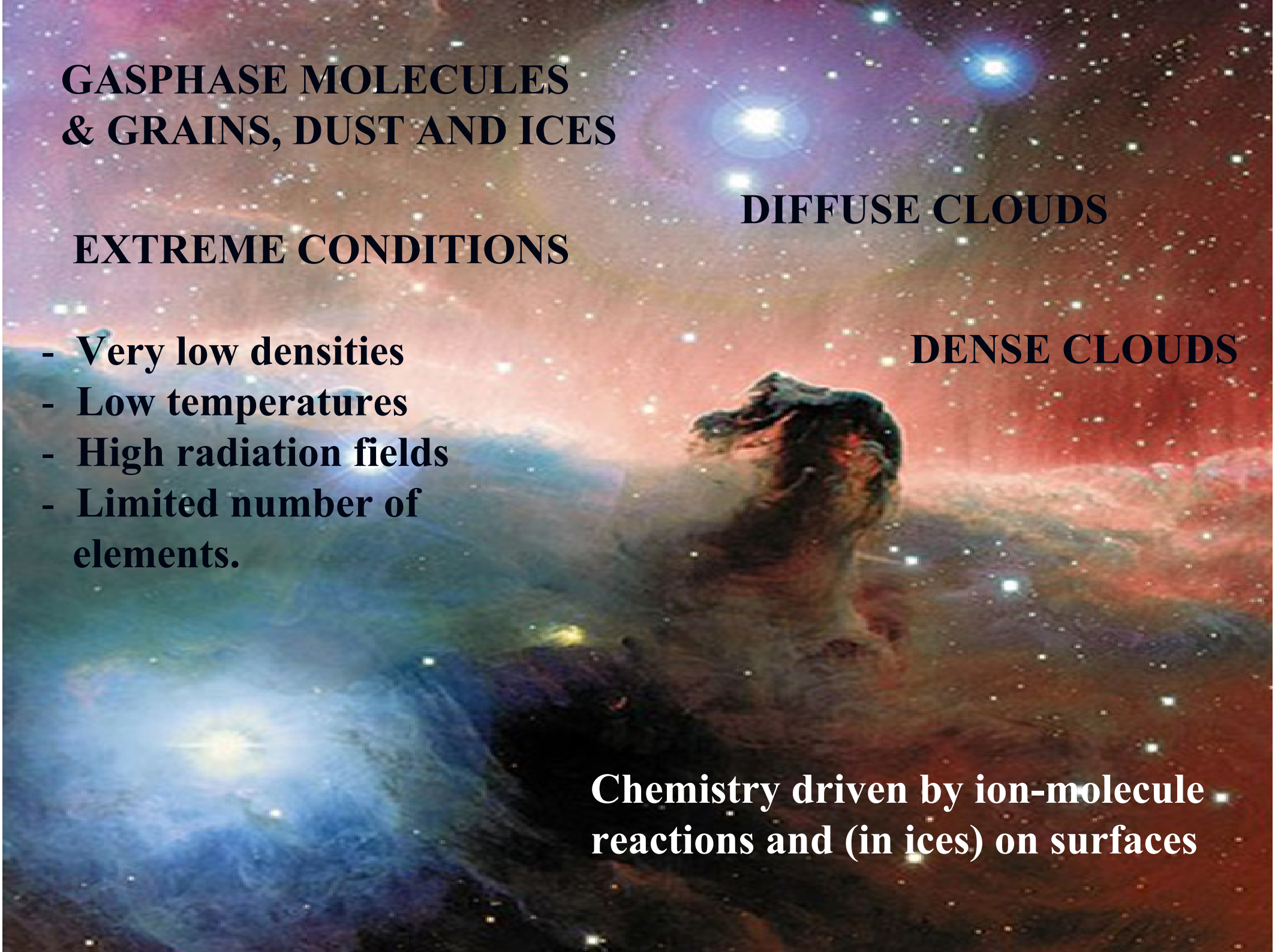
Astrophysics & Astrochemistry
Cavity Ring Down Spectroscopy

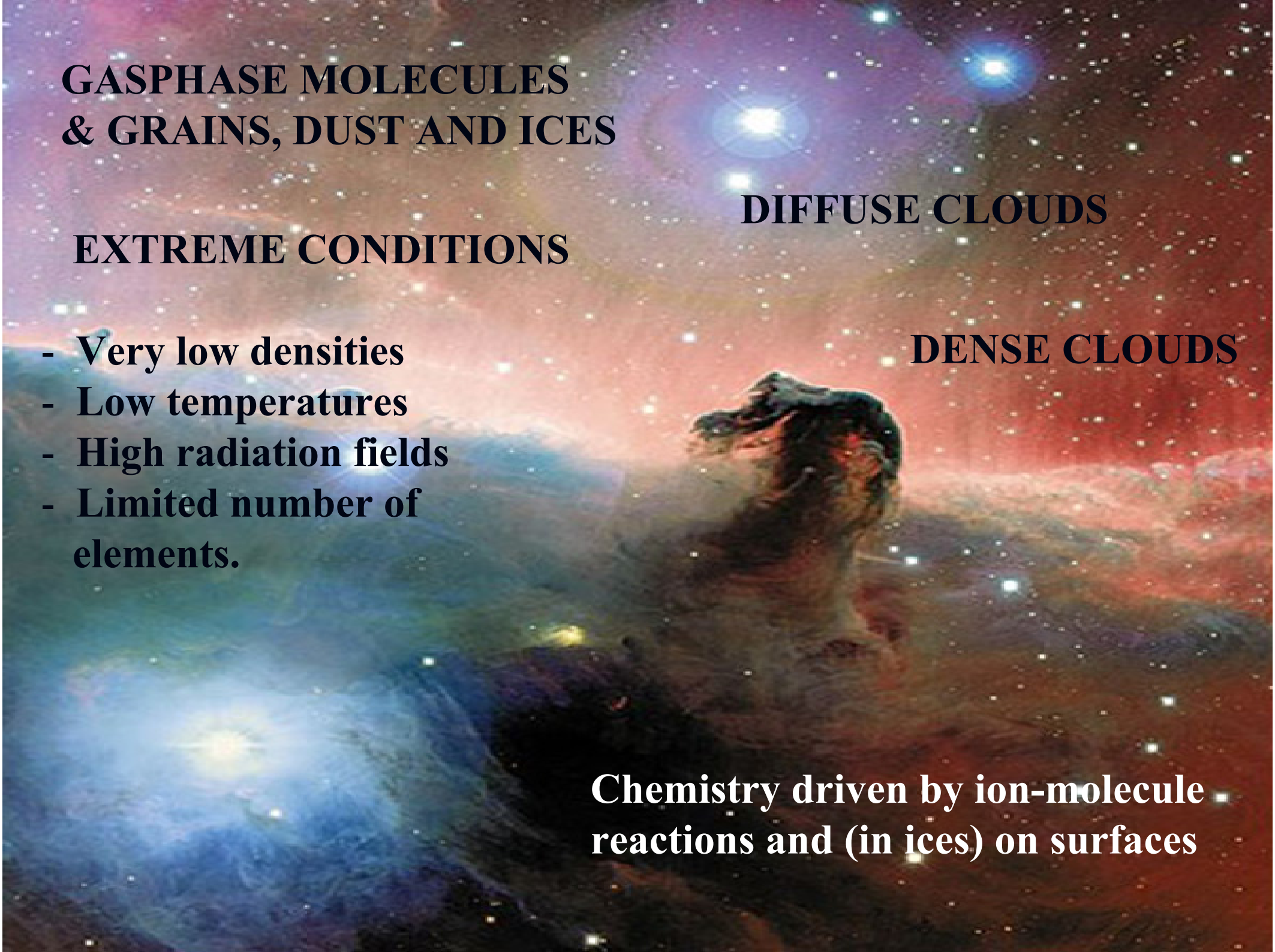
Harold Linnartz

[linnartz@strw.leidenuniv.nl]

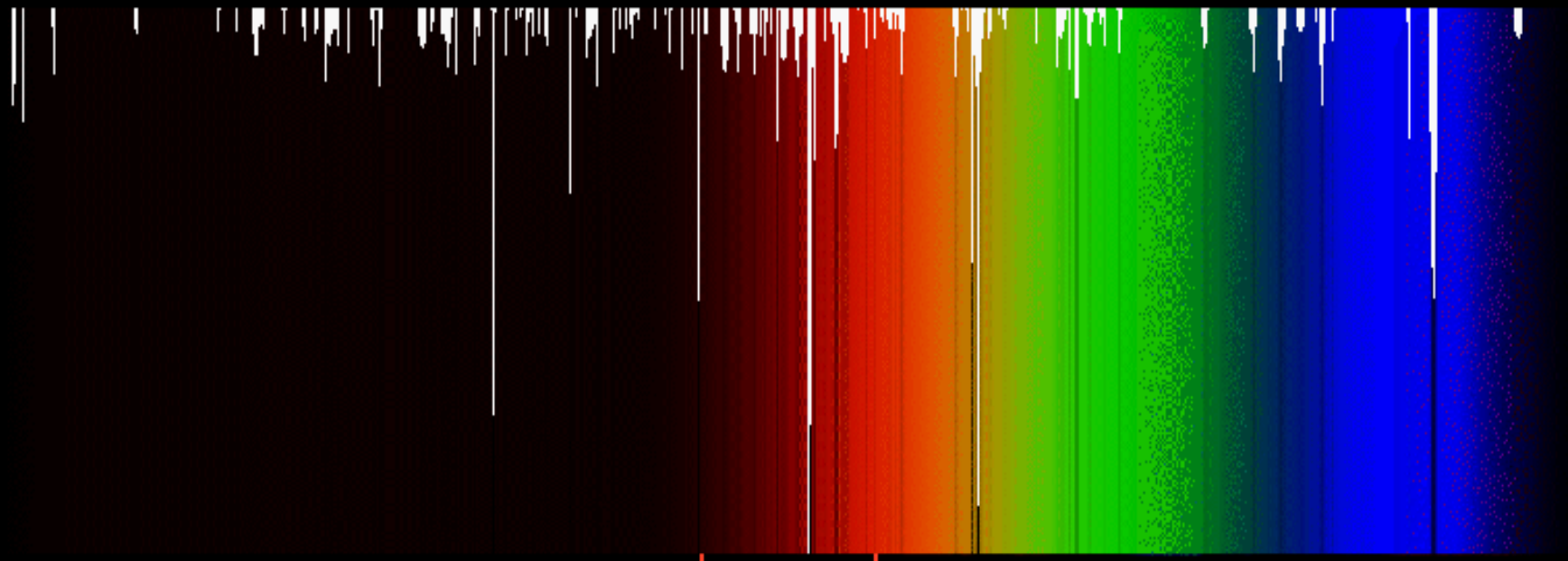
Sackler Laboratory for Astrophysics, Leiden Observatory, the Netherlands

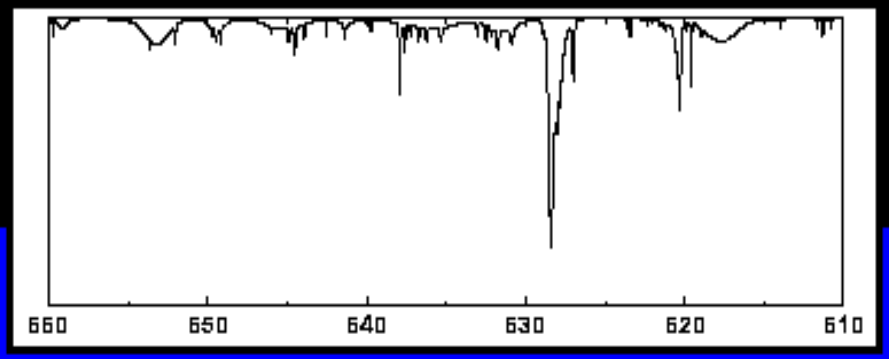

GASPHASE MOLECULES
& GRAINS, DUST AND ICES
EXTREME CONDITIONS
- Very low densities
- Low temperatures
- High radiation fields
- Limited number of elements.
DIFFUSE CLOUDS
DENSE CLOUDS
Chemistry driven by ion-molecule reactions and (in ices) on surfaces

