High Resolution Spectroscopy and Astronomical Detection of Molecular Anions

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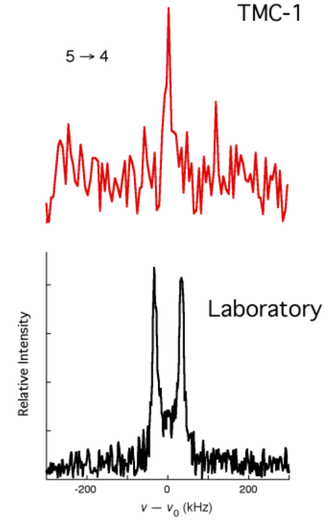
Overview

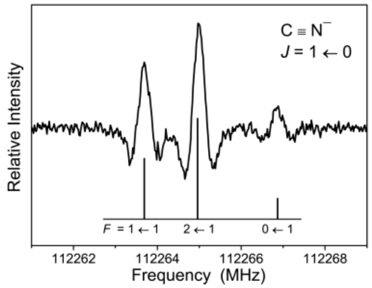
- Introduction
- Identification of the first anion in space

  the story of C_6H^-
- Anions in the laboratory

  six anions now detected
- Anions in space

  four anions detected with surprisingly high abundances
- Discussion and Conclusions





Motivation

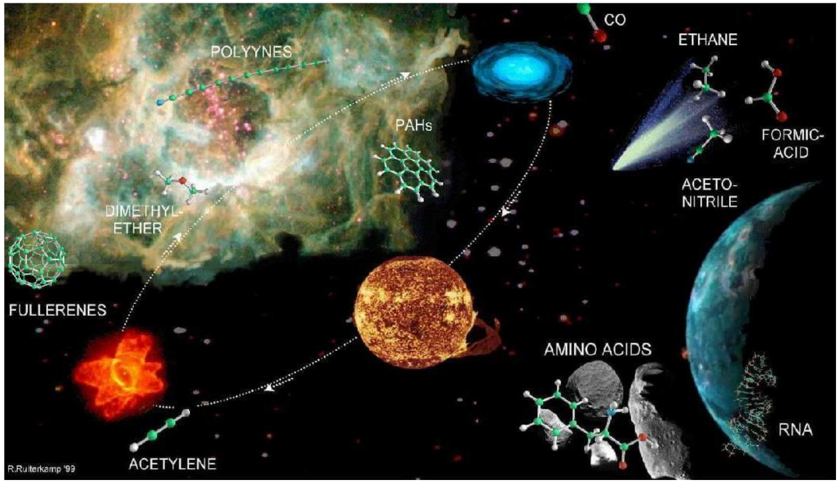
- more than 130 molecules detected in space
- most identified by their rotational spectra

- probe and influence physical properties:

  e.g. cooling

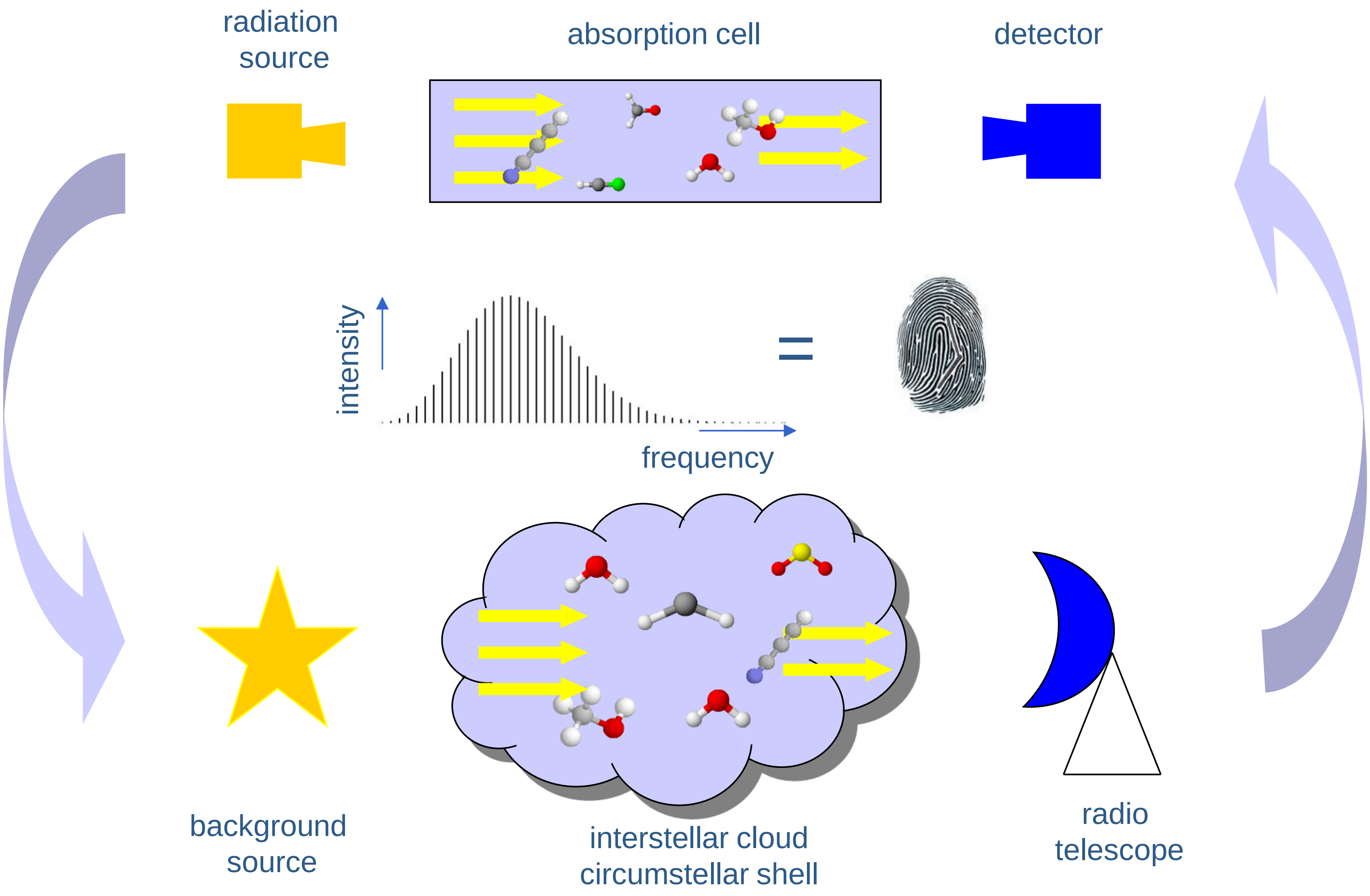
  fractional ionization

- understanding of chemistry and formation processes

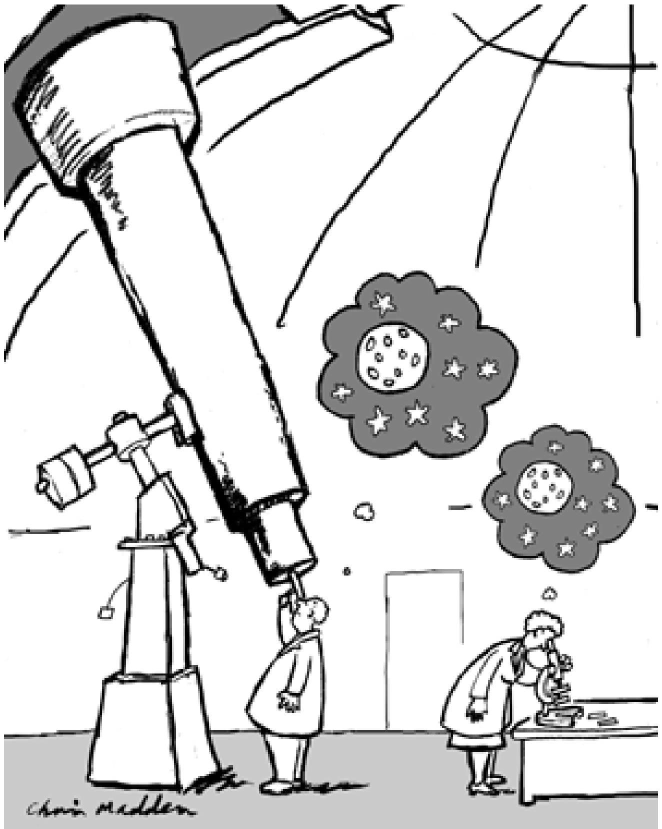


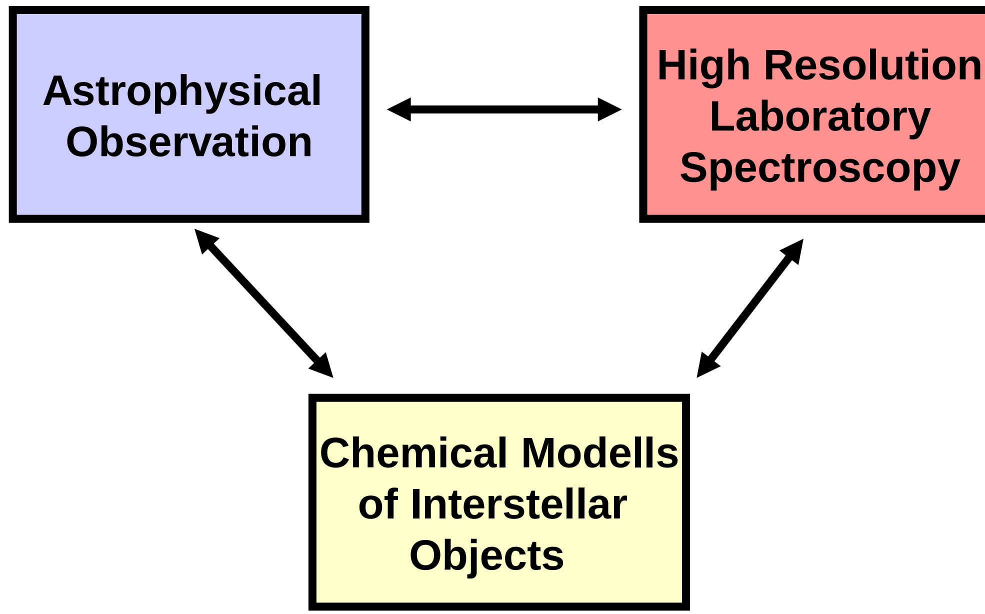
R. Ruiterkamp (2000)

