

Vibrational and rotational spectroscopy in cryogenic ion traps

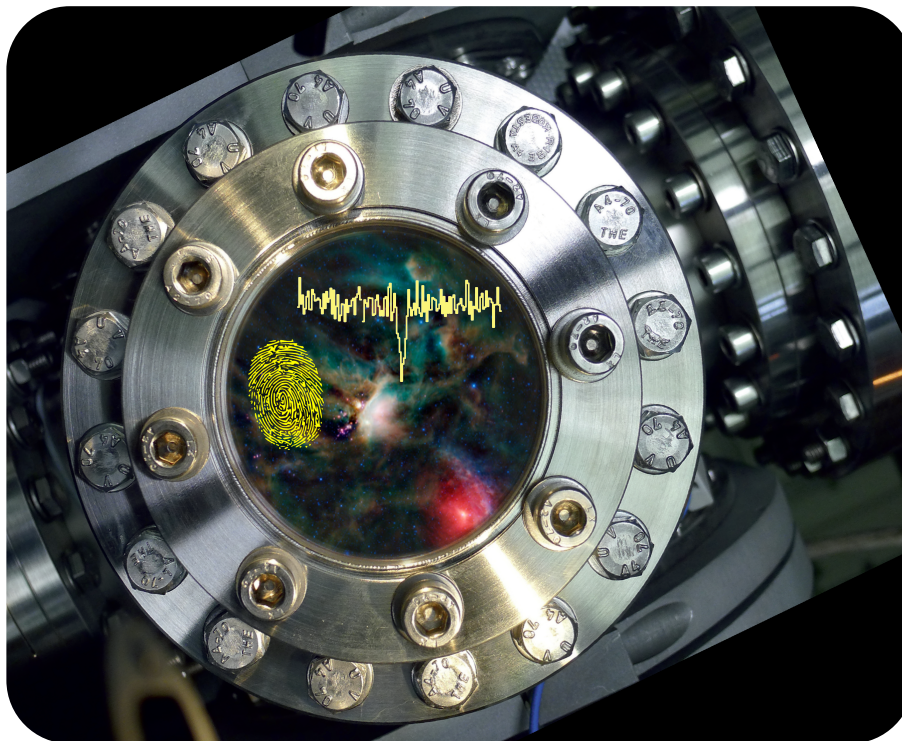
Sandra Brünken, Britta Redlich

FELIX Laboratory, Institute for Molecules and Materials, RU Nijmegen, Netherlands

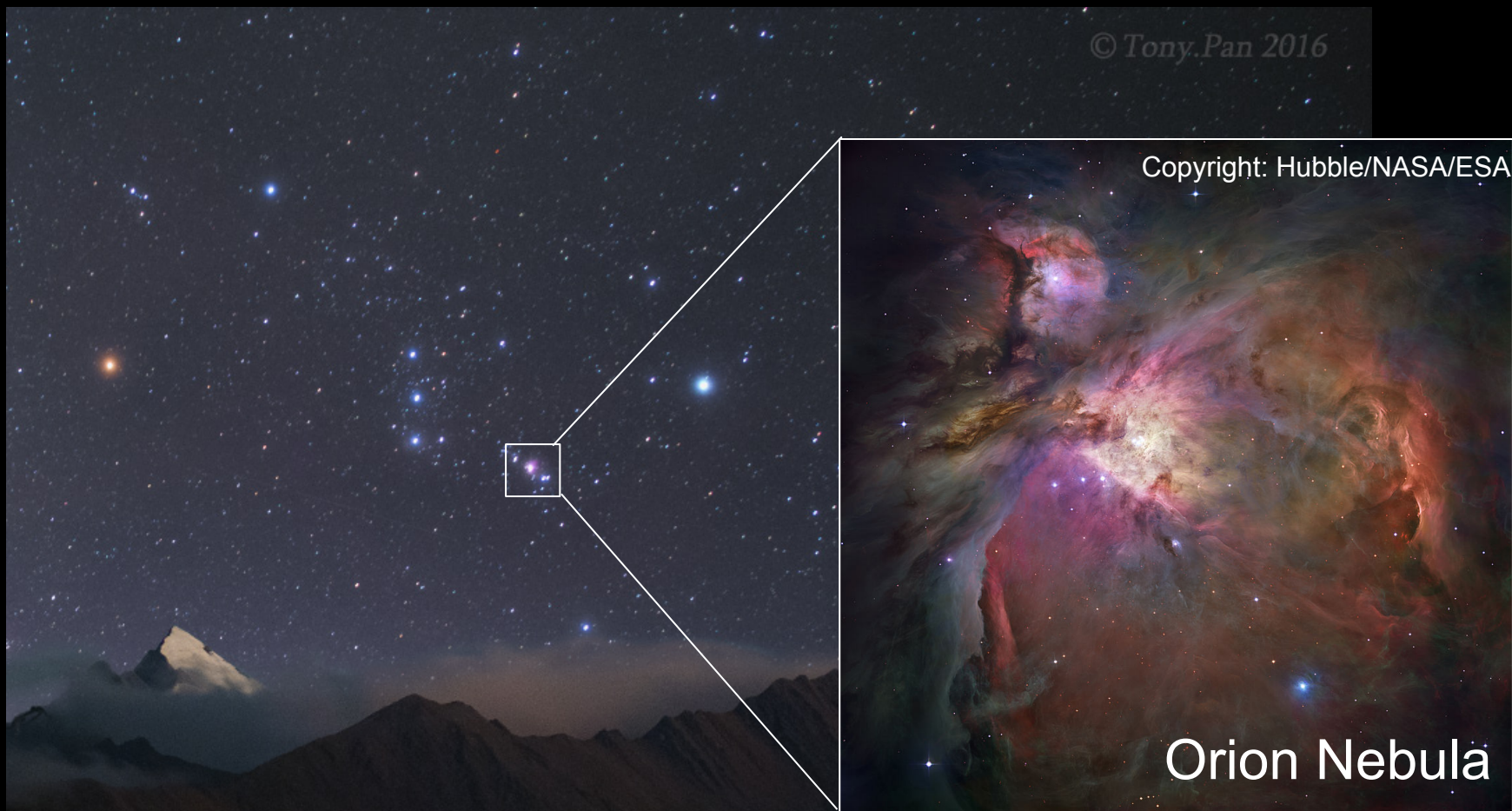
Oskar Asvany, Pavol Jusko*, Stephan Schlemmer

I. Physikalisches Institut, University of Cologne, Germany

*now: IRAP, University of Toulouse, CNRS, CNES, France

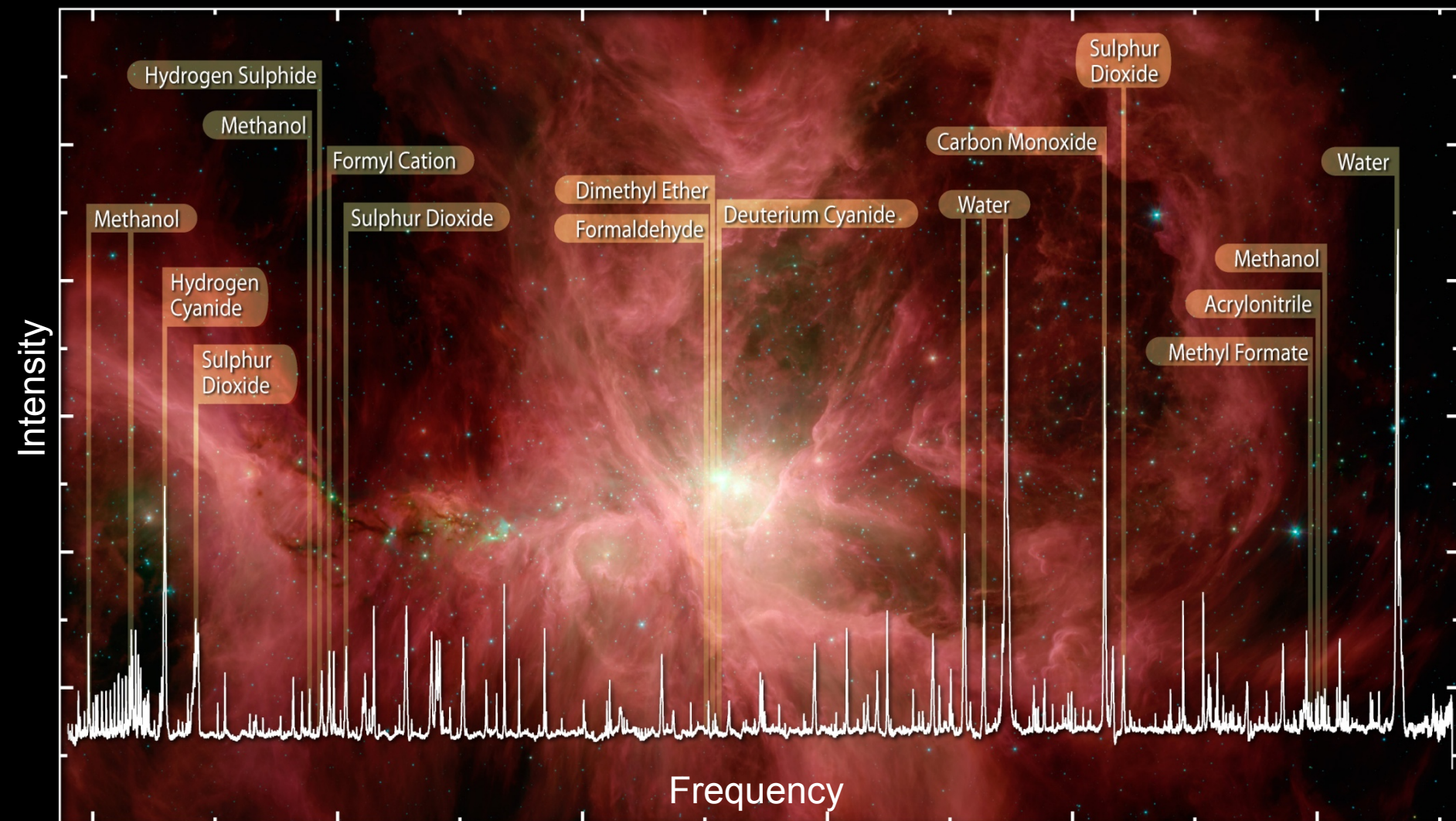


What we see in the sky



Molecular clouds:
Birthplaces of stars, planets, life

Molecular Complexity

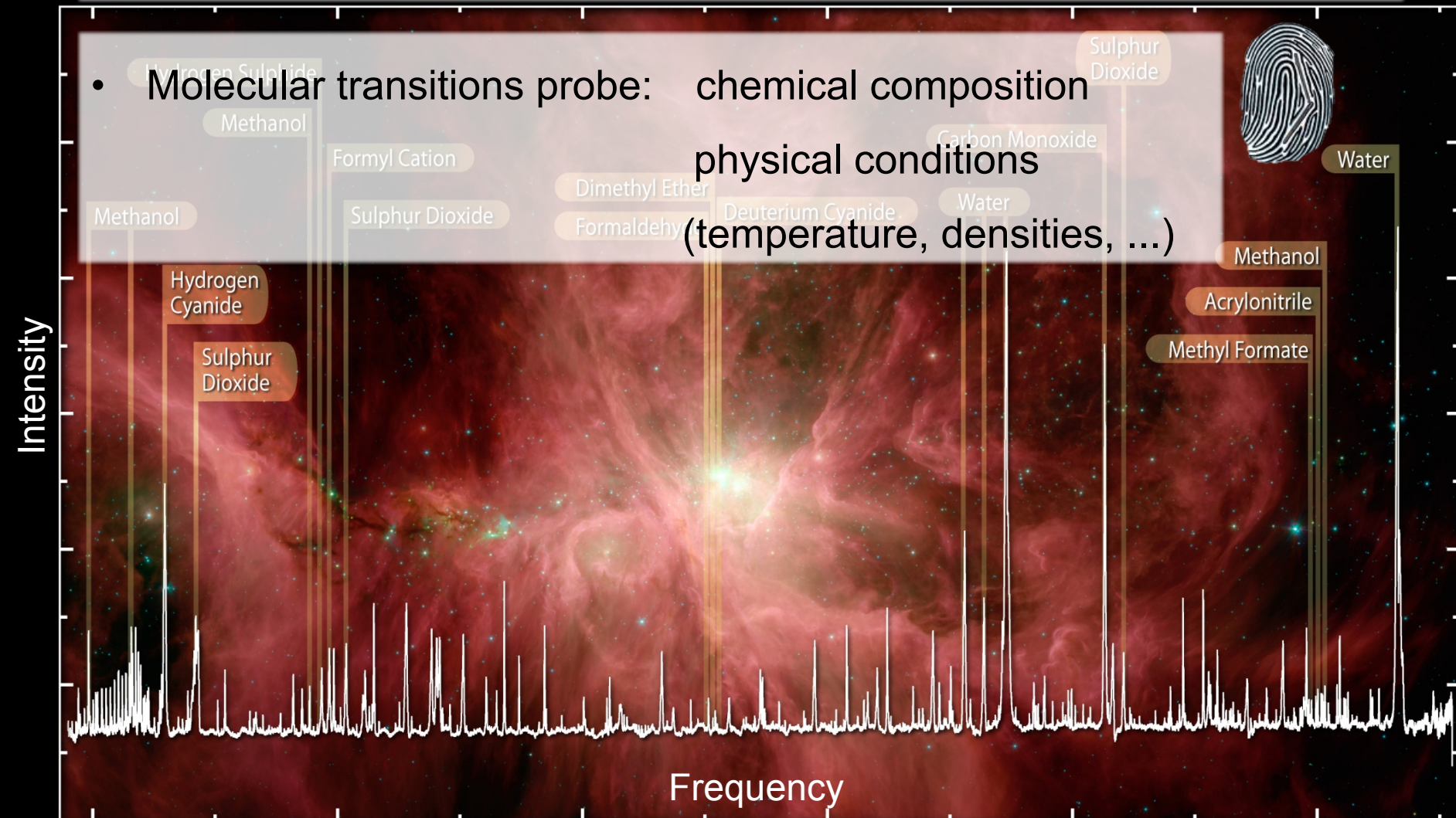


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Molecular Complexity

- Identification relies on laboratory reference data: spectral fingerprint

- Molecular transitions probe: chemical composition
physical conditions
(temperature, densities, ...)

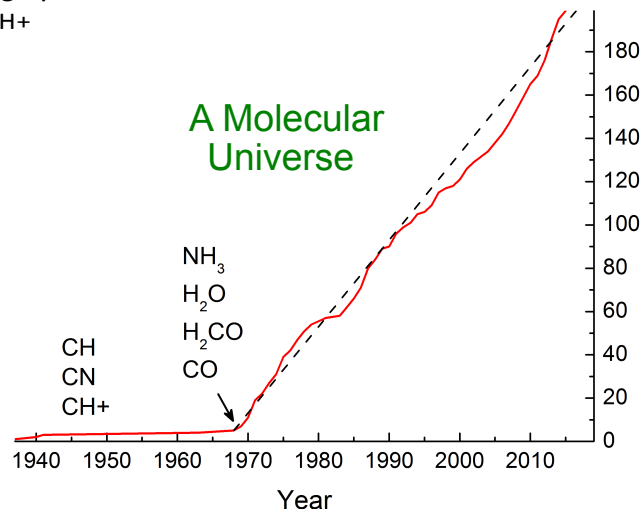


Molecular Complexity in Space

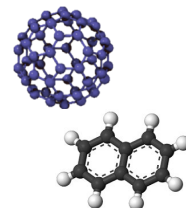
(www.cdms.de 06/2018)

2 atoms	3 atoms	4 atoms	5 atoms	6 atoms	7 atoms	8 atoms	9 atoms
H ₂	C ₃ *	c-C ₃ H	C ₅ *	C ₅ H	C ₆ H	CH ₃ C ₃ N	CH ₃ C ₄ H
AlF	C ₂ H	I-C ₃ H	C ₄ H	I-H ₂ C ₄	CH ₂ CHCN	HC(O)OCH ₃	CH ₃ CH ₂ CN
AlCl	C ₂ O	C ₃ N	C ₄ Si	C ₂ H ₄ *	CH ₃ C ₂ H	CH ₃ COOH	(CH ₃) ₂ O
C ₂ **	C ₂ S	C ₃ O	I-C ₃ H ₂	CH ₃ CN	HC ₅ N	C ₇ H	CH ₃ CH ₂ OH
CH	CH ₂	C ₃ S	c-C ₃ H ₂	CH ₃ NC	CH ₃ CHO	C ₆ H ₂	HC ₇ N
CH ⁺	HCN	C ₂ H ₂ *	H ₂ CCN	CH ₃ OH	CH ₃ NH ₂	CH ₂ OHCHO	C ₈ H
CN	HCO	NH ₃	CH ₄ *	CH ₃ SH	c-C ₂ H ₄ O	I-HC ₆ H *	CH ₃ C(O)NH ₂
CO	HCO ⁺	HCCN	HC ₃ N	HC ₃ NH ⁺	H ₂ CCHOH	CH ₂ CHCHO ?	C ₈ H ⁻
CO ⁺	HCS ⁺	HCNH ⁺	HC ₂ NC	HC ₂ CHO	C ₆ H ⁻	CH ₂ CCHCN	C ₃ H ₆
CP	HOC ⁺	HNCO	HCOOH	NH ₂ CHO	CH ₃ NCO	H ₂ NCH ₂ CN	CH ₃ CH ₂ SH ?
SiC	H ₂ O	HNCS	H ₂ CNH	C ₅ N	HC ₅ O	CH ₃ CHNH	CH ₃ NHCHO?
HCl	H ₂ S	HOCO ⁺	H ₂ C ₂ O	I-HC ₄ H *		CH ₃ SiH ₃	HC ₇ O
KCl	HNC	H ₂ CO	H ₂ CN	I-HC ₄ N			
NH	HNO	H ₂ CN	HNC ₃	c-H ₂ C ₃ O			
NO	MgCN	H ₂ CS	SiH ₄ *	H ₂ CCNH ?			
NS	MgNC	H ₃ O ⁺	H ₂ COH ⁺	C ₅ N ⁻			
NaCl	N ₂ H ⁺	c-SiC ₃	C ₄ H ⁻	HNCHCN			
OH	N ₂ O	CH ₃ *	HC(O)CN	SiH ₃ CN			
PN	NaCN	C ₃ N ⁻	HNCNH				
SO	OCS	PH ₃	CH ₃ O				
SO ⁺	SO ₂	HCNO	NH ₄ ⁺				
SiN	c-SiC ₂	HOCN	H ₂ NCO ⁺ ?				
SiO	CO ₂ *	HSCN	NCCNH ⁺				
SiS	NH ₂	H ₂ O ₂	CH ₃ Cl				
CS	H ₃ ⁺ (*)	C ₃ H ⁺					
HF	SiCN	HMgNC					
HD	AlNC	HCCO					