2	2	3	3	4	5	6	7	8	9	10-13
H_2	SiO	C_3	N_2H	c-C_3H	C_5	C_5H	C_6H	CH_3C_3N	CH_3CH_4	CH_3C_5N ?
AlF	SiS	C_2H	H_3^+	l-C_3H	C_4H	l-H_2C_4	CH_2CHCN	$HCOOCH_3$	CH_3CH_2CN	$(CH_3)_2CO$
AlCl	CS	C_2O	SiCN	C_3N	C_4Si	C_2H_4	CH_3C_2H	CH_3COOH	$(CH_3)_2CO$	NH_2CH_2COOH
C_2	HF	C_2S	H_2S	C_3O	l-C_3H_2	CH_3CN	HC_5N	C_7H	CH_3CH_2OH	CH_3CH_2CHO
CH	SH	CH_2	HNO	C_3S	c-C_3H_2	CH_3NC	$HCOCH_3$	H_2C_6	HC_7N	HC_9N
CH^+	KCl	HCN	MgNC	C_2H_2	CH_2CN	CH_3OH	NH_2CH_3	CH_2OHCHO	C_8H	$HC_{11}N$
CN	NO	HCO	SiCN	CH_2D^+ ?	CH_4	CH_3SH	c-C_2H_4O	CH_2CHCHO		
CO	FeO ?	HCO^+	AlNC	HCCN	HC_3N	HC_3NH^+	CH_2CHOH			
CO^+		HCS^+		$HCNH^+$	HC_2NC	HC_2CHO				
CP		HOC^+		HNCO	HCOOH	NH_2CHO				
CSi		H_2O		HNCS	H_2CHN	C_5N				
HCl		HNC		$HOCO^+$	H_2C_2O					
NH		MgCN		H_2CO	H_2NCN					
NS		N_2H^+		H_2CN	HNC_3					
NaCl		N_2O		H_2CS	SiH_4					
OH		OCS		H_3O^+	H_2COH^+					
PN		NaCN		NH_3						
SO		SO_2		SiC_3						
SO^+		c-SiC_2								
SiN		CO_2								


GASPHASE MOLECULES
& GRAINS, DUST AND ICES
EXTREME CONDITIONS
- Very low densities
- Low temperatures
- High radiation fields
- Limited number of elements.
DIFFUSE CLOUDS
DENSE CLOUDS
Chemistry driven by ion-molecule reactions and (in ices) on surfaces

The Diffuse Interstellar Bands

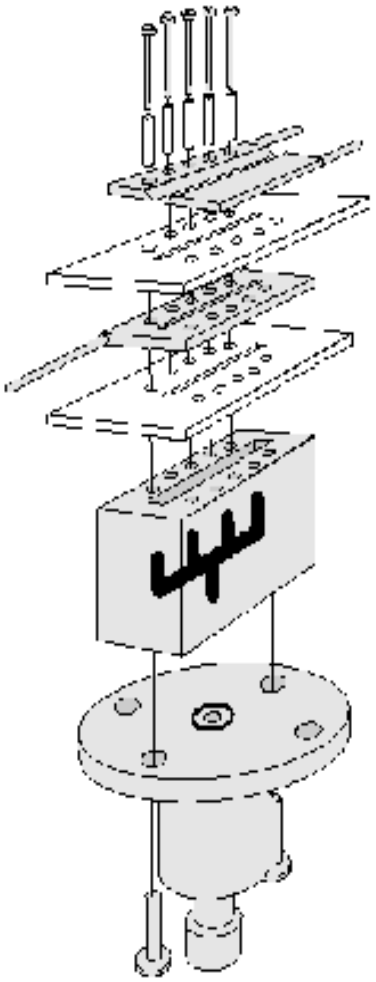




Courtesy: P. Jan[illegible]sens, T. X. Dasart

High pressure slit nozzle discharge

H. Linnartz et al., CPL 292, 188 (1998)



Cathodes

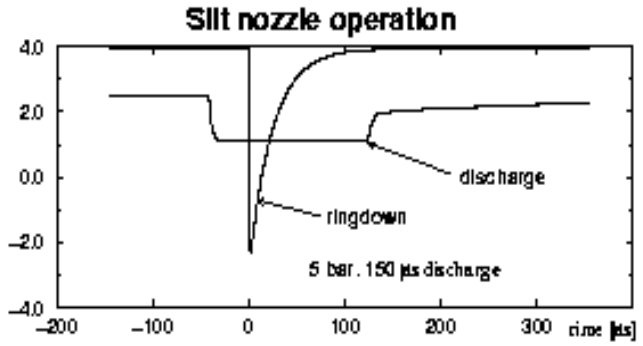
Ceramic insulator

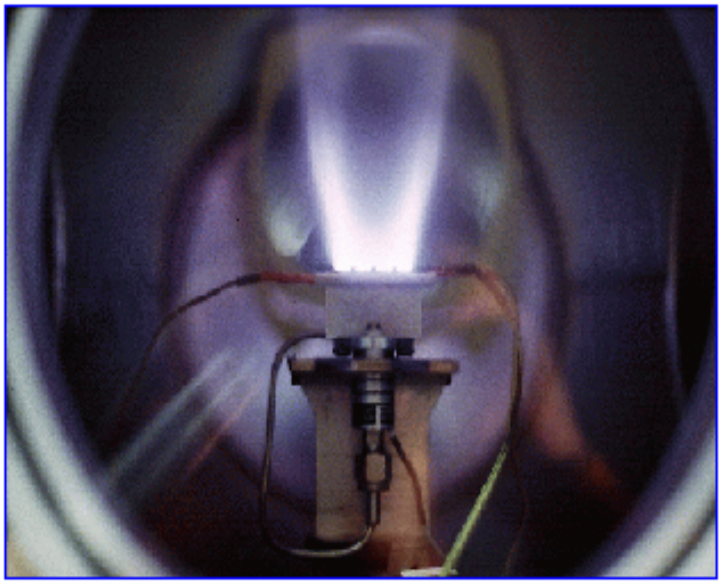
Grounded anode

Ceramic insulator

Multi-channel body

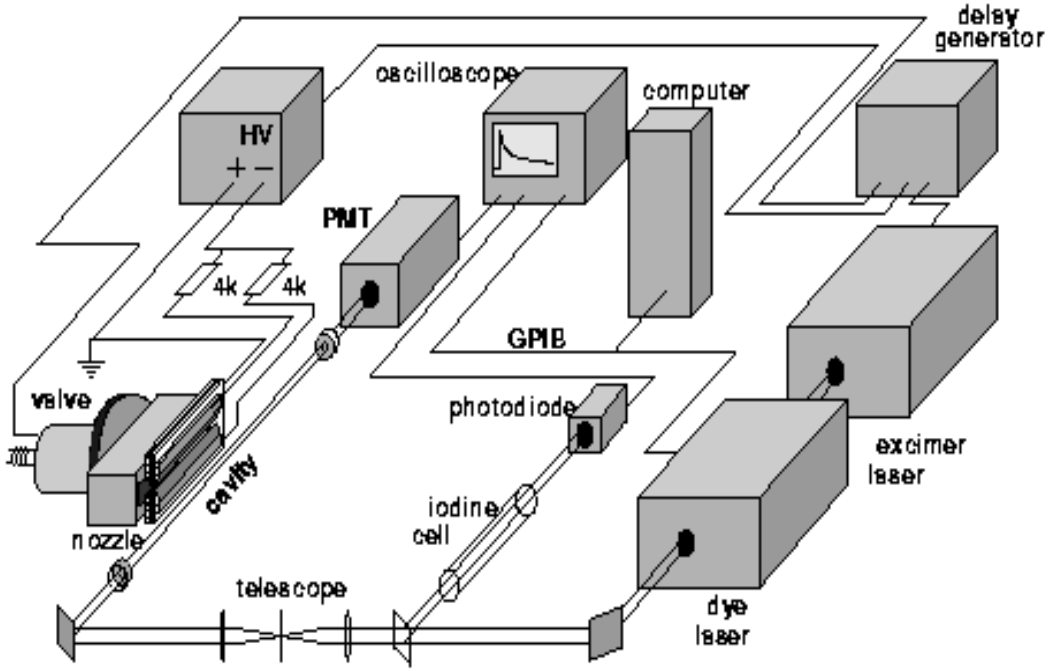
Pulsed valve

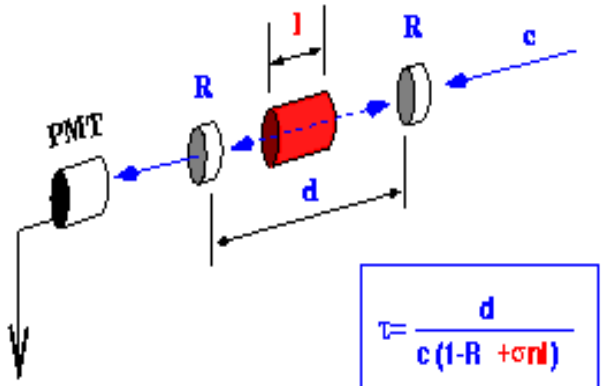


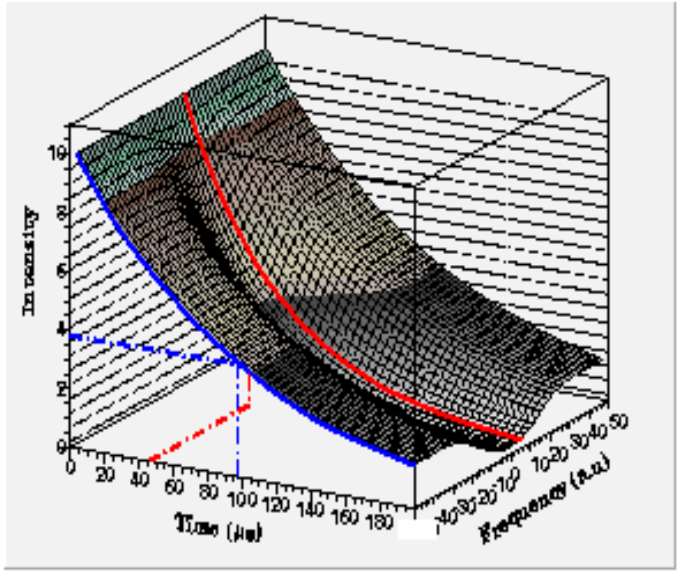


Cavity Ring Down Experiment

T. Motylewski and H. Linnartz, RSI 70 (2000) 1305.





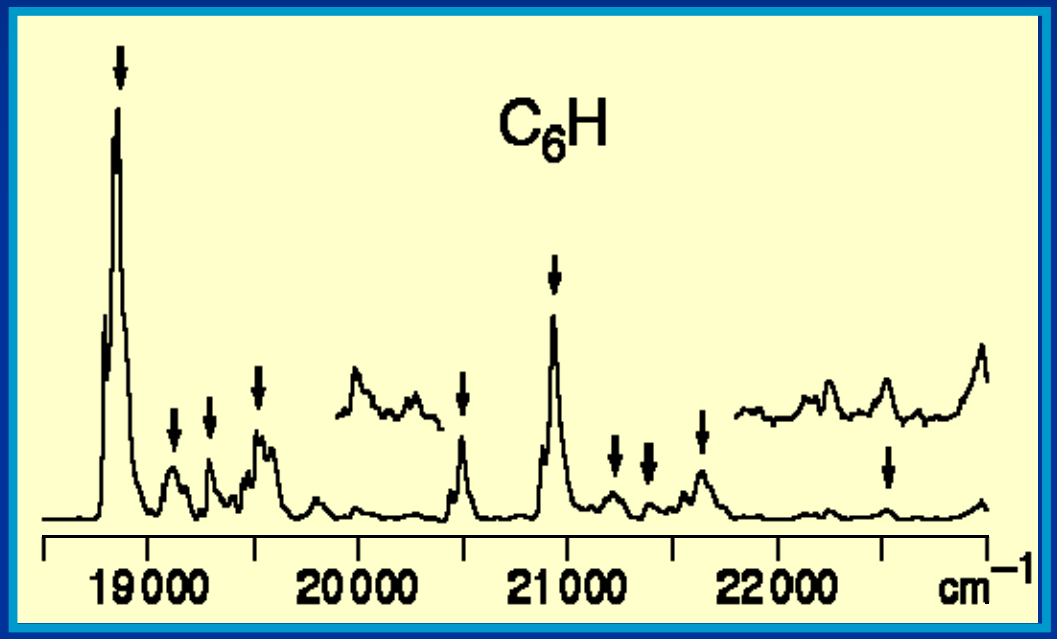


Principle of CRDS:

Confine a light pulse to an optical cavity

and detect the rate of light leaking out.

