Anions in Space and in the Laboratory

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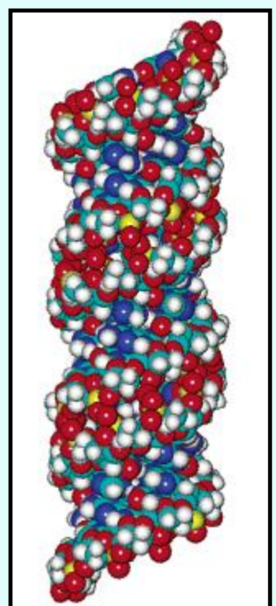
University of Colorado

Ions are ubiquitous!



Interstellar Molecules

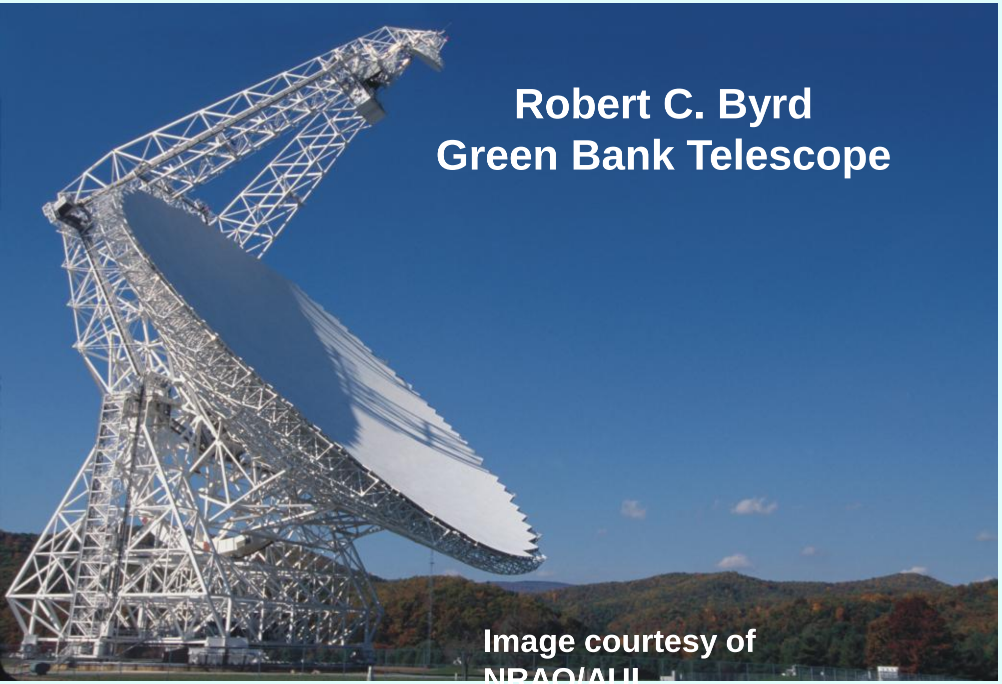
CH	CN	CH^+	OH	NH_3	H_2O	H_2CO
CO	H_2	HCO^+	CH_3OH	HC_3N	HCN	HCOOH
SiO	CS	CH_3CN	OCS	NH_2CHO	H_2S	HNCO
CH_3CHO	CH_3CCH	CH_2NH	H_2CS	HNC	SO	CH_3OCH_3
CH_3NH_2	N_2H^+	C_2H	CH_2CHCN	CH_3CH_2OH	$HCOOCH_3$	SO_2
HDO	SiS	NS	NH_2CN	HCO	C_3N	H_2CCO
C_2	HNO	CH_3CH_2CN	HC_7N	HC_5N	HC_9N	C_4H
NO	OCN^-	CH_3SH	HNCS	C_2H_4	HCS^+	$HOCO^+$
HOC^+	CH_3C_3N	SiH_4	CH_3C_4H	c-SiC_2	C_3H	HCl
C_3O	c-C_3H_2	C_6H	$HCNH^+$	MgNC	C_5H	H_3O^+
C_2S	C_3S	$(CH_3)_2CO$	NaCl	AlCl	KCl	AlF
PN	CH_3NC	C_3	c-C_3H	CH_2CN	HC_2CHO	C_5
SiC	C_2H_2	SiC_4	CO_2	CH_2	CP	l-C_3H_2
HC_2N	NH	CH_4	C_2O	HCCNC	SiN	HNCCC
SO^+	NH_2	CO^+	HC_3NH^+	H_2CN	NaCN	N_2O
MgCN	C_8H	H_3^+	H_2COH^+	C_7H	CH_3COOH	$HC_{11}N$
HF	c-C_2H_4O	LiH	C_5N	SiC_3	SH	CH_3
CH_2OHCHO	SiCN	C_4H_2	C_6H_2	C_6H_6	CH_2CHOH	AlNC
FeO	$HOCH_2CH_2OH$	NH_2CH_2COOH	N_2	CH_2CHCHO	CH_3CH_2CHO	SiNC
HC_4N	$CO(CH_2OH)_2$	CH_2CCHCN	c-H_2C_3O	CH_3CONH_2	CH_3C_6H	CH_2CNH
CF^+	CH_3C_5N	C_6H^-	O_2	C_4H^-	HCP	C_8H^-
CH_2CHCH_3	PO	CNCHO	CCP	C_3N^-	NH_2CH_2CHN	PH_3
C_5N^-	HCNO	AlO	HOCN	C_2H_5OCHO	C_3H_7CN	HSCN
AlOH	CN^-	H_2O^+	OH^+	C_{60}	C_{70}	H_2Cl^+
KCN	SH^+	FeCN				

http://www.astrochymist.org/astrochymist_ism.html

Laboratory and Astronomical Identification of the Negative Molecular Ion C_6H^-

McCarthy, Gottlieb, Gupta and Thaddeus

Harvard-Smithsonian Center for Astrophysics



***Astrophysical Journal 652, L141 December 2006*.**

17 rotational lines between 8 & 187 GHz

Identified C_6H^- in IRC +10216 & TMC-1

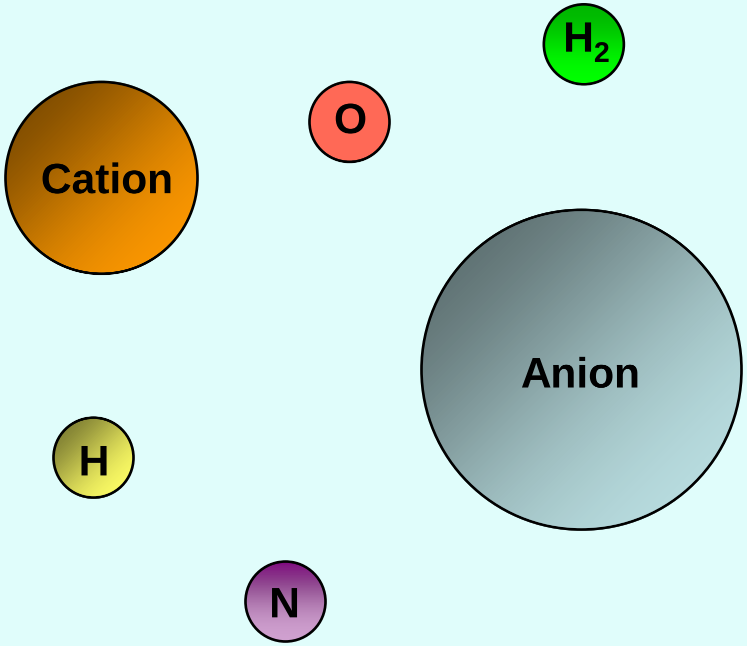
C_4H^- C_6H^- C_8H^- CN^- C_3N^-

Interstellar Molecules

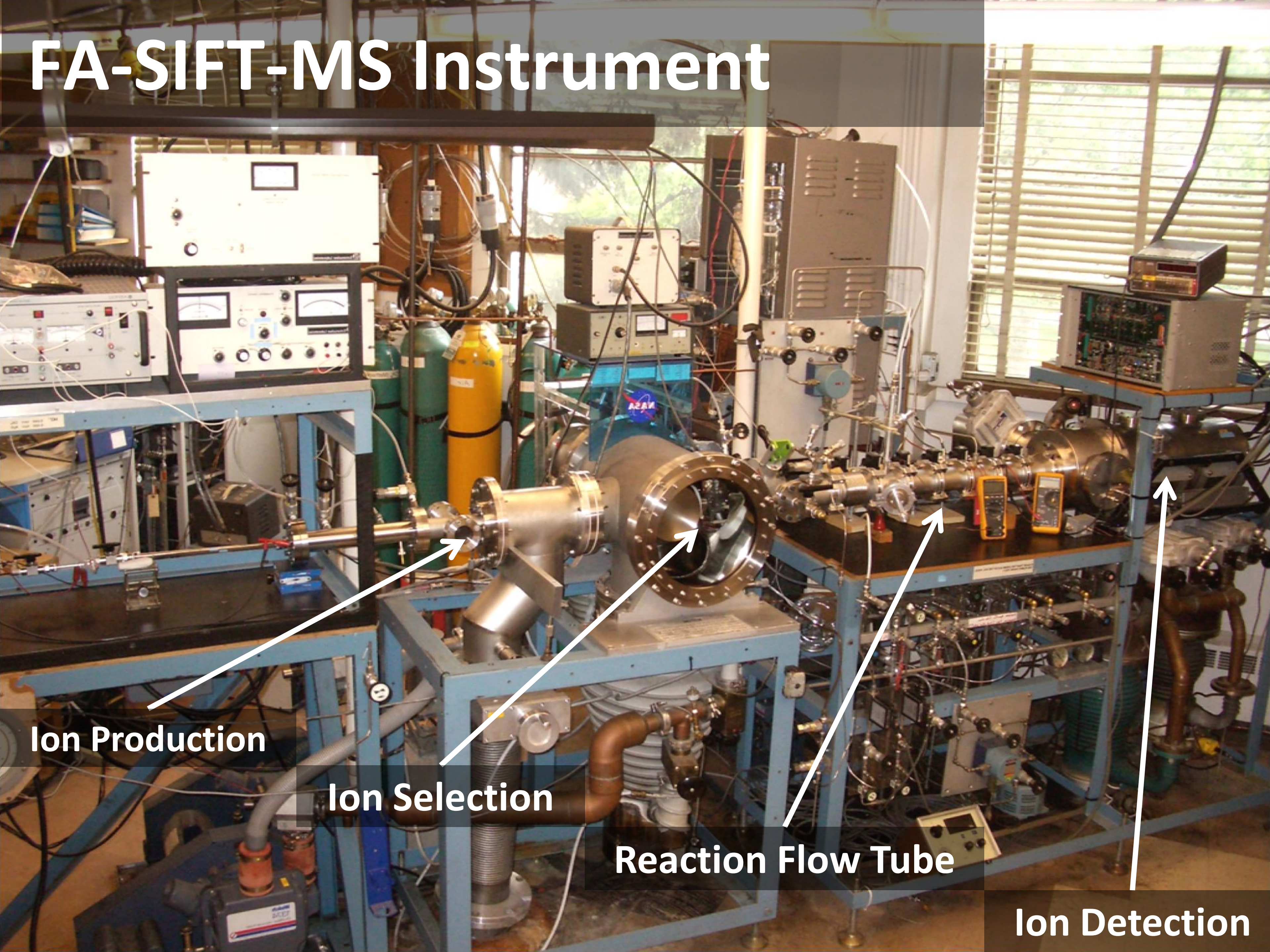
CH	CN	CH^+	OH	NH_3	H_2O	H_2CO
CO	H_2	HCO^+	CH_3OH	HC_3N	HCN	HCOOH
SiO	CS	CH_3CN	OCS	NH_2CHO	H_2S	HNCO
CH_3CHO	CH_3CCH	CH_2NH	H_2CS	HNC	SO	CH_3OCH_3
CH_3NH_2	N_2H^+	C_2H	CH_2CHCN	CH_3CH_2OH	$HCOOCH_3$	SO_2
HDO	SiS	NS	NH_2CN	HCO	C_3N	H_2CCO
C_2	HNO	CH_3CH_2CN	HC_7N	HC_5N	HC_9N	C_4H
NO	OCN^-	CH_3SH	HNCS	C_2H_4	HCS^+	$HOCO^+$
HOC^+	CH_3C_3N	SiH_4	CH_3C_4H	c-SiC_2	C_3H	HCl
C_3O	c-C_3H_2	C_6H	$HCNH^+$	MgNC	C_5H	H_3O^+
C_2S	C_3S	$(CH_3)_2CO$	NaCl	AlCl	KCl	AlF
PN	CH_3NC	C_3	c-C_3H	CH_2CN	HC_2CHO	C_5
SiC	C_2H_2	SiC_4	CO_2	CH_2	CP	l-C_3H_2
HC_2N	NH	CH_4	C_2O	HCCNC	SiN	HNCCC
SO^+	NH_2	CO^+	HC_3NH^+	H_2CN	NaCN	N_2O
MgCN	C_8H	H_3^+	H_2COH^+	C_7H	CH_3COOH	$HC_{11}N$
HF	c-C_2H_4O	LiH	C_5N	SiC_3	SH	CH_3
CH_2OHCHO	SiCN	C_4H_2	C_6H_2	C_6H_6	CH_2CHOH	AlNC
FeO	$HOCH_2CH_2OH$	NH_2CH_2COOH	N_2	CH_2CHCHO	CH_3CH_2CHO	SiNC
HC_4N	$CO(CH_2OH)_2$	CH_2CCHCN	c-H_2C_3O	CH_3CONH_2	CH_3C_6H	CH_2CNH
CF^+	CH_3C_5N	C_6H^-	O_2	C_4H^-	HCP	C_8H^-
CH_2CHCH_3	PO	CNCHO	CCP	C_3N^-	NH_2CH_2CHN	PH_3
C_5N^-	HCNO	AlO	HOCN	C_2H_5OCHO	C_3H_7CN	HSCN
AlOH	CN^-	H_2O^+	OH^+	C_{60}	C_{70}	H_2Cl^+
KCN	SH^+	FeCN				