Identifying molecules in space

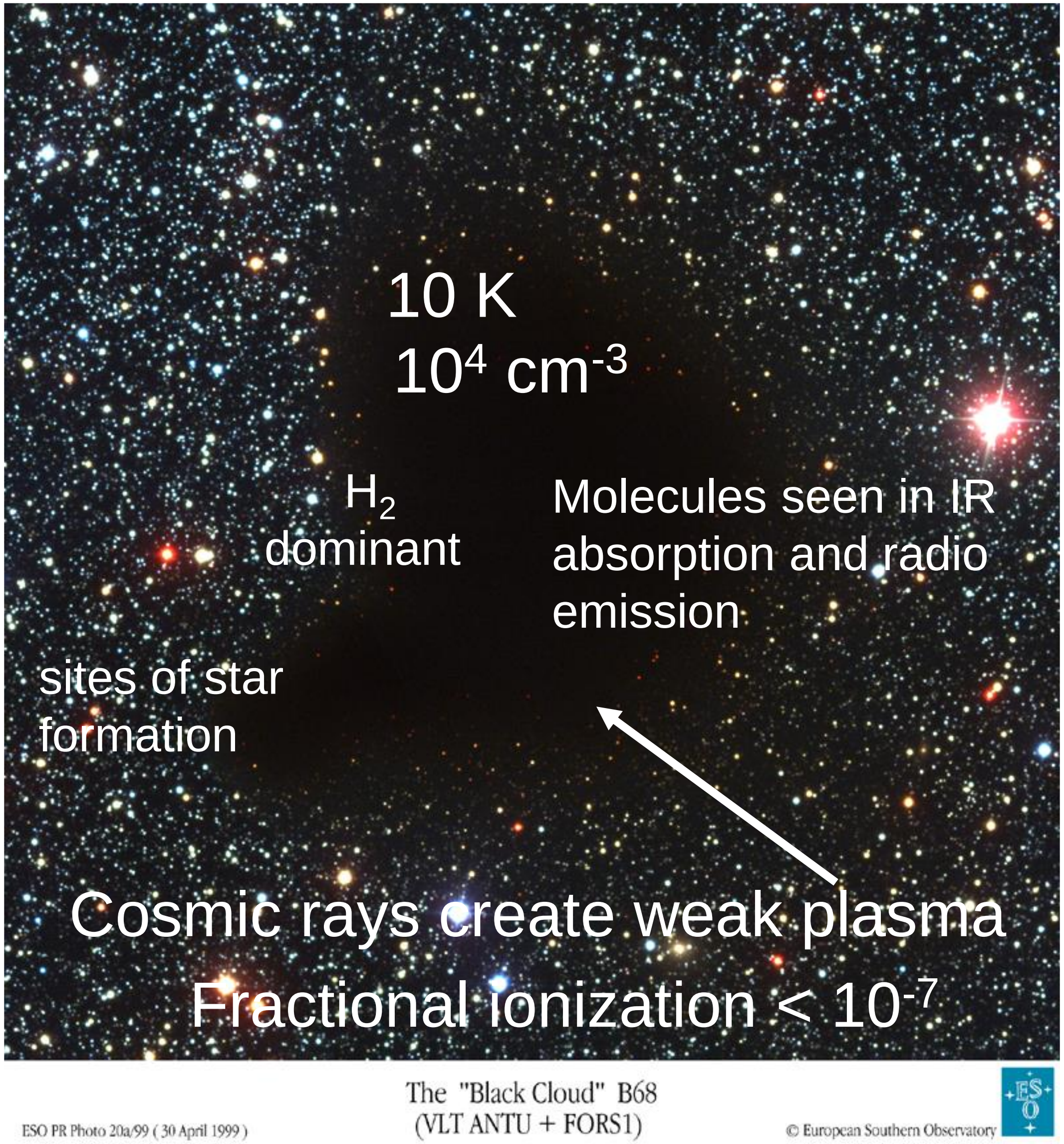


Identifying molecules in space



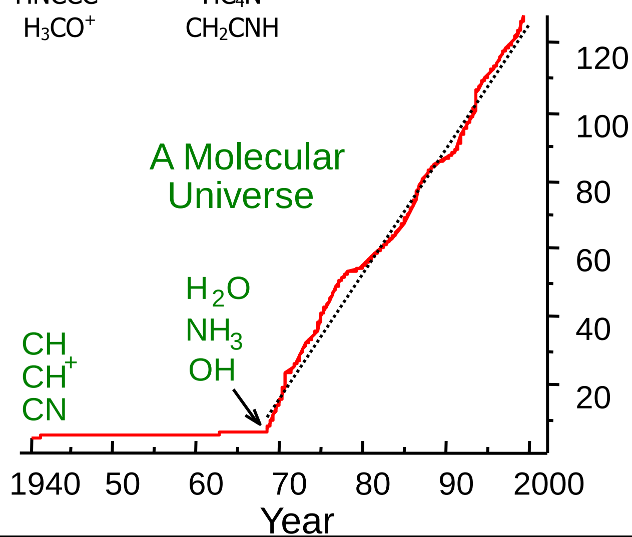


Dense Interstellar Cloud Cores



Molecules in space

Number of Atoms							
2	**3**	**4**	**5**	**6**	**7**	**8**	**9**
H_2	H_2O	NH_3	SiH_4	CH_3OH	CH_3CHO	$HCOOCH_3$	CH_3CH_2OH
OH	H_2S	H_3O^+	CH_4	NH_2CHO	CH_3NH_2	CH_2OHCHO	$(CH_3)_2O$
SO	SO_2	H_2CO	CHOOH	CH_3CN	CH_3CCH	CH_3C_2CN	CH_3CH_2CN
SO^+	HN_2^+	H_2CS	$HC{\equiv}CCN$	CH_3NC	CH_2CHCN	C_7H	$H(C{\equiv}C)_3CN$
SiO	HNO	HNCO	CH_2NH	CH_3SH	HC_4CN	H_2C_6	$CH_3(C{\equiv}C)_2H$
SiS	SiH_2	HNCS	NH_2CN	C_5H	C_6H	HC_6H	C_8H
NO	NH_2	CCCN	H_2CCO	HC_2CHO	c-CH_2OCH_2	CH_3CO_2H	$CH_3(C{\equiv}C)_2CN$
NS	H_3^+	HCO_2^+	C_4H	$CH_2{=}CH_2$	CH_2CHOH	C_6H_2	
HCl	NNO	CCCH	c-C_3H_2	H_2CCCC			**10**
NaCl	HCO	c-CCCH	CH_2CN	HC_3NH^+			CH_3COCH_3
AlCl	OCS	CCCS	SiC_4	HC_4H			$CH_3(C{\equiv}C)_2CN$
AlF	CCH	HCCH	H_2CCC	C_5S			$HOCH_2CH_2OH$
PN	HCS^+	$HCNH^+$	HCCNC	C_4H_2			CH_3CH_2CHO
SiN	c-SiCC	HCCN	HNCCC	HC_4N			
NH	CCO	H_2CN	H_3CO^+	CH_2CNH			
SH	CCS	c-SiC_3					**11**
HF	C_3	CH_3					$H(C{\equiv}C)_4CN$
CN	MgNC	CH_2D^+					
CO	NaCN	AlNC					**12**
CS	CH_2						c-C_6H_6
C_2	MgCN						
SiC	HOC^+						**13**
CP	HCN						$H(C{\equiv}C)_5CN$
CO^+	HNC						
CH^+	CO_2						
CH	SiCN						Total: 136
N_2	AlCN						
CF^+	SiNC						
	KCN						
	HCO^+						



December 2006

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SO^+	**HN_2^+**	H_2CS	$HC\equiv CCN$	CH_3NC	CH_2CHCN	C_7H	$H(C\equiv C)_3CN$
SiO	HNO	$HNCO$	CH_2NH	CH_3SH	HC_4CN	H_2C_6	$CH_3(C\equiv C)_2H$
SiS	SiH_2	$HNCS$	NH_2CN	C_5H	C_6H	HC_6H	C_8H
NO	NH_2	$CCCN$	H_2CCO	HC_2CHO	$c\text{-}CH_2OCH_2$	CH_3CO_2H	$CH_3(C\equiv C)_2CN$
NS	**H_3^+**	**HCO_2^+**	C_4H	$CH_2{=}CH_2$	CH_2CHOH	C_6H_2	
HCl	NNO	$CCCH$	$c\text{-}C_3H_2$	H_2CCCC			**10**
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CF^+	$SiNC$						
	KCN						
	HCO^+						

15 positive molecular ions

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N_2	AlCN						
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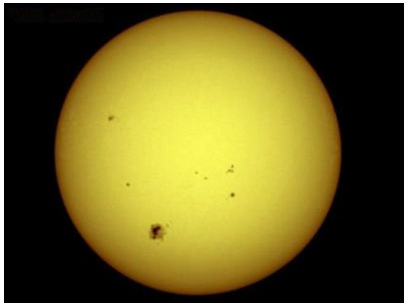
	KCN						
	HCO^+						

NO negative molecular ions!