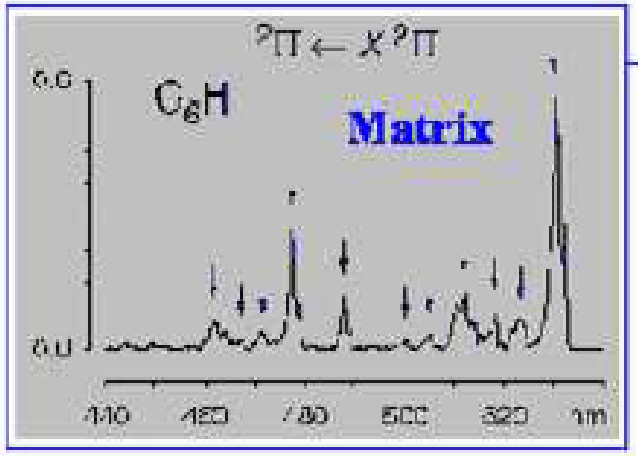
Matrix (solid state) work



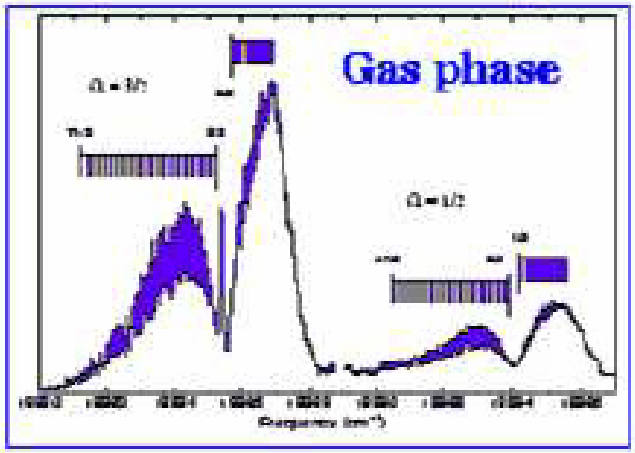
J.P. Maier, Chem. Soc. Rev. 26 (1997) 21

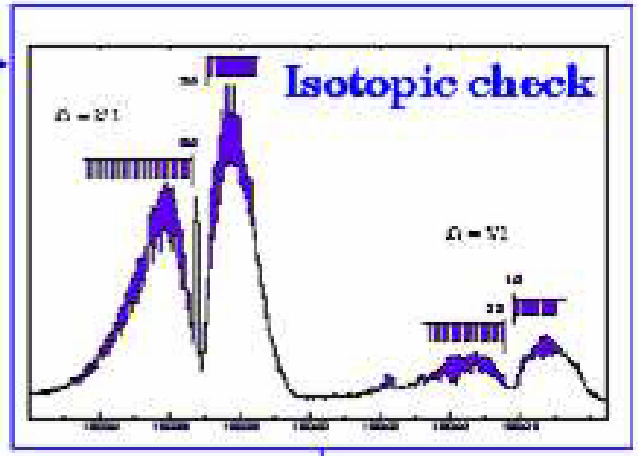
- Mass selective spectra.
- High molecular densities (10^{15} / 10^{16} part./cm^3).
- Low resolution.
- Interaction with matrix environment:
  - no rotational spectra
  - matrix shifts
- However, indication for region of absorption.

Experimental procedure



J.P. Maier, Chem. Soc. Rev. 26 (1997) 21.





Look for excited states

Check electronic profile

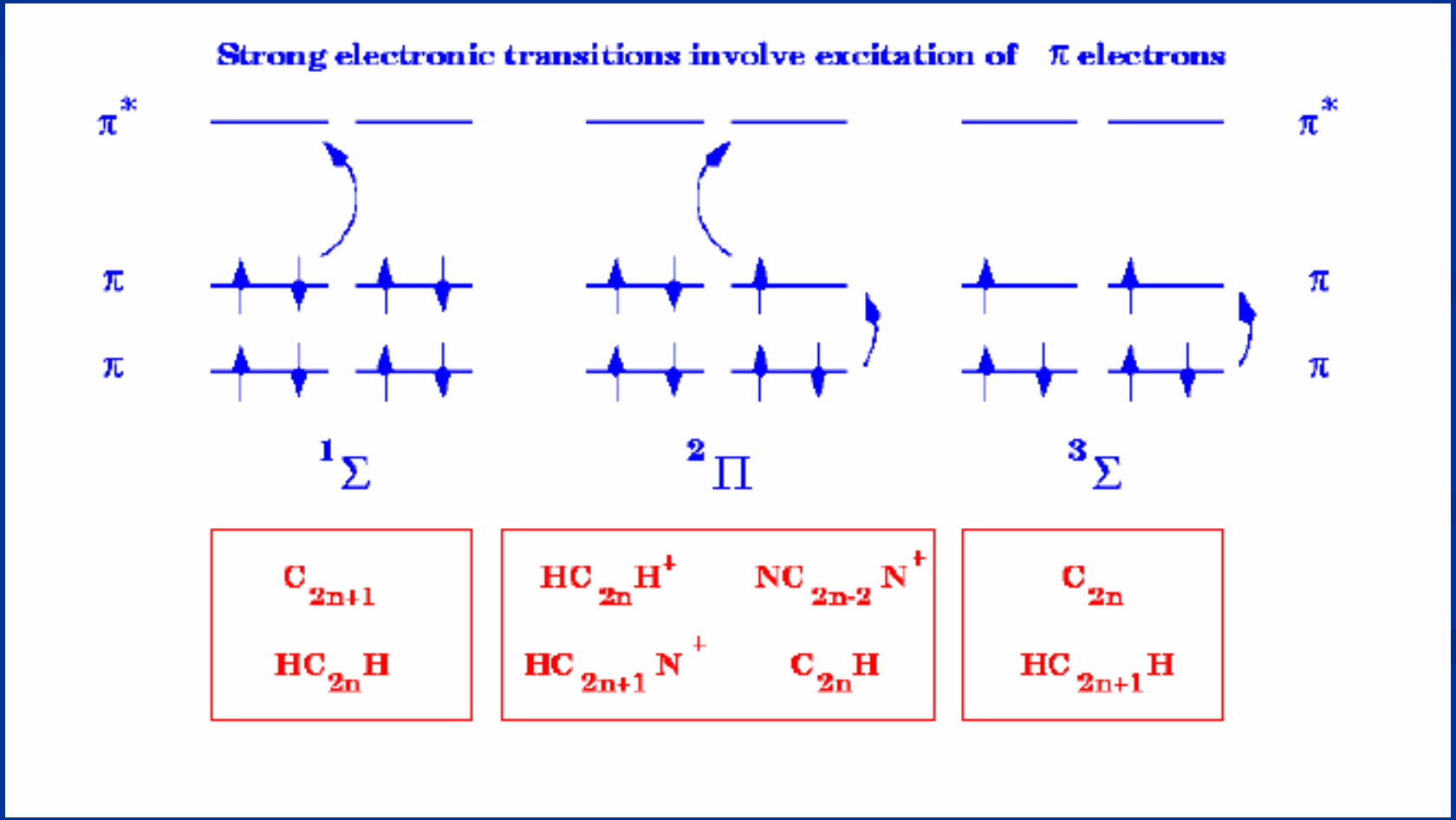
Compare with MW and IR data.

P. Thaddeus et al. Faraday Disc. 109 (1998) 121.

A. van Orden, R.J. Saykally, Chem. Rev. 98 (1998) 2313.

Origin of the electronic transition

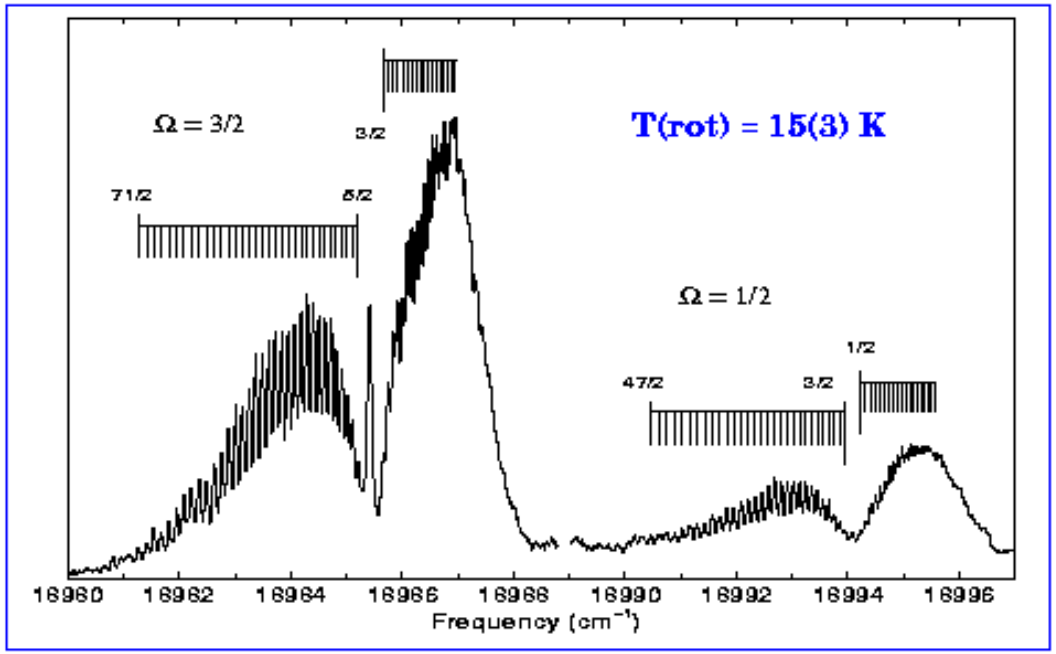
Rovibronic spectra give information on the electronic excitation, on the internuclear modes and on the moment of inertia of the molecule.