http://www.astrochymist.org/astrochymist_ism.html

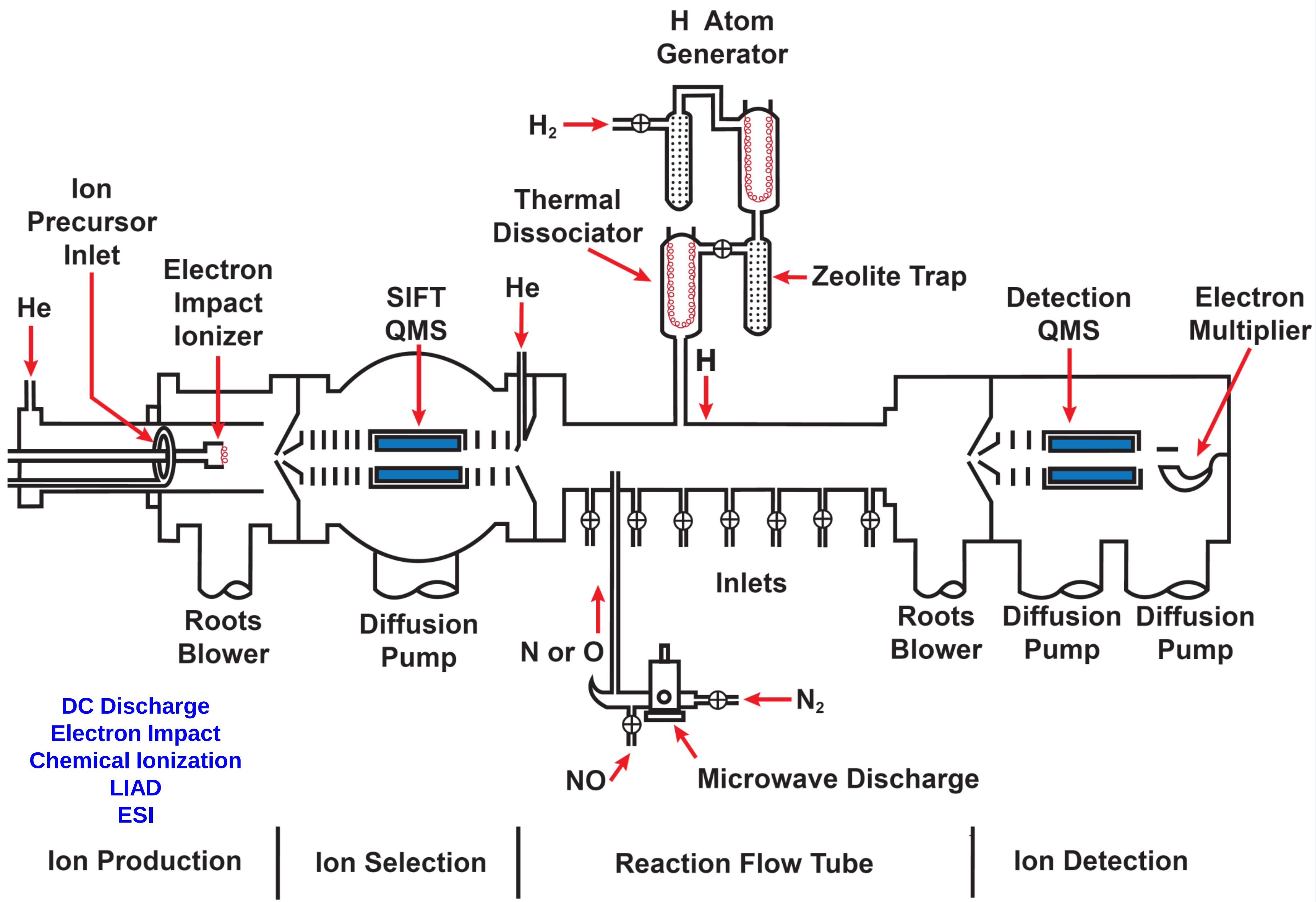
Interstellar Molecular Synthesis



FA-SIFT-MS Instrument



Flowing Afterglow-Selected Ion Flow Tube (FA-SIFT)



Features of the Flowing Afterglow

- Thermal energy
- Energy variability
- Kinetic analysis
- High ion density/sensitivity

Coupling with other techniques

- Chemical versatility

Ionic and neutral reactants

Negative Ion Chemistry

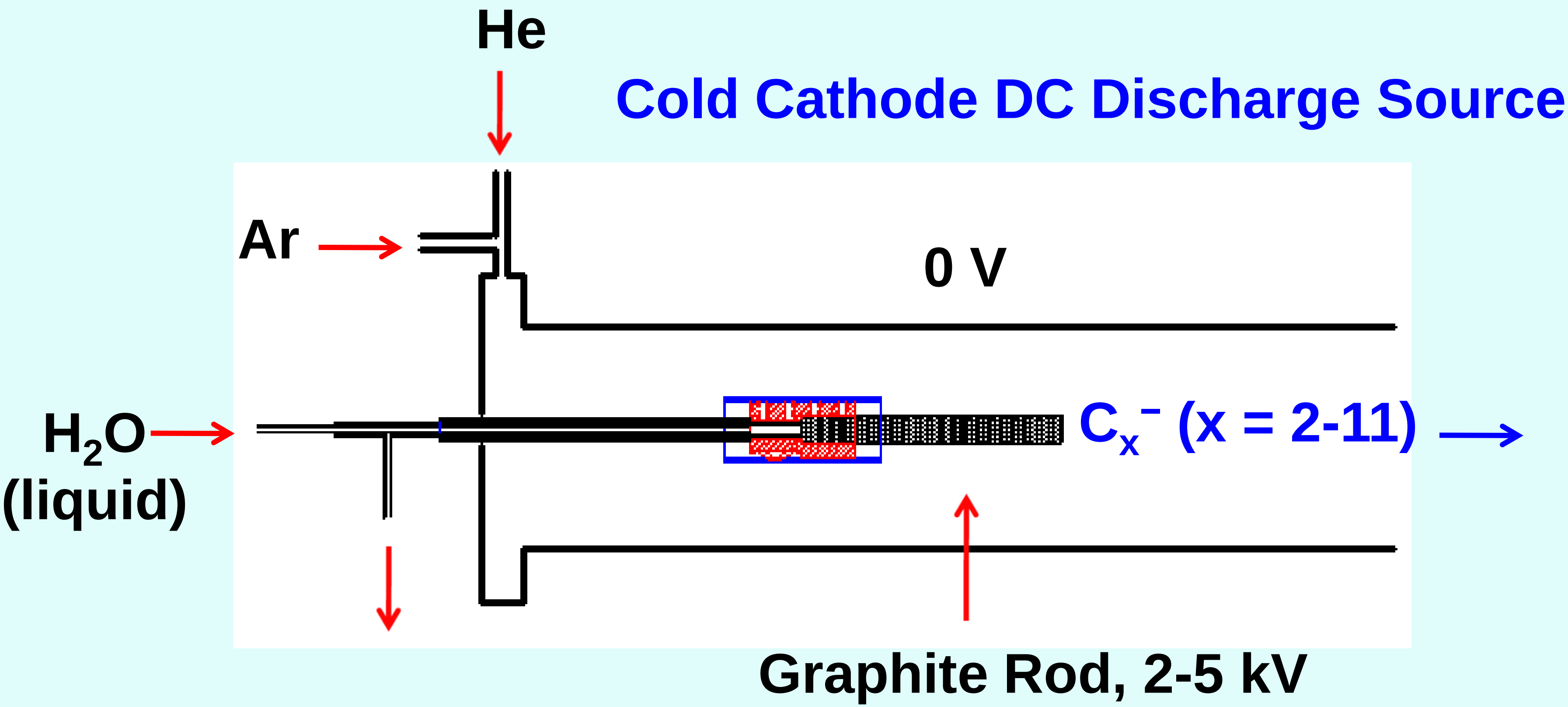
✈ Reactions of Negative Ions

1. Carbon chains (C_x^-)
2. Hydrogenated carbon chains (HC_x^-)
3. Organic anions ($H_wC_xN_yO_z^-$)
4. Nitrogen-containing carbanions ($C_xN_y^-$)
5. Hydride anion (H^-)