Anions in space – not such a bad idea

- H^- shown to be the main source of opacity in the solar atmosphere. (Wildt, ApJ, 1939)



- Molecular anions long postulated to be constituents of the interstellar gas.
  - ✓ cold, dense clouds
  - ✓ circumstellar shells
  - ✓ diffuse interstellar medium

(Herbst, Nature, 1981; Lepp & Dalgarno, ApJ, 1988; Petrie, MNRAS, 1996; Petrie & Herbst, ApJ 1997; Millar et al., MNRAS, 2000, Tulej et al., ApJL, 1998)

- 1000+ anions studied by low resolution methods in the laboratory.

(e.g. Rienstra-Kiracofe et al., Chem. Rev., 2002)

Anions in space – lack of laboratory data

But:

- only two anions studied by rotational spectroscopy:
  (Liu & Oka, JCP, 1986; Civis *et al.*, JCP, 1998).

  OH^- and SH^-

- a few more by IR spectroscopy:

  NCS^-, NCO^-, NH_2^-, NH^-, HNO^-

  (Owrutsky *et al.*, Phil Trans. R. Soc. Lond., 1987; Miller *et al.*, JMS, 1989; Al Za'al *et al*., Phys. Rev. A, 1987)

- and rotationally resolved electronic spectroscopy:

  C_4H^-, CH_2CN^-, l-$C_3H_2^-$

  (Pachkov et al., Mol. Phys., 2003; Lykke *et al*., JCP, 1987; Yokoyama *et al*., JCP, 1996)

- only one published (unsuccessful) search in space:
  (Morisawa *et al*., PASJ, 1995)

  CCH^-, NCS^-, NCO^-

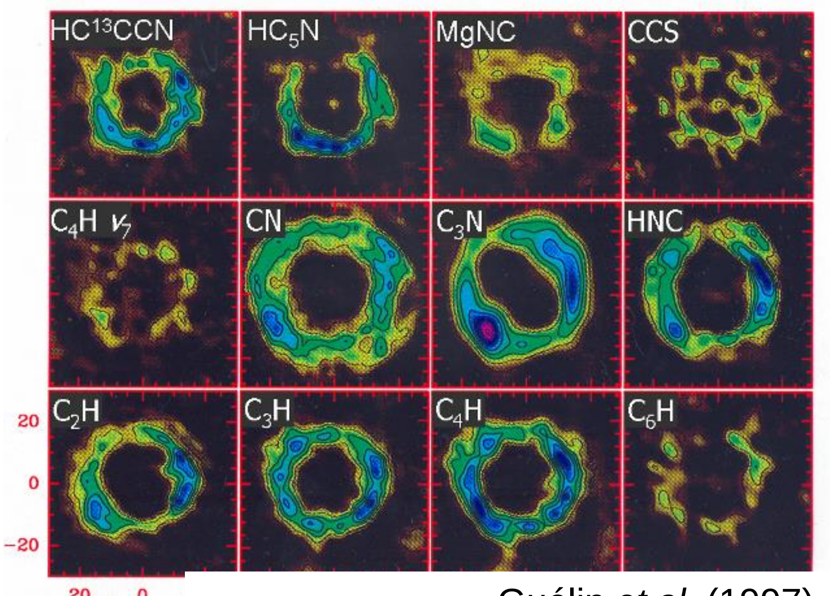
B1377: An unidentified sequence of astronomical lines

Line survey of IRC+10216

(Kawaguchi *et al.*, PASJ, 1995)

7 lines (Nobeyama 45m)

- circumstellar envelope around carbon rich star
- extremely rich chemistry: >50 molecules



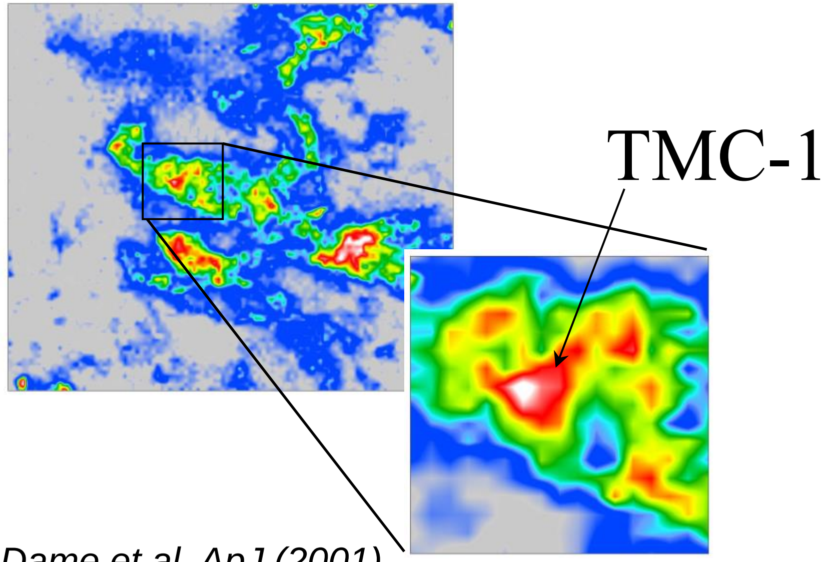
Guélin *et al*. (1997)

TMC-1 (Taurus-Auriga Molecular Cloud)

(McCarthy *et al*., ApJL, 2006)

2 lines (GBT 100m)

- cold (10 K), dense (10^4 cm^{-3})
- rich in carbon-chains
- no metal-bearing molecules



Dame et al. ApJ (2001)

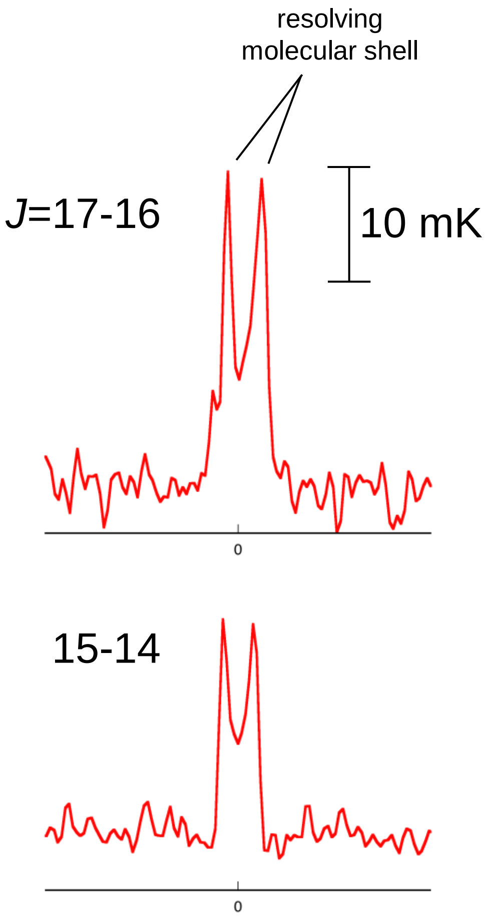
B1377: An unidentified sequence of astronomical lines

- rotational lines are harmonic: separated in frequency by ratio of integers

→ carrier almost certainly a closed-shell ($^1\Sigma$) linear molecule

- likely a rather fundamental molecule
- rotational constant about 1% lower than C_6H (B=1391 MHz), an abundant radical in this source
- C_6H^- suggested as carrier based on ab initio calculations (Aoki, Chem. Phys. L., 2000)