10 atoms	11 atoms	12 atoms	>12 atoms
CH ₃ C ₅ N	HC ₉ N	c-C ₆ H ₆ *	HC ₁₁ N
(CH ₃) ₂ CO	CH ₃ C ₆ H	n-C ₃ H ₇ CN	C ₆₀ *
(CH ₂ OH) ₂	C ₂ H ₅ OCHO	i-C ₃ H ₇ CN	C ₇₀ *
CH ₃ CH ₂ CHO	CH ₃ OC(O)CH ₃	C ₂ H ₅ OCH ₃	C ₆₀ ⁺ *
CH ₃ CHCH ₂ O			c-C ₆ H ₅ CN
CH ₃ OCH ₂ OH			

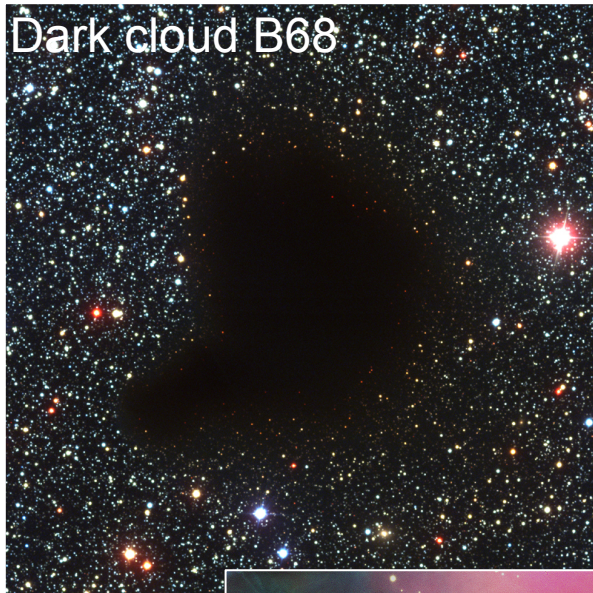


~ 200 total
~ 70 % organic
~ 15 % ions

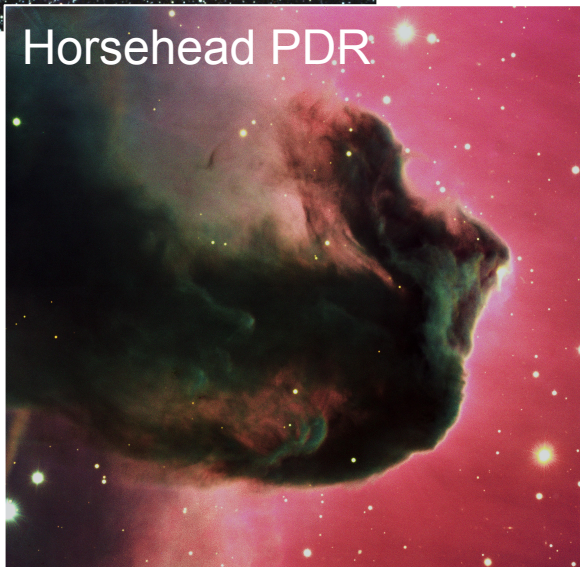


Most species detected by their rotational lines!

Molecular clouds – factories of complex molecular synthesis



Dark cloud B68

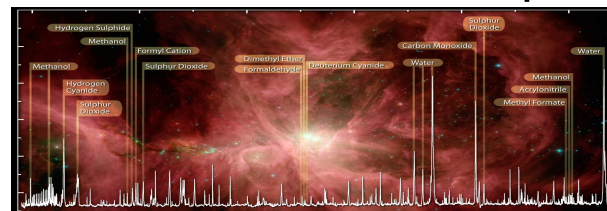


Horsehead PDR

Physical conditions from observations:

- cold ($T = 10 - 100$ K)

Why do we see chemical complexity?



- UV photons or cosmic rays create **ions**
- **ion-molecule reactions** proceed also at low temperatures

Ions drive the chemistry!

**accurate (rotational) spectroscopic data
mandatory for astronomical detection**

Copyright: ESO

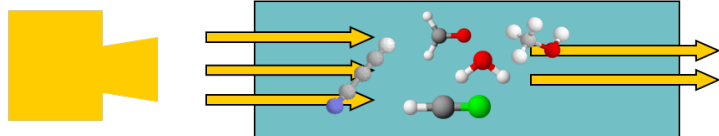
Spectroscopy of (Reactive) Molecular Ions

Typical absorption experiment

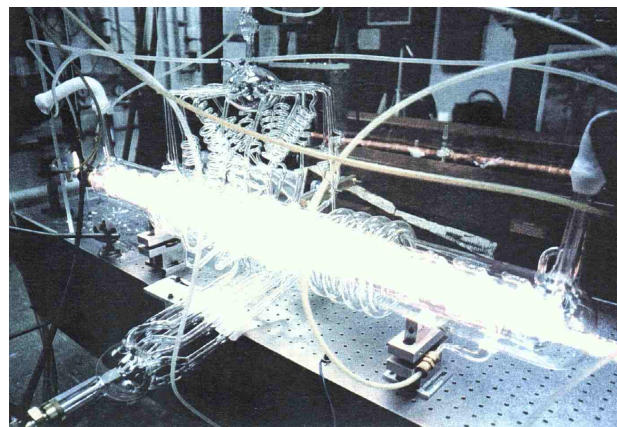
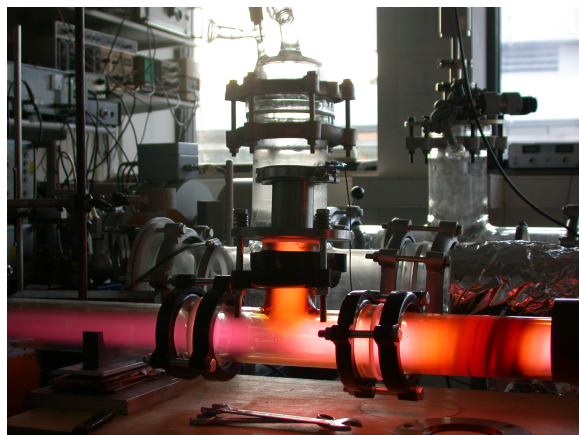
tunable, monochromatic
radiation source

absorption cell

Broadband
photon detector



- high number densities necessary
→ **difficult for reactive ions**
- line contamination
- high temperatures



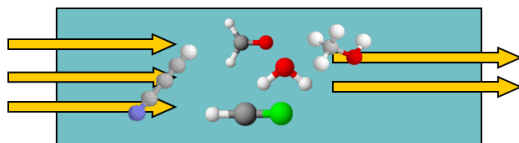
Spectroscopy of (Reactive) Molecular Ions

Typical absorption experiment

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Broadband
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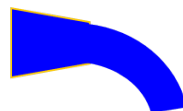
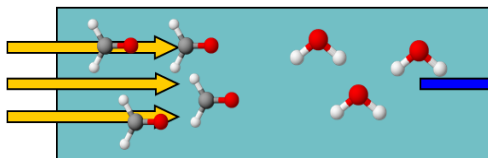
- high number densities necessary
→ **difficult for reactive ions**
- line contamination

Action Spectroscopy in Cryogenic Ion Traps

tunable, monochromatic
radiation source

ion trap (> 4K)

ion detector



- **sensitive** (only few 1000 ions)
- **mass selection**
- **isolation** of reactive ions
- **low ion temperatures**
 - less congested spectra
 - higher S/N & accuracy
- **long interaction times**

Action spectroscopic schemes: Vibration

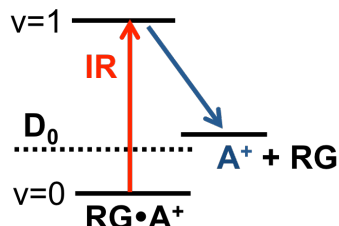
detection via change of ions chemical composition, e.g. dissociation

photon energy (IR): $300 - 3000 \text{ cm}^{-1} \approx 1/10 - 1/100 D_0$

1985 – IR-PD

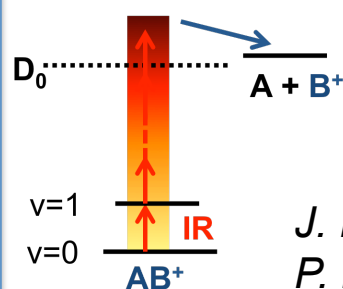
weakly bound messenger
predissociation

*Y. T. Lee, M. Duncan, M. A
Johnson, K. Asmis, O. Dopfer,
J. Roithova, ...*



1970, 1996 – IRMPD

IR multiple photon
dissociation

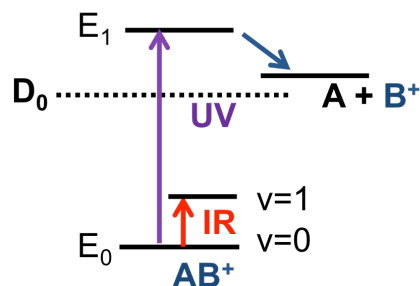


*J. L. Beauchamp, J. R. Eyler,
P. Maitre, G. von Helden,
G. Meijer, J. Oomens, ...*

1988 – IR-UV

double resonance
dissociation

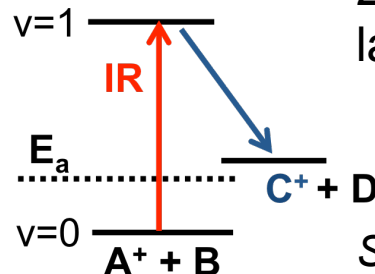
*Y. T. Lee, M. De Vries,
T. Zwier, T. Rizzo, A. Rijs*



2002 – LIR

laser induced reactions

*S. Schlemmer
D. Gerlich, F. Merckt*



Action spectroscopic schemes: Rotation

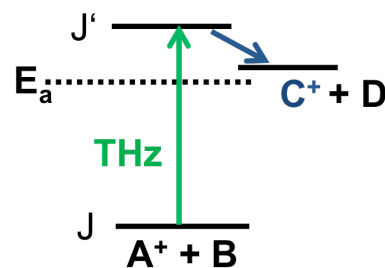
detection via change of ions chemical composition, e.g. dissociation

$$\text{photon energy} < 100 \text{ cm}^{-1} \ll D_0, < E_a$$

2008 laser induced reaction (LIR)

only H_2D^+ , D_2H^+

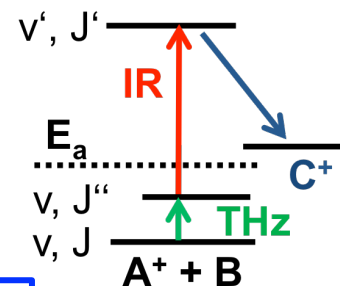
Asvany et al. 2008, Phys Rev Lett.



2014 double resonance LIR

H_2D^+ , OH^+ , CH_2D^+ , ...

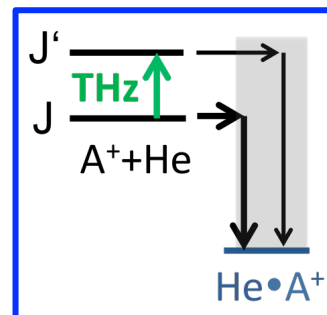
*Gärtner et al. 2013, J Phys Chem A; Jusko et al. 2014, Phys Rev Lett.;
Töpfer et al. 2016, Astron. Astrophys.; Jusko et al. 2017, J Mol Spectrosc.*



2014 state-dependent He-attachment

C_3H^+ , NH_3D^+ , SiH^+ , CO^+ , CH^+ (iso), CF^+ , d-CH_3^+ , ...

*Brünken et al. 2014, ApJ Lett.; Brünken et al. 2017, J Mol Spectrosc.;
Domenech et al. 2017, ApJ*

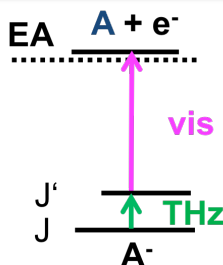


2016 double resonance

e^- -detachment

OD^- , NH_2^-

Lee, Wester, et al. 2016, Phys Rev A

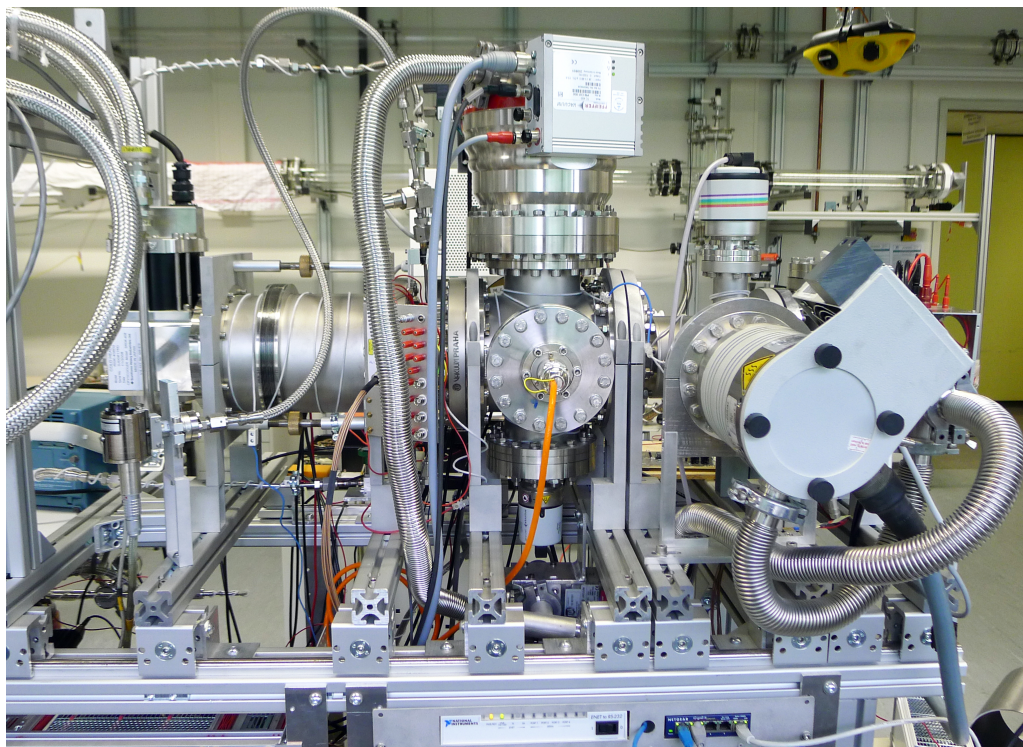
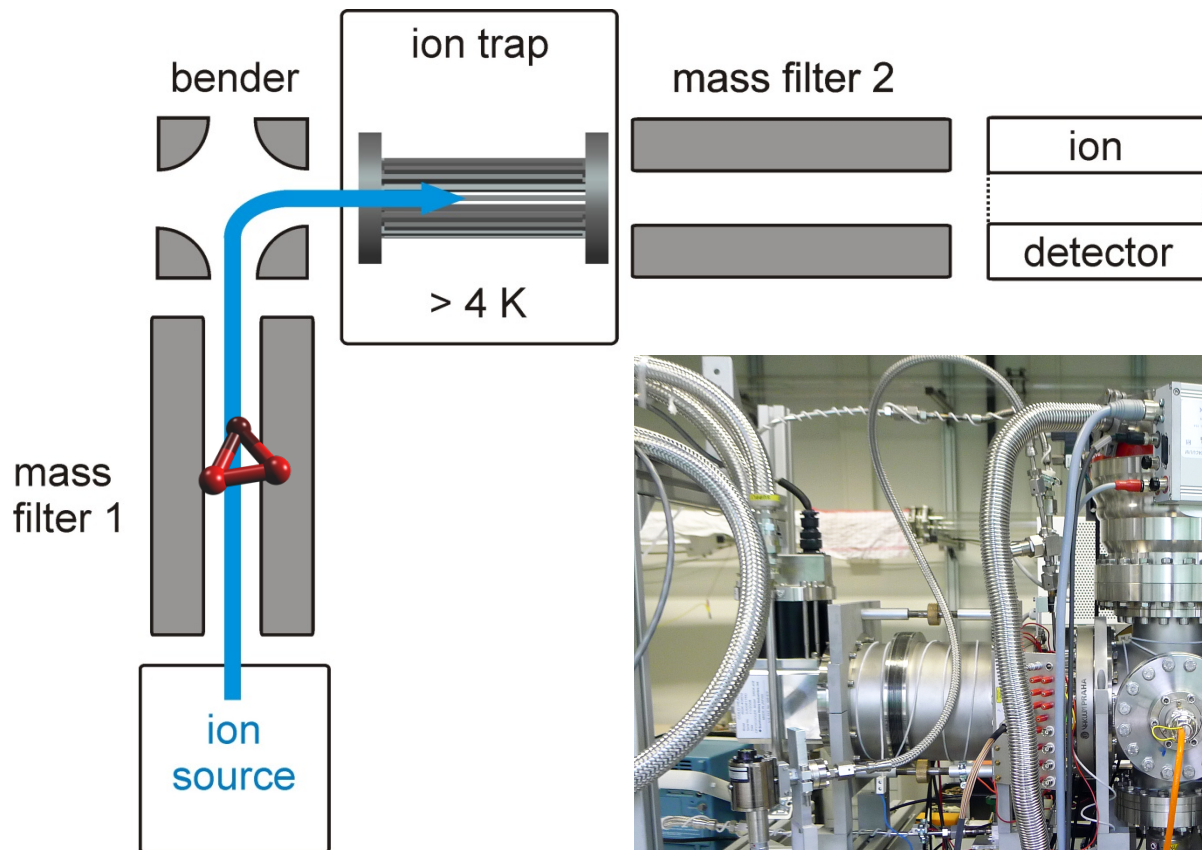


