded with our instruments are intended to be published and made available in the *Cologne Data Base for Molecular Spectroscopy* (CDMS). The Figure shows the coverage and resolution of our light sources.



High-Resolution Spectroscopy: A Curse and a Blessing



Rotation

$B \sim 1/\mu r^2$

Vibration

$\omega \sim \sqrt{k/\mu}$

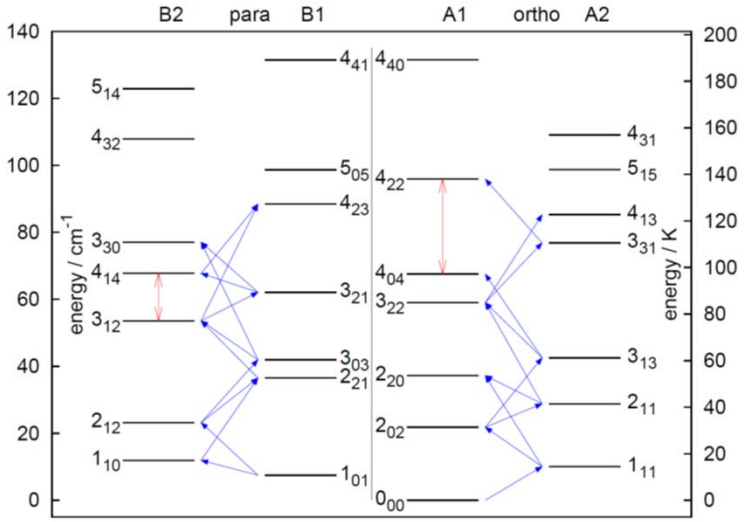
Structure:	Symmetry (C_{2v})
Bond Lengths	r
Bond Strengths	k

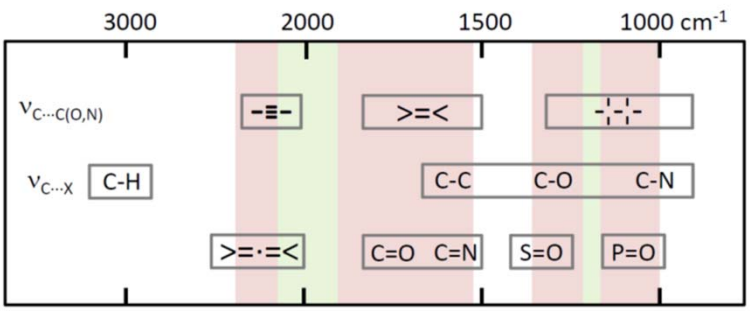
Accurate bond strengths and the molecular structure are derived from high-reso-lution measurements. The light sources of the CCTS shown on the opposite page provide exceptional spectral coverage at medium and highest resolution to record vibrational, ro-vibrational and pure rotational spectra of many molecules.

Molecular Parameters

Parameter	Ground State
A	217431.5125(11)
B	140618.0669(16)
C	84406.6900(12)
Δ_K	20.2019(2)
Δ_{JK}	-3.5430(3)
Δ_J	3.03725(9)
δ_K	4.2321(6)
δ_J	1.25076(6)
Φ_K	0.00787(5)
Φ_{KJ}	-0.00303(6)
Φ_{JK}	
Φ_J	0.000313(5)
ϕ_K	0.00640(5)
ϕ_{JK}	0.00010(3)
ϕ_J	0.000165(2)

Term Diagrams

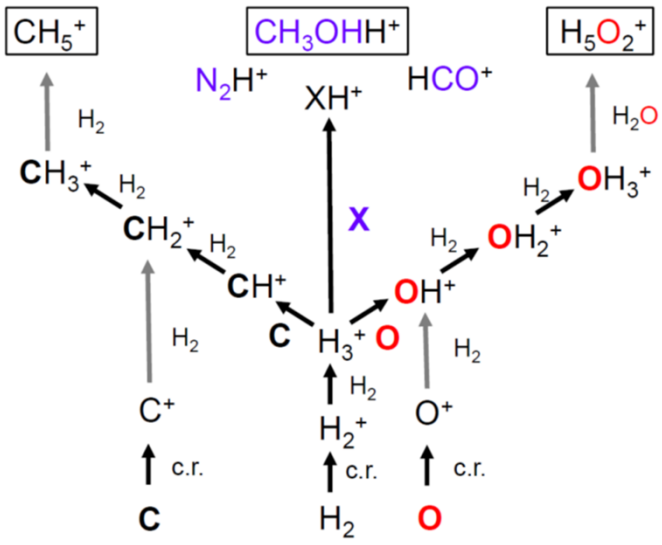




Bands of typical molecular vibrations lying in the range of 1000 – 3000 cm^{-1}. Marked are spectral regions which are now accessible thanks to a new high-resolution QCL system.

MissIons for Astrophysics

The cosmic cycle of star and planet formation is linked to molecular ions. Laboratory spectra for Missing Ions (MissIons) which are key players in interstellar chemistry are the subject of this ERC advanced grant project.

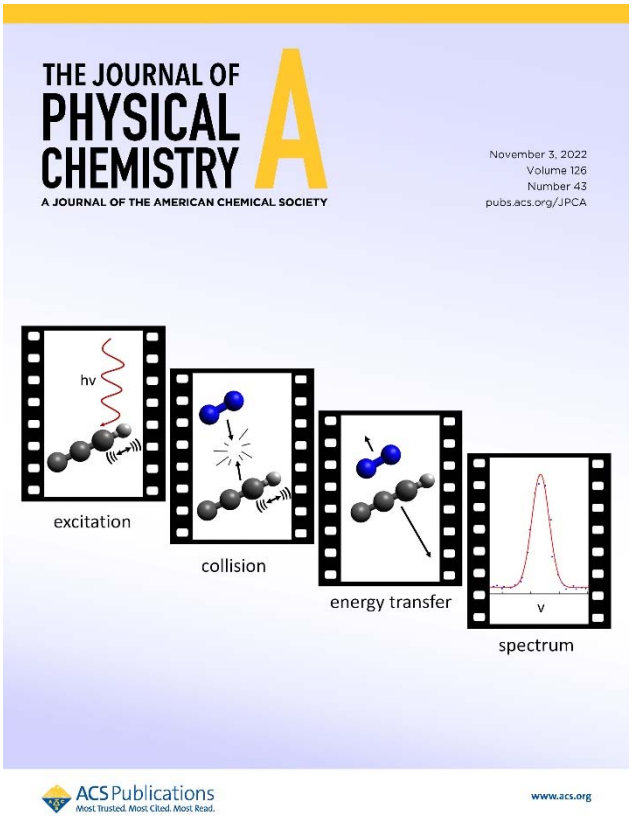


Much of the ion chemistry starts with the omnipresent hydrogen. The Figure shows initial steps of interstellar ion chemistry where the initial H_3^+ ion acts as a universal proton donor.

Elusive molecules like protonated methane, CH_5^+ and protonated methane are predicted but could not be identified in space because laboratory spectra are still (largely) missing.

The new method of leak-out-spectroscopy (LOS) in cryogenic ion traps is the tool which enables us to record spectra of the missing ions. The title page of J.Phys.Chem.A shows the sequence of events acting in the LOS technique. A patent on this method is pending.

Removing structural and nuclear spin isomers or other isobaric species from the finite ensemble of trapped ions gives us a powerful handle in assigning the very dense spectra of the ions of interest.



Molecular Astrophysics
Schlemmer Group