But: positive ions (HCO^+) not abundant in these sources

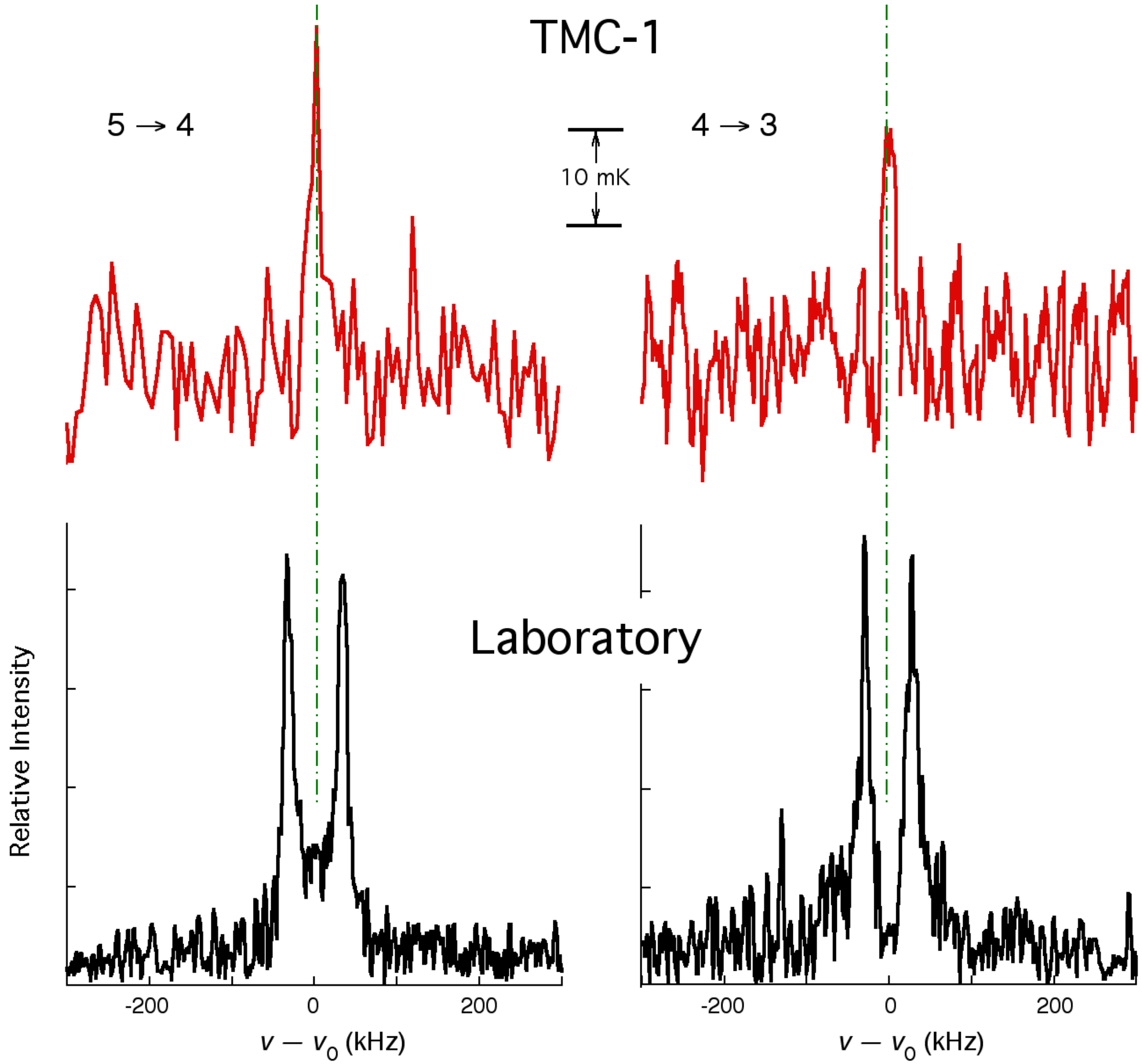


B1377 in the laboratory

- Exact match to astronomical lines has now been achieved using two hydrocarbon gases
- 15+ lines detected over two decades of frequency

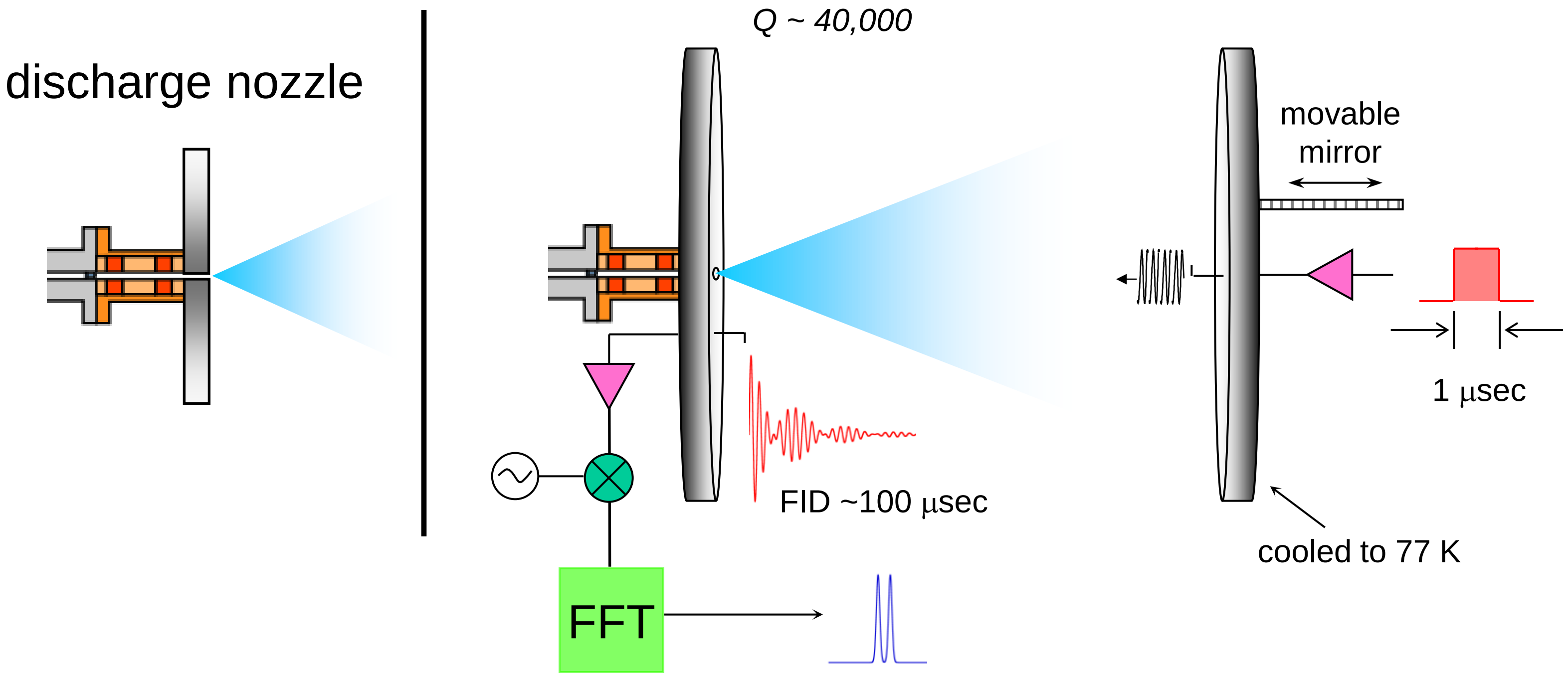
Constant (MHz)	Laboratory	Astronomical
B	1376.86298(7)	1376.86248(294)
$10^6 D$	32.35(1)	33.35(993)

B1377 in the laboratory and in space



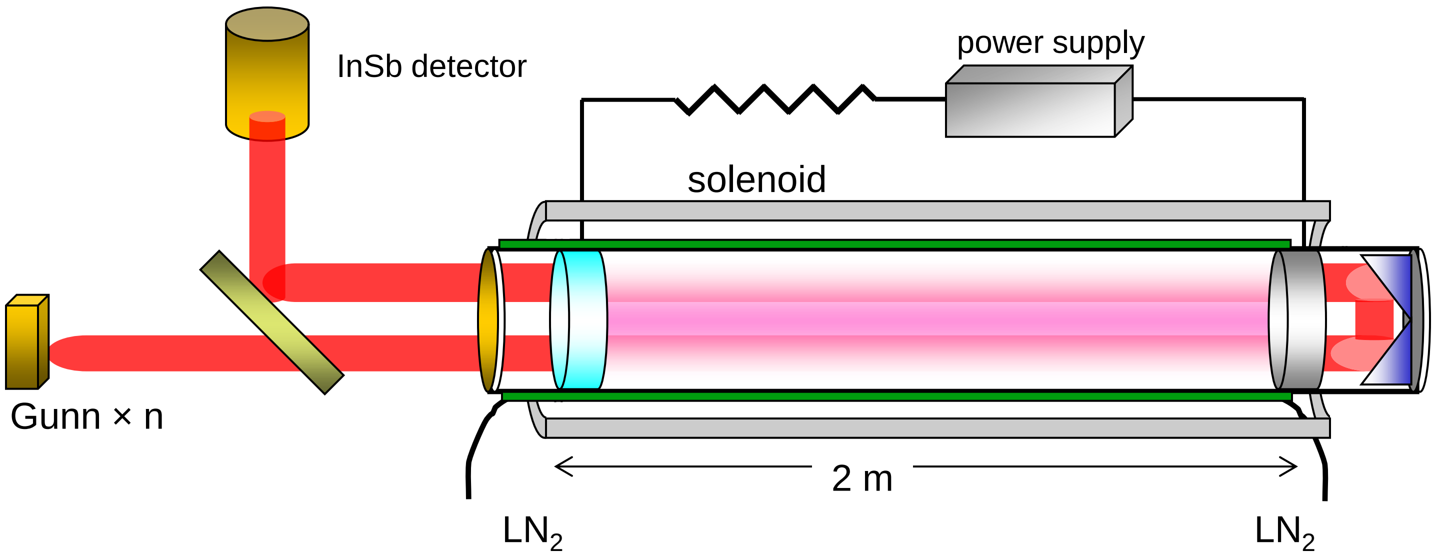
Experimental setup - FTM

supersonic nozzle coupled to a high-*Q* Fabry-Perot cavity



- frequency range: 5 – 42 GHz resolution: 20 kHz accuracy: 1-2 kHz
- low current (~20 mA) discharge of C_4H_2 or C_2H_2 (0.1 %) in Ne (He, H_2)

Experimental setup – mm-wave absorption spectrometer



- low current dc glow discharge of C_2H_2 (85 %) + Ar (15 %)
- frequency coverage: 68 – 600 GHz
- frequency accuracy: 10 – 50 kHz
- cell walls cooled by LN_2 to 150 K

Identification of B1377 as C_6H^-

- composed of both **C** and **H**
- harmonic relation of lines requires **linear geometry**
- *B* constant requires chain of **six carbon atoms**; one more of less yields *B* 40% too high or low
- Isotopic shift observed on deuteration requires **one H** at end of carbon chain (4.53% vs. 4.55% for C_6H)
- Neutral C_6H ($^2\Pi$) and C_6H^+ ($^3\Sigma$) lack required **symmetry**