2018 double resonance IR-PD

$\text{HCO}^+\text{-He}$, $\text{CH}_3^+\text{-He}$

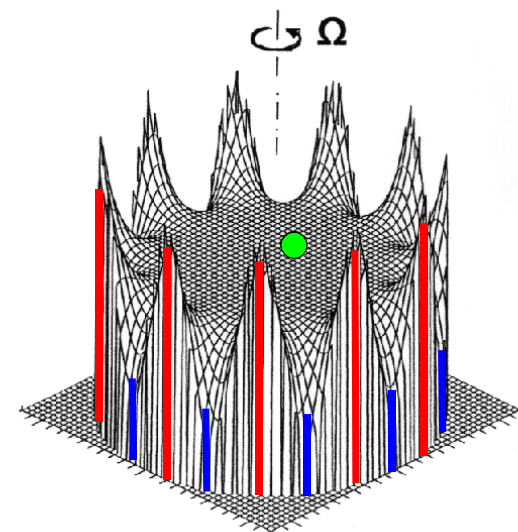
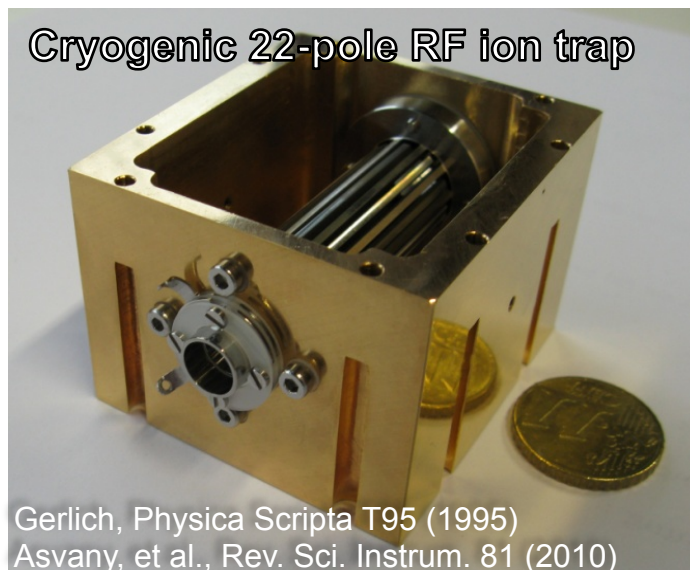
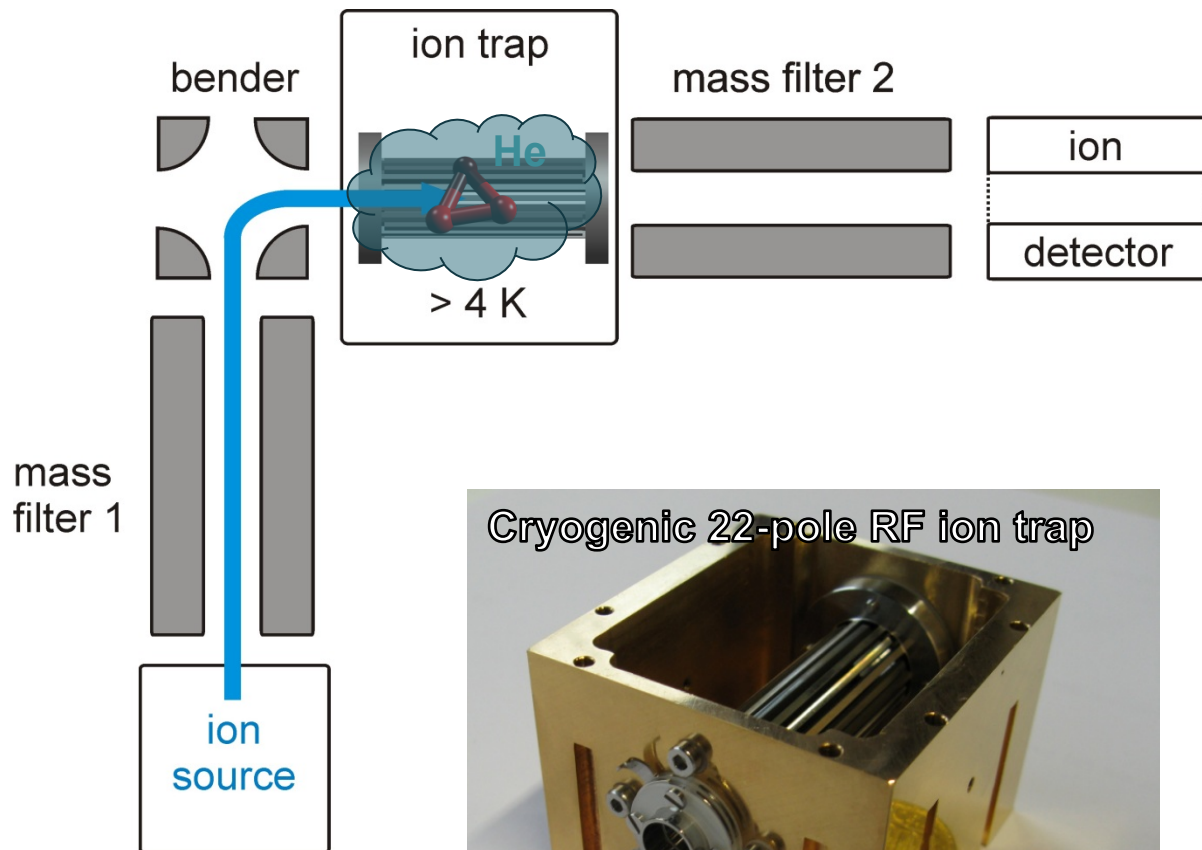
see Talks FC03, FD07 S. Schlemmer

Experimental Approach: Cryogenic Ion Trap Instrument

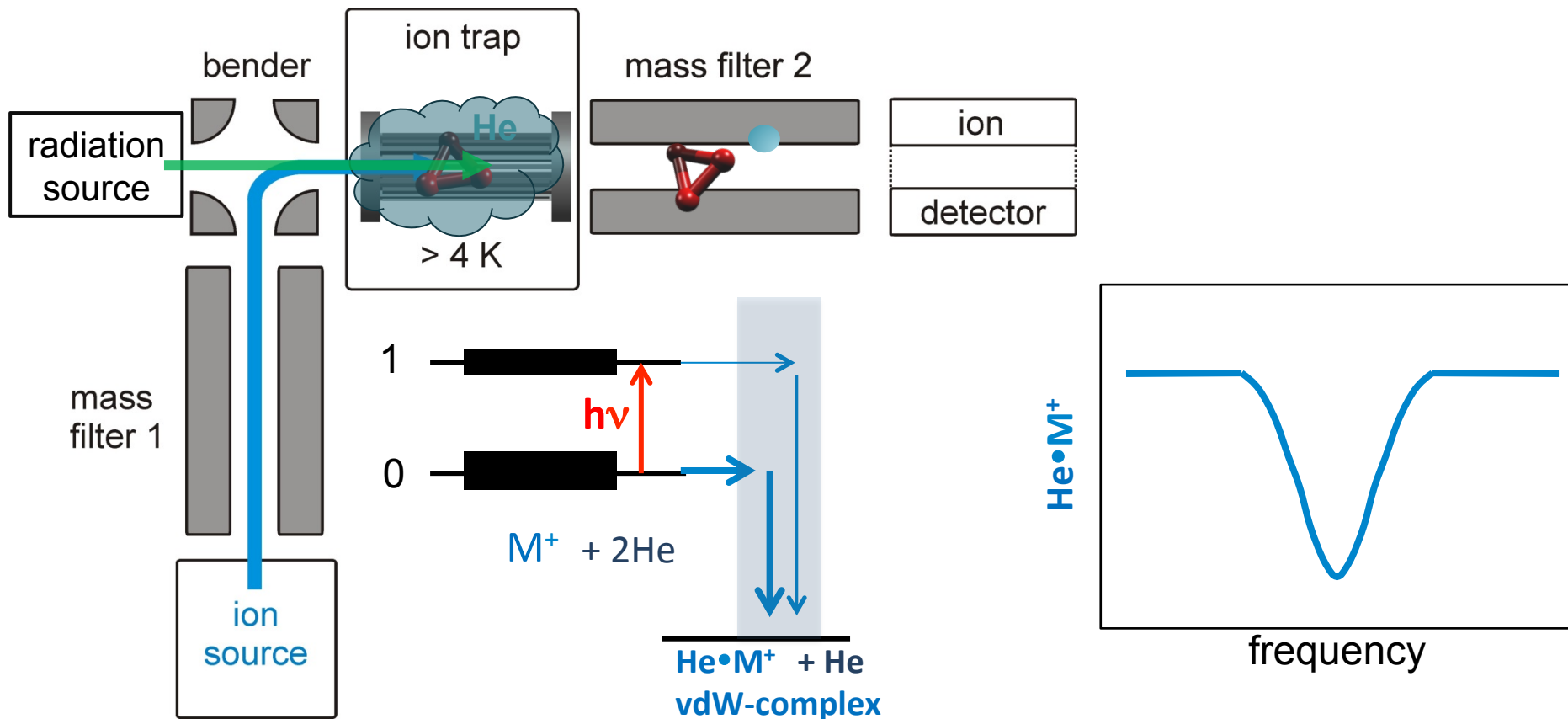


FELion – developed & built in Cologne, now at FELIX

Experimental Approach: Cryogenic Ion Trap Instrument



Methods: Rotational State-Dependent Attachment of He Atoms (ROSAA) Laser Induced Inhibition of Cluster Growth (LIICG)



Electronic: Chakrabarty et al., *JPC Lett.* 4 (2013)
Vibrational: Asvany et al., *Science* 347 (2015)
LIICG & *Appl. Phys. B* 114 (2014)
Rotational: Brünken et al. *ApJL* 783 (2014)
ROSAA & *JMS* 332 (2017);
 Stoffels et al., *A&A* 593, A56 (2016)

General method:

- any kind of excitation (even rotation)
- large class of ions
- spectra of bare ions!

A first example: $\text{CF}^+ J = 1-0$ hfs

Astrochemistry: CF^+ important F tracer in photon-dominated regions (PDRs)

detection of CF^+ in Orion Bar and Horsehead PDR
Guzman et al., A&A 543 (2012)

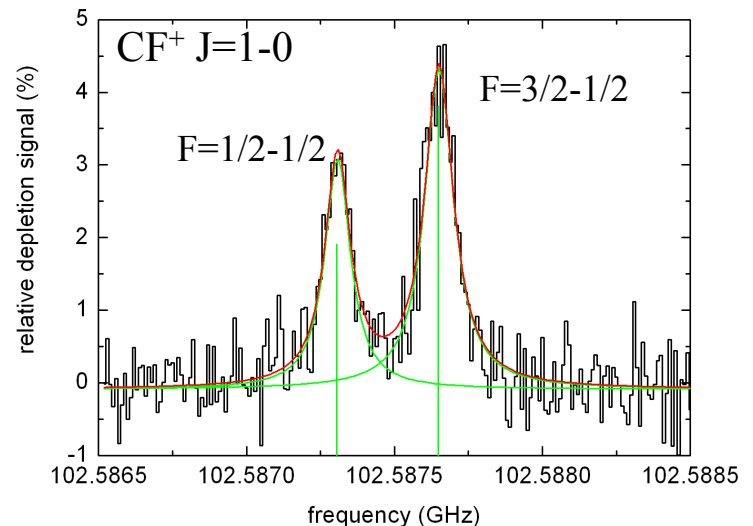
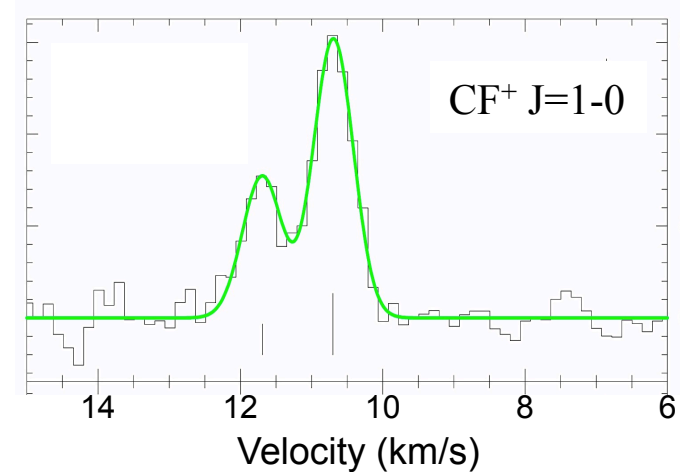
CF^+ ($^1\Sigma^+$) well characterized for $J>1$
Cazzoli et al., ApJS 203 (2012)

structure in $J=1-0$ due to I_F - rotation interaction:
 $C_I = 229.2$ kHz from AI calculations
Guzman et al., A&A 548 (2012);

low ion temperatures = narrow lines
resolved hfs structure:

$C_I = 229(3)$ kHz from experiment

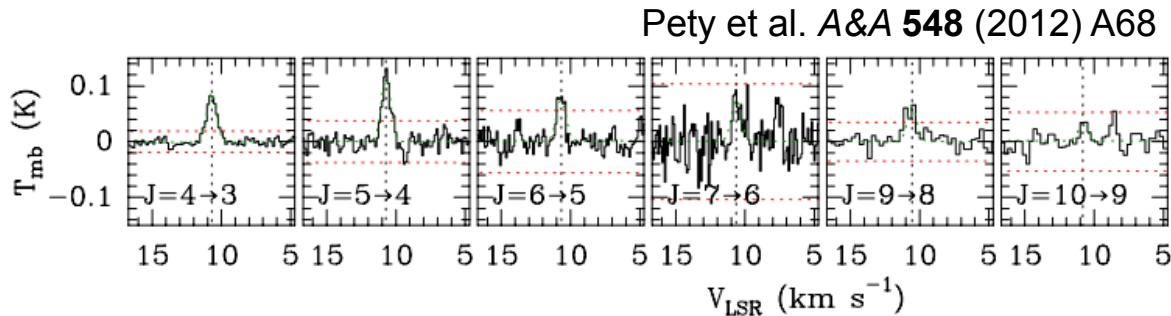
$\text{FWHM}_{\text{Lor}} = 110$ kHz @ $3\mu\text{W}$
expected Doppler width (10K): 45 kHz



Stoffels et al., A&A 593, A56 (2016)

Identification of interstellar I-C₃H⁺

Series of rotational emission lines observed in the

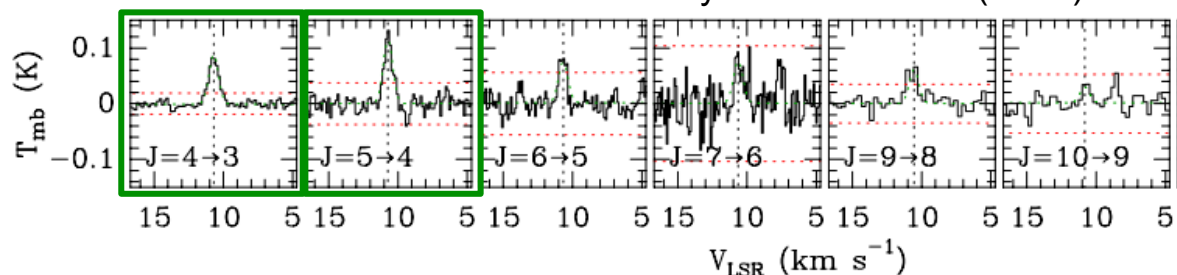


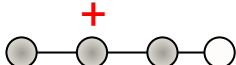
- No laboratory reference data available at time of observation
- *Ab initio* calculations disagreed on charge state:
not clear if lines from **C₃H⁺** or **C₃H⁻**
Huang et al. ApJL 768 (2013) L25; Fortenberry et al. ApJ 772 (2013) 39
- Further astronomical observations favoured C₃H⁺ as carrier
McGuire et al. ApJ 774 (2013) 56; McGuire et al. MNRAS 442 (2014)

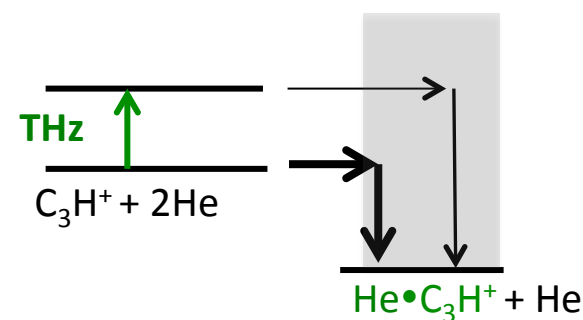
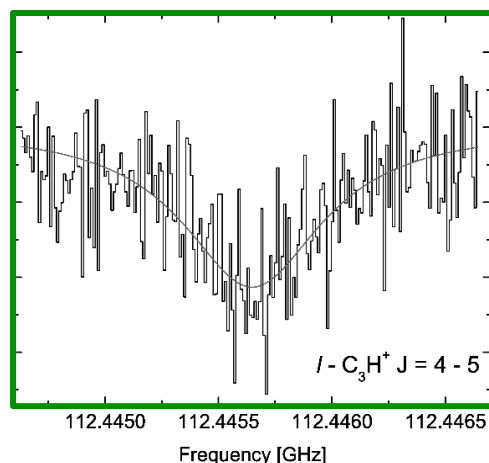
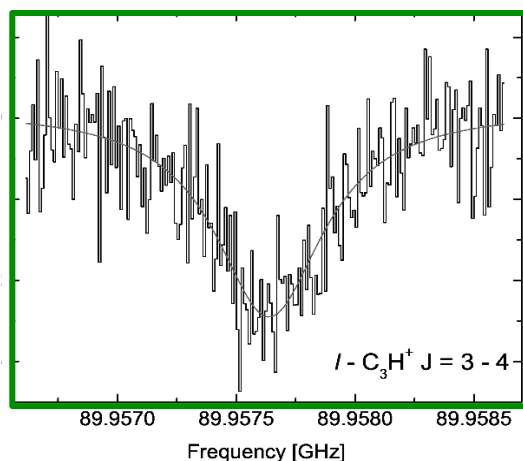
Identification of interstellar $\text{l-C}_3\text{H}^+$