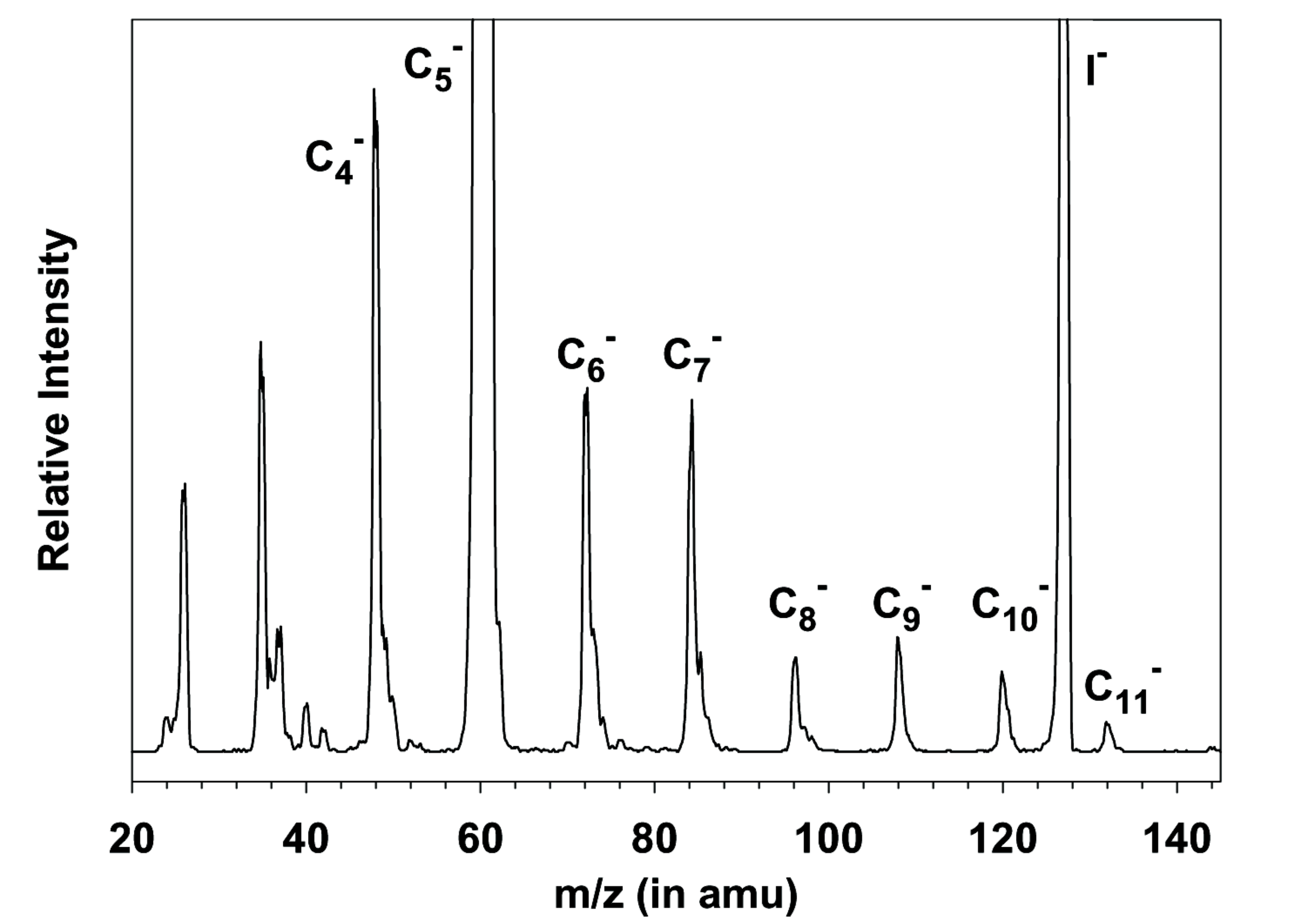
✈ Summary

✈ Future Directions (including PAH$^-$)

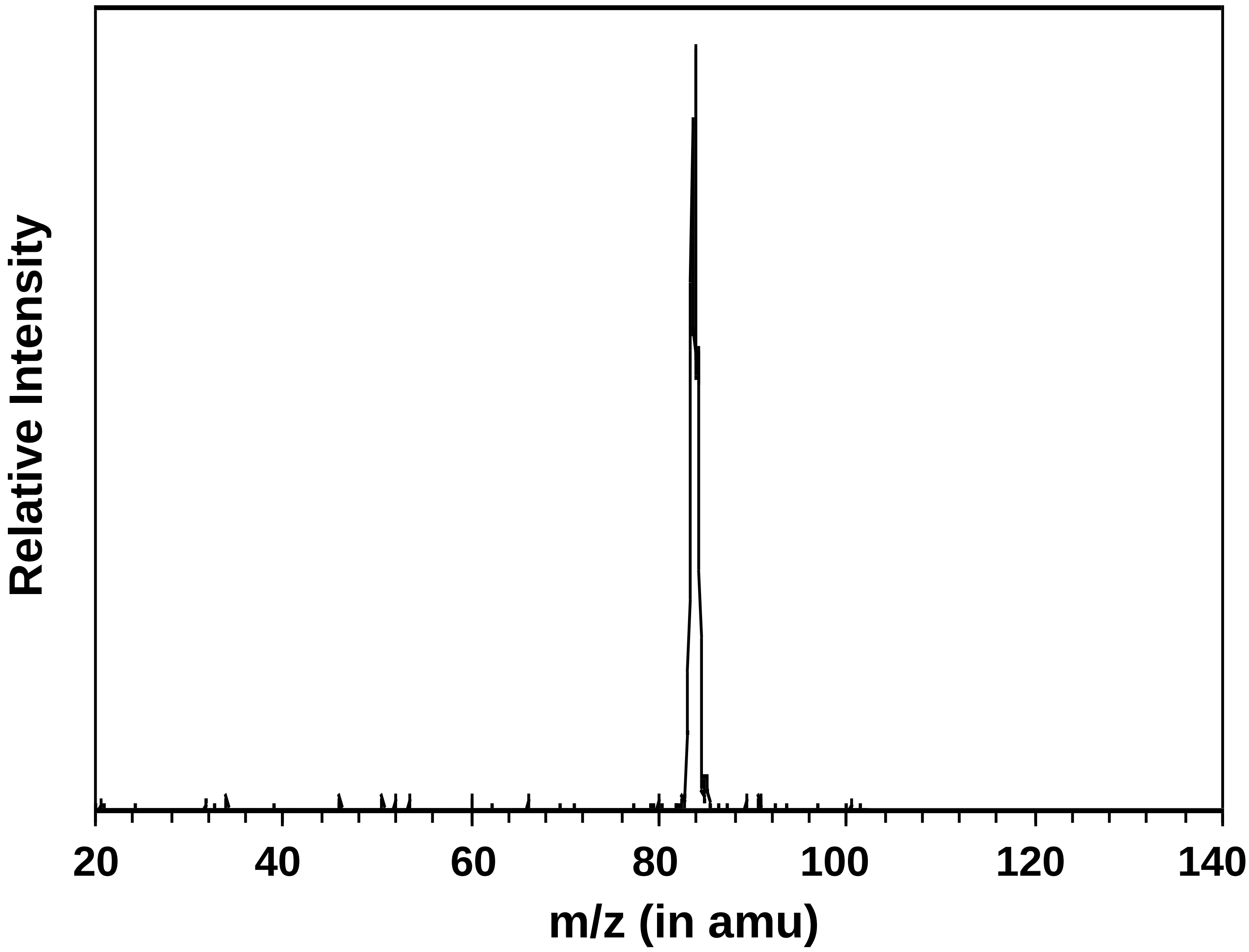
Formation of C_x^-



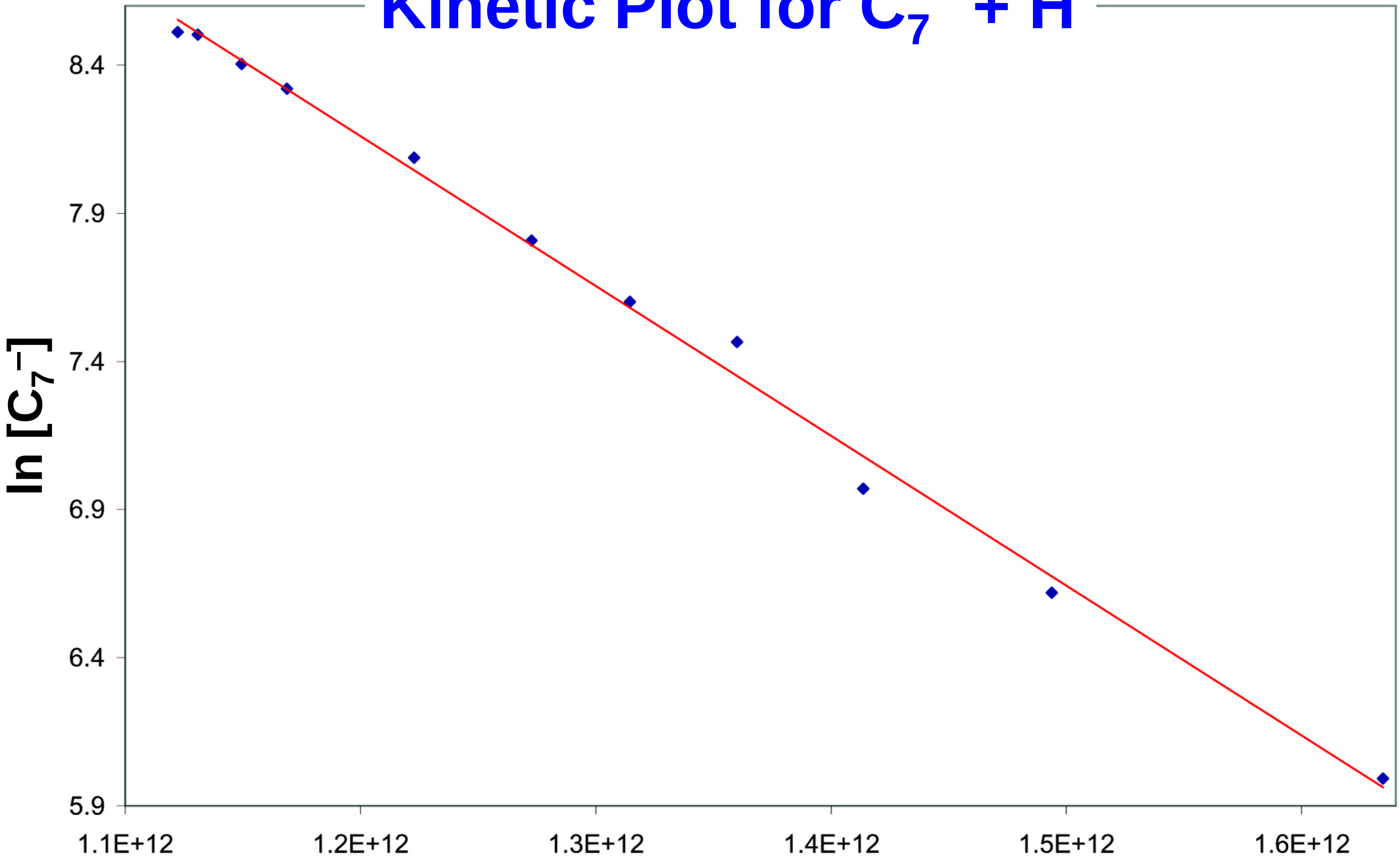
Mass Spectrum for Cold Cathode DC Discharge



Mass Selecting and Injecting C_7^-



Kinetic Plot for C_7^- + H



H Atom Flow (atom/cm^3)

Reactions of Carbon Chain Anions with H Atom

Reactant	Products	BR	k (cm^3/s)
C_4^-			
C_5^-			
C_6^-			
C_7^-			
C_8^-			
C_9^-			
C_{10}^-			

Reactions of Carbon Chain Anions with H Atom

Reactant	Products	BR	k (cm^3/s)
C_4^-	$C_4H + e^-$		6.2×10^{-10}
C_5^-	$C_5H + e^-$		6.2×10^{-10}
C_6^-	$C_6H + e^-$		6.1×10^{-10}
C_7^-			
C_8^-			
C_9^-			
C_{10}^-			

Reactions of Carbon Chain Anions with H Atom

Reactant	Products	BR	k (cm^3/s)
C_4^-	$C_4H + e^-$		6.2×10^{-10}
C_5^-	$C_5H + e^-$		6.2×10^{-10}
C_6^-	$C_6H + e^-$		6.1×10^{-10}
C_7^-	$C_7H + e^-$	0.41	6.9×10^{-10}
	C_7H^-	0.59	
C_8^-	$C_8H + e^-$	0.33	7.3×10^{-10}
	C_8H^-	0.67	
C_9^-	$C_9H + e^-$	0.17	7.2×10^{-10}
	C_9H^-	0.83	
C_{10}^-	$C_{10}H + e^-$	0.24	7.5×10^{-10}
	$C_{10}H^-$	0.76	