→ carrier must be C_6H^-

one of the most securely identified astronomical molecules

Why hexatriyne, C_6H^- ?

larger than most of the neutral molecules and all of the cations

Four factors favor formation:

- ✓ radical is abundant in both IRC+10216 and TMC-1
- ✓ exceptionally stable: high electron binding (3.8 eV)

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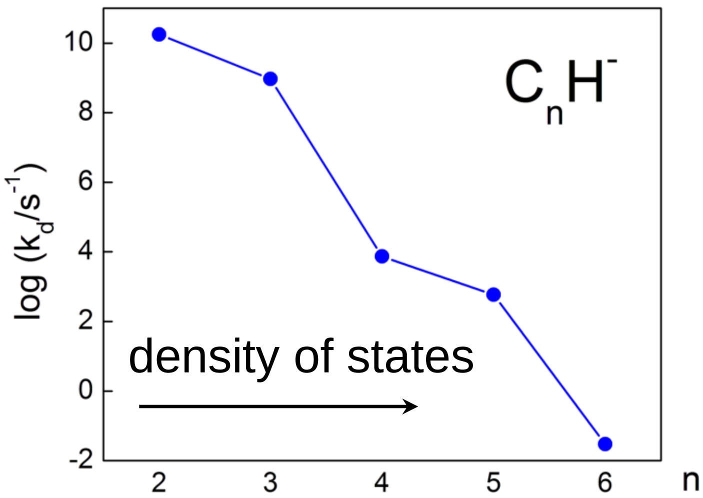
- ✓ exceptionally stable: high electron binding (3.8 eV)
- ✓ size confers stability: C_6H apparently large enough where e^- attachment becomes efficient (Taylor *et al*., JCP, 1998)

e^- radiative attachment versus size

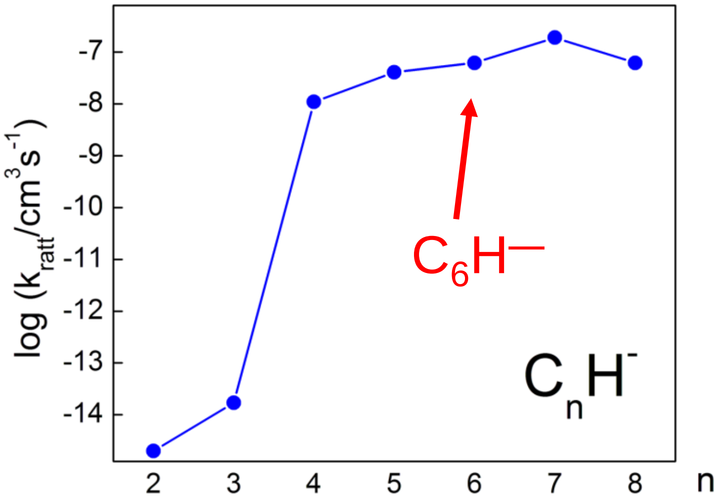
Statistical Treatment:

$$C_nH + e^- \xrightarrow[k_f]{} [C_nH^-]^* \begin{array}{l} \xrightarrow{k_d} C_nH + e^- \\ \xrightarrow[k_{rad}]{} C_nH^- + h\nu \end{array}$$

autodetachment vs. size



total radiative attachment



Herbst *et al*. ApJ, in press

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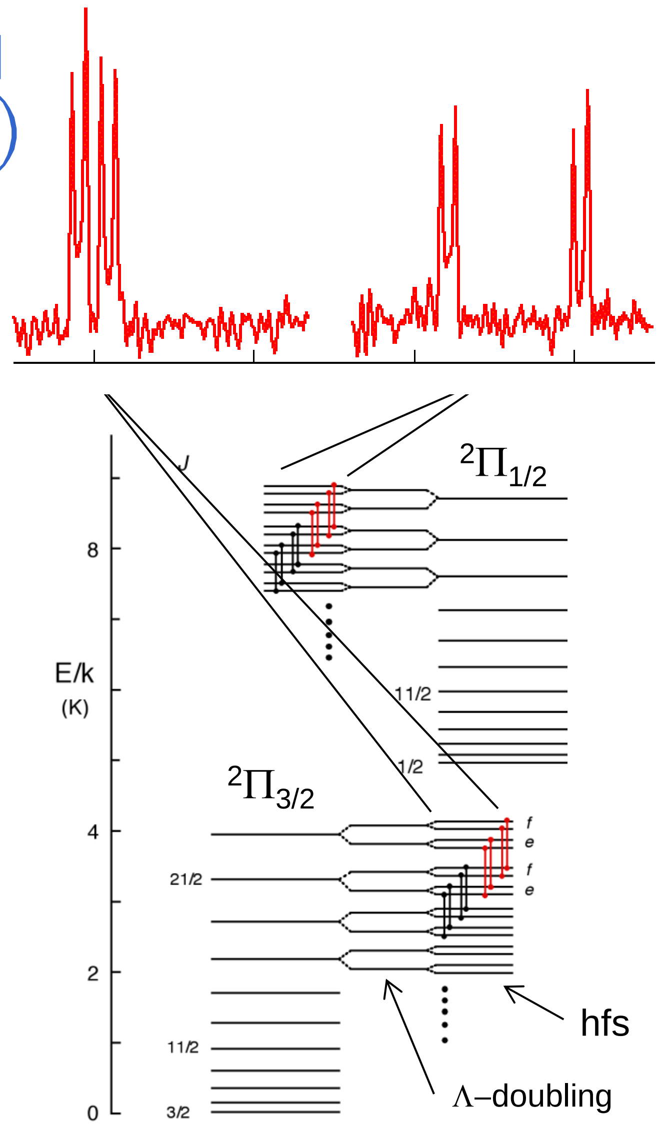
- ✓ exceptionally stable: high electron binding (3.8 eV)
- ✓ size confers stability: C_6H apparently large enough where e^- attachment becomes efficient (Taylor *et al*., JCP, 1998)
- ✓ spectral simplification: lines of anion *x10* more conspicuous than those of neutral !

Spectral compression

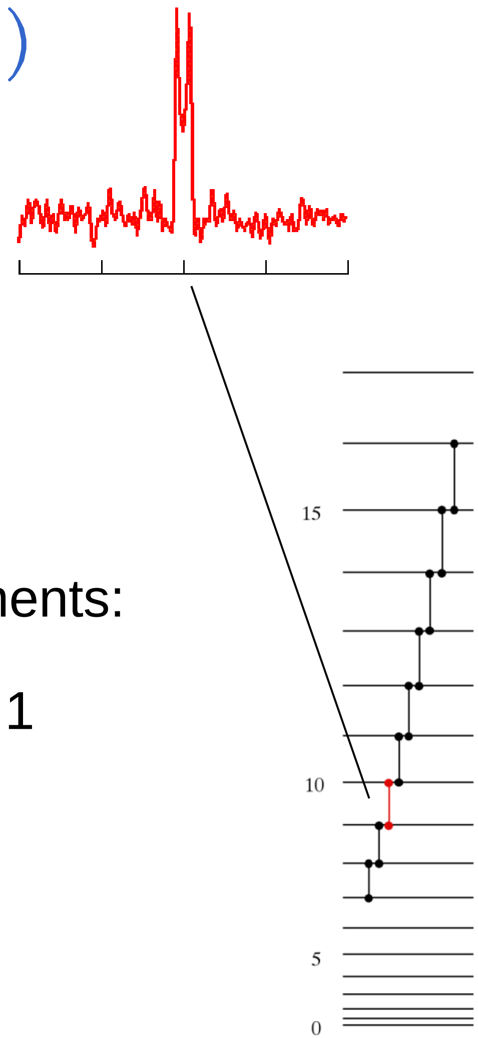
C_6H ($^2\Pi$)



$\xrightarrow{e^-}$ C_6H^- ($^1\Sigma$)

10 mK

IRC+10216



Dipole Moments:

$$\left[\frac{8.2}{5.6}\right]^2 = 2.1$$

More anions

discovery of C_6H^- suggested specific anions to target

- closed-shell $^1\Sigma$ ground states and large dipole moments (μ)
- large electron affinities (EA)
- radicals are detected in astronomical sources
- anions do not react with H_2 (Barckholtz et al., ApJL, 547, 2001)

		EA (eV)	μ (D)			μ (D)	B (MHz)
CCH	$^2\Sigma$	2.97	0.8	**CCH^-**	$^1\Sigma$	3.1	41,639
C_4H	$^2\Sigma$	3.56	0.9	**C_4H^-**	$^1\Sigma$	6.1	4,656
C_6H	$^2\Pi$	3.81	5.6	**C_6H^-**	$^1\Sigma$	8.2	1,377
C_8H	$^2\Pi$	3.97	6.3	**C_8H^-**	$^1\Sigma$	11.9	583
CN	$^2\Sigma$	3.8	1.5	**CN^-**	$^1\Sigma$	0.7	56,133
C_3N	$^2\Sigma$	4.59	2.9	**C_3N^-**	$^1\Sigma$	3.1	4,852

Ab initio calculations

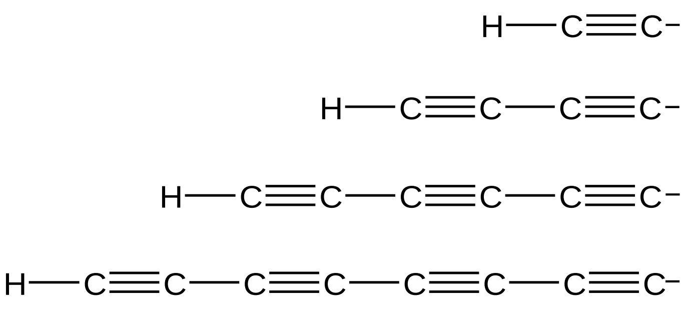
- laboratory searches guided by high level CCSD(T) *ab initio* calculations (cc-PVTZ or higher) (Gupta & Stanton, private communication)
- calculated rotational constants B_0 accurate to better than 0.1 %