Series of rotational emission lines observed in the

Pety et al. *A&A* **548** (2012) A68



laboratory 



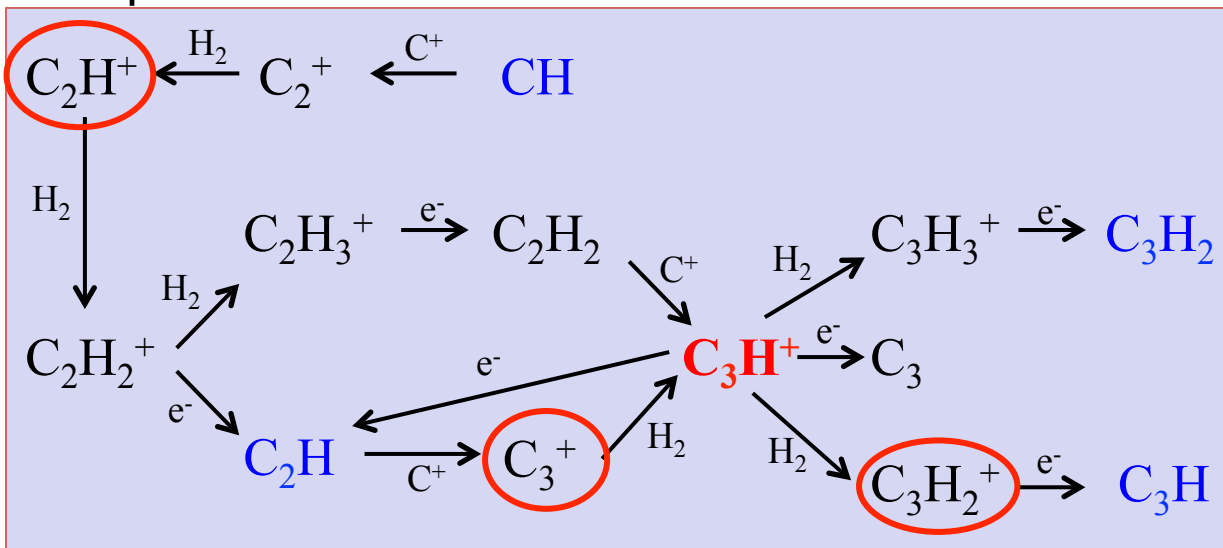
Brünken et al. *ApJL* **783** (2014)

Laboratory rotational spectra confirm detection of linear C_3H^+ in space

Also: McCarthy et al. *ApJSS* **217** (2015); Botschwina et al. *ApJ* **787** (2014); Mladenovic *JCP* **141** (2014)

C_3H^+ as integral intermediate in interstellar organic synthesis

Gas-phase reaction network:

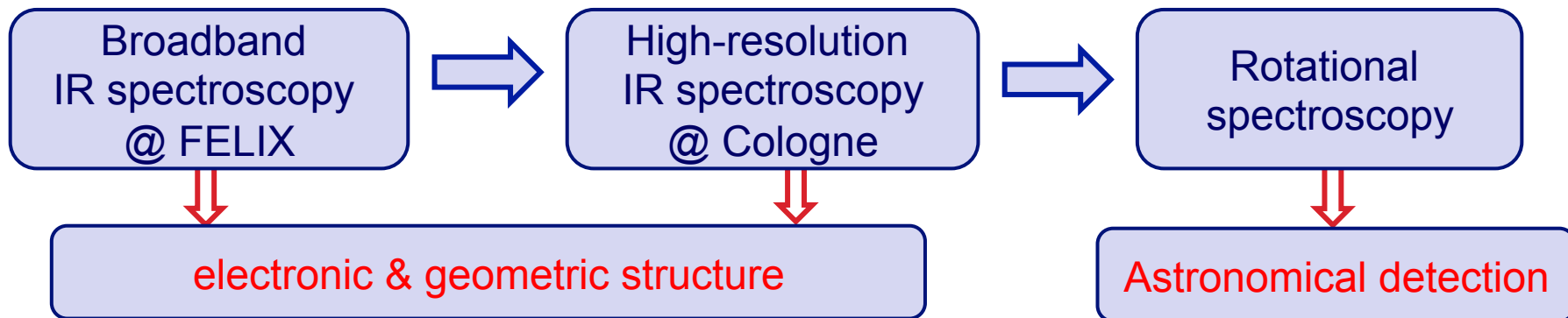


- virtually no spectral data available on C_2H^+ , C_3^+ & $C_3H_2^+$

Guzman et al., *ApJL* 800 (2015)

See also: Cuadrado et al. *A&A* 575 (2015) A82; McGuire et al. *MNRAS* 442 (2014) 2901

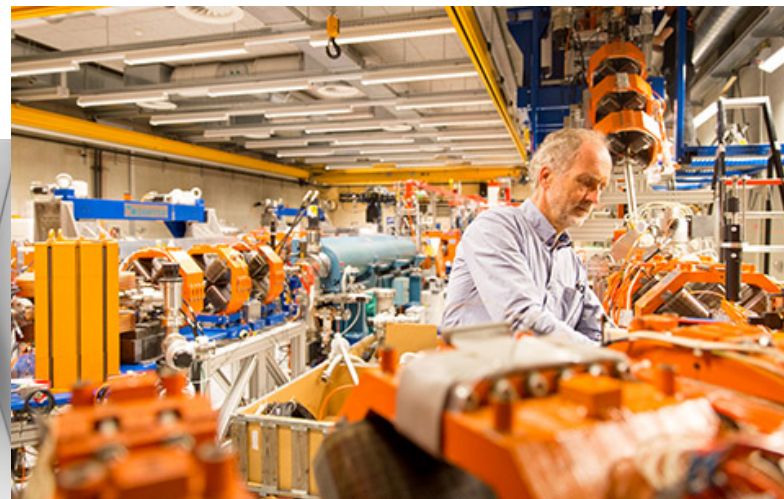
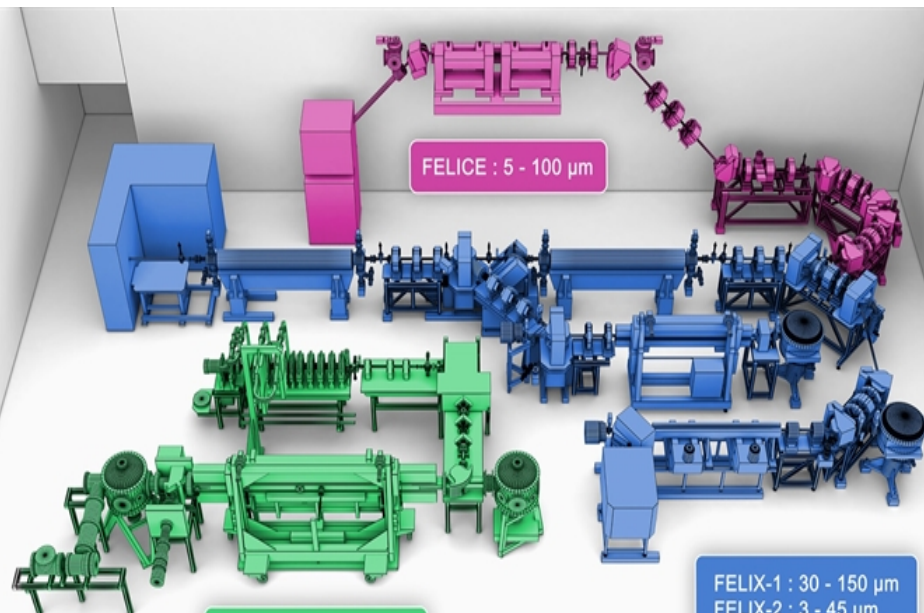
Experimental Strategy:



Free Electron Laser Laboratory

FELIX

Free Electron Lasers for
Infrared eXperiments



FEL 1 + 2:

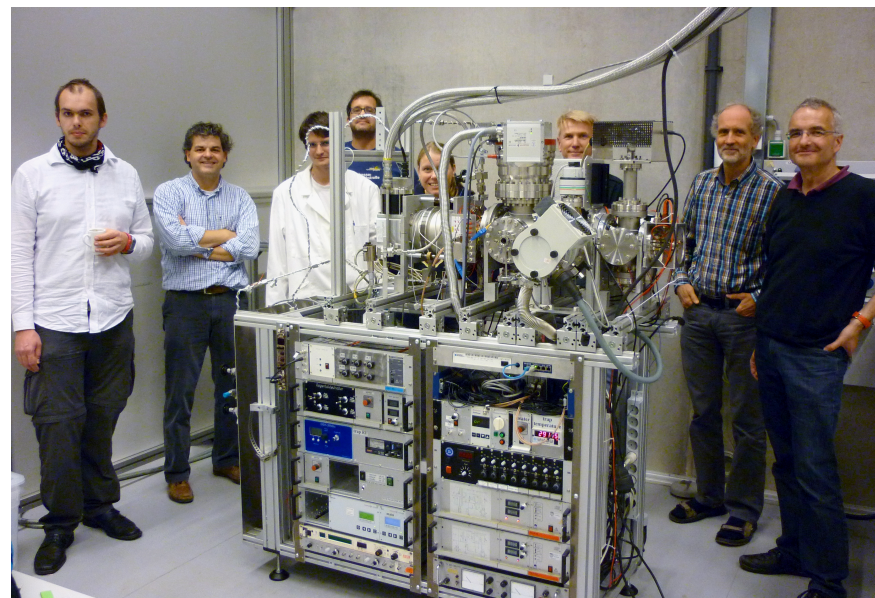
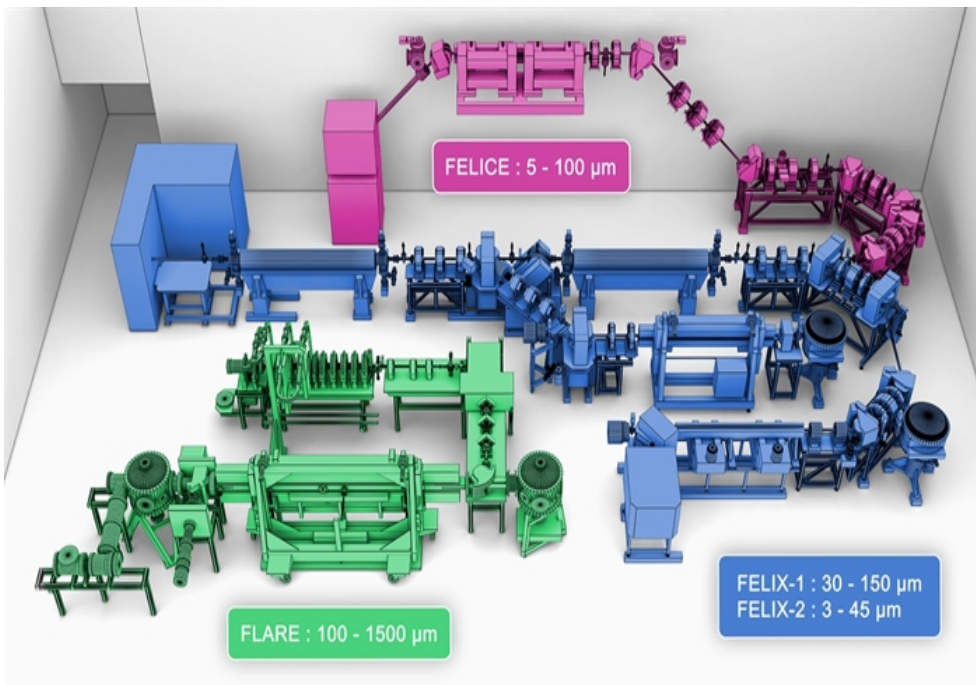
Wavelength tunable	3 - 150 μm
Pulse energy	<100mJ in 10 μs pulse
FWHM bandwidth	> 0.2 %

- international user facility
- large suite of gas-phase beam stations

Cryogenic trap instrument FELion @

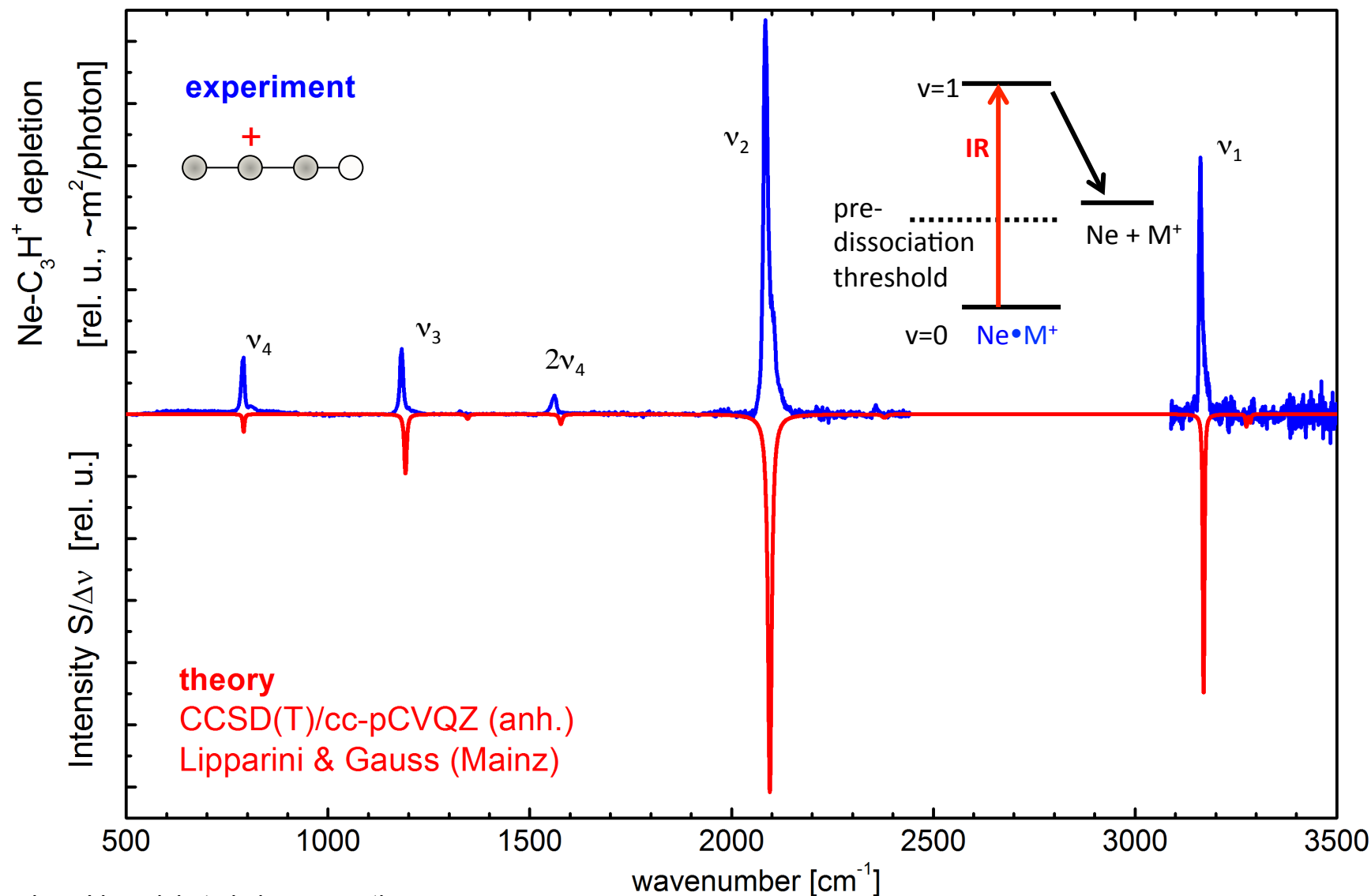


Collaboration S. Schlemmer (Cologne) & FELIX laboratory



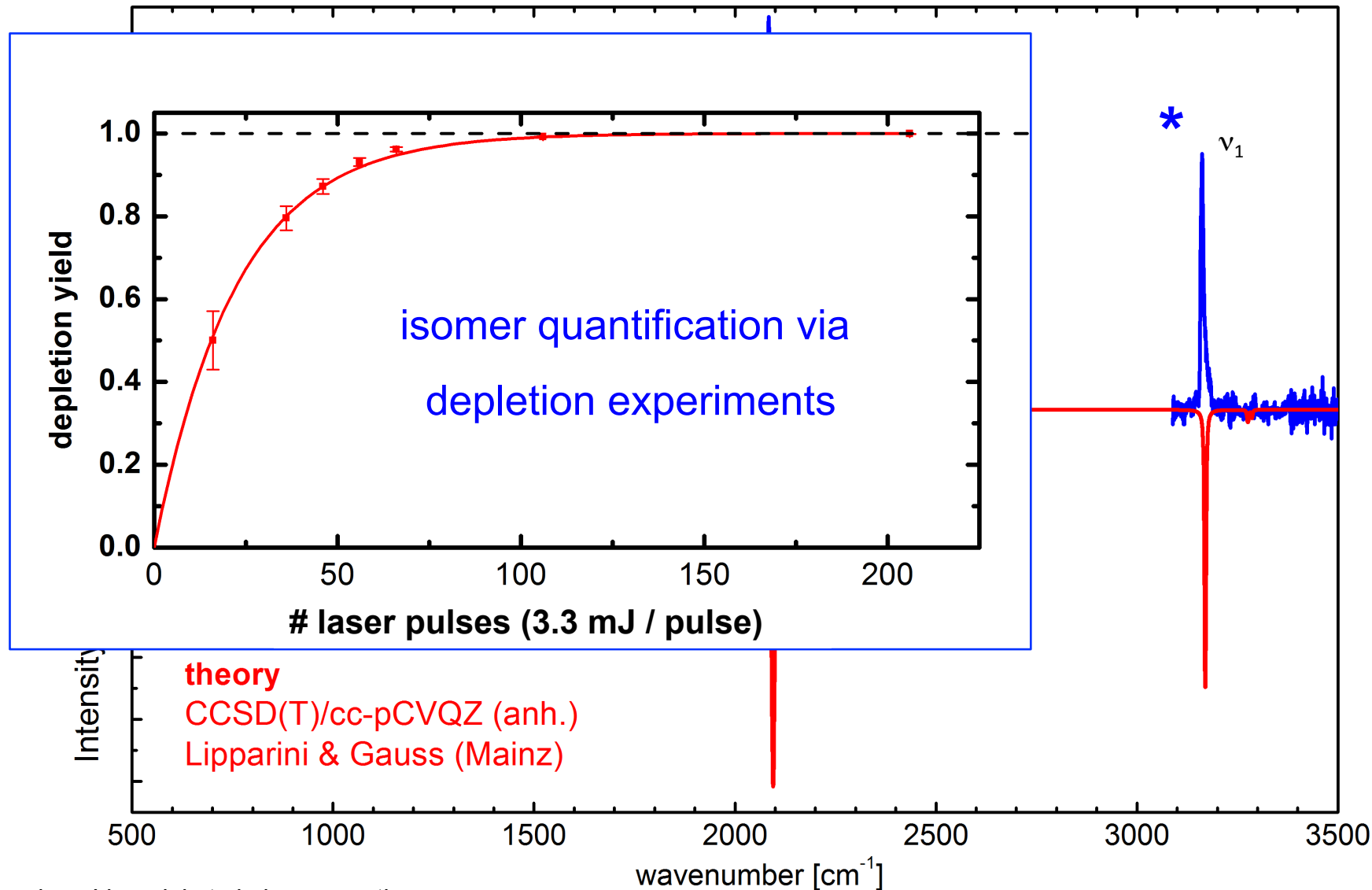
- Cryogenic 22-pole ion trap installed at FELIX in October 2014
- Unique combination with FELIX for gas-phase IR spectroscopic studies