Reactions of C_x^- with O Atom

Reactant	Products	k (cm^3/s)
C_2^-		
C_4^-		
C_5^-		
C_6^-		
C_7^-		

Reactions of C_x^- with O Atom

Reactant	Products	k (cm^3/s)
C_2^-	C^- + CO	5.8×10^{-10}
C_4^-	C_3^- + CO	5.6×10^{-10}
C_5^-	C_4^- + CO	6.4×10^{-10}
C_6^-	C_5^- + CO	4.7×10^{-10}
C_7^-	C_6^- + CO	5.3×10^{-10}

Reactions of C_x^- with N Atom

Reactant	Products	k (cm^3/s)
C_2^-		
C_4^-		
C_5^-		
C_6^-		
C_7^-		

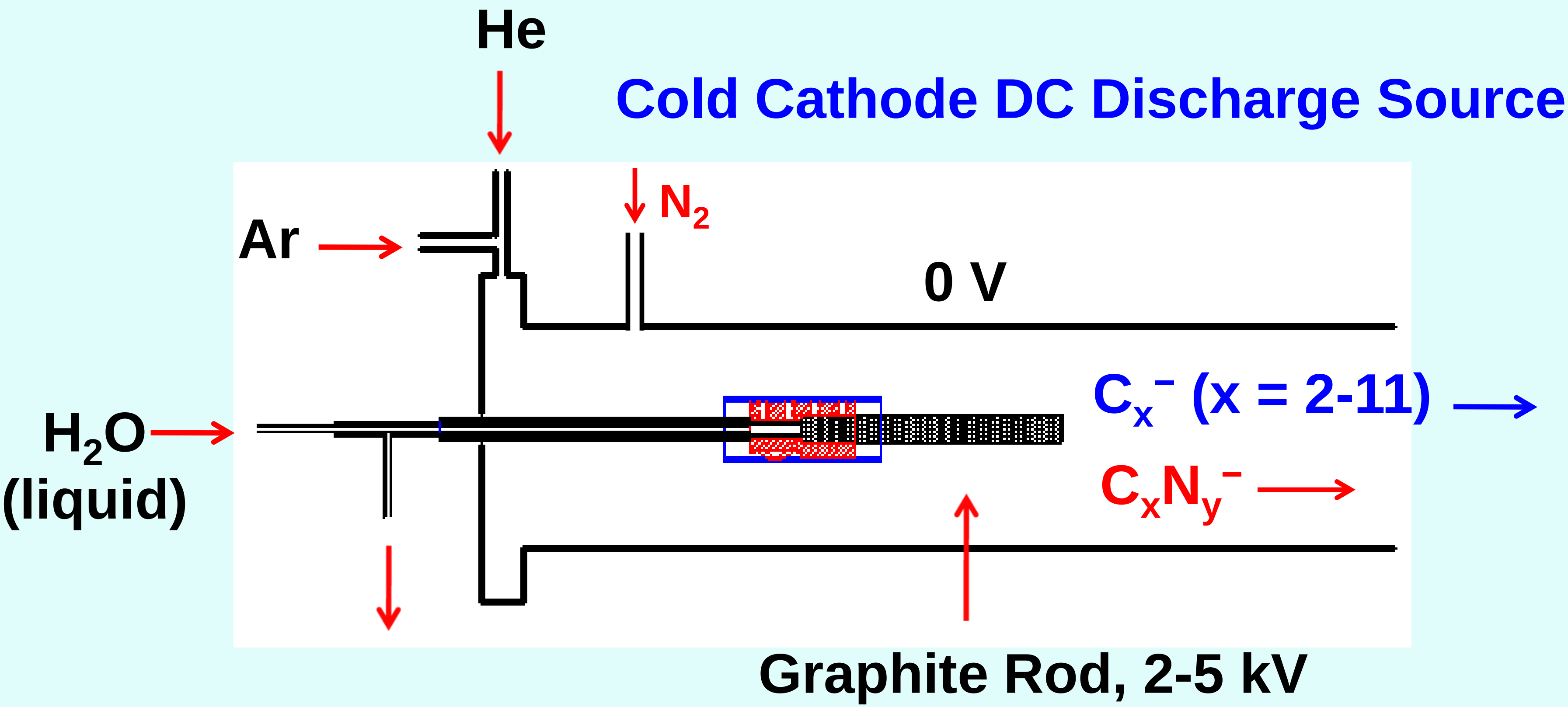
Reactions of C_x^- with N Atom

Reactant	Products	k (cm^3/s)	EA(C_x) eV
C_2^-	CN^- + C	2.3×10^{-10}	3.27
C_4^-	CN^- + C_3 C_3^- + CN	2.0×10^{-10}	3.88
C_5^-	CN^- + C_4 C_4^- + CN C_3N^- + C_2	2.7×10^{-10}	2.84
C_6^-	CN^- + C_5 C_5^- + CN C_3N^- + C_3	1.5×10^{-10}	4.19
C_7^-	CN^- + C_6 C_6^- + CN C_3N^- + C_4 C_5N^- + C_2	2.2×10^{-10}	3.39

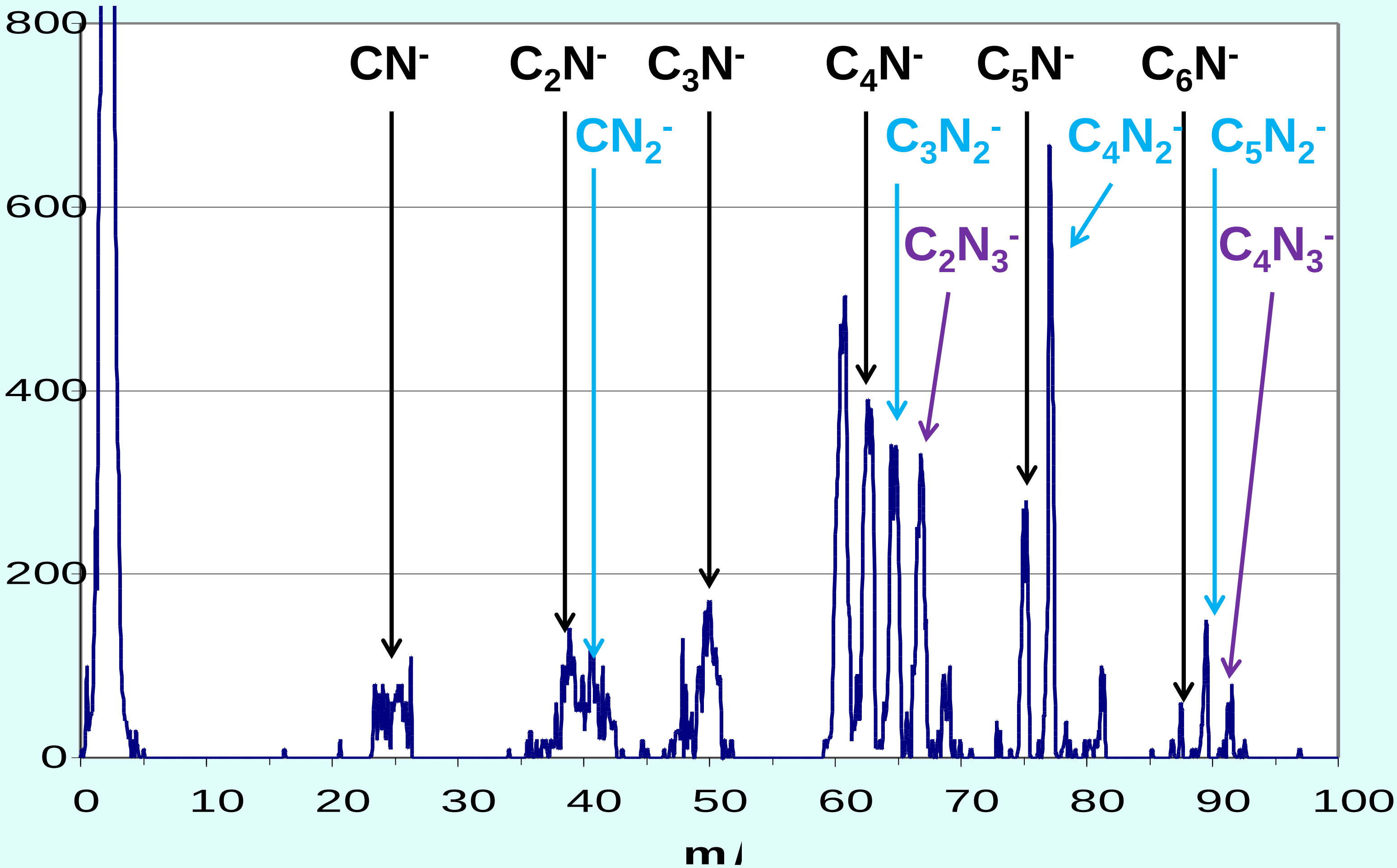
Negative Ion Chemistry

- **Reactions of Negative Ions**
  1. Carbon chains (C_x^-)
  2. Hydrogenated carbon chains (HC_x^-)
  3. Organic anions ($H_wC_xN_yO_z^-$)
  4. Nitrogen-containing carbanions ($C_xN_y^-$)
  5. Hydride anion (H^-)
- **Summary**
- **Future Directions** (including PAH^-)