→ calculations considerably speed up laboratory searches

- additional information: centrifugal distortion constants
  quadrupole coupling constants
  dipole moments

Laboratory measurements

- **six molecular anions detected in less than one year**



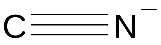
CCH^-

C_4H^-

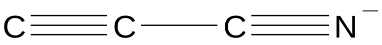
C_6H^-

C_8H^-

CN^-



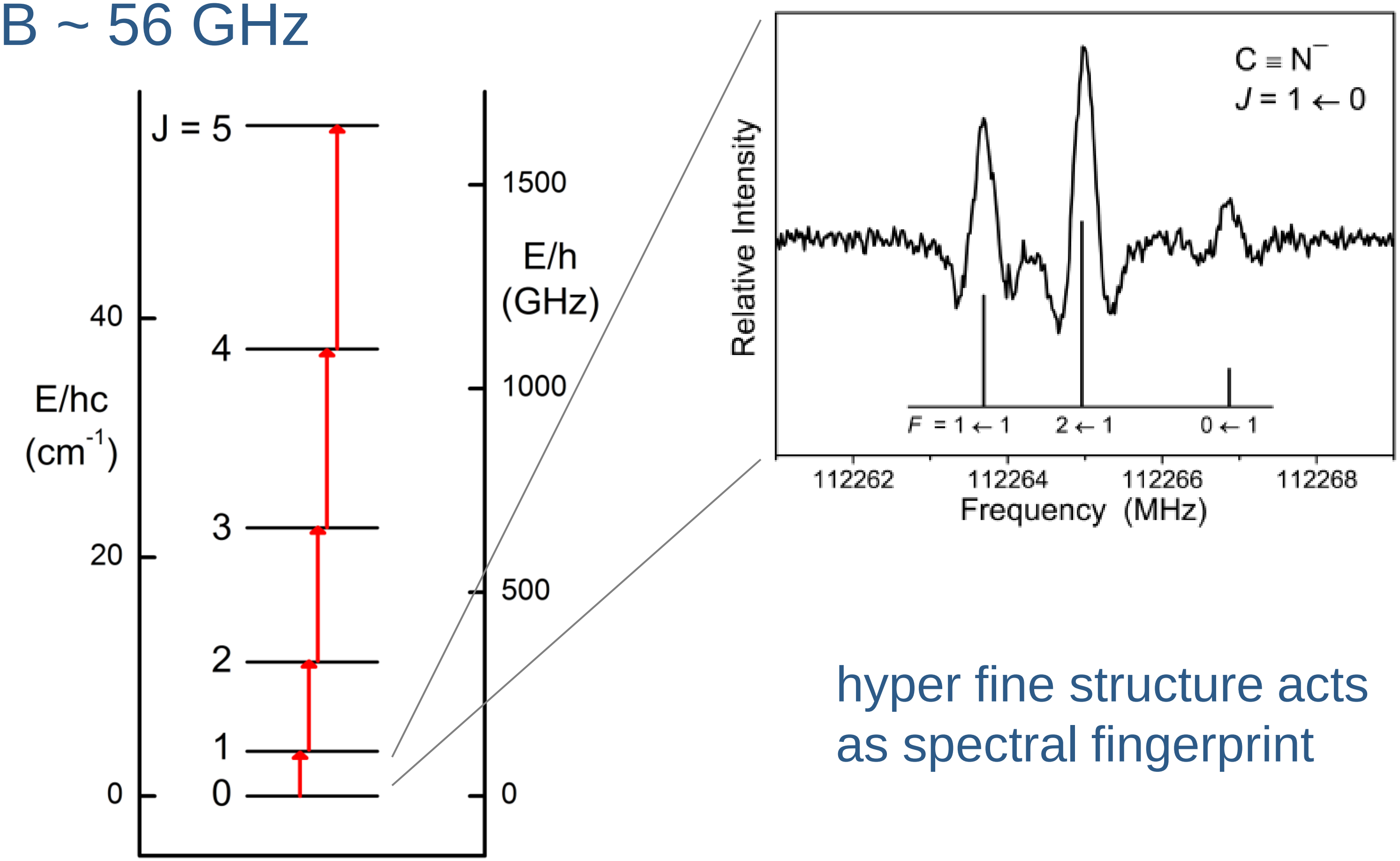
C_3N^-



- detections secured by:
  - ✓ elemental composition
  - ✓ harmonicity
  - ✓ close agreement with calculations
  - ✓ isotopic shift
  - ✓ determination of charge state

Cyanide, CN^-

B ~ 56 GHz



hyper fine structure acts as spectral fingerprint

5 transitions in 112 – 560 GHz range
(Gottlieb et al., JCP 2007)

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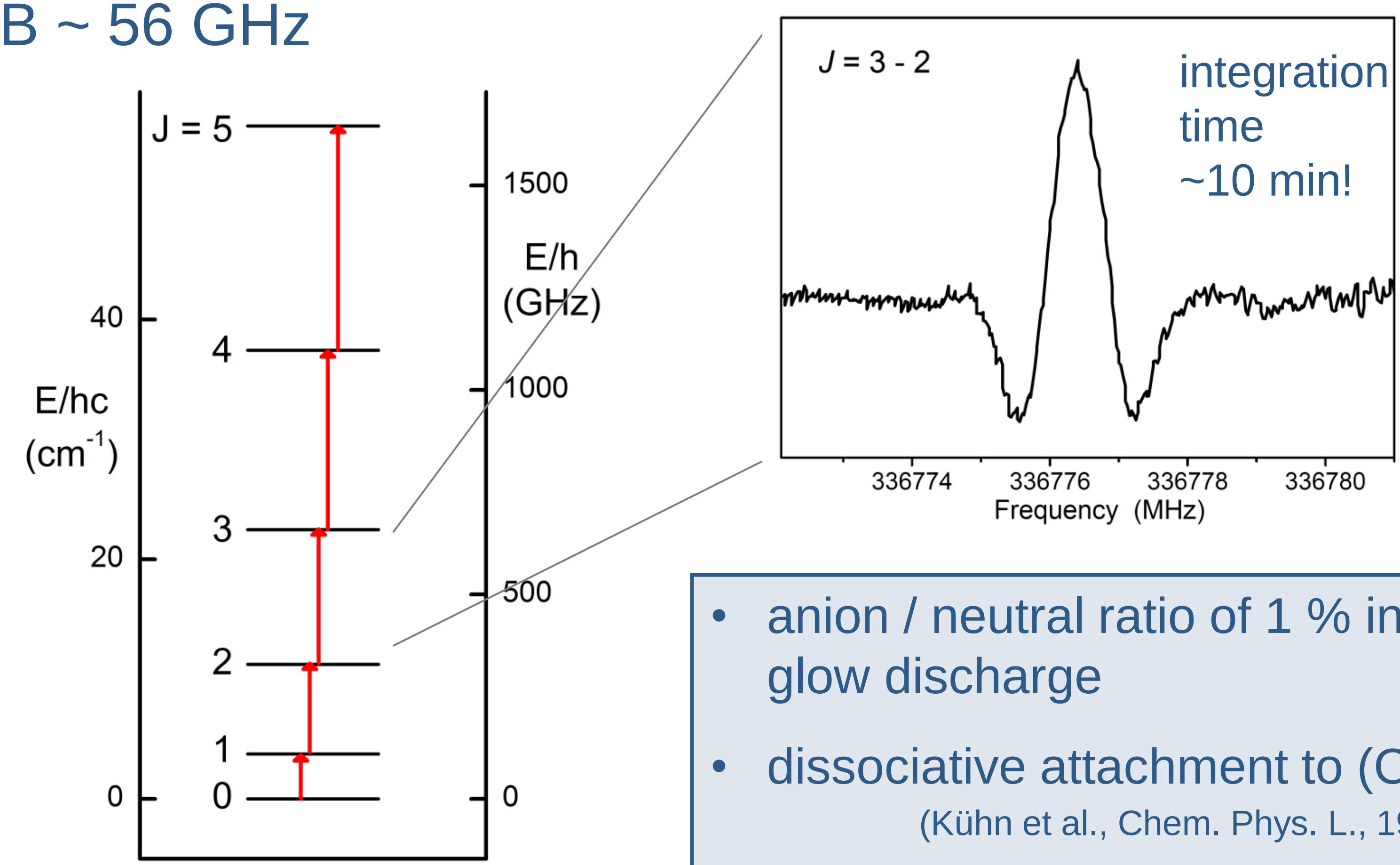
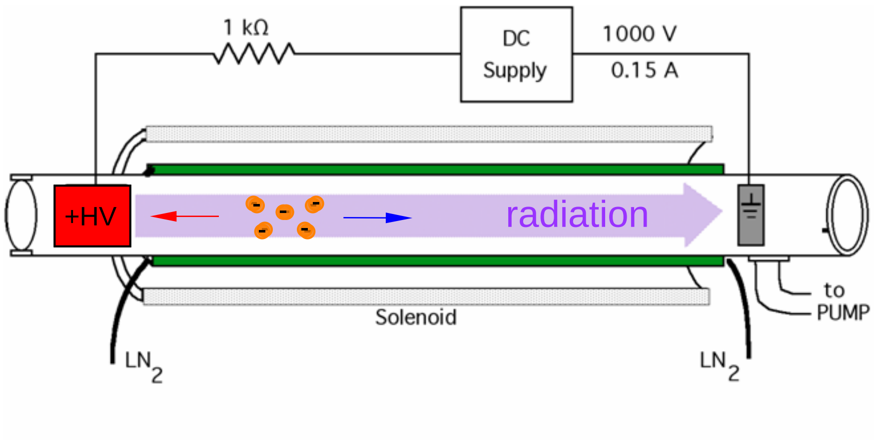


integration time ~10 min!