IR-PD spectrum of linear C_3H^+ ($^1\Sigma^+$) @ FELIX



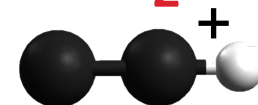
Brünken, Lipparini et al., in preparation

IR-PD spectrum of linear C_3H^+ ($^1\Sigma^+$) @ FELIX



Brünken, Lipparini et al., in preparation

Only limited previous work on ethynyl cation C_2H^+



Ab initio studies, e.g.:

- HF/6-31G^{**}: **$^3\Pi$ ground state**
Renner-Teller-split π bending mode ($^3A'$, $^3A''$): 540 & 930 cm^{-1}
two σ modes CC stretch: 1810 cm^{-1}
 CH stretch: 3442 cm^{-1}

Largo & Barrientos *CP* 138 (1989) 291

Experimental:

- Ar (Ne) **matrix IR** spectroscopy & CCSD(T)/aug-cc-pVDZ ab initio **calculations**
Andrews et al. *JCP* 110 (1999) 4457

549.5 cm^{-1} (1 comp.)
1820.4 (1832.2) cm^{-1}

RT-split π bending mode: **201 & 747 cm^{-1}**
CC stretch: 1830 cm^{-1}
CH stretch: 3247 cm^{-1}

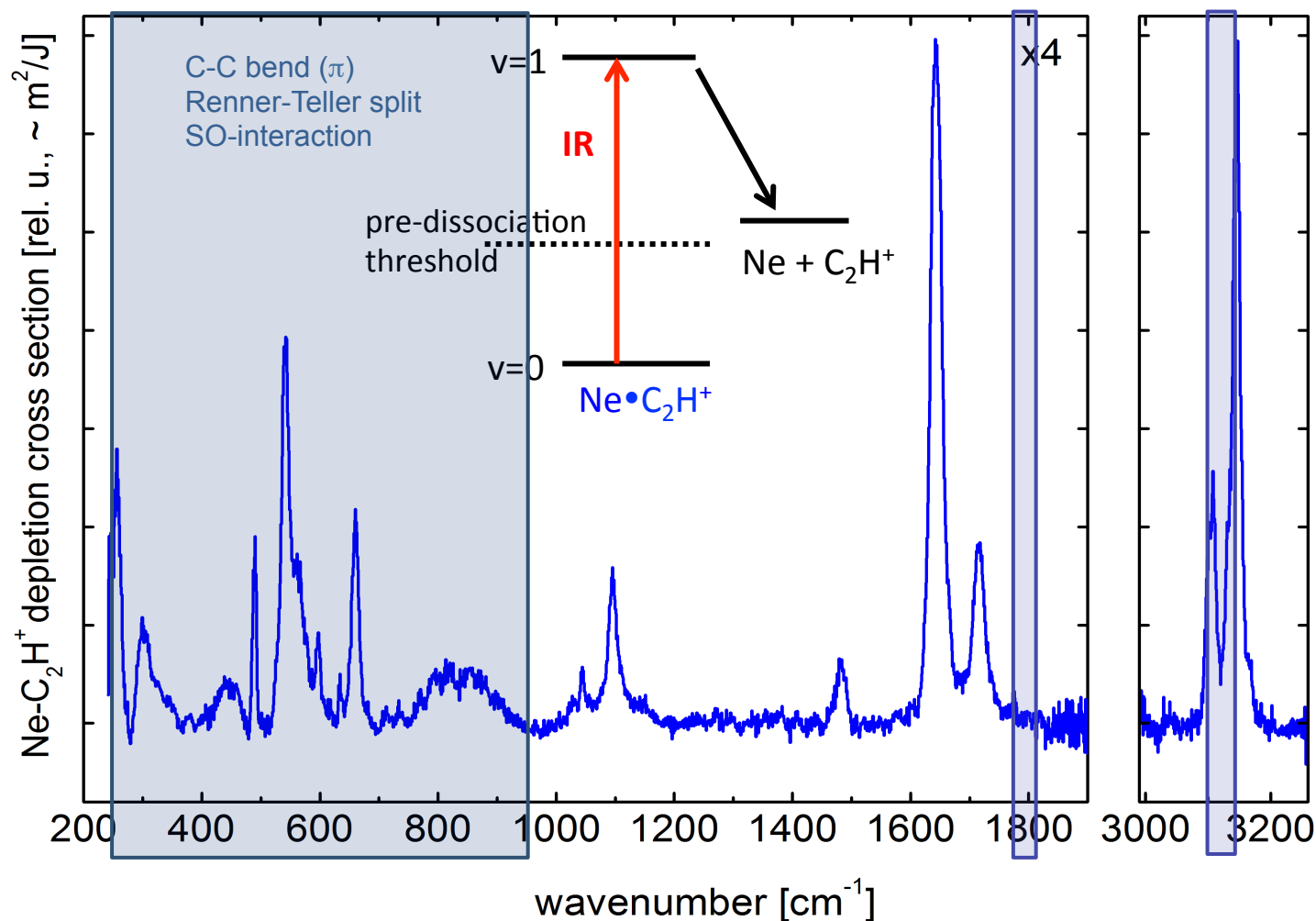
- (S)PES gas phase**

& MRCI/CASSCF ab initio calculations
Gans et al. *JCP* 146 (2017) 011101

1620(40) cm^{-1}

RT-split π bending mode: 347 & 719 cm^{-1}
CC stretch: **1839 cm^{-1}**
CH stretch: 3242 cm^{-1}

Ne - IRPD spectrum of linear C_2H^+ ($^3\Pi$)



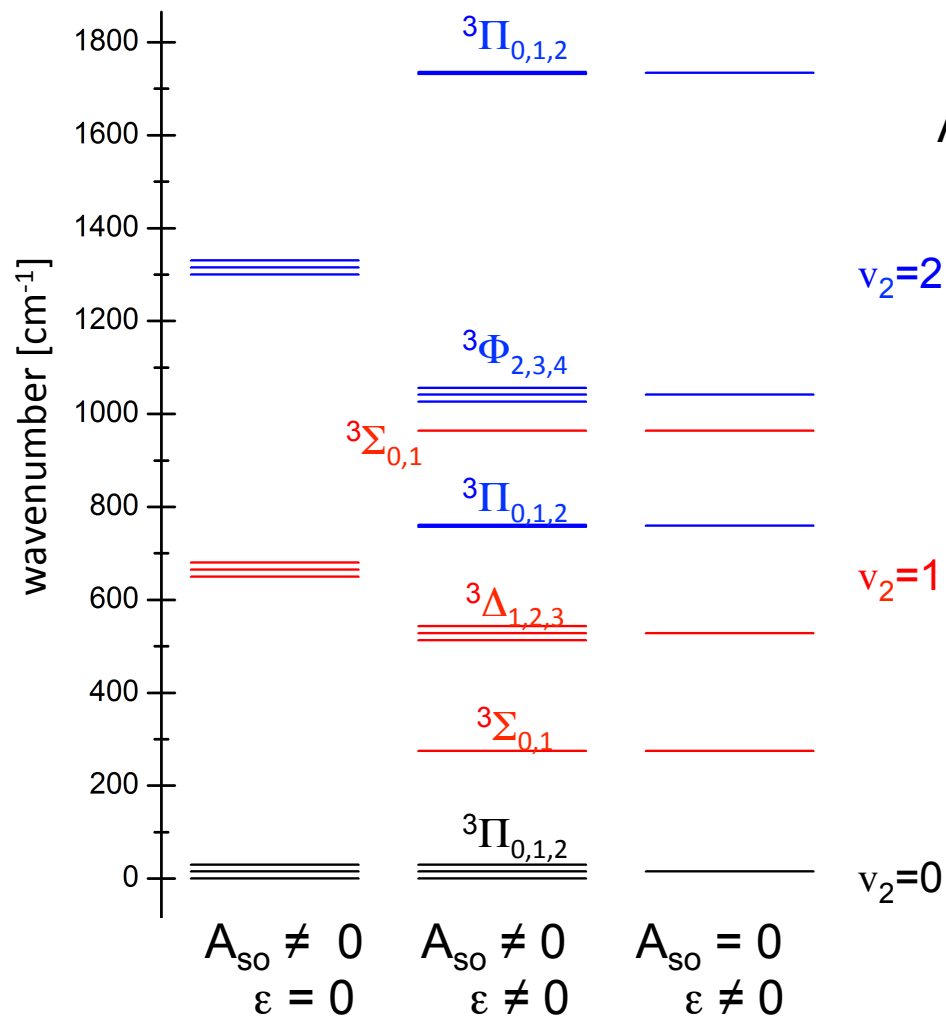
harmonic EOM-IP-CCSD(T)/cc-pCVTZ
Gauss / Lipparini / Stanton

C-C stretch (σ_g) C-H stretch (σ_g)

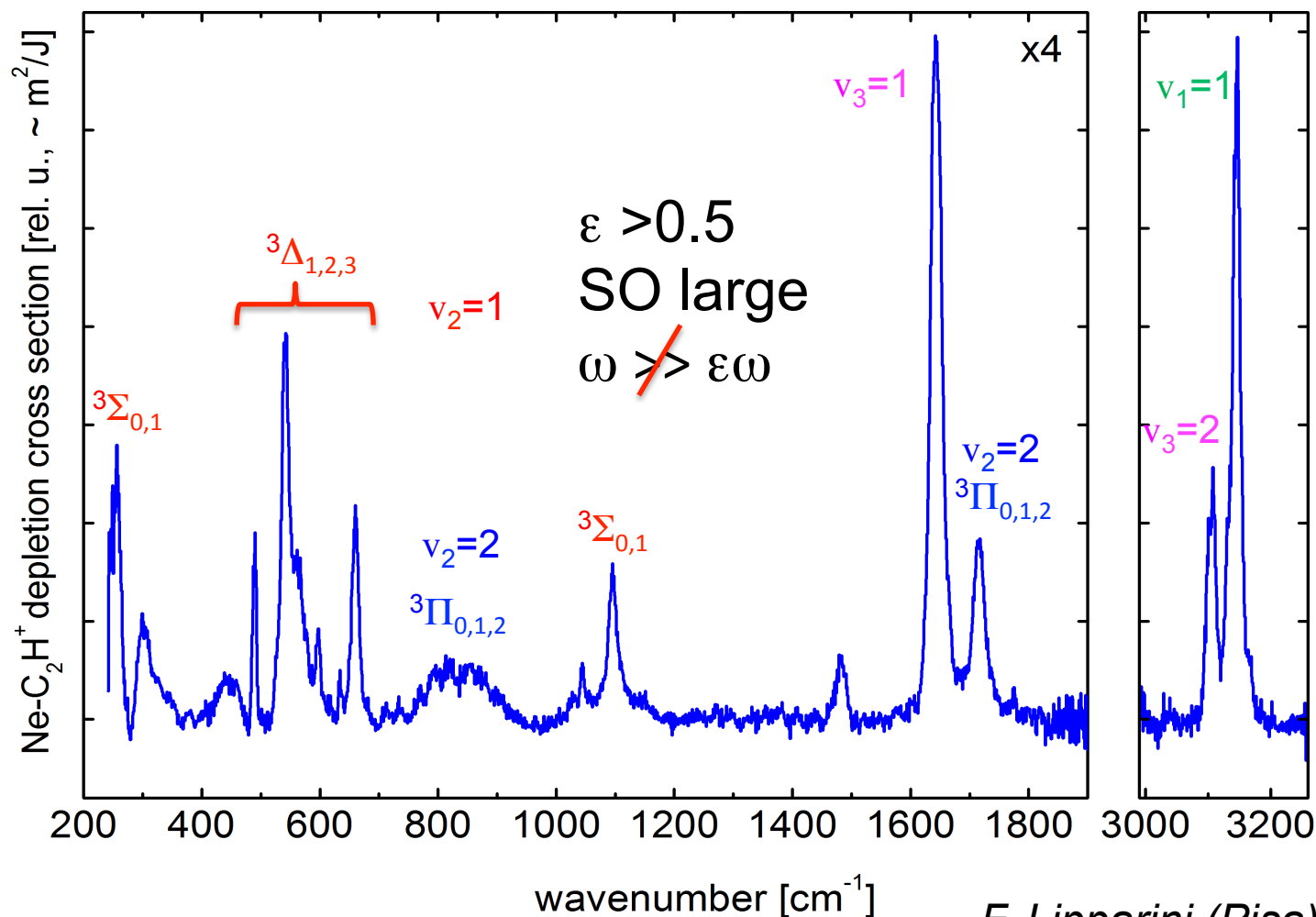
RT and SO effects in linear C_2H^+ ($^3\Pi$)

Perturbative approach by J. Hougen

J. Chem. Phys. 36, 1874 (1962)



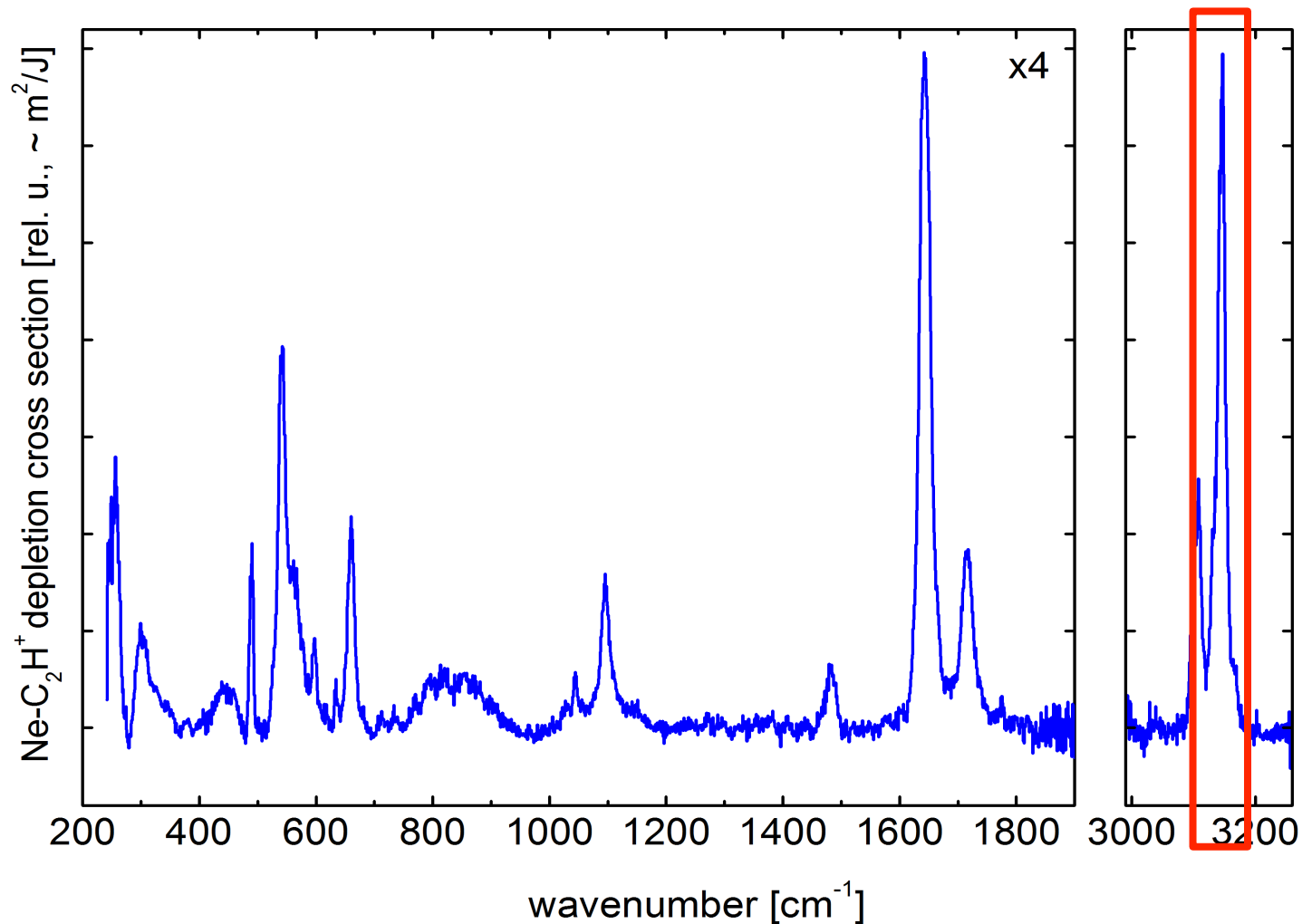
Ne - IRPD spectrum of linear C_2H^+ ($^3\Pi$)