Formation of $C_xN_y^-$ Ions

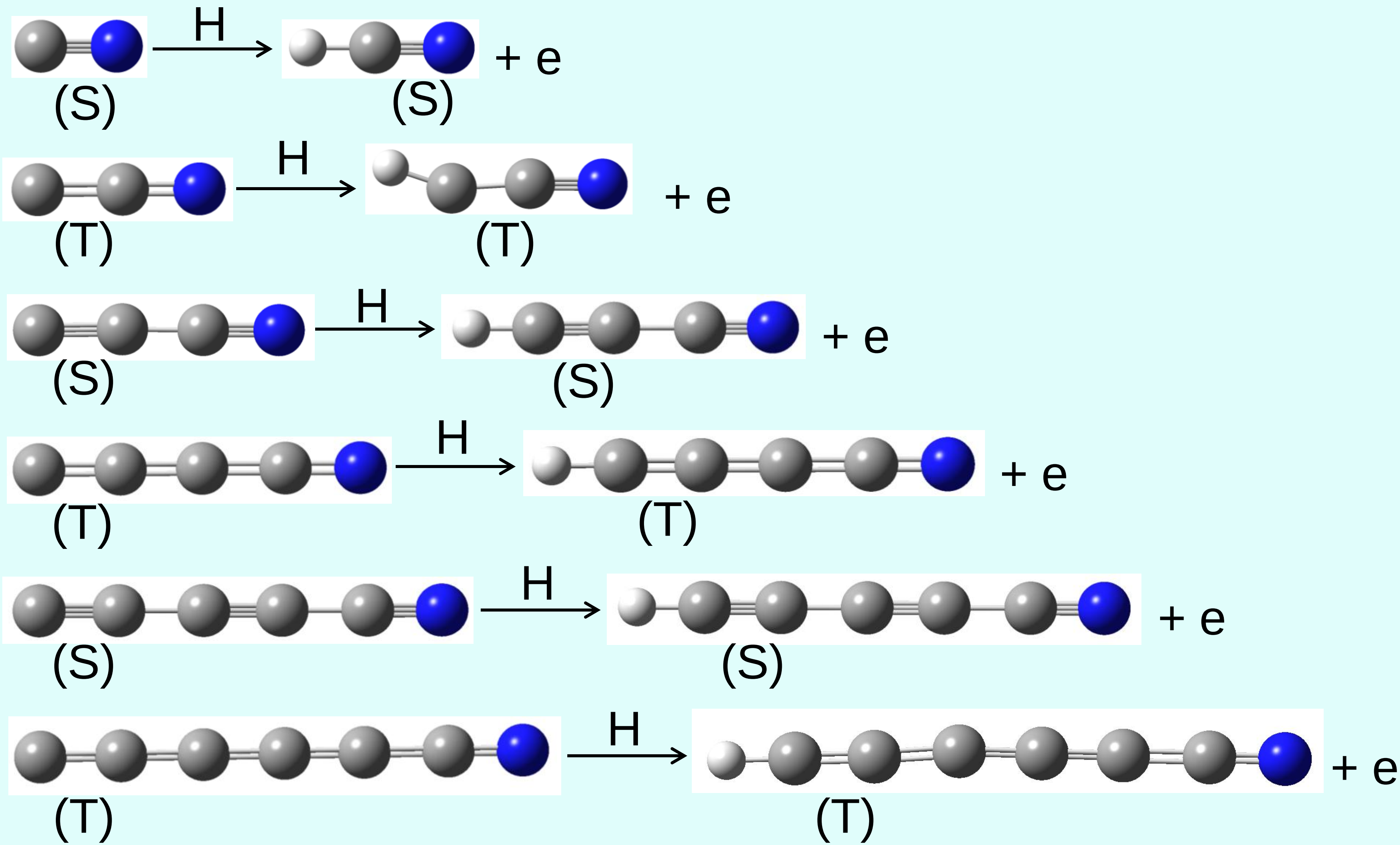


Nitrogen-Containing Carbanions



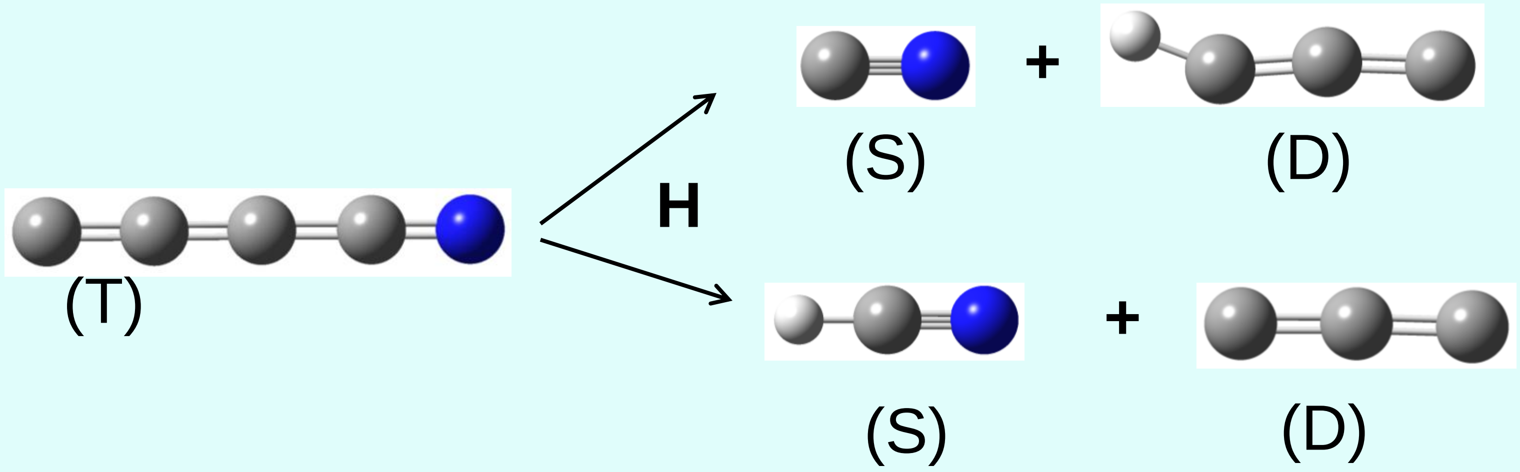
Reactions of $C_xN_y^-$ with H atoms

C_xN^- (x = 1 – 6)

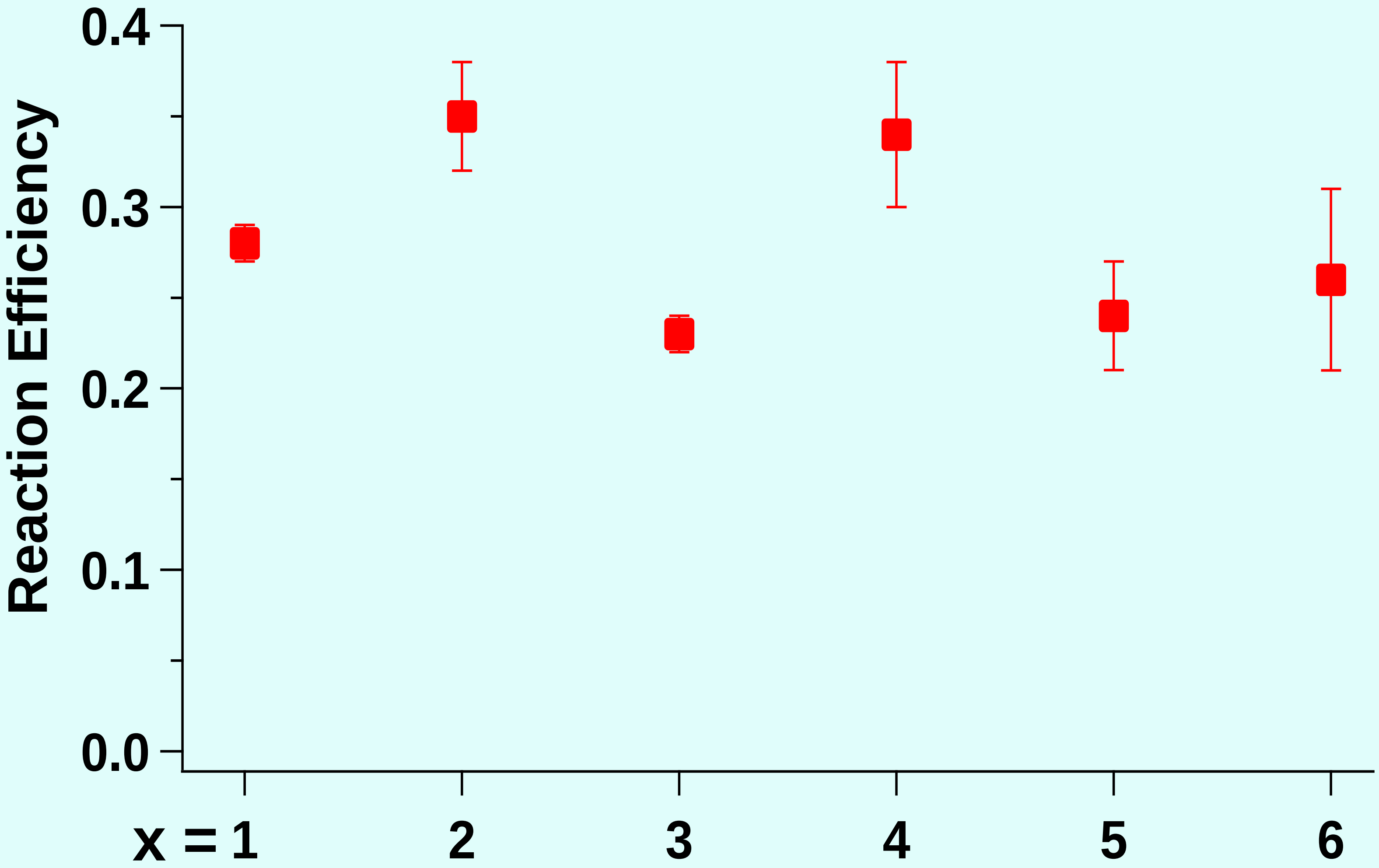


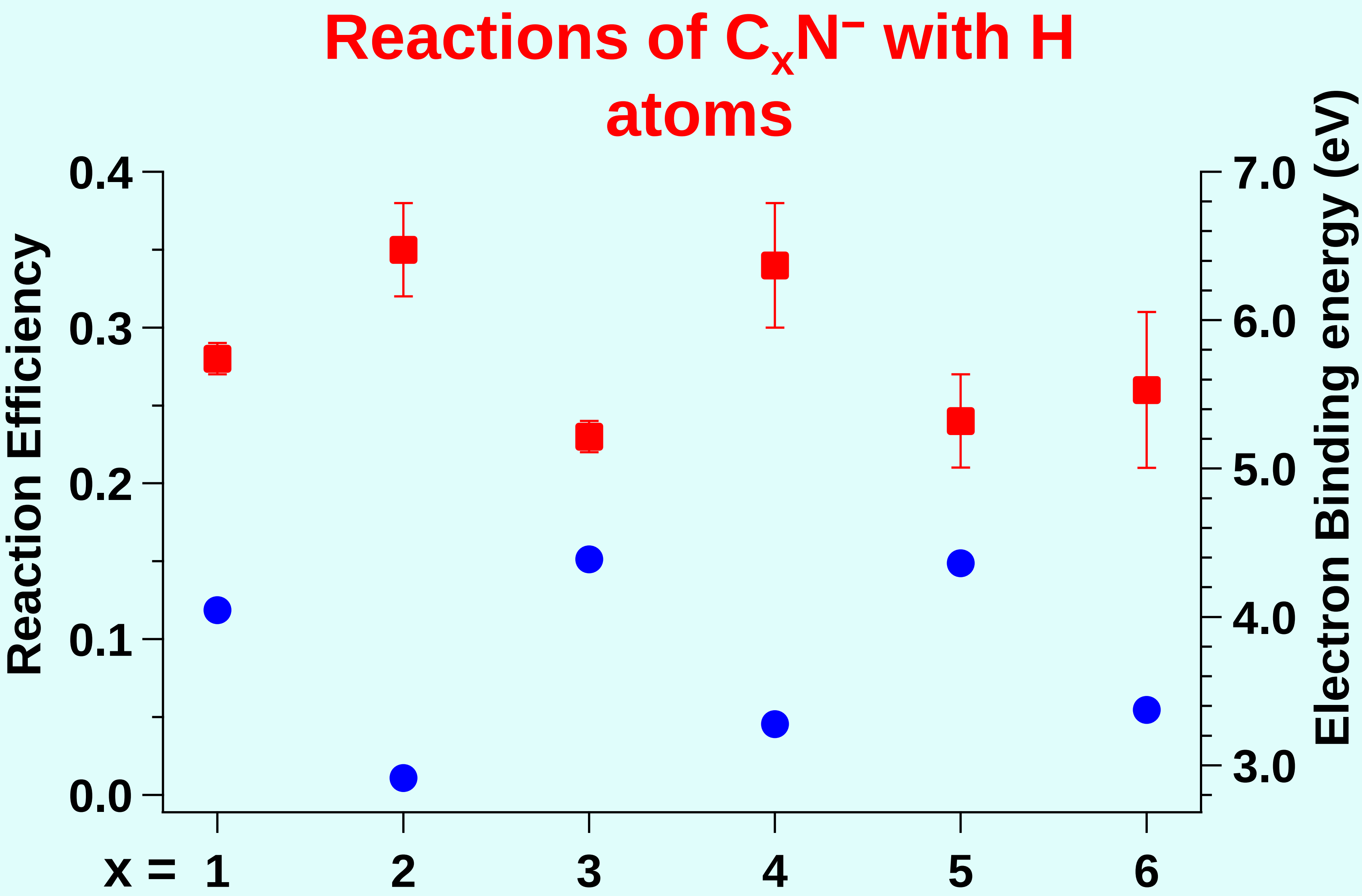
Reactions of $C_xN_y^-$ with H atoms

C_xN^- (x = 1 – 6)