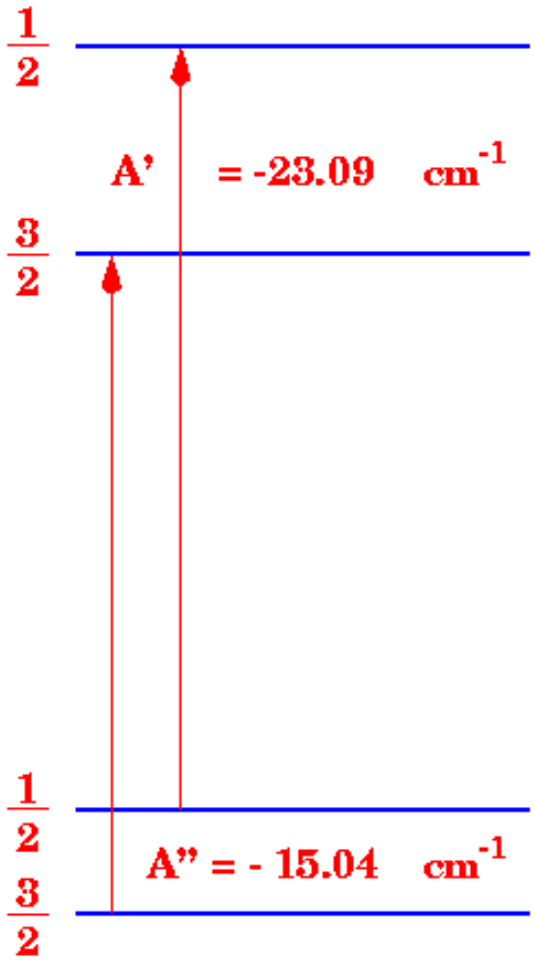
Results: linear :C=C=C=C=C=C-H

H. Linnartz et al., J. Molec. Spectrosc. 197 (1999) 1.

$A\,^2\Pi \leftarrow X\,^2\Pi$



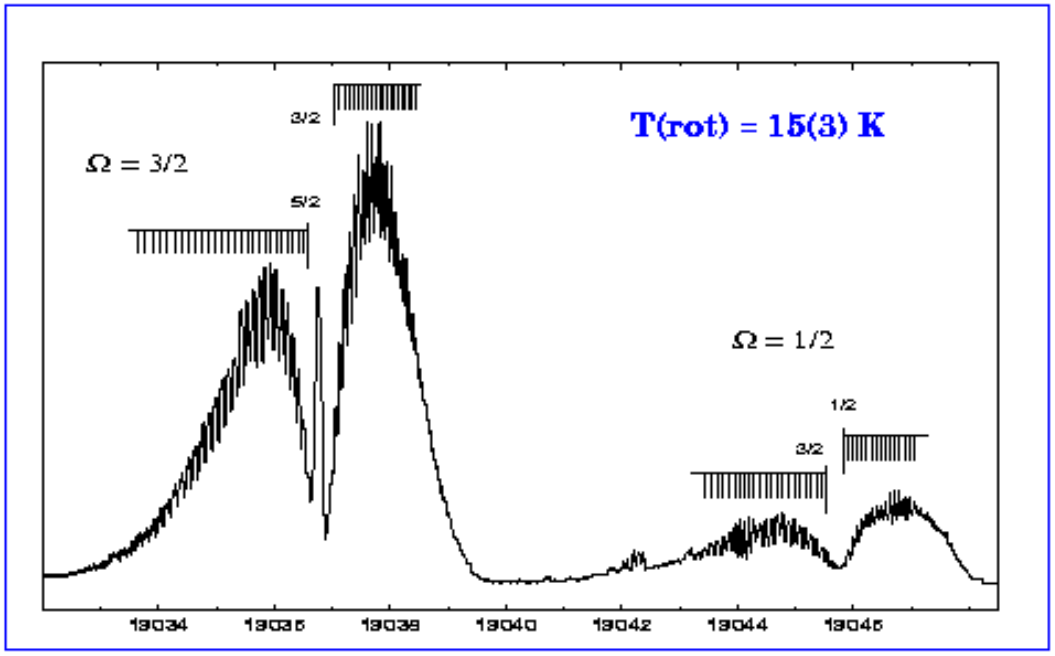
$\Delta A = 8.05\ cm^{-1}$



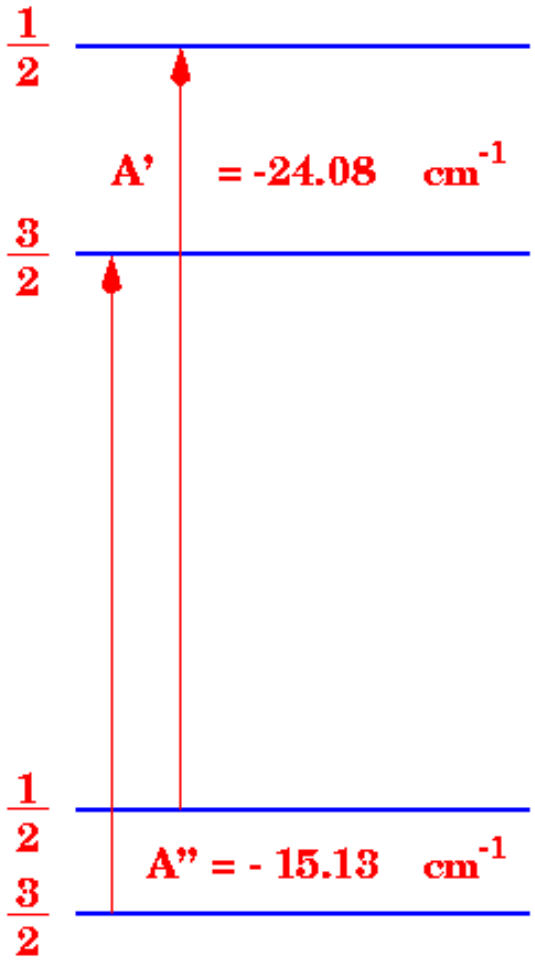
Results: linear :C=C=C=C=C=C-D

H. Linnartz et al., J. Molec. Spectrosc. 197 (1999) 1.

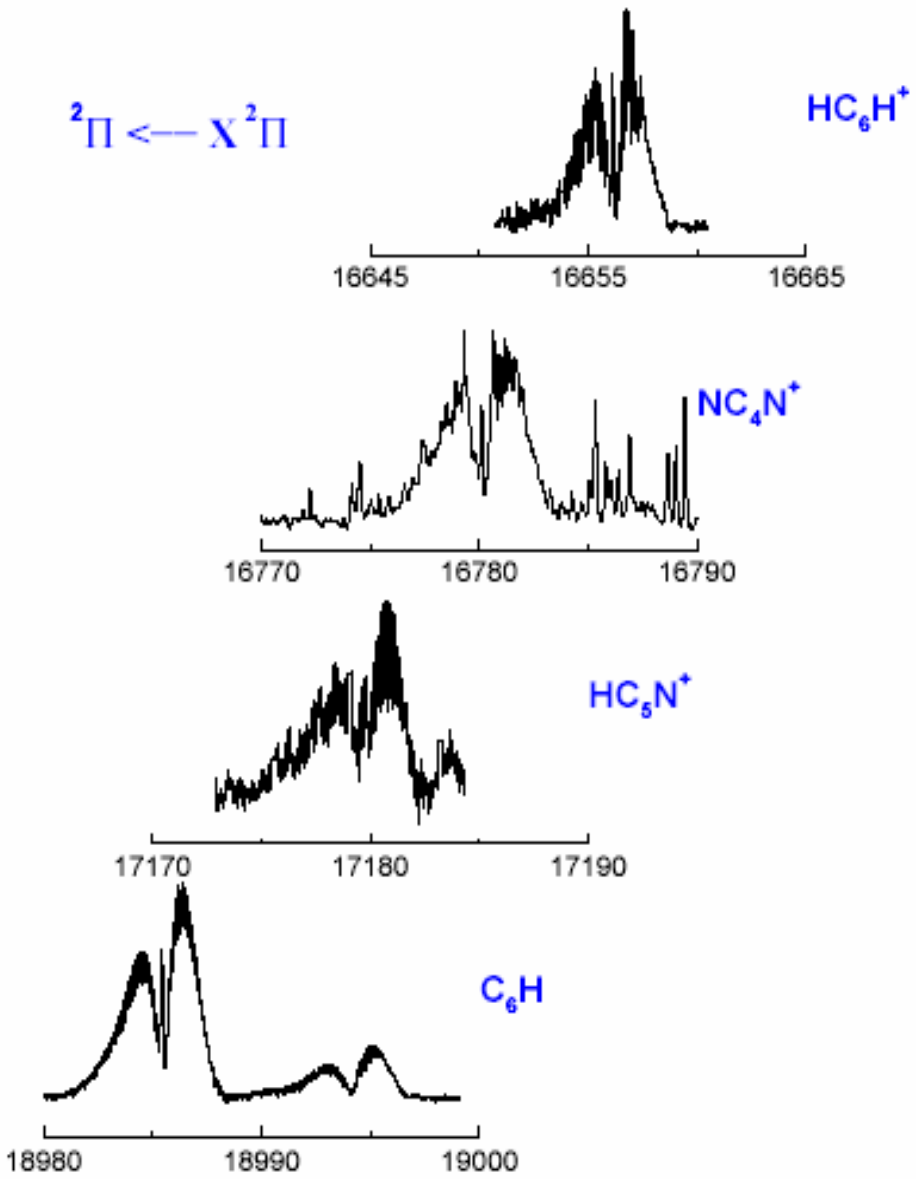
$A\,^2\Pi \leftarrow X\,^2\Pi$



$\Delta A = 8.95\ cm^{-1}$



Iso-electronic species



Triacetylene cation

CPL 313, 171 (1999)
JCP 110, 296 (1999)

Dicyano–acetylene cation

ApJ 531, 312 (2000)

Cyano–diacetylene cation

ApJ 521, 312 (2000)

Hexatrinyl radical

JMS 197, 1 (1999)

CW CRDS & Pulsed Plasma

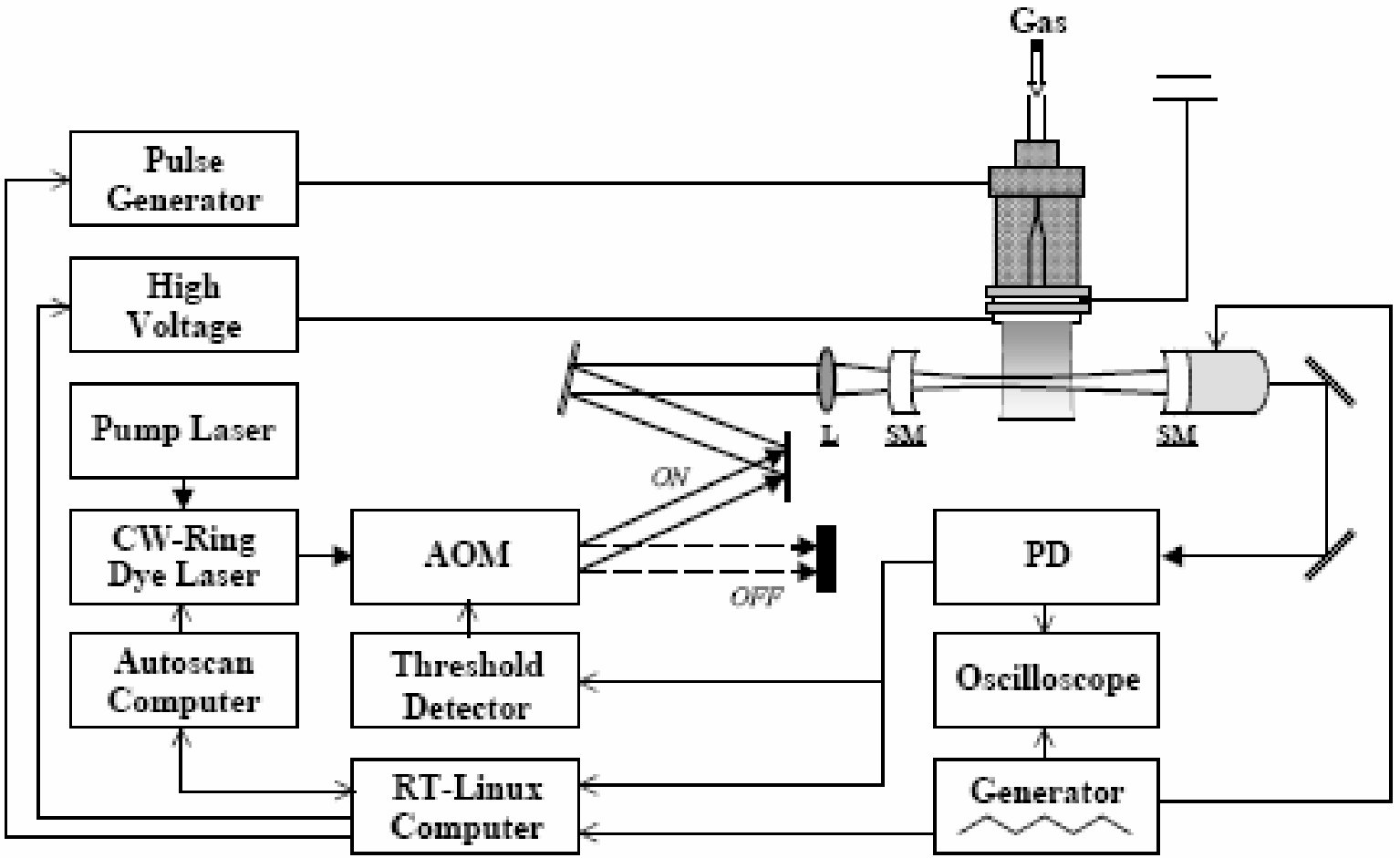
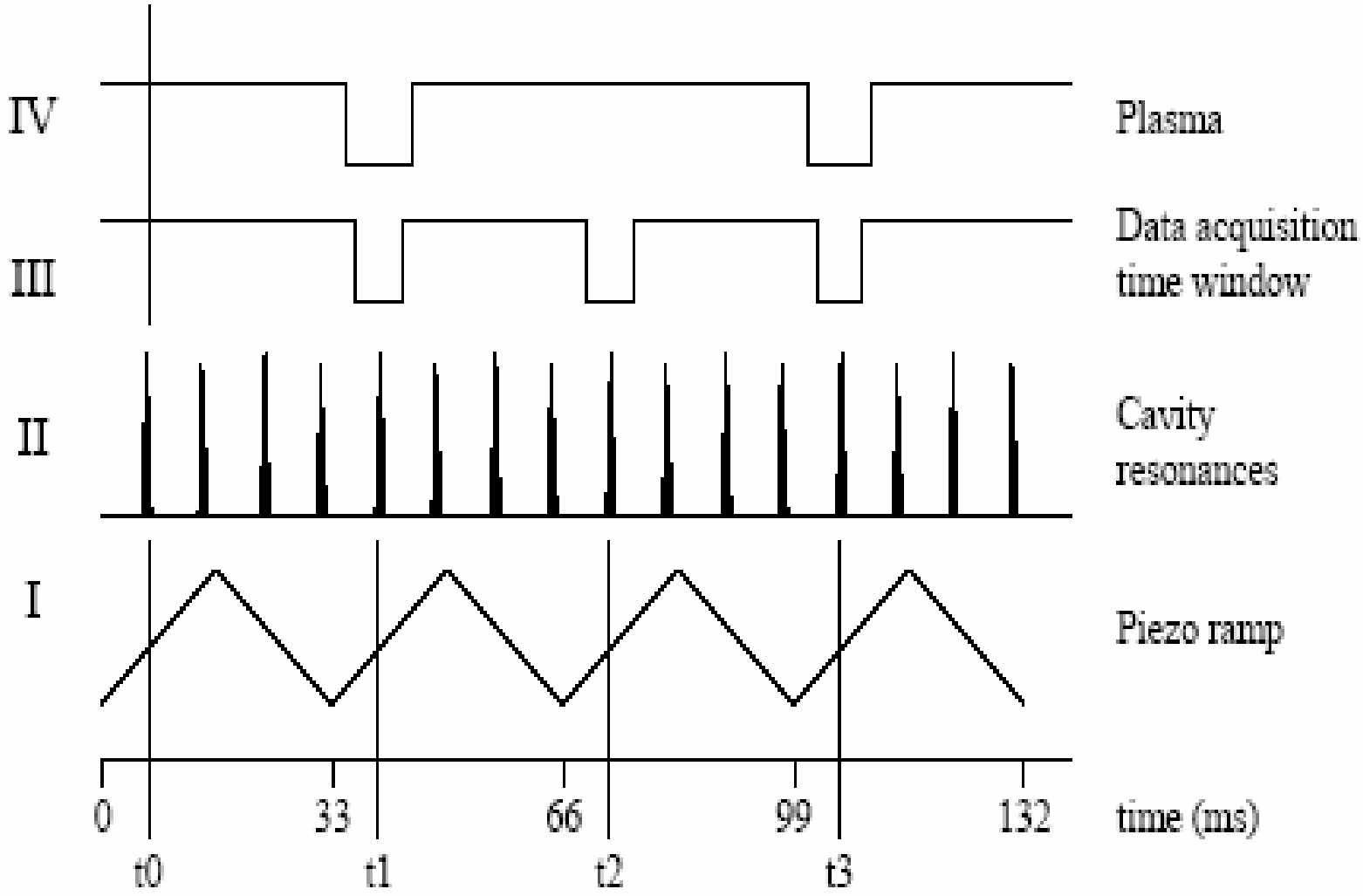