Benchmarking of quantum-chemical calculations

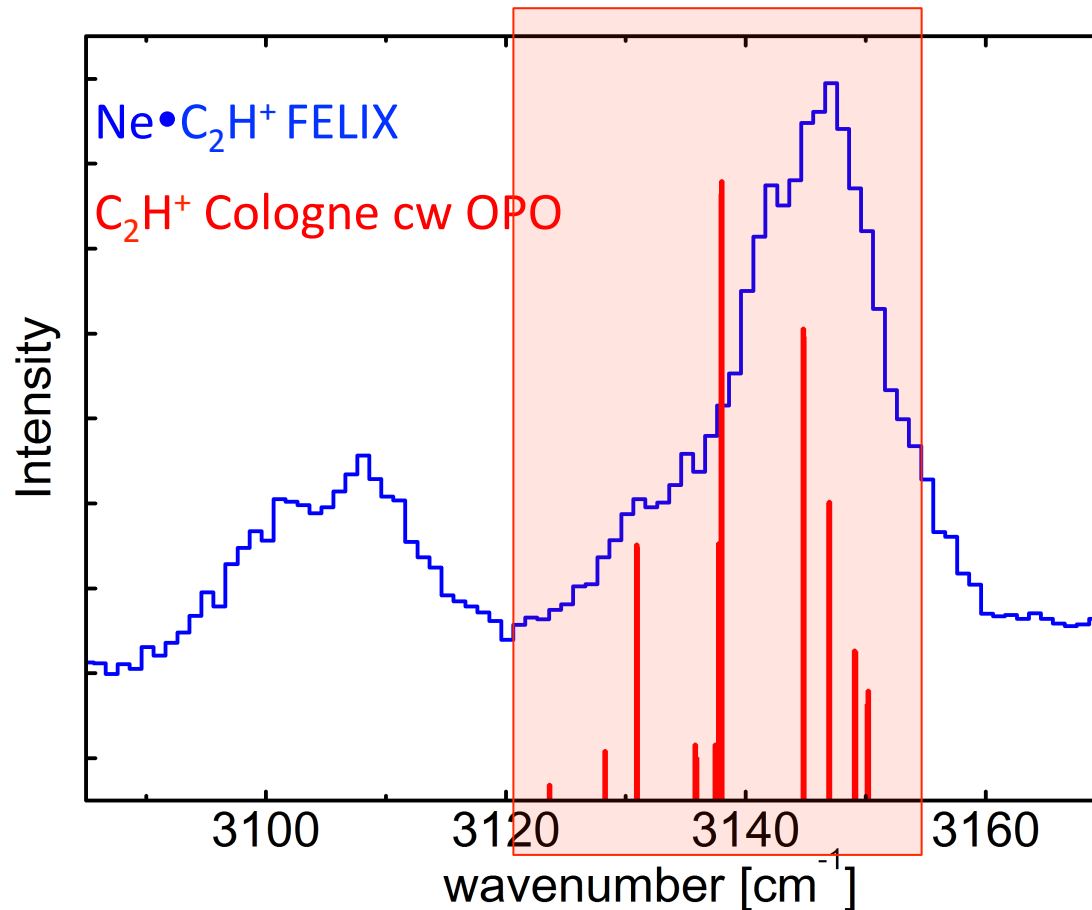
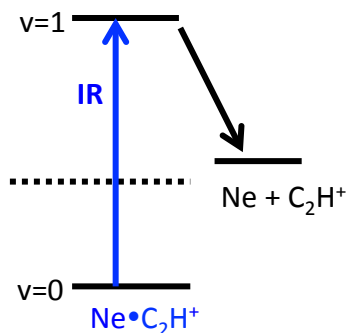
F. Lipparini (Pisa)
J. Gauss (Mainz)
J. Stanton (Gainesville)

Ne - IRPD spectrum of linear C_2H^+ ($^3\Pi$)

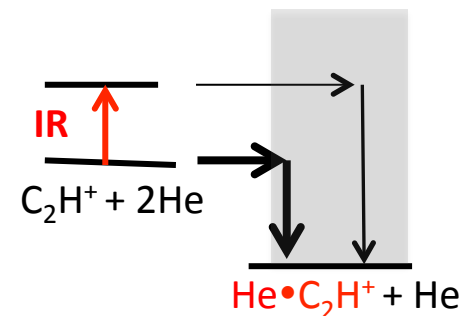


C_2H^+ : From broadband to high-resolution

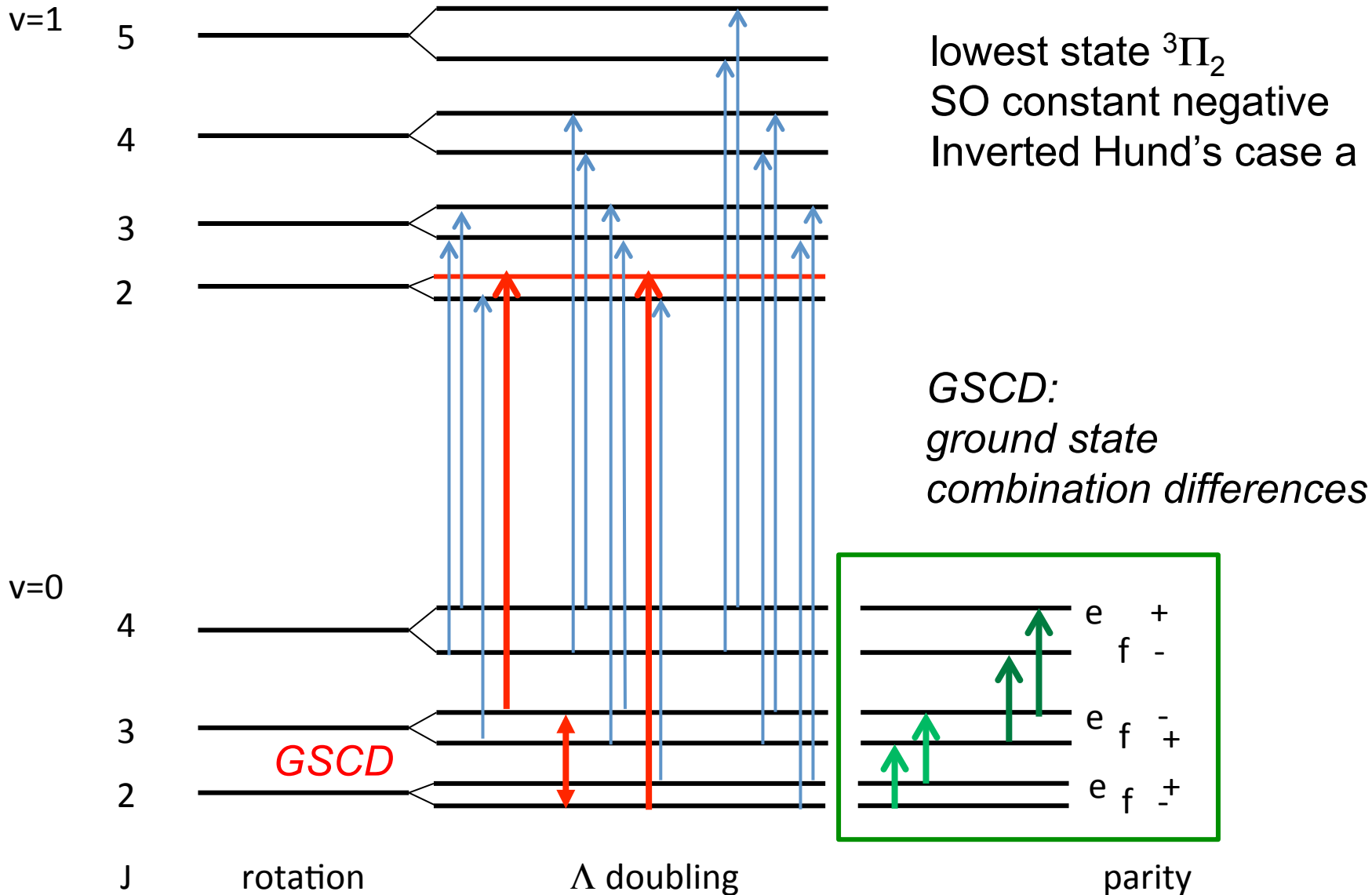
IR-PD



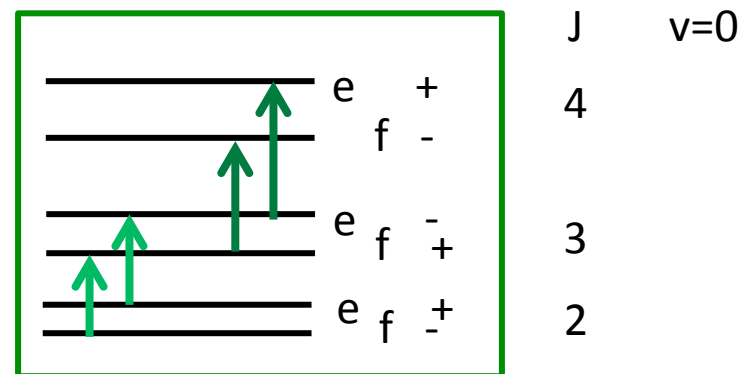
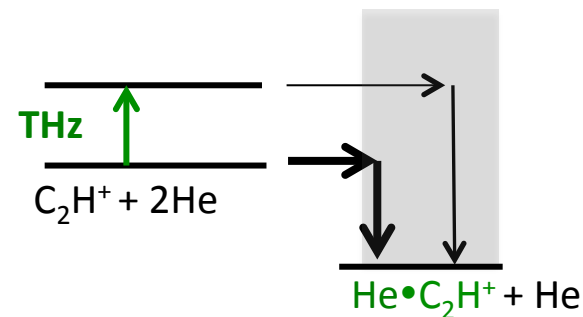
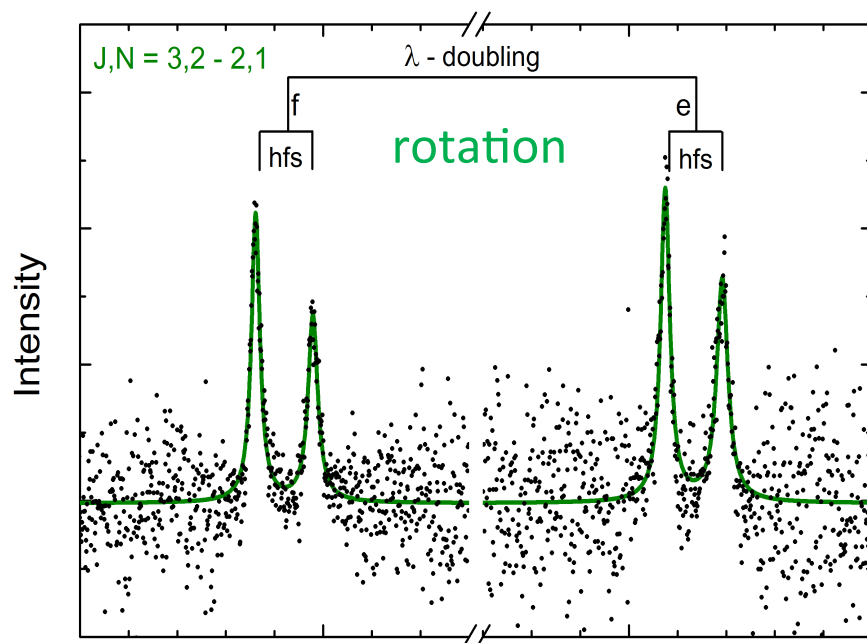
LIICG



C₂H⁺: Analysis of ro-vib data constrains search for rotational lines

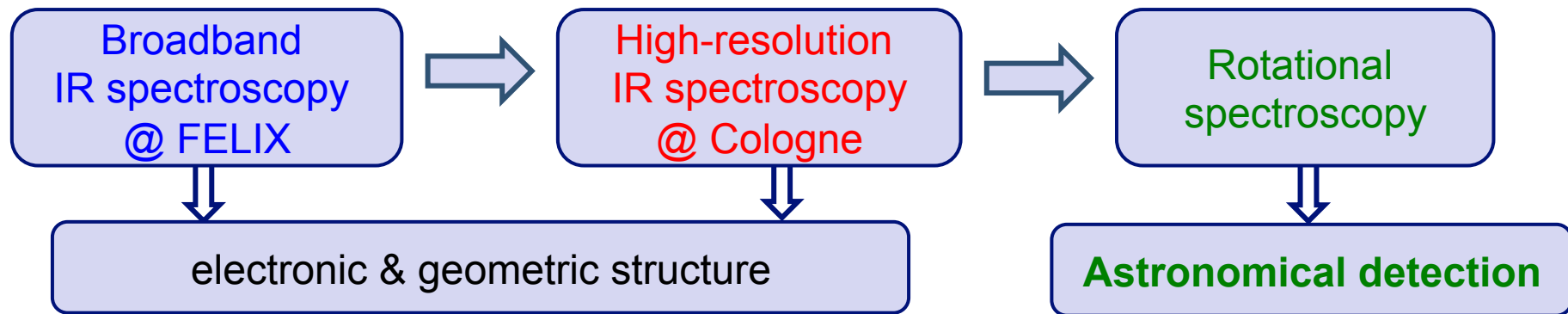
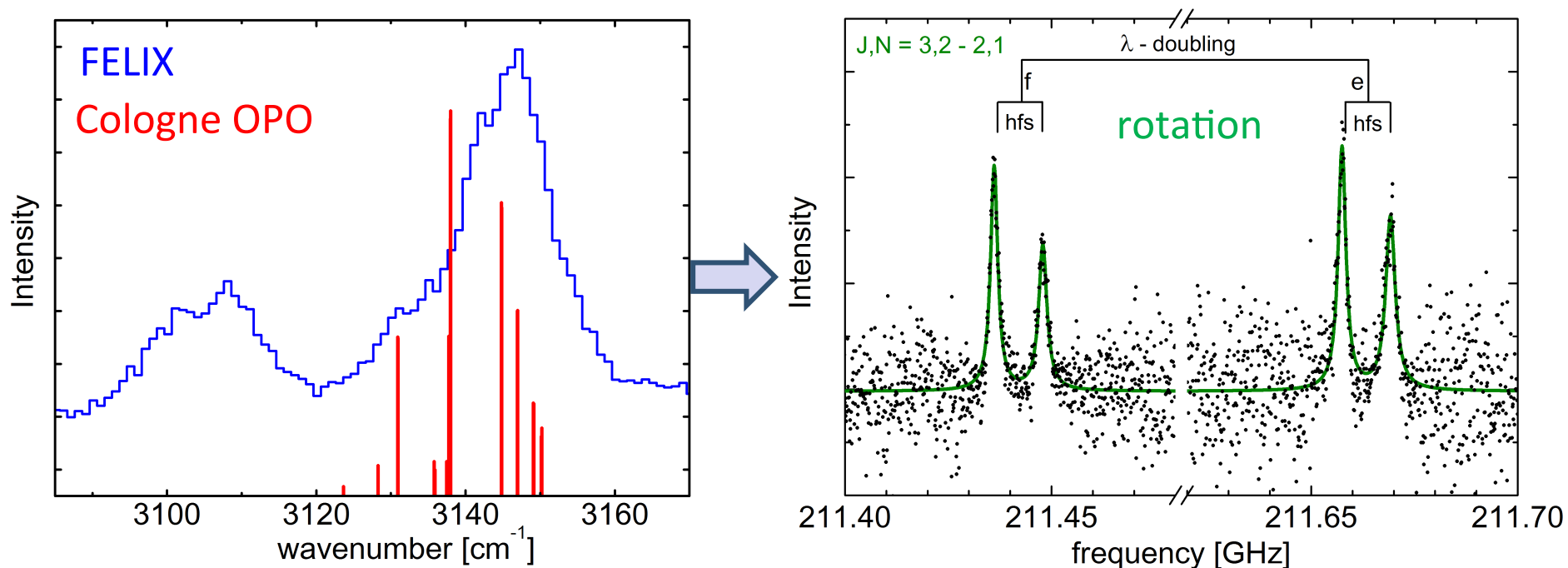


C_2H^+ : Pure rotational transitions via state-dependent attachment of He



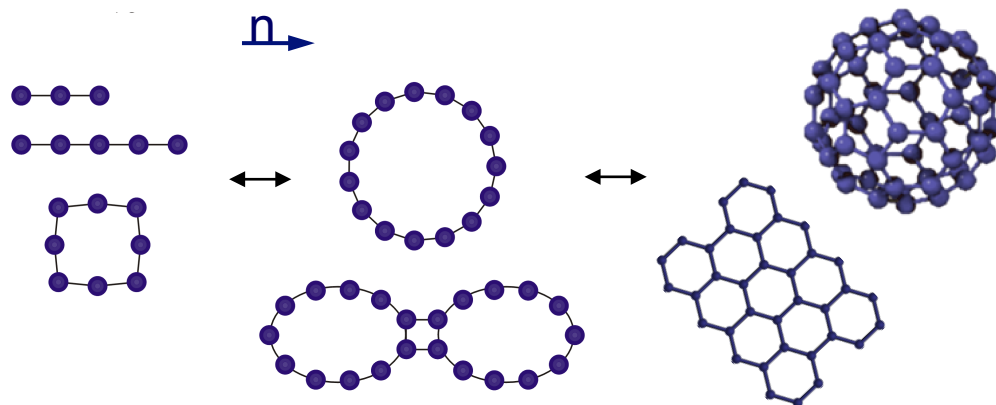
Brünken et al., in preparation

C_2H^+ : From broadband vibration to rotation

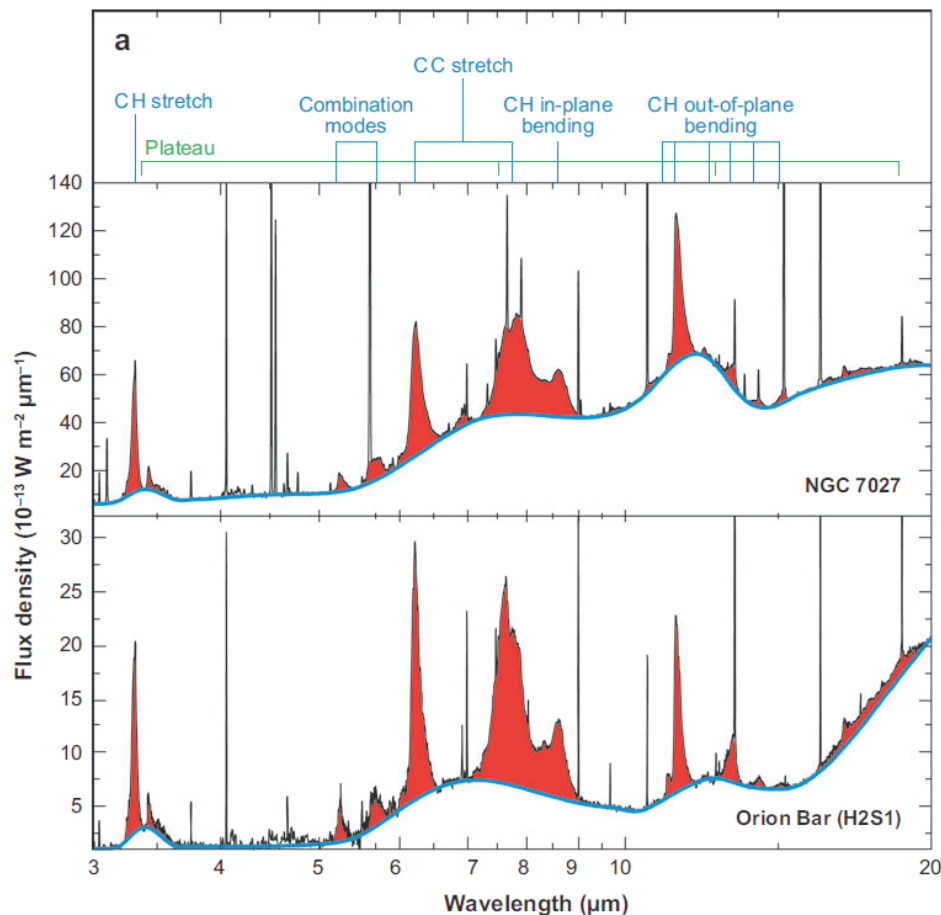
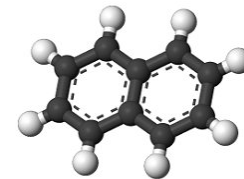