Reactions of C_xN^- with H atoms

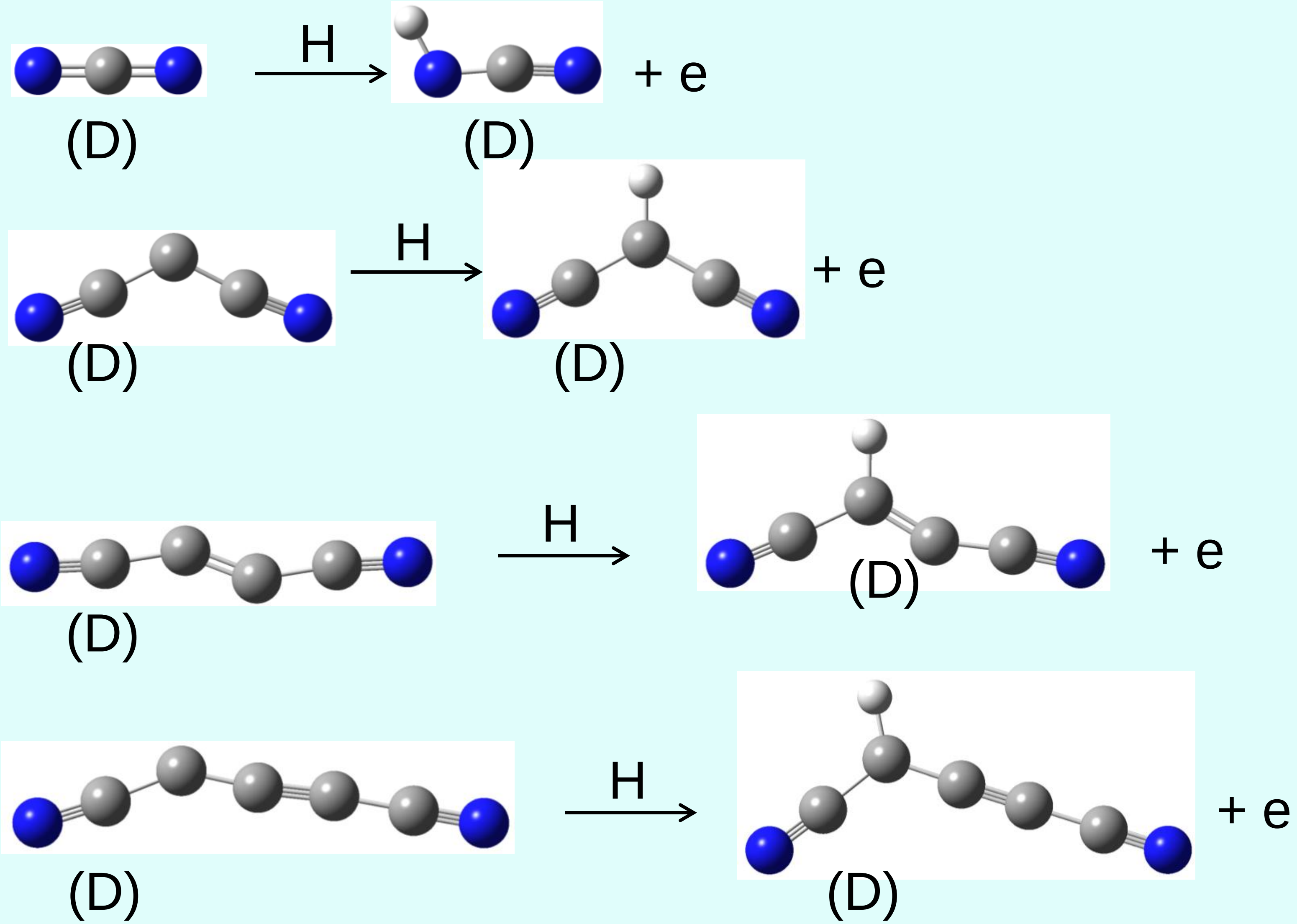




Reactions of C_xN^- with H atoms
Reaction Efficiency
Electron Binding energy (eV)
0.4
0.3
0.2
0.1
0.0
7.0
6.0
5.0
4.0
3.0
x = 1
2
3
4
5
6

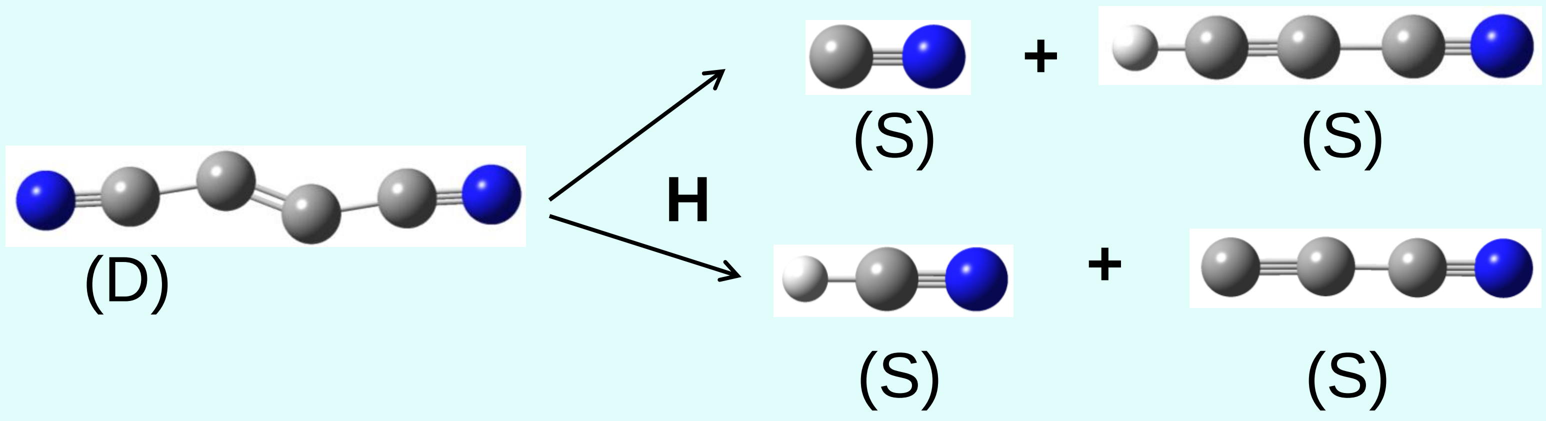
Reactions of $C_xN_y^-$ with H atoms

$C_xN_2^-$ (x = 1, 3 – 5)



Reactions of $C_xN_y^-$ with H atoms

$C_xN_2^-$ (x = 1, 3 – 5)

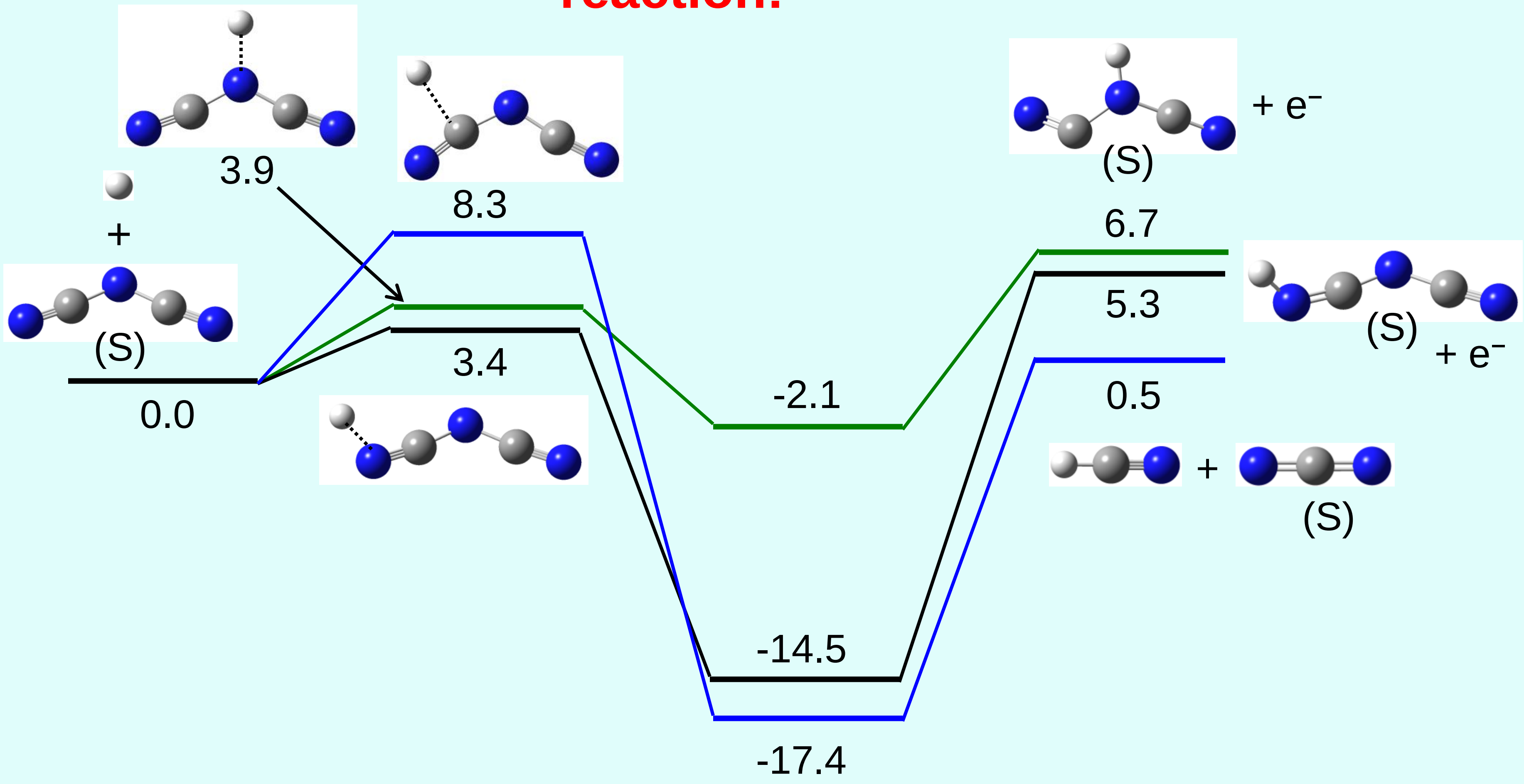


Reactions of $C_xN_3^-$ with H atoms

$C_xN_3^-$ (x = 2, 4)

a) $C_2N_3^-$ + H

No reaction!