- anion / neutral ratio of 1 % in glow discharge
- dissociative attachment to $(CN)_2$ (Kühn et al., Chem. Phys. L., 1987)
- $CN^- / (CN)_2 = 4 \times 10^{-6}$

Ion Drift Measurements – CN^-

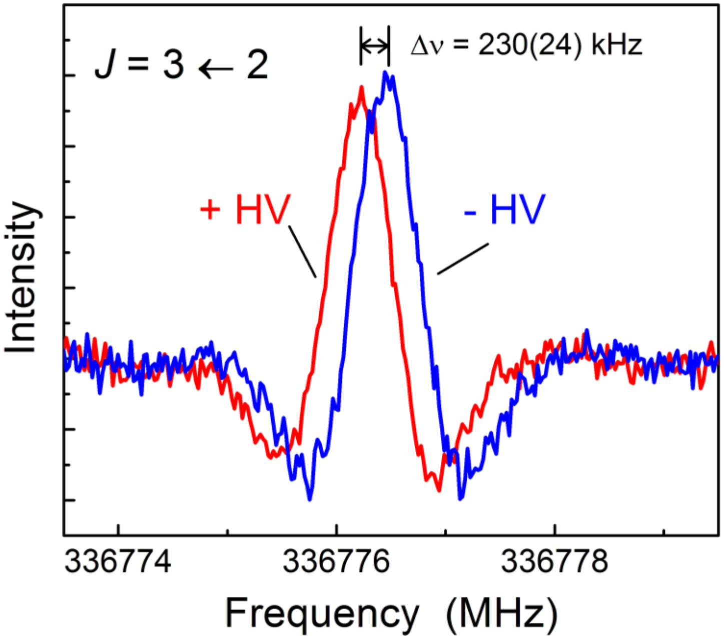


measurements in single pass

with alternating polarity

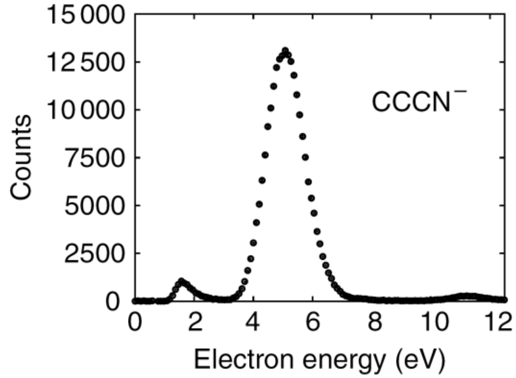
direct proof of the charge

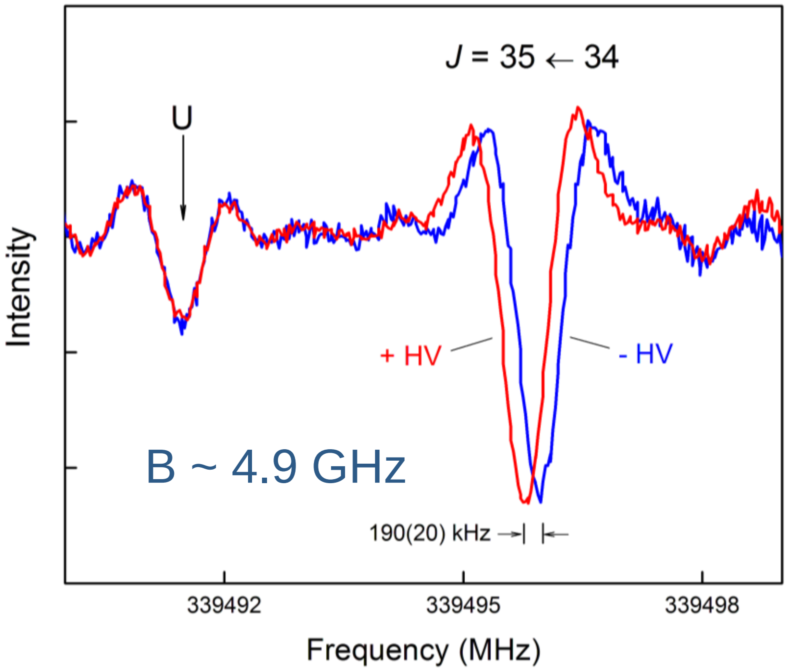
state of the carrier



C_3N^-

- Petrie & Herbst (ApJ, 1997) predicted C_3N^- to have abundance ~1 % of neutral C_3N in TMC-1
- discharge production: dissociative attachment to HCCCN (Graupner et al., New J. Phys., 2006)





- 12 transitions detected up to 380 GHz
- C_3N^- / HC_3N = 5 x 10^{-6}
- C_3N^- / C_3N = 2 %

Formation in the laboratory

- in the laboratory dissociative attachment possible $[E_{kin}(e^-) \sim 3eV]$

$$e^- + HCCH \rightarrow CCH^- + H$$

$$CCH^- + HCCH \rightarrow C_4H^- + H_2$$

threshold 1.76 eV
(De Bleecker *et al*., Phys. Rev. E , 2006)

Questions to be addressed:

- plasma characteristics, influence of carrier gas, suitable precursors?
- wall surface chemistry, metallization of discharge cell?
- DC discharge vs. H^+ or H_2^+ abstraction

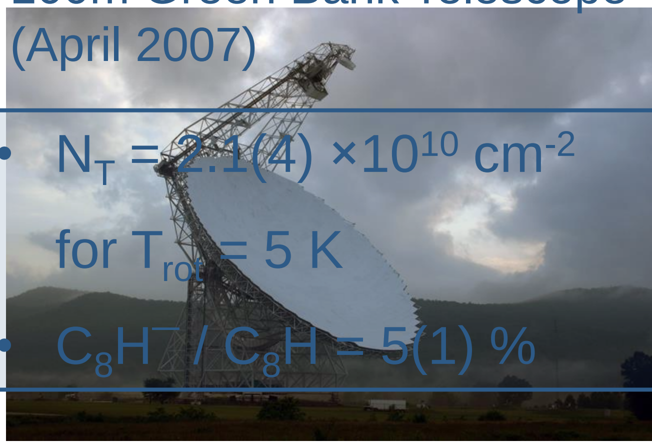
$$HC_{2n}H + OH^- \rightarrow C_{2n}H^- + H_2O$$

reduction of background lines?

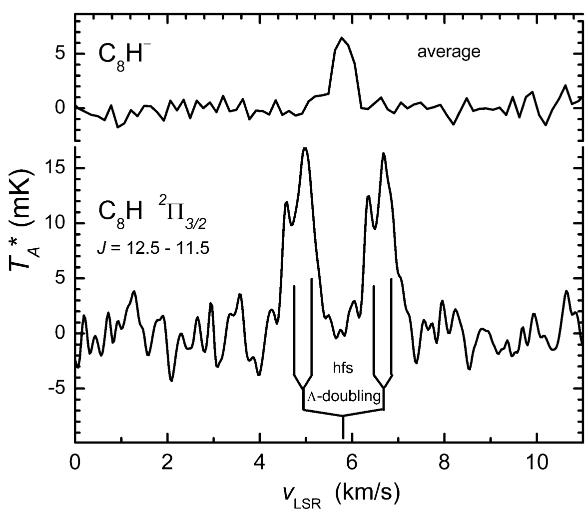
- velocity modulation

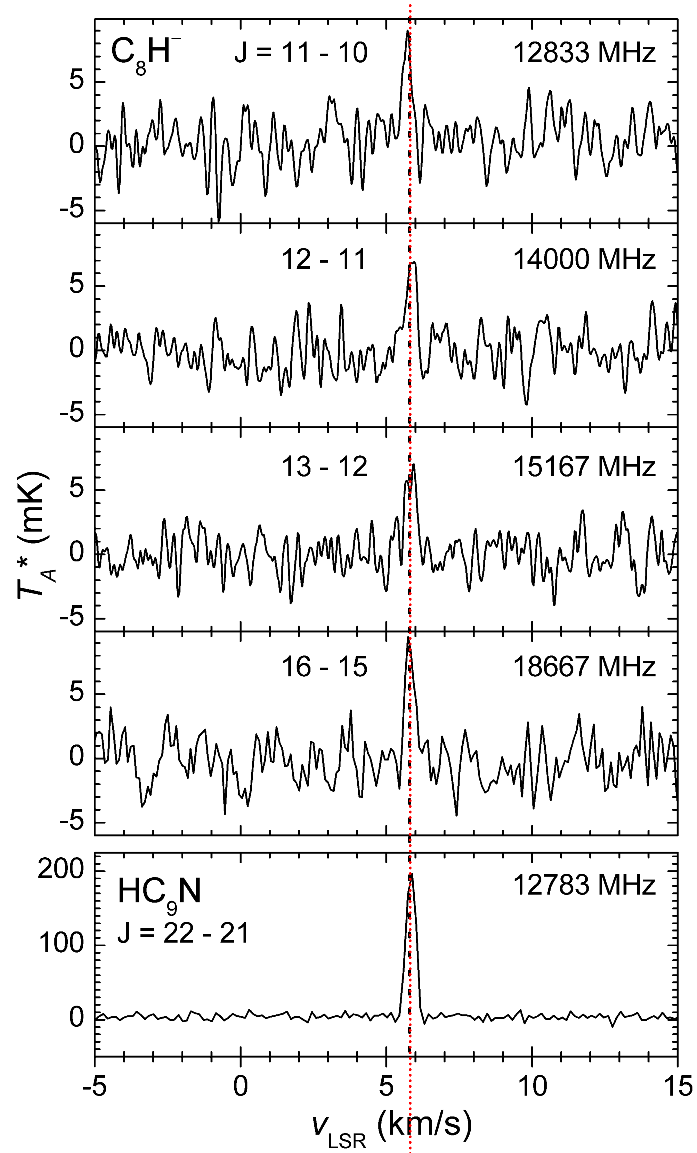
Detection of C_8H^- in TMC-1

100m Green Bank Telescope (April 2007)