Perspectives: increasing the structural complexity

- Pure carbon and hydrocarbon ions :
 C_n^+ ; $C_nH_m^+$, **PAH (polycyclic aromatic hydrocarbon) ions**



The PAH hypothesis

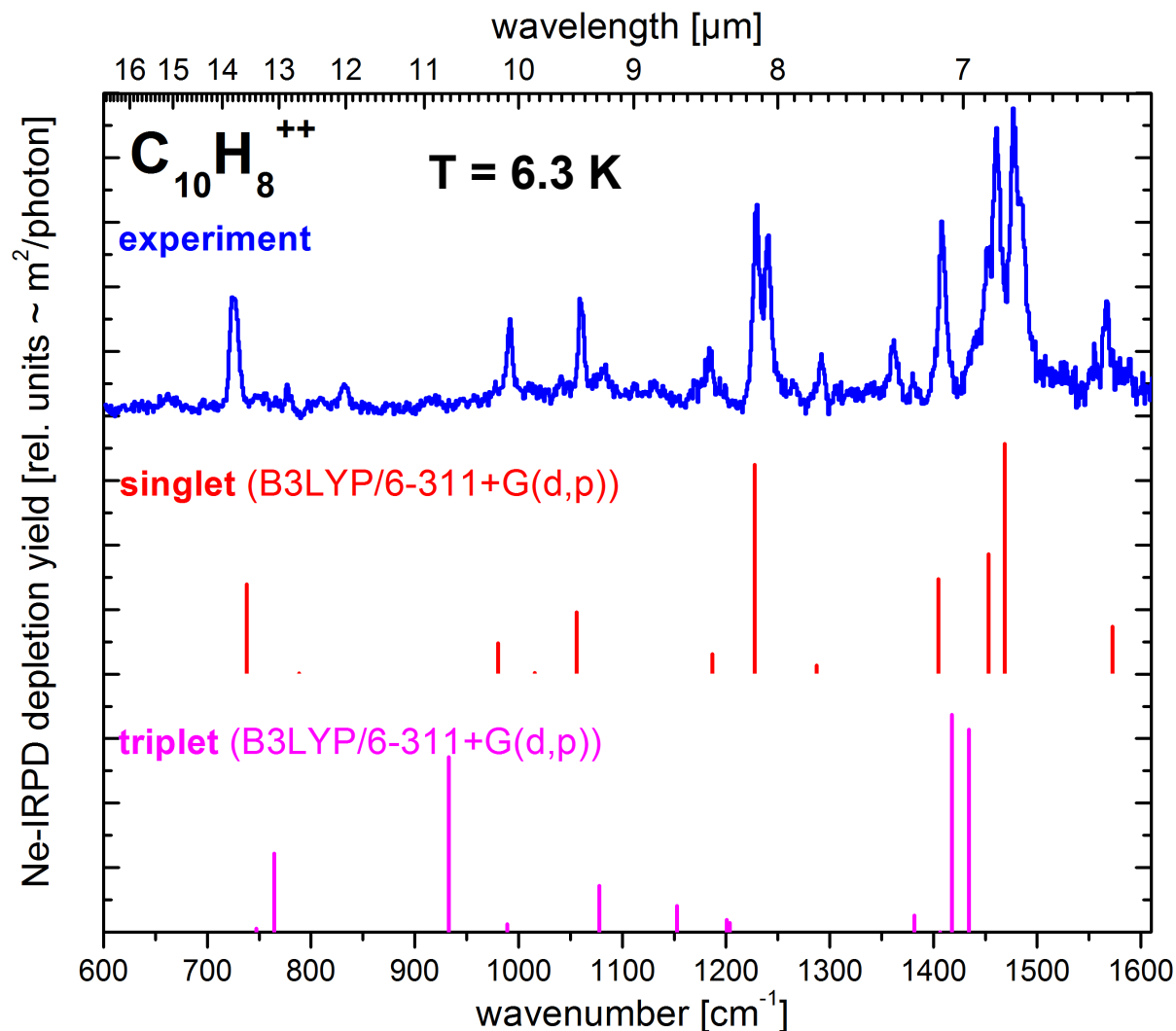
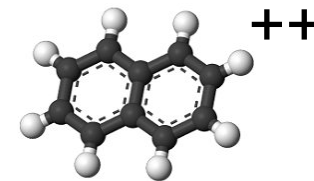


- Ubiquitous infrared emission features seen in many different environments
- Attributed to IR fluorescence of Polycyclic Aromatic Hydrocarbons (PAHs)
- Variation in observations attributed to heterogeneity of PAH family:
 - Charge state
 - Size
 - Hydrogenation state

IR Spectroscopic laboratory data needed!

Combination of FELIX and temperature-variable ion trap perfect match!

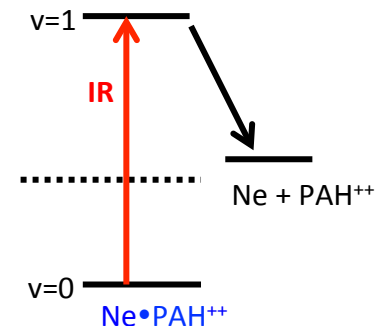
First results of a cold PAH dication



Collaboration with J. Oomens (RU Nijmegen)

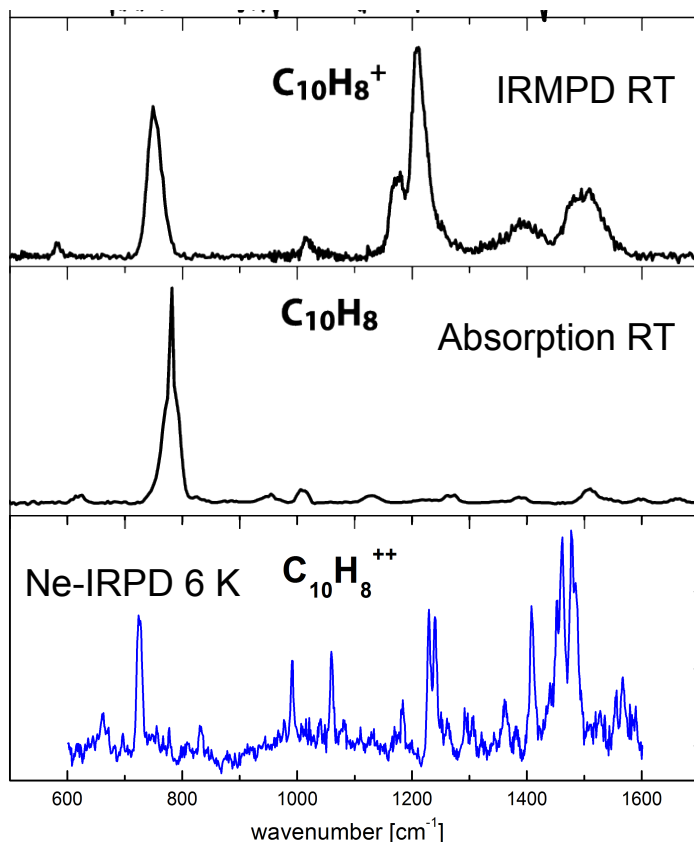
- Electron impact ion source allows efficient production of **doubly charged** PAHs
- Narrow line-widths only limited by FELIX bandwidth:

➤ Benchmarking of ab-initio calculations



First results of a cold PAH dication

Vibrational spectra of different **classes** of PAH molecules

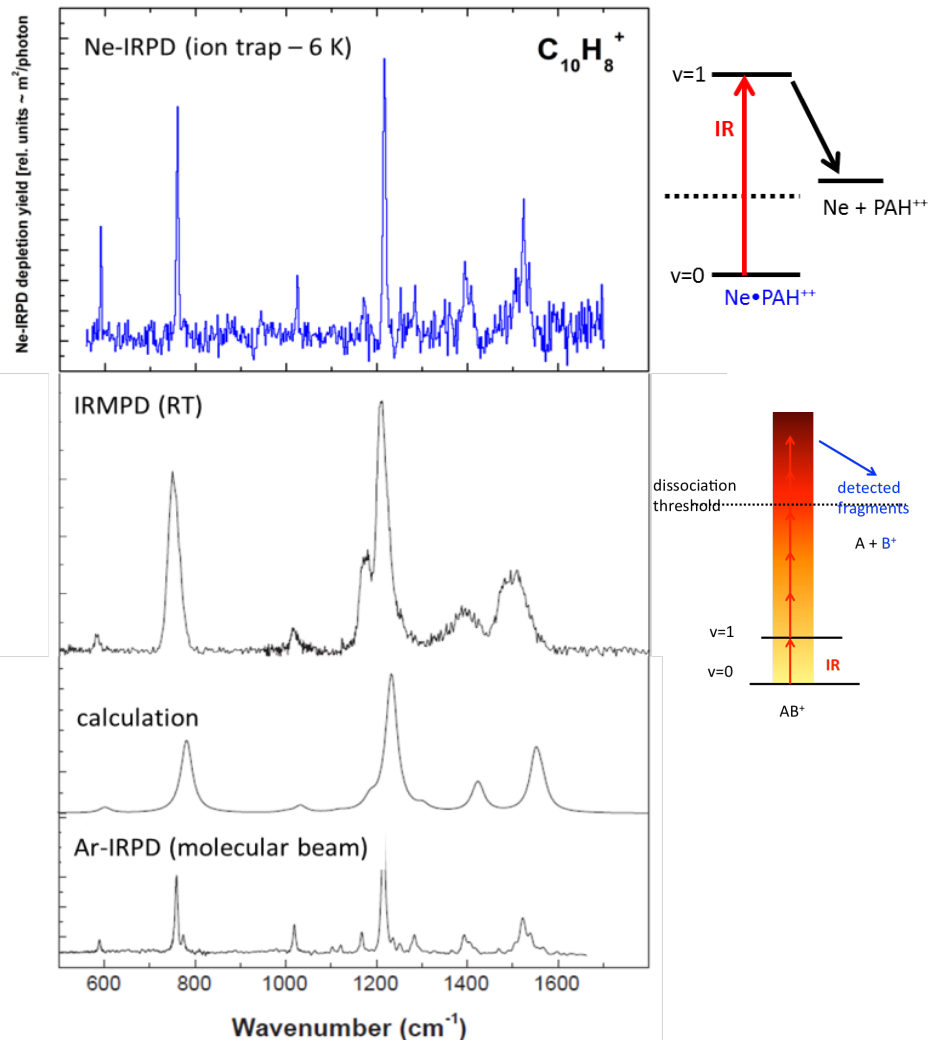


NIST & Szczepanski et al. ApJ 646 (2008) & this work



europaH

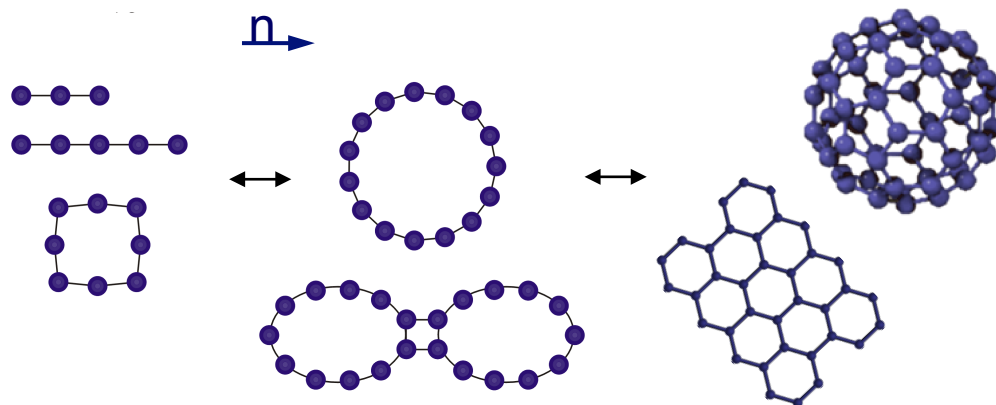
Influence of **temperature and methods** (single vs. multiphoton) on spectra



Oomens et al. ApJ 591 (2003) & this work

Perspectives: increasing the structural complexity

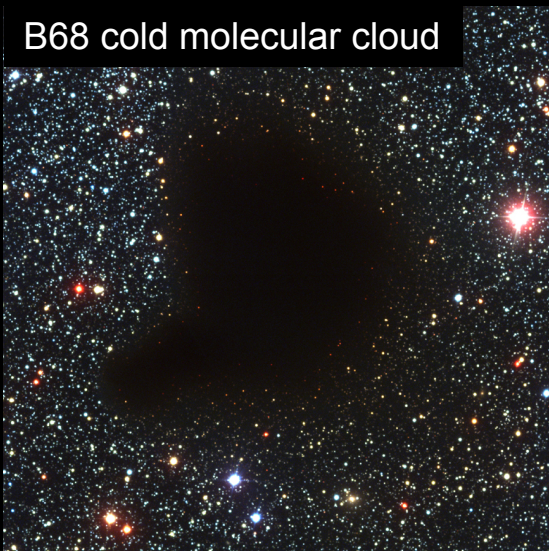
- Pure carbon and hydrocarbon ions :
 C_n^+ ; $C_nH_m^+$, **PAH (polycyclic aromatic hydrocarbon) ions**



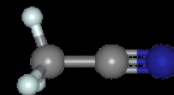
- Nitrogen-substituted ions $HC_{2n+1}N^+$, $HC_{2n+1}NH^+$, **CH_nCN^+**

Astrochemical Motivation – Interstellar Medium

B68 cold molecular cloud

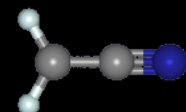


CH_3CN methyl cyanide – Solomon 1971



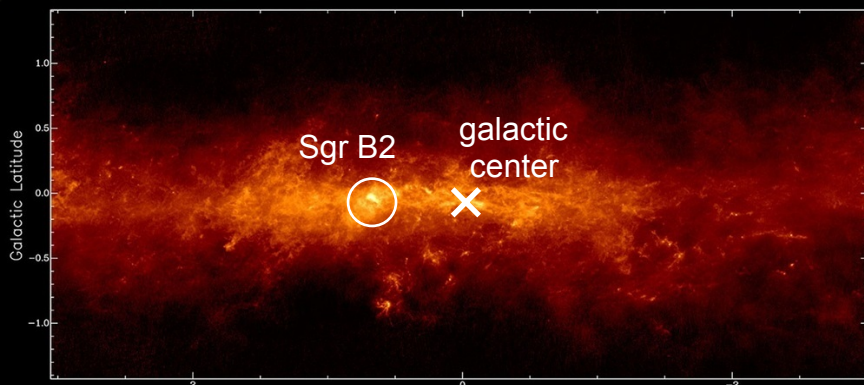
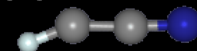
CH_3NC methyl isocyanide – Cernicharo 1988

CH_2CNH ketenimine – Lovas 2006



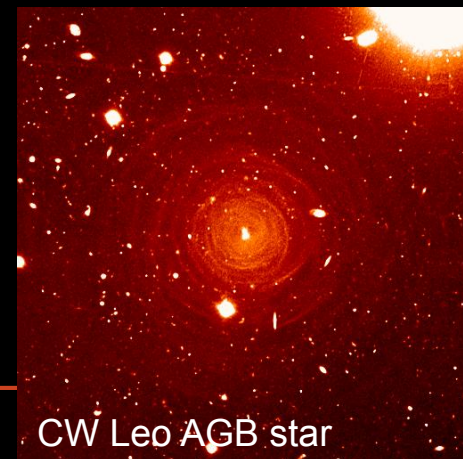
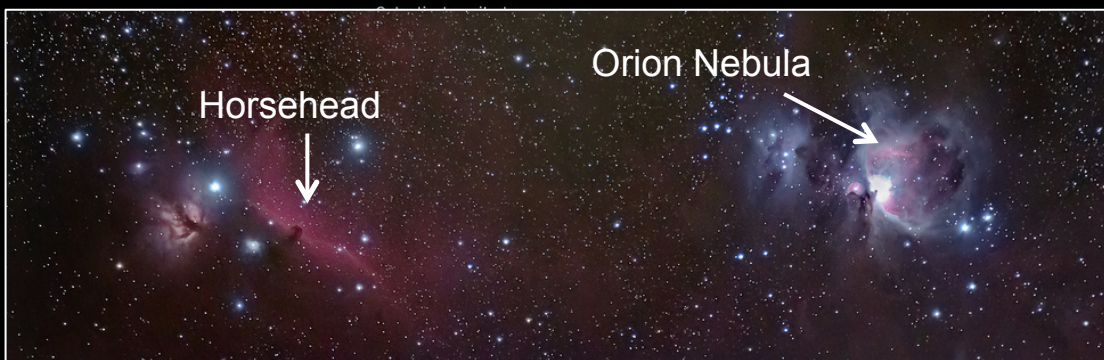
H_2CCN cyanomethyl radical – Irvine 1988