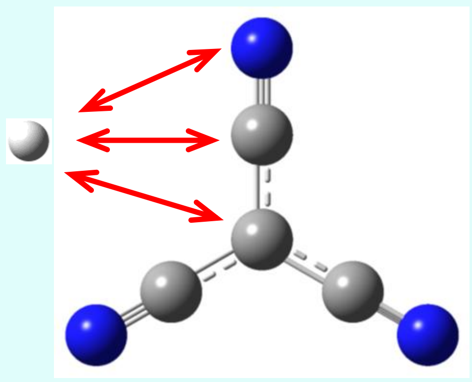


kcal/mol, CCSD(T)/aug-cc-pVDZ//B3LYP/aug-cc-pVTZ

Reactions of $C_xN_y^-$ with H atoms

$C_xN_3^-$ (x = 2, 4)

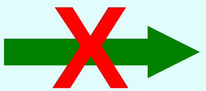
b) $C_4N_3^-$ + H



High energy TS

and

Endothermic pathways



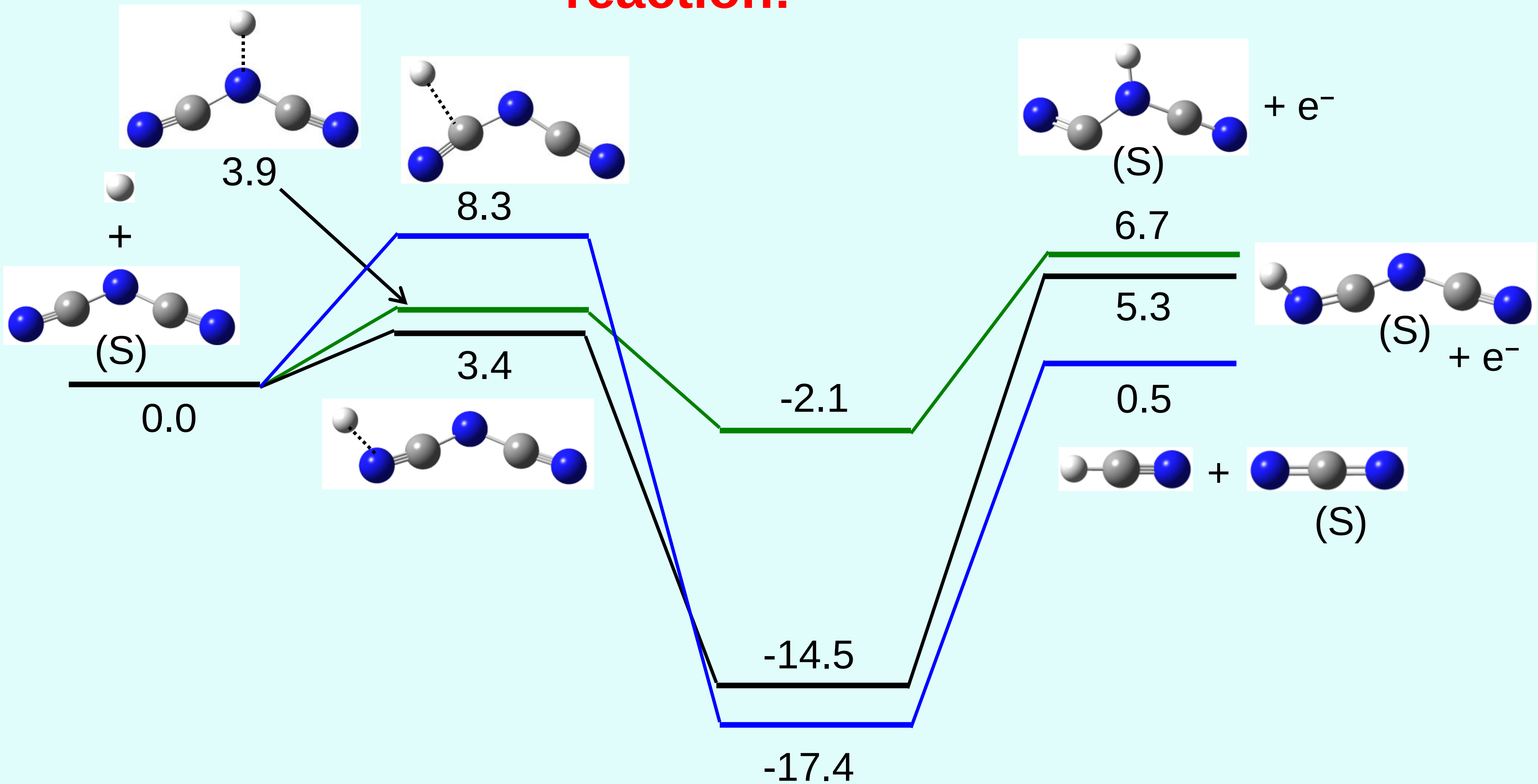
Reaction

Reactions of $C_xN_3^-$ with H atoms

$C_xN_3^-$ (x = 2, 4)

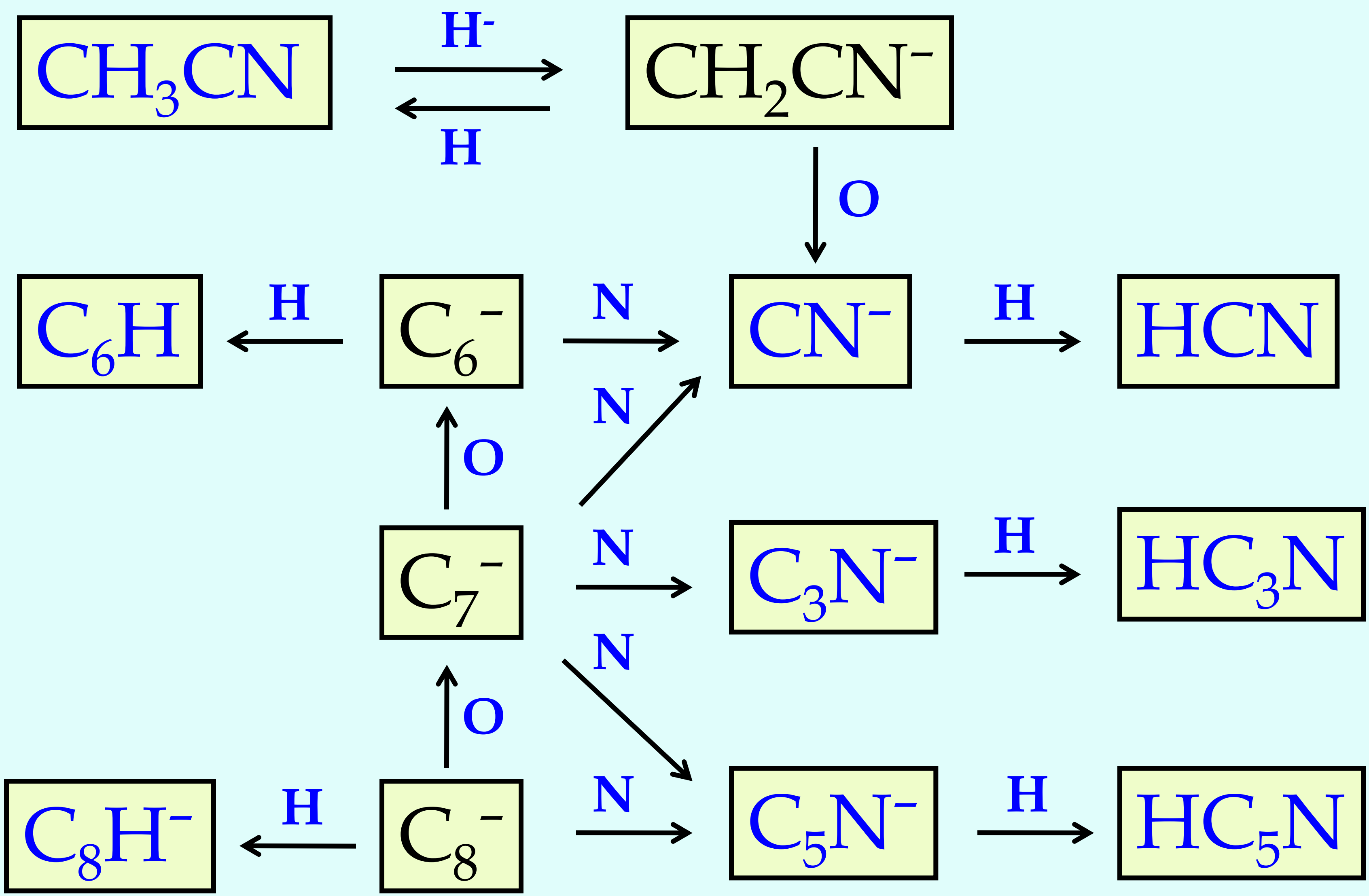
a) $C_2N_3^-$ + H

No reaction!



kcal/mol, CCSD(T)/aug-cc-pVDZ//B3LYP/aug-cc-pVTZ

Interstellar Molecular Synthesis



Summary – General Themes
Reactions of Negative Ions

C_x^-

HC_x^-

Nitriles

Aldehydes

Ketones

Esters

Acids

Alcohols

Glycine

$C_xN_y^-$

- Unreactive with H_2
- React with H by associative detachment
  - Rate often correlates with exothermicity
  - Some fragmentation pathways
  - Alternation in reactivity for x=even or odd
- React with N and O
  - Rich variety of pathways
  - O-atom more rapid than N-atom
- Computations
  - Provide insight to products & energies
  - Importance of spin conservation
- Processes provide routes to neutrals and ions observed in interstellar clouds

Future Directions

- **Quantify product ratios for anion reactions**

  Account for associative detachment and ionic products,
  mass discrimination, secondary reactions
- **Study additional reactions of $C_xN_y^-$**

  With N and O and other reagents
- **Study PAH^- (and larger PAH^+/PAH^-)**

  Develop and implement LIAD and ESI sources

PAH Anions

Inclusion of PAHs in dense clouds

- **PAH^- become the dominant carriers of negative charge**

  Free e^- are replaced by PAH^-

- **Reduces overall ionization fraction**

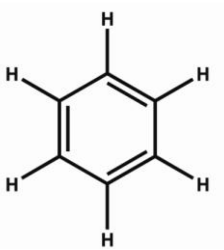
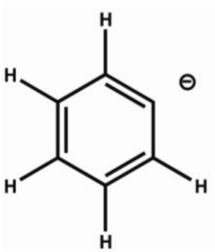
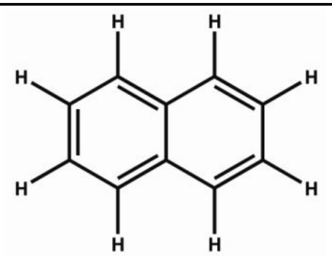
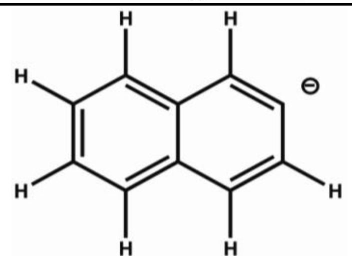
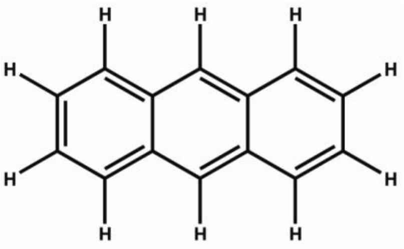
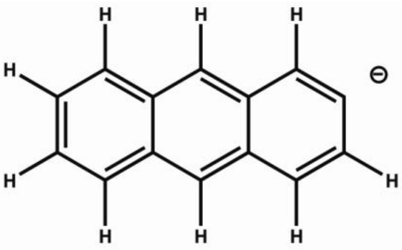
  Neutralization of atomic cations is enhanced

  Wakelam & Herbst, ApJ 680, 371 (2008)