Fig. 2. Schematic of the experimental setup. Details are given in the text.

CW CRDS & Pulsed Plasma



CW CRDS & Pulsed Plasma

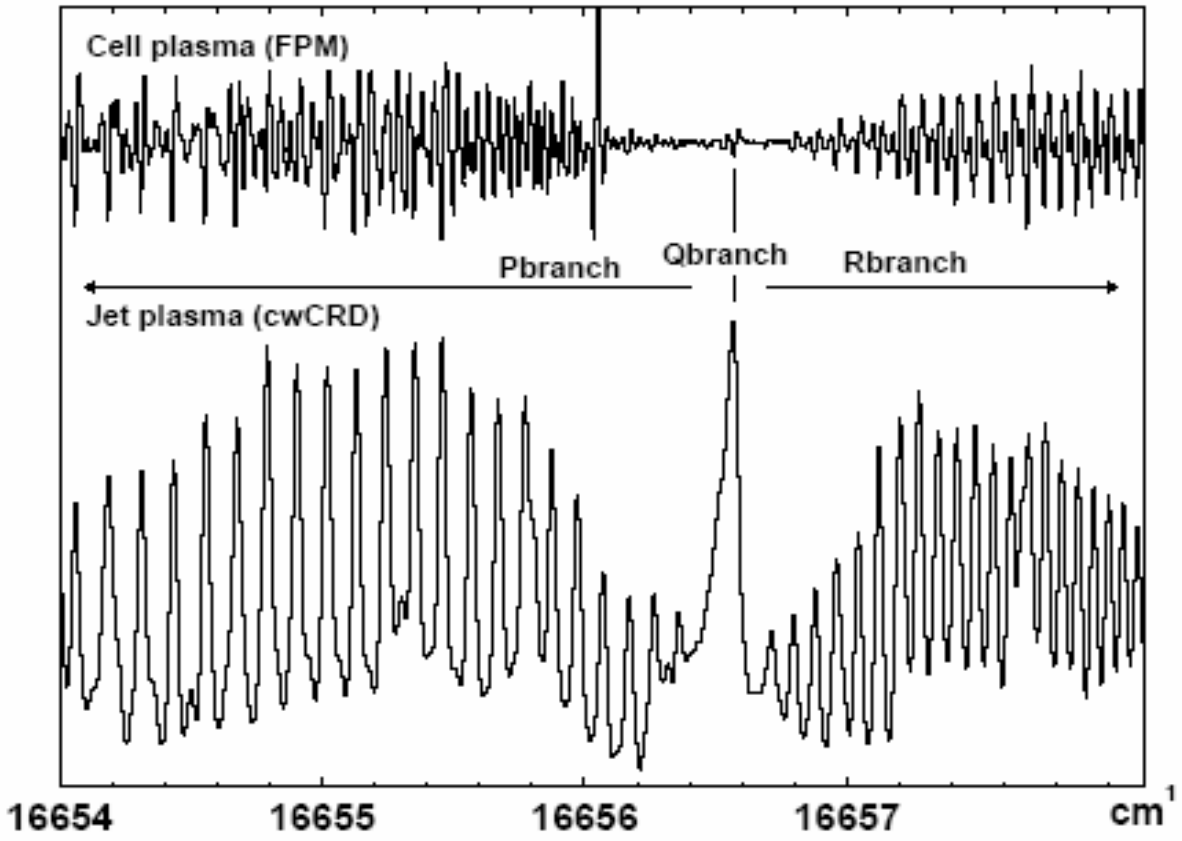
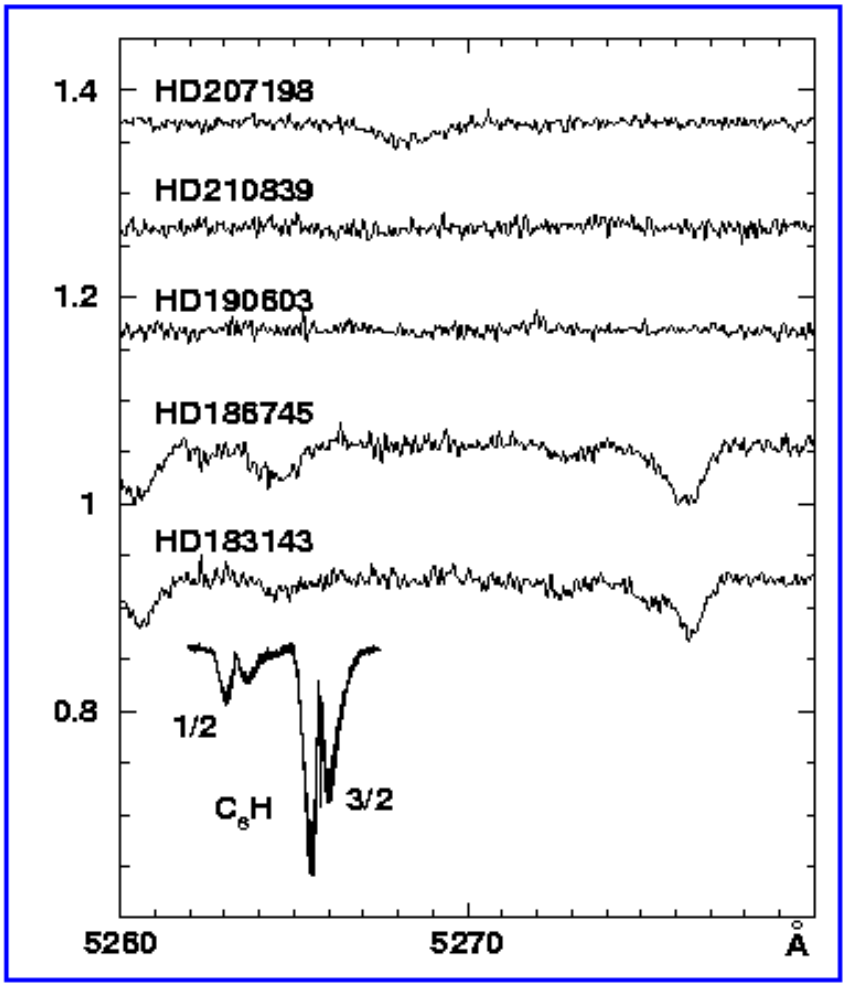
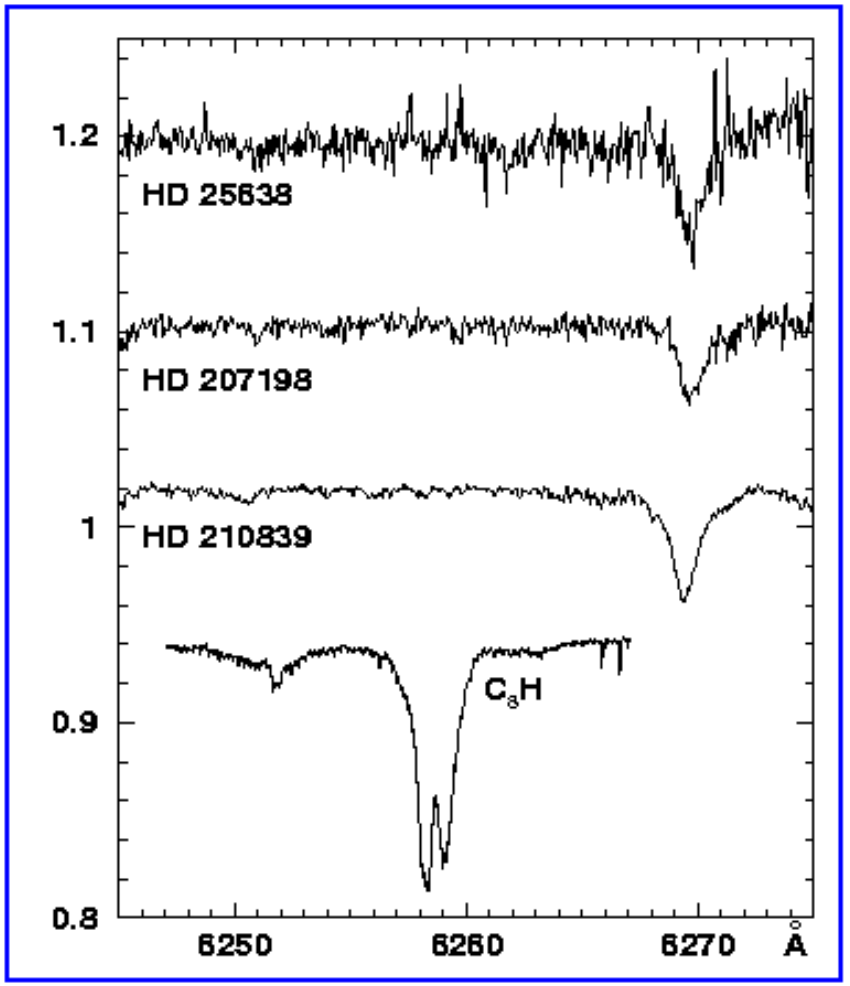