HCCN cyanomethylene radical – Guelin 1991

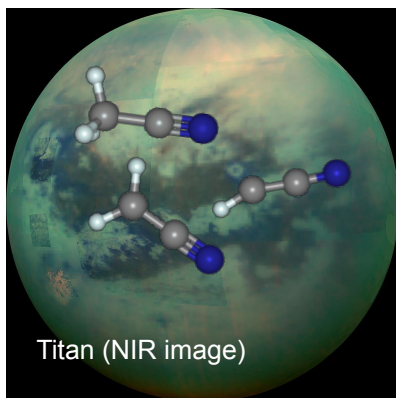


Ionized forms likely present

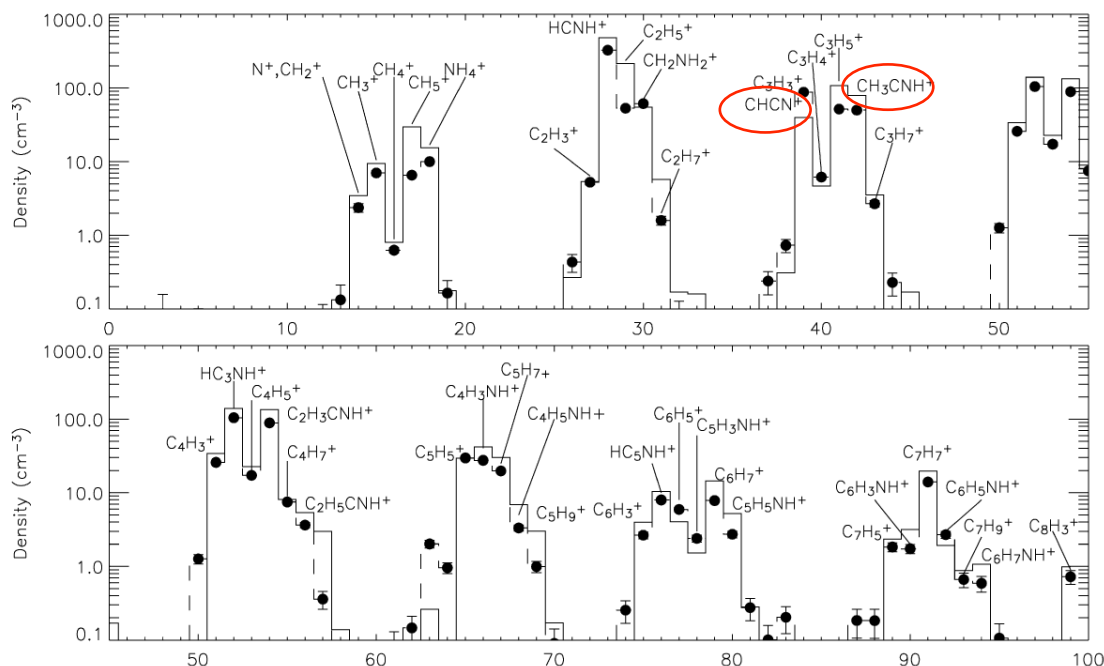
- Spectroscopic data needed
- Reaction pathways needed



Astrochemical Motivation – Planetary Atmospheres

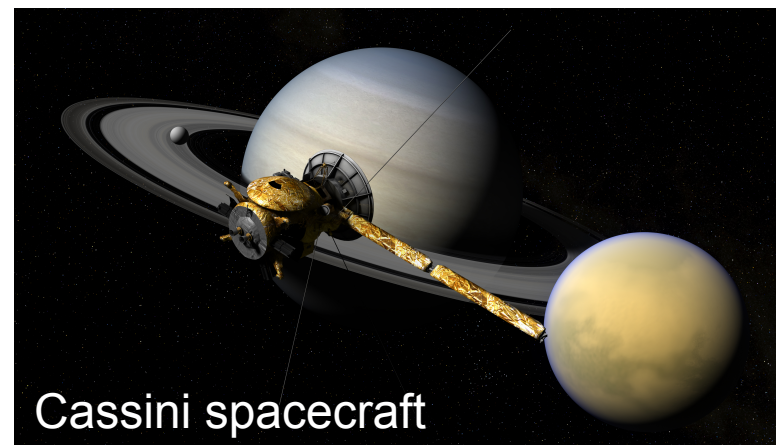


- Dissociation and ionization of N_2 and CH_4 in Titan's upper atmosphere initiate rich chemistry
- Ion-neutral reactions more important than previously thought
- Reactive $[C_2 H_n N]^+$ ions important intermediates



Spectroscopic IR database needed for isomer specific probing of reaction products

Collaboration W. Geppert, D. Ascenzi

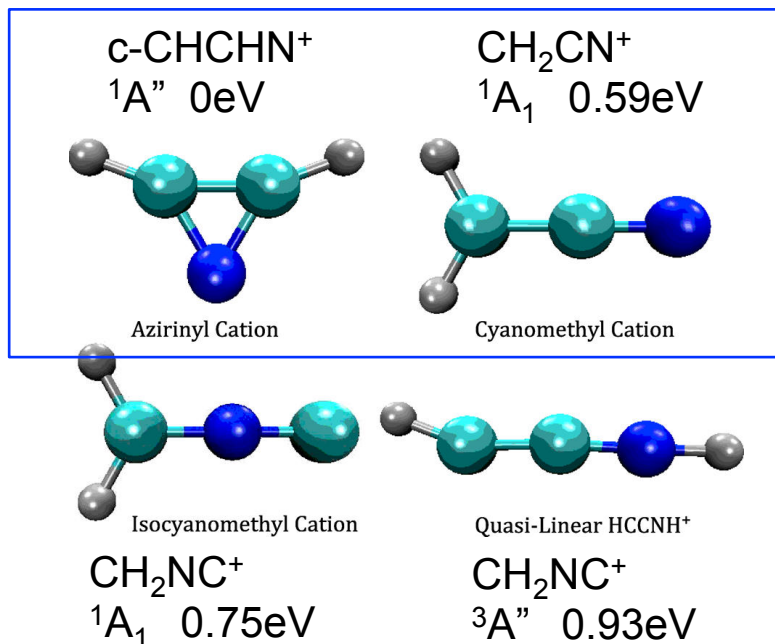


Cassini INMS (Ion and Neutral Mass Spectrometer) data
Vuitton et al., Icarus 2007

Spectroscopic/Chemical Motivation: $[\text{C}_2\text{H}_2\text{N}]^+$ isomers

So far only limited spectroscopic data.

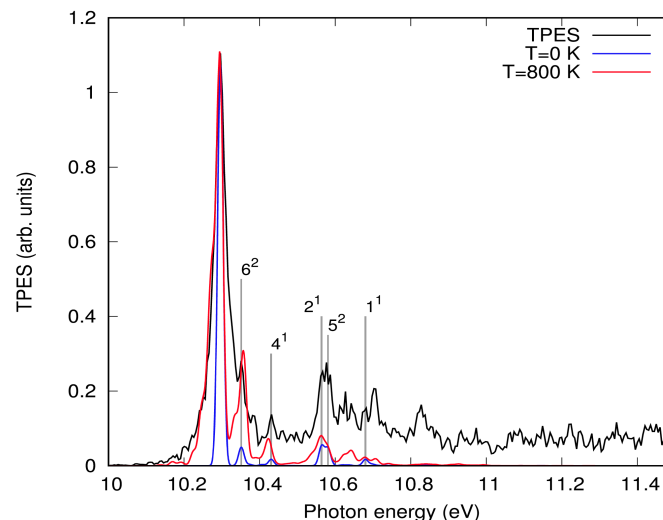
- Presence of four stable isomers:
two lowest should be accessible



**Ab initio structures
and vibrational frequencies**

Kokkila et al., J. Phys. Chem. A 2016

- **TPEPICO**



Garcia et al., JCP 2017

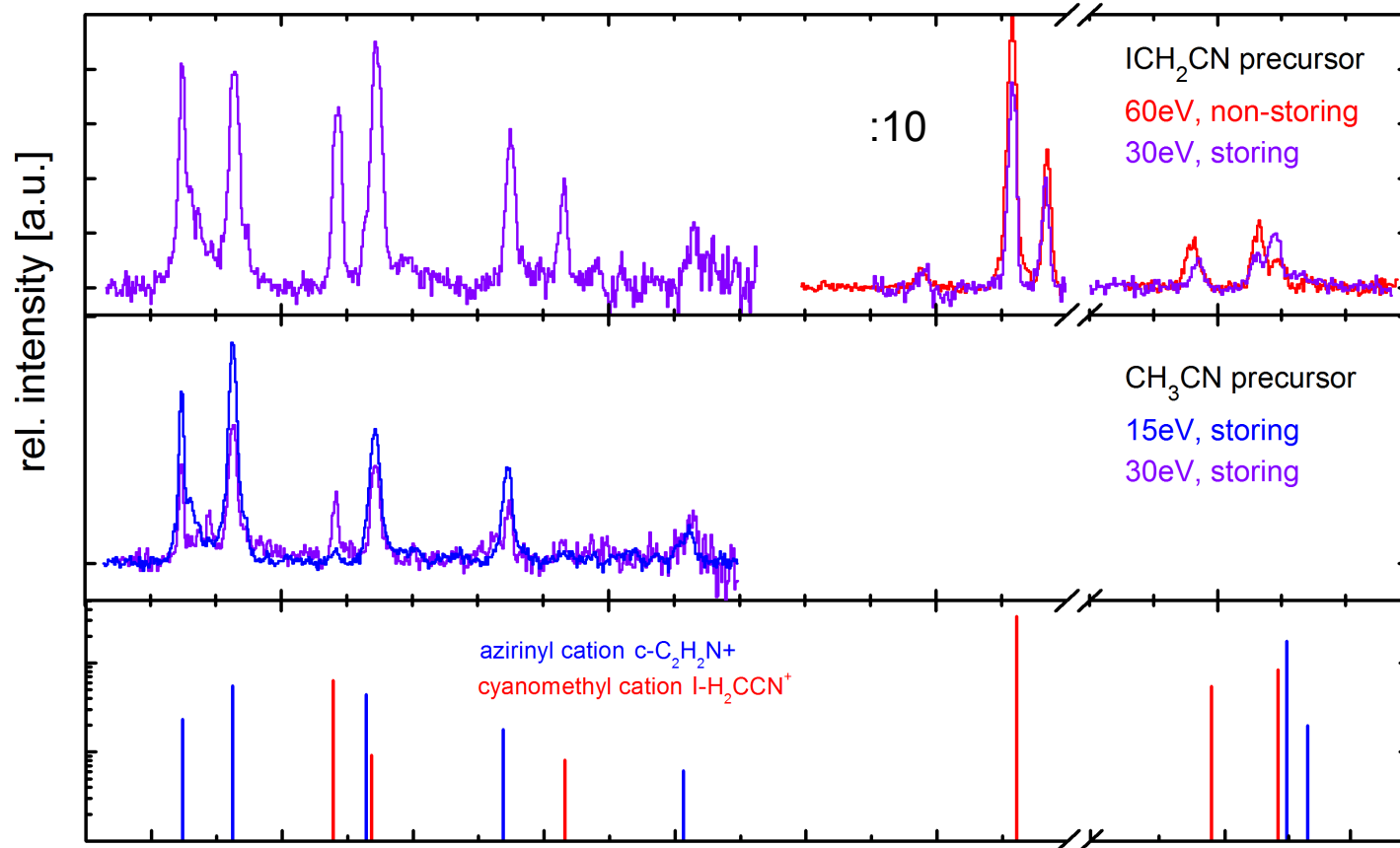
Steinbauer et al., Chem. Phys. Lett. 2010

- **Ne-matrix FT-IR spectroscopy**

1-2 bands only

Frankowski et al., PCCP 2005

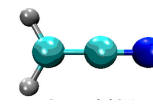
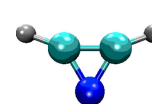
Ne-IR-PD spectra of $[\text{C}_2\text{H}_2\text{N}]^+$ isomers



Depletion analysis:

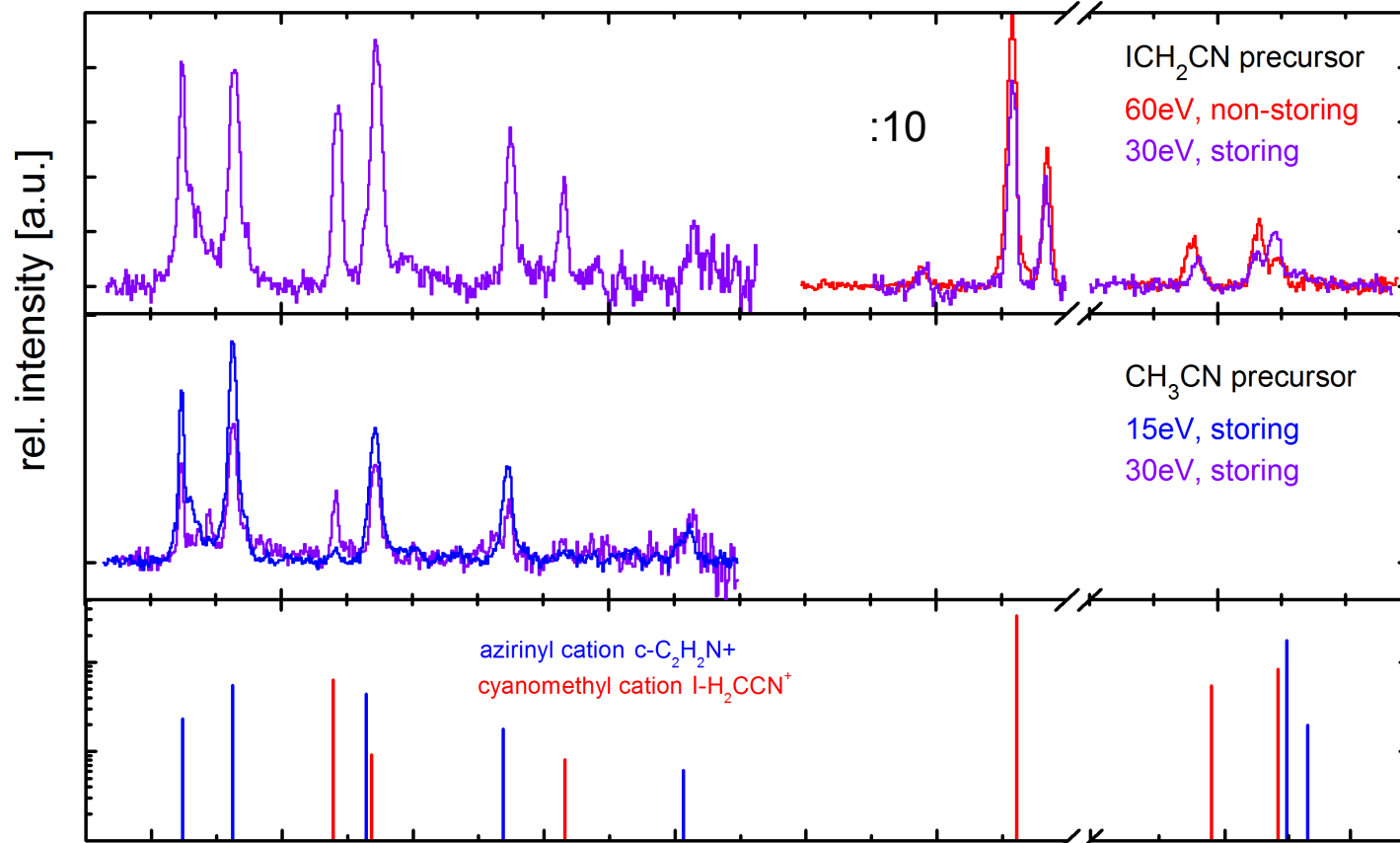
$\text{I-H}_2\text{CCN}^+$
73(3) %
40(2) %

c-CHCHN^+ $\text{I-H}_2\text{CCN}^+$
95(5) %
55(5) % 30(10) %



Theory collaboration with S. Thorwirth (Cologne):
anharmonic frequencies CCSD(T)/cc-pVTZ, harmonic intensities B3LYP/cc-pVTZ

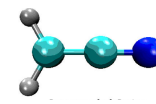
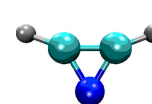
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Depletion analysis:

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73(3) %
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c-CHCHN^+ $\text{I-H}_2\text{CCN}^+$
95(5) %
55(5) % 30(10) %



- Basis for follow up high-resolution studies → radio-astronomical detection
- Isomer specific educt formation pathways → follow up reactivity studies
- IR database for reaction product probing

take home messages



- Laboratory spectroscopy prerequisite to interpret astronomical observation
 - Cryogenic ion trap experiments sensitive tools for rotational, vibrational (and electronic) spectroscopy on molecular ions
 - Development of action spectroscopic schemes for purely rotational spectroscopy provides accurate data for astronomical searches
- See also:
Talk TL19
J. Domenech*
- Combination of cryogenic ion trap with FELIX unique combination for study of reactive ions!
 - Possibility of isomer specific reaction probing

Many Thanks to Colleagues and Collaborators!

FELIX Laboratory team



Britta Redlich

Lex van der Meer

Jos Oomens & Giel Berden

Thijs Janssen & Frank Huis in't Veld

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Jürgen Gauss & Filippo Lipparini
John Stanton



Astronomy:

Karl Menten & Arnaud Belloche



Laboratory Astrophysics Group University of Cologne



Stephan Schlemmer

Oskar Asvany & Pavol Jusko

Sven Thorwirth

Alexander Stoffels (FELIX) & Lars Kluge

Shreyak Banhatti (EUROPAH)

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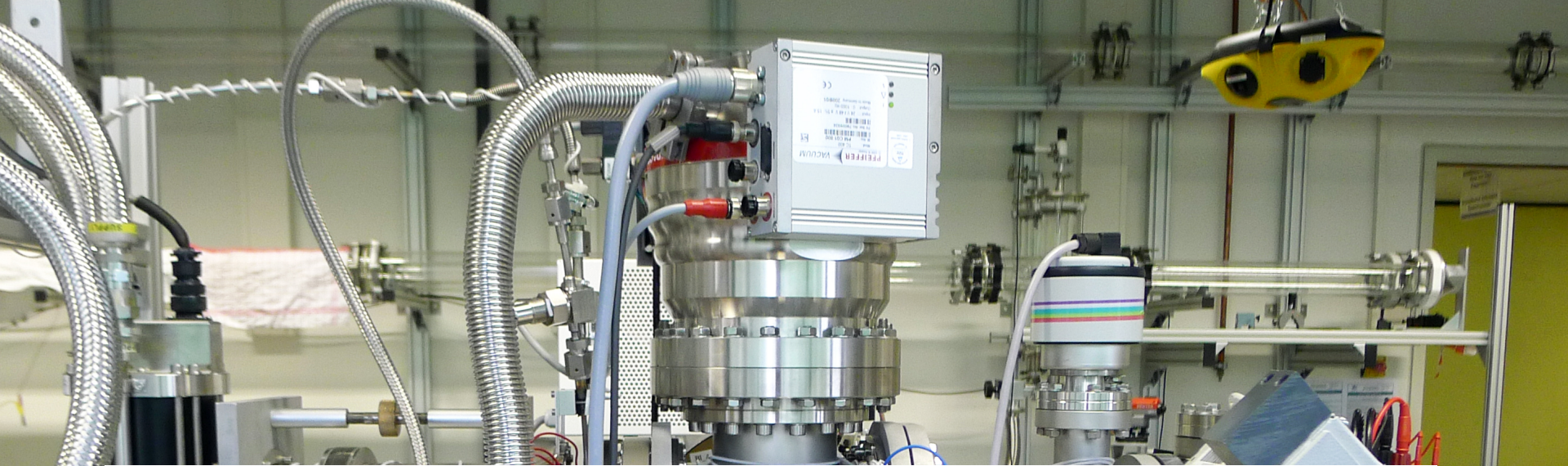


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Thank you for your attention!