- N_T = 2.1(4) ×10^{10} cm^{-2} for T_{rot} = 5 K
- C_8H^- / C_8H = 5(1) %





Brünken *et al.*, ApJL, 2007

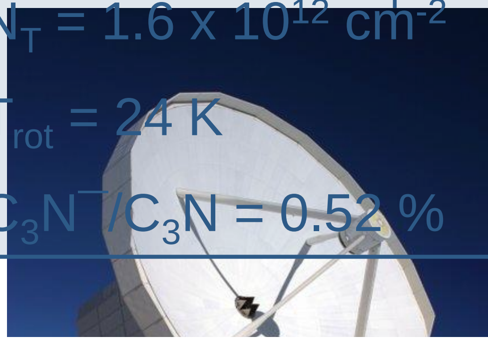
Detection of C_3N^- in IRC+10216

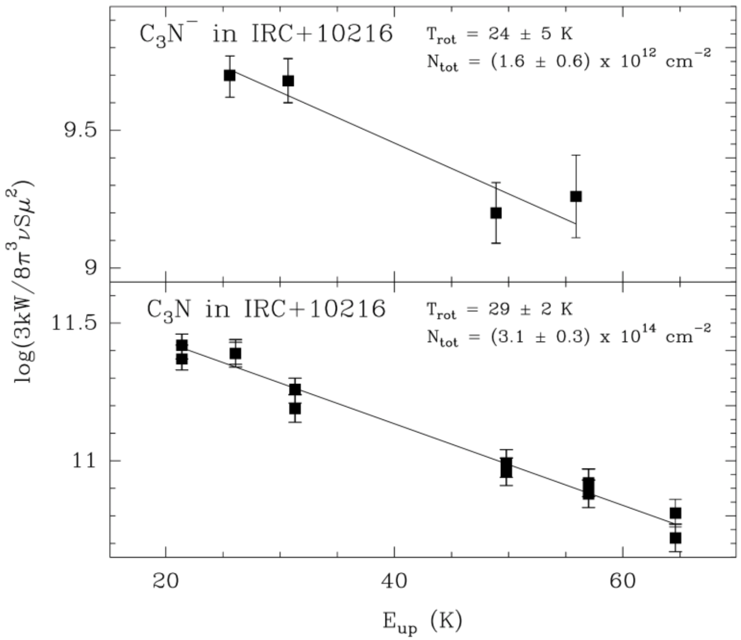
IRAM 30m telescope

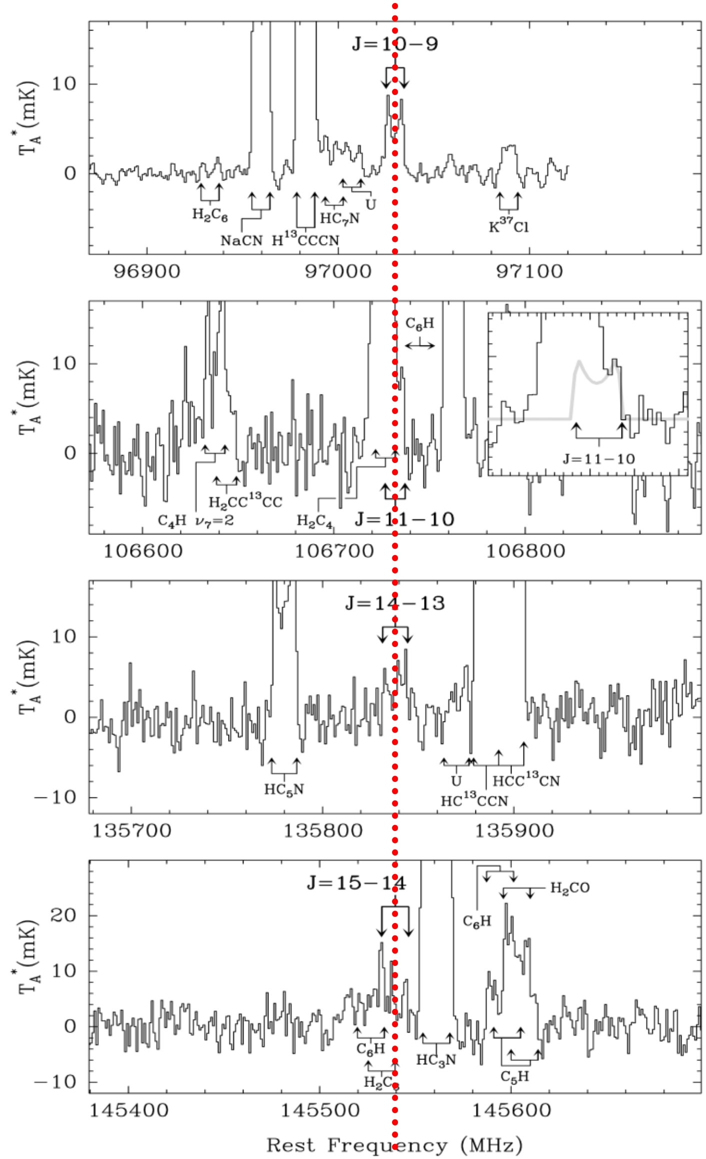
N_T = 1.6 x 10^{12} cm^{-2}

T_{rot} = 24 K

C_3N^-/C_3N = 0.52 %







Thaddeus *et al.*, ApJ 2008

Anions in space

- C_6H^- and C_8H^- detected in TMC-1

- C_4H^-, C_6H^- , C_8H^- and C_3N^- now been detected in IRC+10216
  (Cernicharo *et al*. ApJL, 2007; Remijan *et al*., ApJL, 2007, Kawaguchi *et al*., PASJ, 2007, Thaddeus et al., ApJ 2008)

  C_8H^- anion to neutral ratio 28-37% !

- detection of C_4H^-, C_6H^- in a third source: IRAS 04368+2557 in L1527
  (Agundez et al. A&A, 2008; Sakai et al. ApJL, 2007, 2008)

- tentative detection of J = 2-1 of CN^- in IRC+10216
  (Guelin, private communication)

Abundances of anions in space

	TMC-1		IRC+10216	
C_nH^- / C_nH	obs.	calc.[e]	obs.	calc.[e]
8	**5**	5.4	**28/37**[a]	28
6	**1.6**	8.9	**8.6**[b]	30
4	**< 0.004**[f]	0.7	**0.024**[c]	4
C_3N^- / C_3N	**< 0.8**[f]		**0.52**[f]	≅0.05[e,f]

all ratios in %, [a]Remijan *et al*., ApJL, 2007; Kawaguchi *et al*., PASJ, acc.; [b] Kasai *et al*. ApJL, 2007, [c]Cernicharo *et al*. ApJL, 2007; [d] Agundez et al. ApJ 2008., [e] Millar *et al*. ApJL, 2007, Herbst et al. ApJ 2008, [f]Thaddeus et al. ApJ 2008

- formation and destruction processes not fully understood
- lack of laboratory data

What can we learn?

- radiative electron attachment most likely formation process in space:

$$\mathbf{A + e^- \rightarrow (A^-)^* \rightarrow A^- + h\nu} \qquad k_{ratt}$$

- dominant destruction processes:

$$\mathbf{A^- + H \xrightarrow{k_{aa}} AH + e^-} \qquad \mathbf{A^- + B^+ \xrightarrow{k_{neu}} A + B}$$

$$\rightarrow \quad \frac{[\mathbf{A}^-]}{[\mathbf{A}]} = \frac{k_{ratt}\,[\mathbf{e}^-]}{k_{aa}\,[\mathbf{H}] + k_{neu}\,[\mathbf{B}^+]} \approx \frac{k_{ratt}}{k_{aa}}\,\frac{[\mathbf{e}^-]}{[\mathbf{H}]}$$

fractional ionization

- fractional ionization dependent upon:
  - cosmic ray ionization rate
  - hydrogen density
  - grain characteristics
  - PAH and metal abundance

Flower *et al*., A&A, 2007

Conclusions

- accurate transition frequencies available for all six anions
- C_4H^-, C_6H^-, C_8H^- and C_3N^- have already been detected in space with surprisingly high abundances
- many other anions likely to be detected in the laboratory and in space (CH_2CN^-, l-$C_3H_2^-$, $C_3H_3^-$, CH_3O^-)
- a galactic survey of molecular anions, i.e. C_6H^- is timely
  - other, better sources
  - abundance as function of temperature, density and composition
- laboratory studies of reaction and formation rates of anions necessary

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