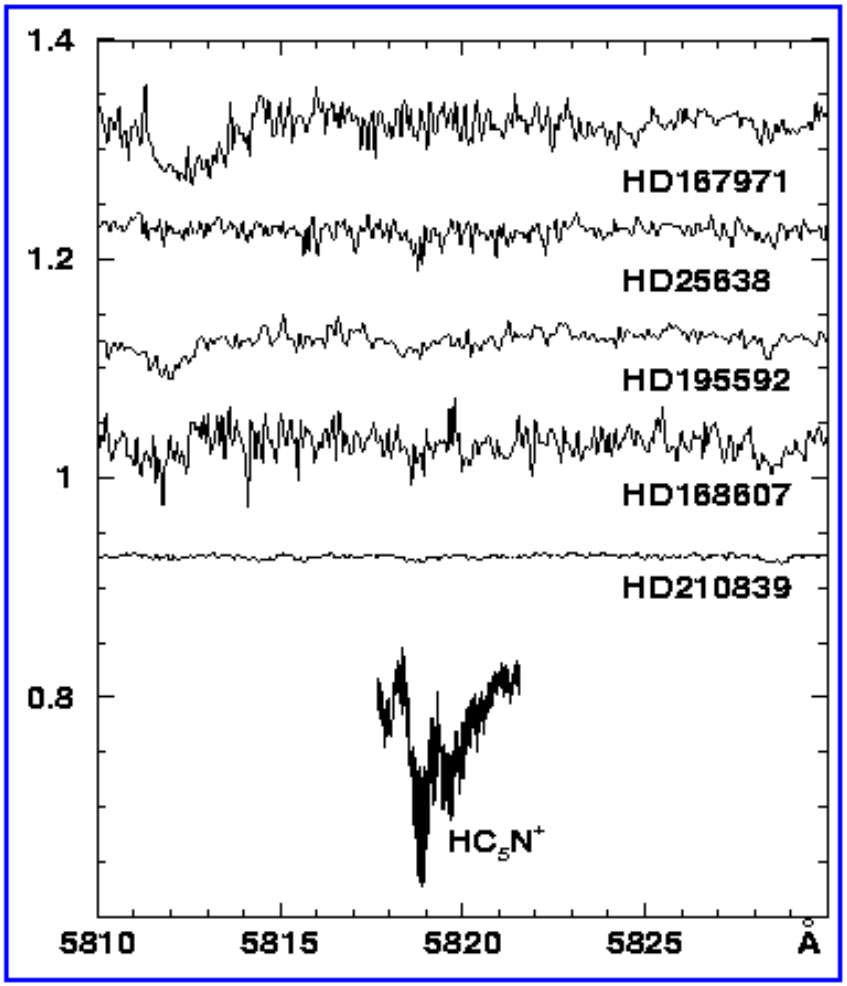
Fig. 4. The origin band of the $A^2\Pi_g - X^2\Pi_u$ electronic spectrum of triacetylene cation, HC_6H^+, measured by cw CRD spectroscopy through a supersonic pulsed planar plasma with $T_{rot} \sim 15$ K (lower trace). The upper trace shows the corresponding cell spectrum using frequency-plasma double modulation spectroscopy with $T_{rot} \sim 170$ K [21].

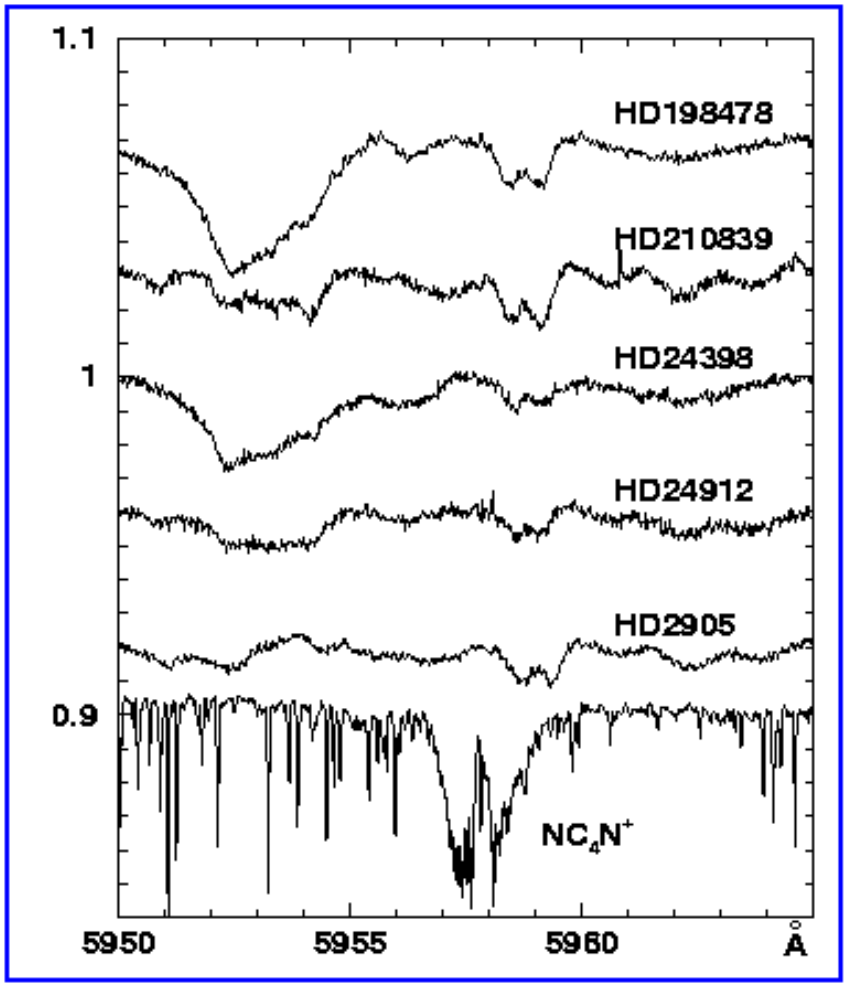
Laboratory vs. Astronomical Data



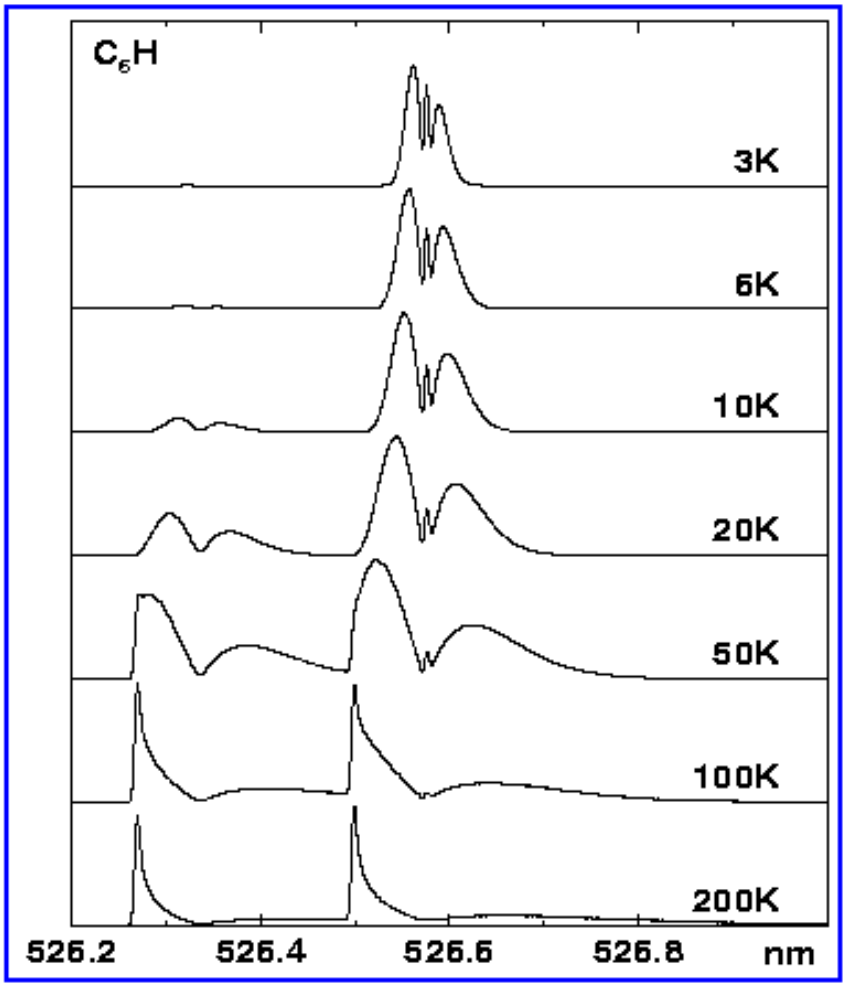


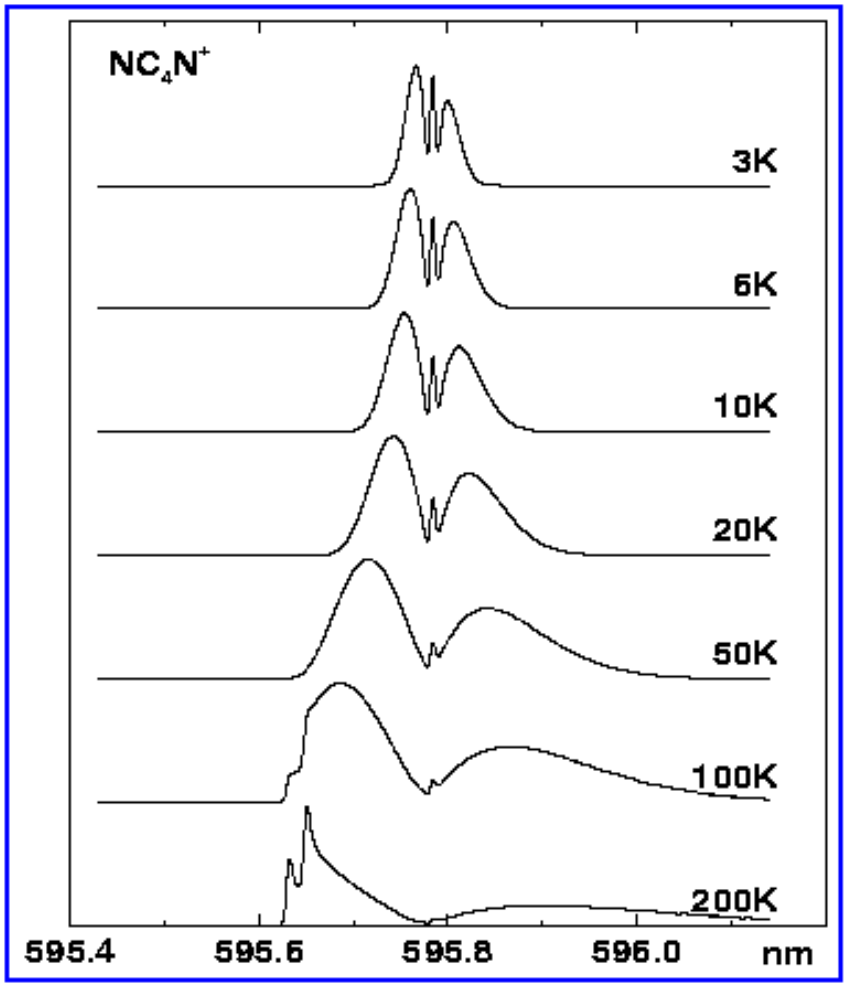
Laboratory vs. Astronomical Data



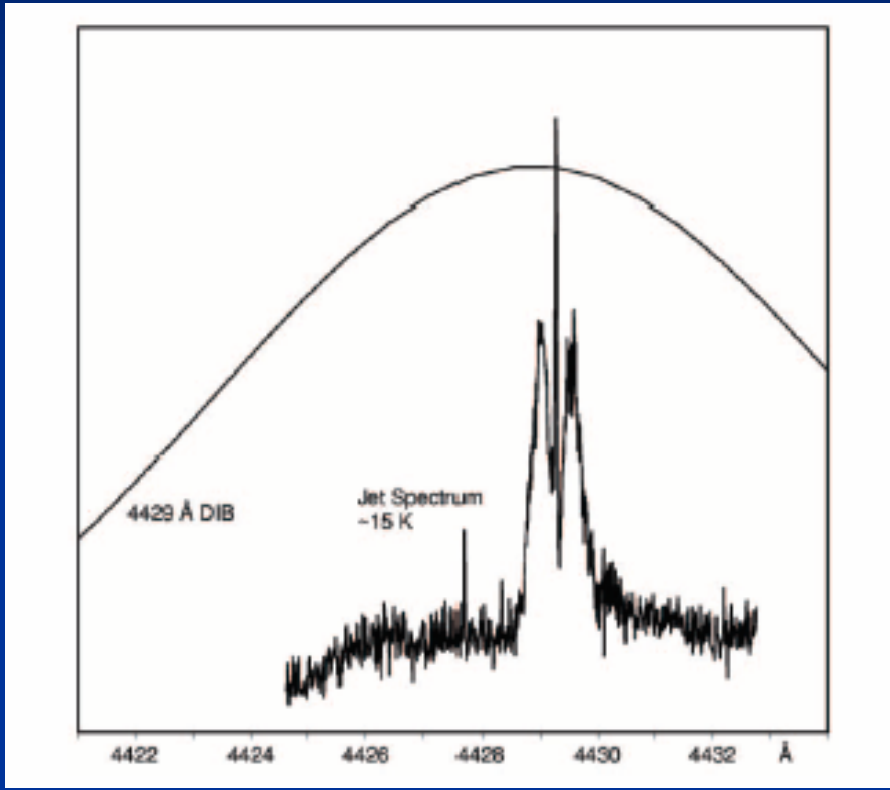


Temperature effects



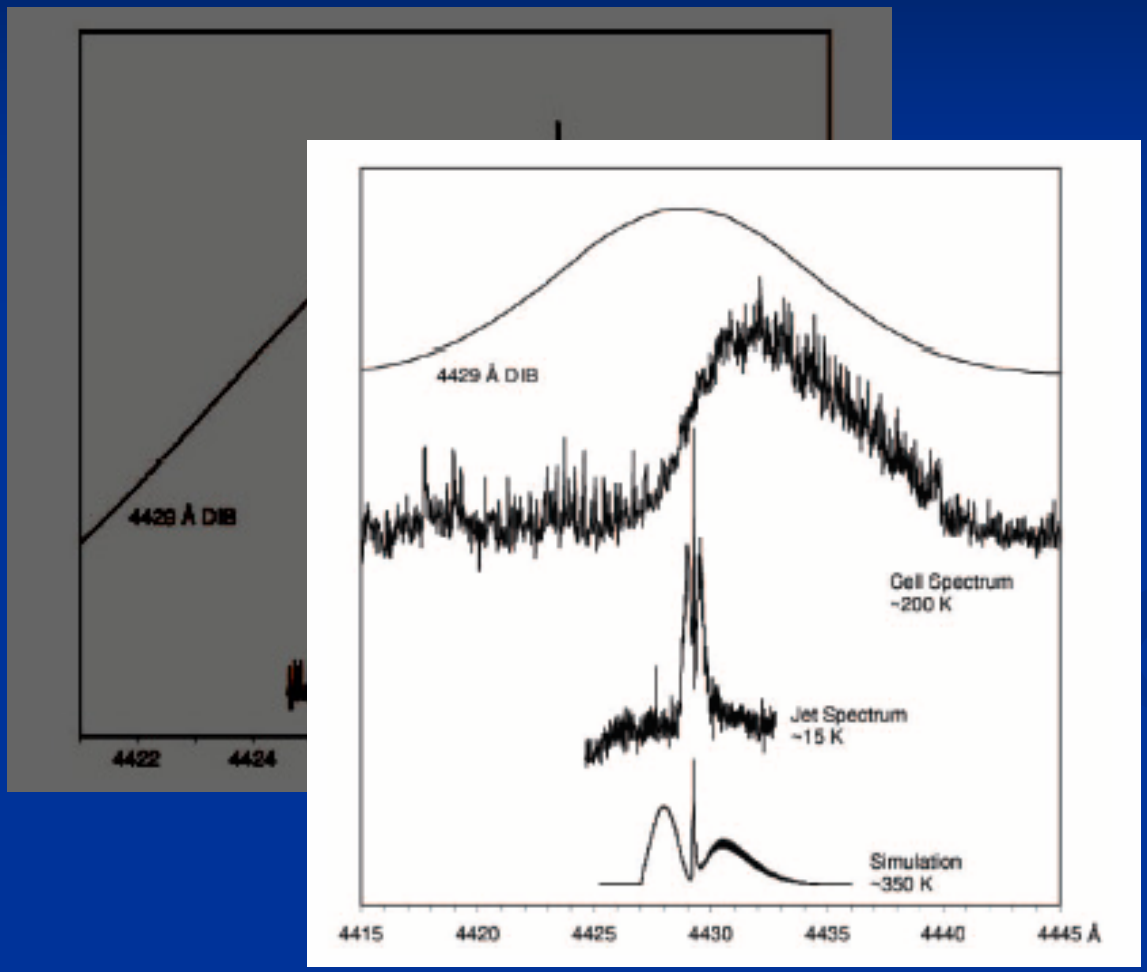


Benzene plasma and 4429 DIB



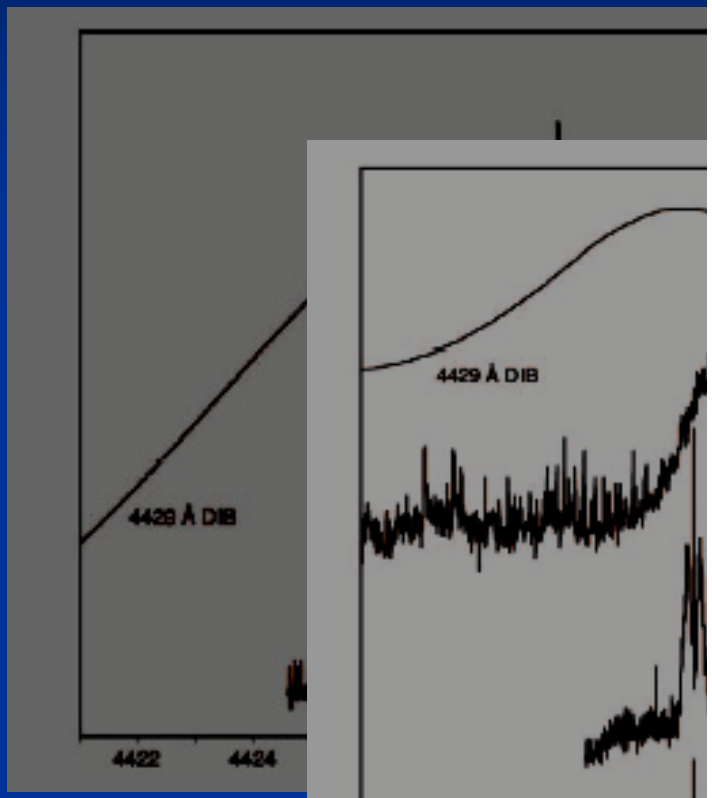
C.D. Ball, M.C. McCarthy, P. Thaddeus, ApJ. 528 (2000) L61

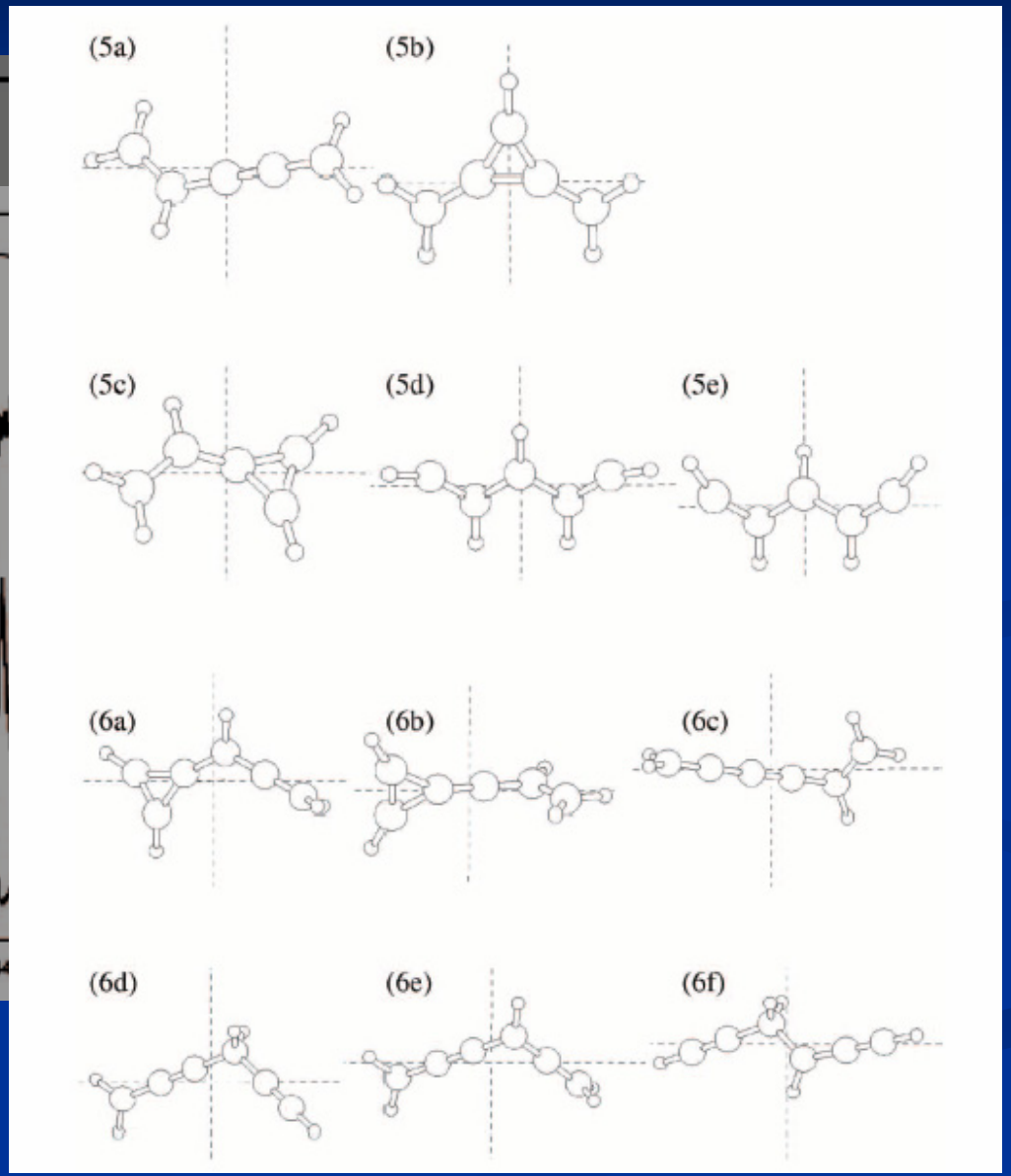
Benzene plasma and 4429 DIB



M. Araki et al. ApJ 616 (2004) 1301.

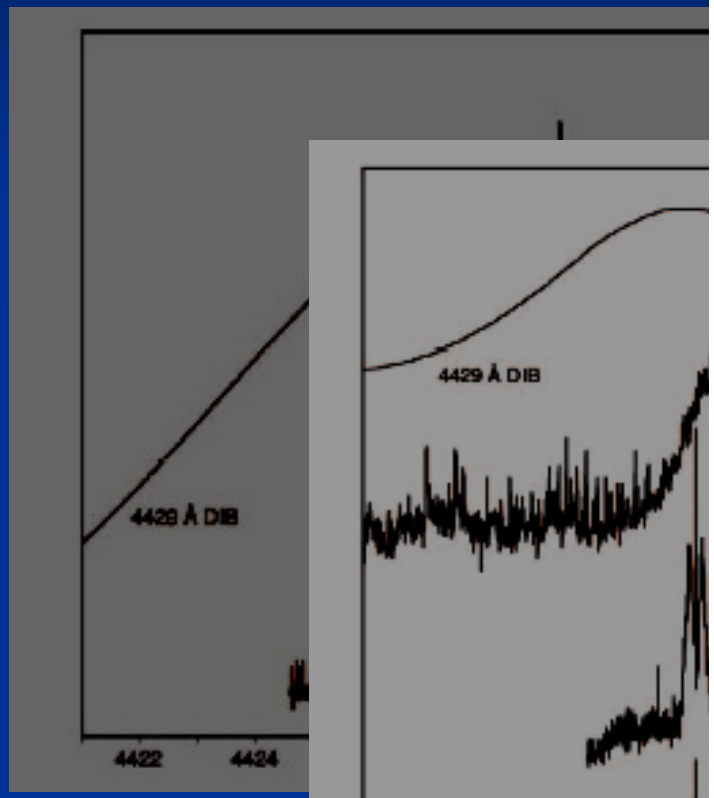
Benzene plasma and 4429 DIB

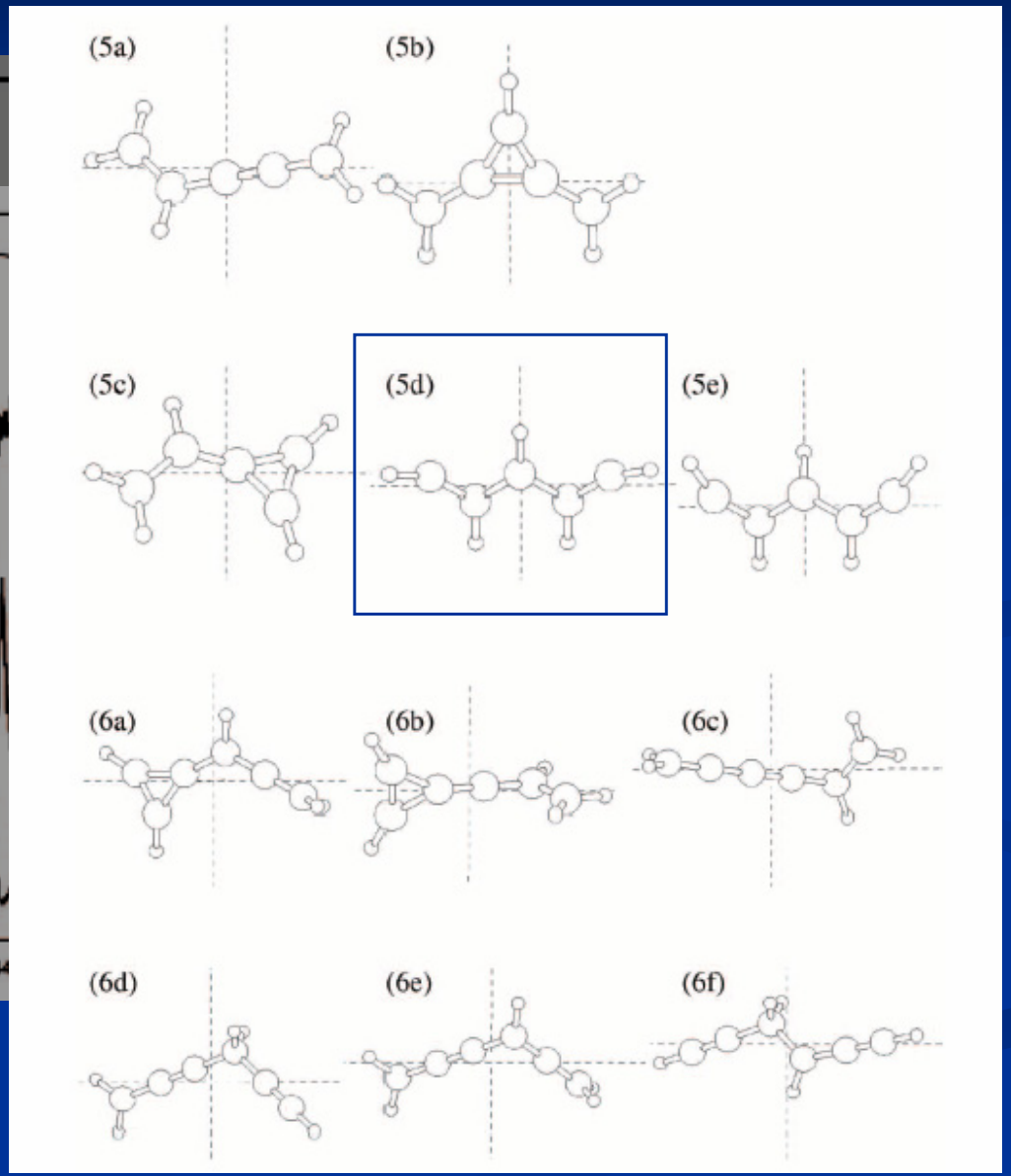




M. Araki et al. ApJ 616 (2004) 1301.

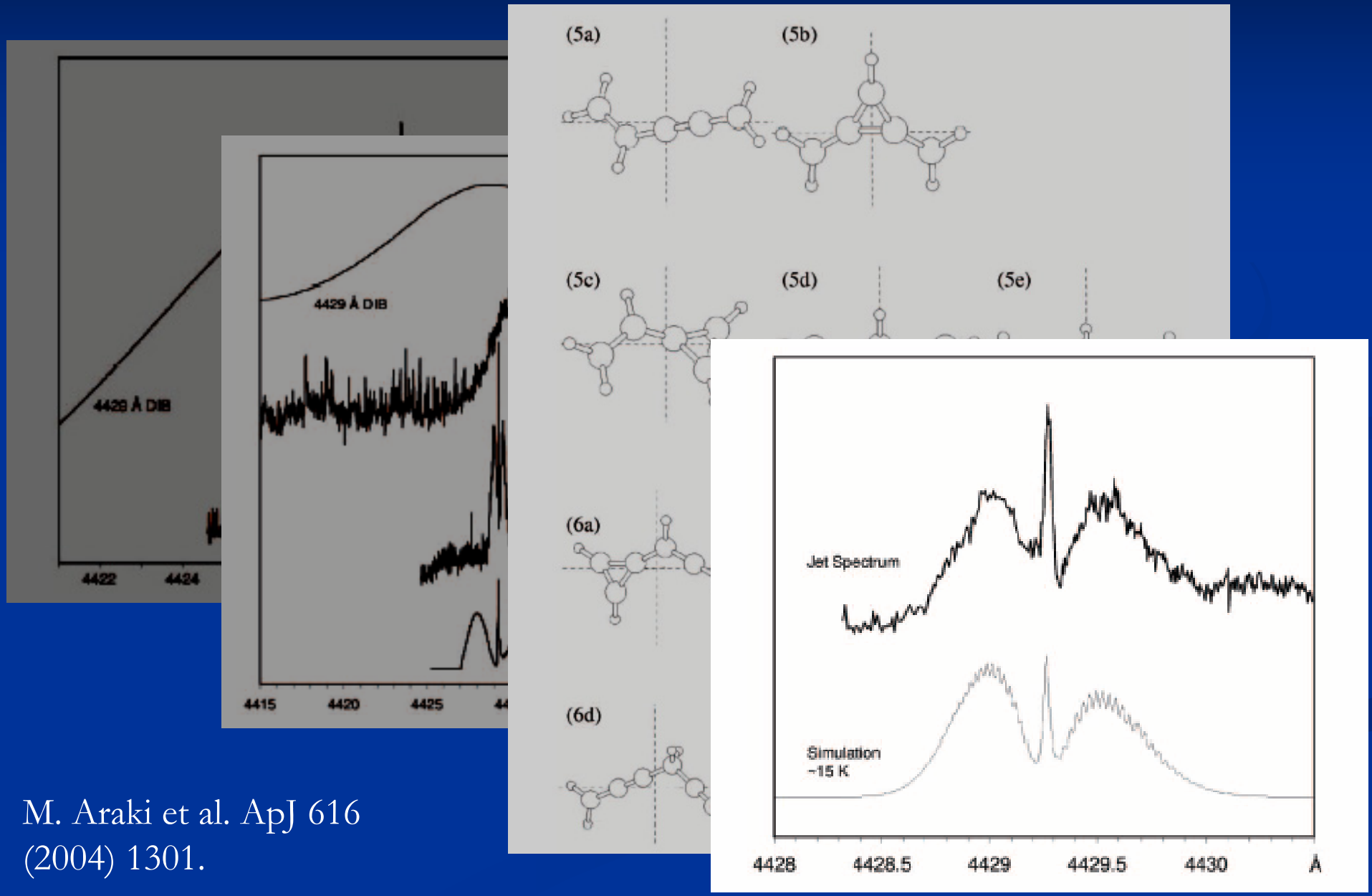
Benzene plasma and 4429 DIB





M. Araki et al. ApJ 616 (2004) 1301.

Benzene plasma and 4429 DIB

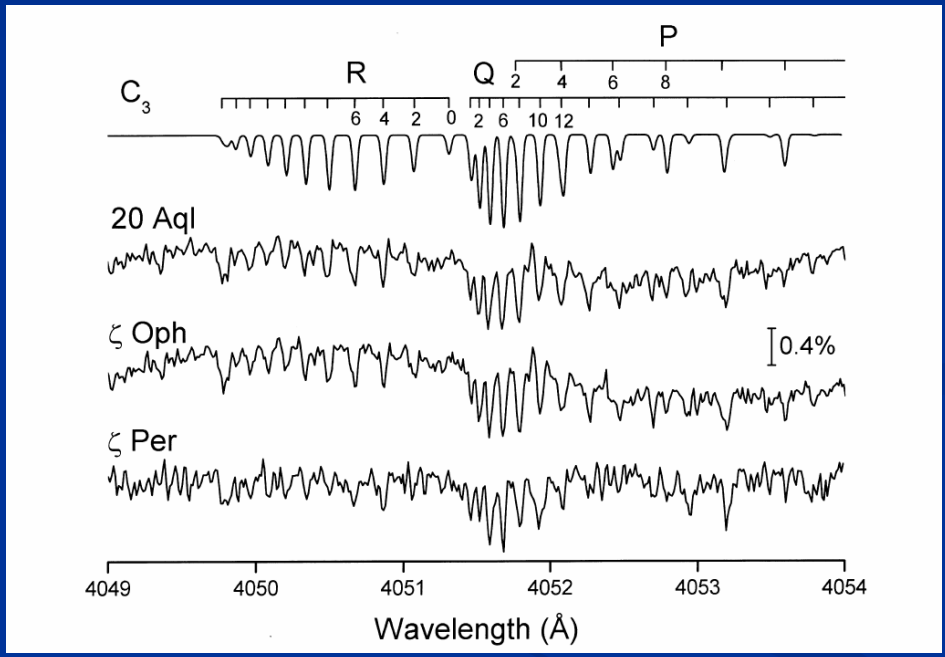


M. Araki et al. ApJ 616 (2004) 1301.

A story without a happy end ?

- The strong DIBs are not due to electronic transitions of carbon chain radicals.
- We learnt a lot about carbon chain radicals, and
- The new spectra allow for a guided search of these species in diffuse interstellar clouds.
- Recently, C_3 has been detected in the diffuse interstellar medium.

  Column densities are of the order of $< 10^{12}$ cm^2.



Astrophys. J. 553 (2001) 267

Conclusion ?!

T. Motylewski et al. ApJ. 531 (2000) 312.

TABLE 1

LABORATORY AND ASTRONOMICAL DATA OF CARBON CHAIN RADICALS WITH INFERRED UPPER LIMITS OF THE COLUMN DENSITY N_{max} IN DIFFUSE CLOUDS TOWARDS SELECTED STARS.

Laboratory					Astronomical			
Chain	λ_{air} [Å]	Ref.	f_{0-0}	FWHM [Å]	Star	RMS	$W_{\lambda,max}$	N_{max} [10^{12} cm^{-2}]
C_8H	5265.756(3)[a]	1	0.06	1.0	HD190603	0.0043	0.021	1.43
					HD207198	0.0032	0.016	1.09
C_8H	6258.66(8)[b]	2	0.08	1.7	HD210839	0.0017	0.014	0.50
					HD207198	0.0037	0.031	1.12
$C_{10}H$	7140.9(5)[b]	2	0.10	4.0	HD207198	0.0036	0.072	1.59
					HD210839	0.0044	0.088	1.95
$C_{12}H$	7904.5(3)[b]	3	0.12	2.8	HD210839	0.0066	0.092	1.39
					HD207198	0.0076	0.106	1.60
HC_4H^+	5068.650(3)[a]	3,4	0.04	2.0	HD207198	0.0046	0.046	5.06
HC_6H^+	6002.138(3)[a]	3,5	0.06	1.2	HD210839	0.0015	0.009	0.47
HC_8H^+	7067.82(2)[a]	3,4	0.08	1.9	HD207198	0.0036	0.034	0.96
					BD+40° 4220	0.0058	0.055	1.55
NC_4N^+	5957.738(3)[a]	3,6	0.06	1.4	HD210839	0.005[c]	0.007[c]	0.37
NC_6N^+	6557.52(3)[a]	3	0.08	1.2	obscured by Hα line			
HC_5N^+	5819.27(2)[a]	3,6	0.06	1.6	HD207198		0.011[d]	0.61

Take home message

Cavity Ring Down

&

Molecular Laboratory Astrophysics

Basel:

John P. Maier

Pulsed CRD

Tomasz Motylewski

Olga Vaizert

Pawel Cias

Alexey Denisov

Mitsunori Araki

CW CRD

Petre Birza

FPM

Wayne Sinclair

David Pfluger

Dmitriy Khoroshev

Amsterdam:

Pulsed CRD

Wim Ubachs

Dmitriy Ityaksov

Jordy Bouwman

Tomas Foldes

Leiden:

IBBCEAS

Jordy Bouwman

CW-IR CRDS

Harald Verbraak

Anthony Ngai

Stefan Persijn

Frans Harren

RUN

Thank you !

Additional information available from

http://www.strw.leidenuniv.nl/~linnartz

Or via e-mail

linnartz@strw.leidenuniv.nl