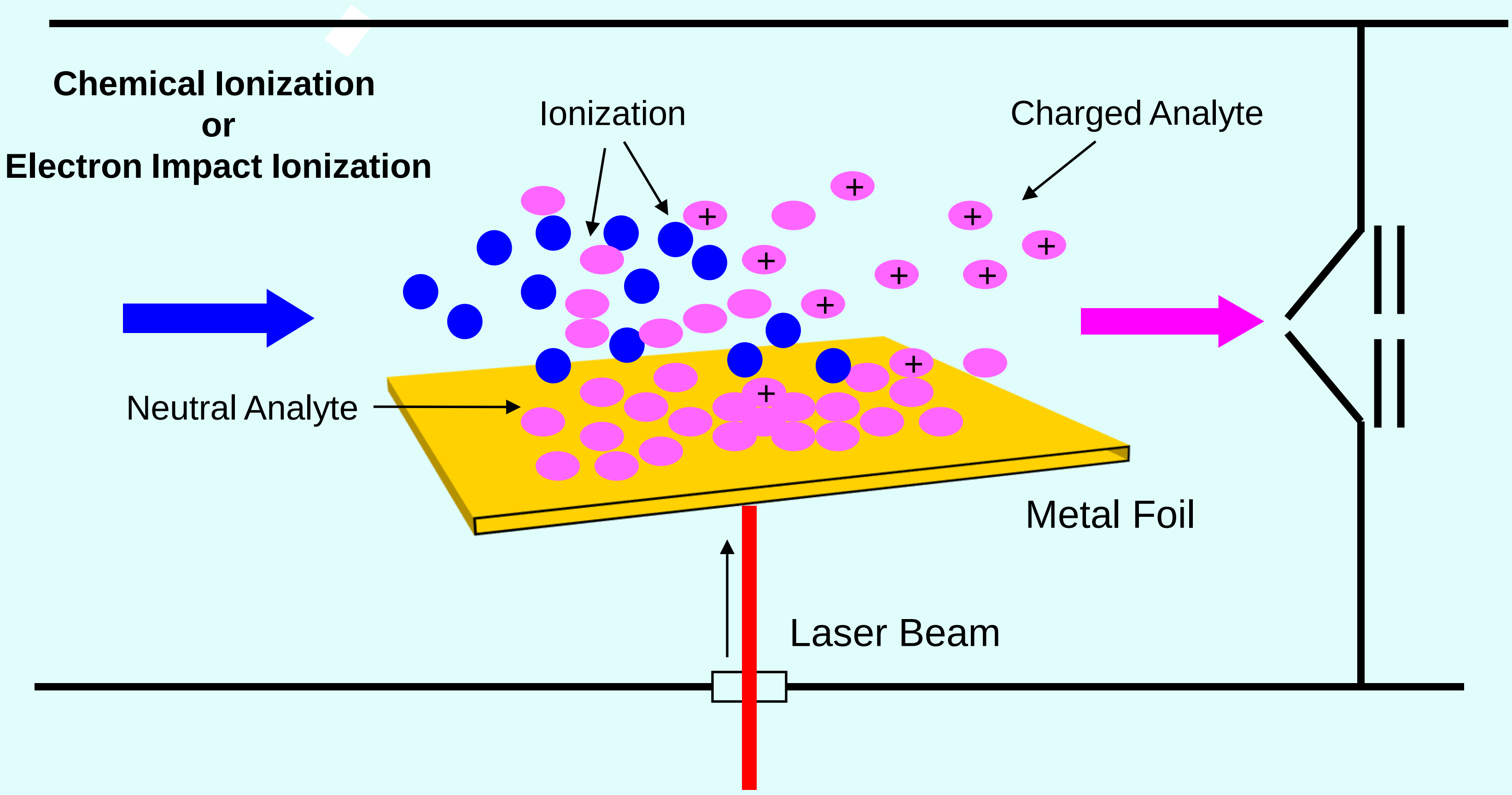
- **Deprotonated PAHs are more stable than the parent radical anions**

  Hammonds & Sarre, Poster 1.34

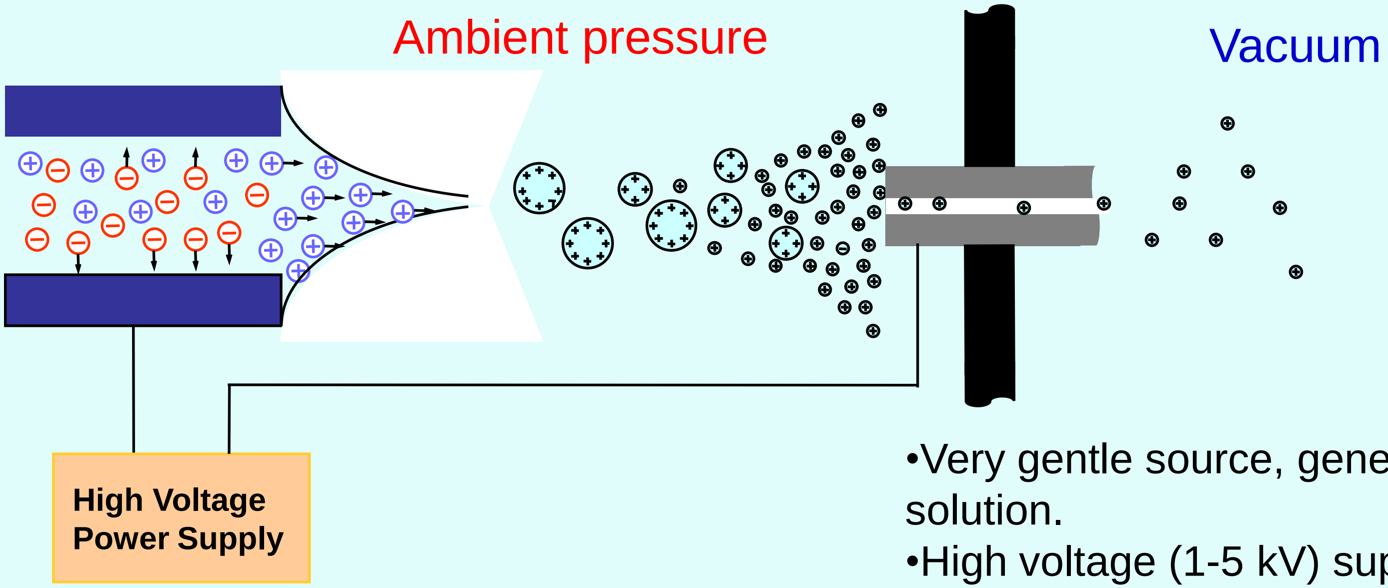
Electron affinities of PAHs and dehydrogenated PAH radicals

M	EA (M) (eV)	$[M\text{-}H]^-$	EA ([M-H]) (eV)
	Unbound		1.096
	Unbound		1.431
	0.60		Predicted > 1.431

Laser Induced Acoustic Desorption

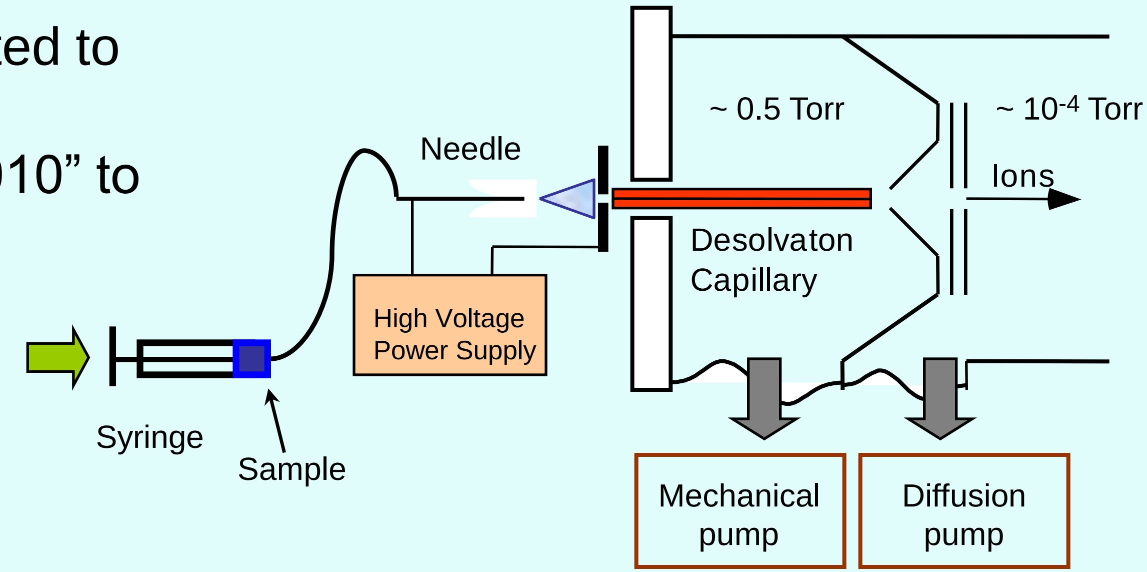


Electrospray Ionization



- Very gentle source, generates ions from solution.
- High voltage (1-5 kV) supplied to needle.

- Desolvation capillary heated to 80-200 ° C.
- Capillaries range from 0.010” to 0.040” in diameter.



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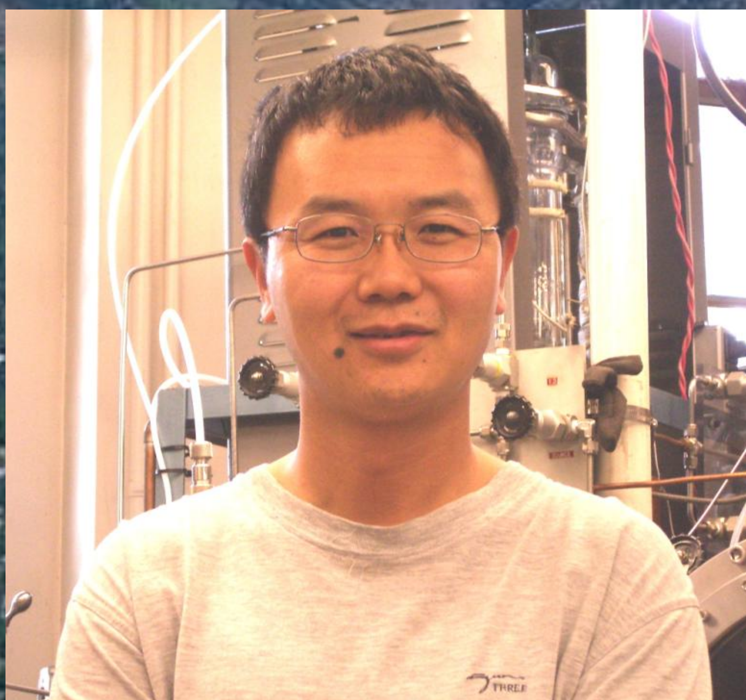
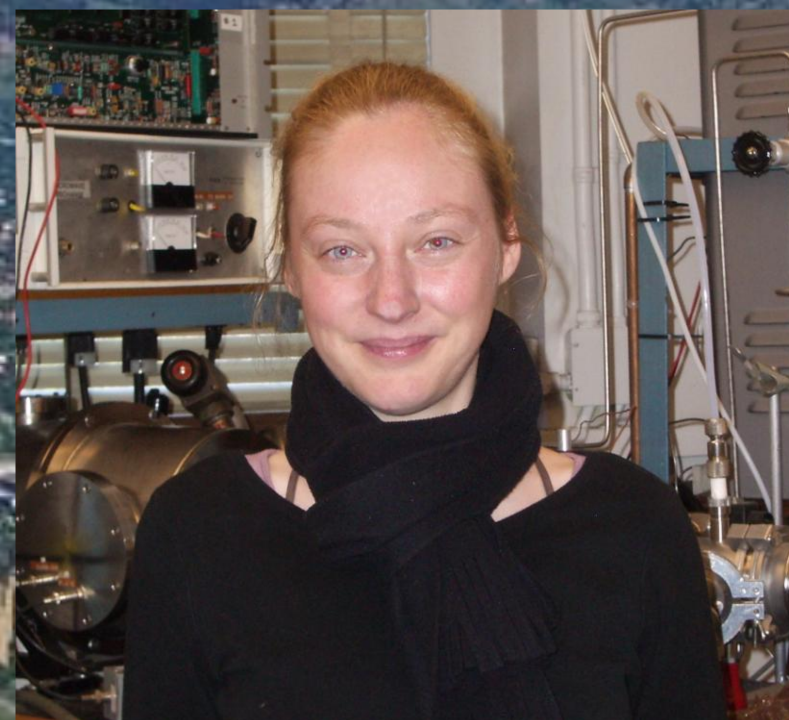
University of Colorado, Boulder



Zhibo Yang



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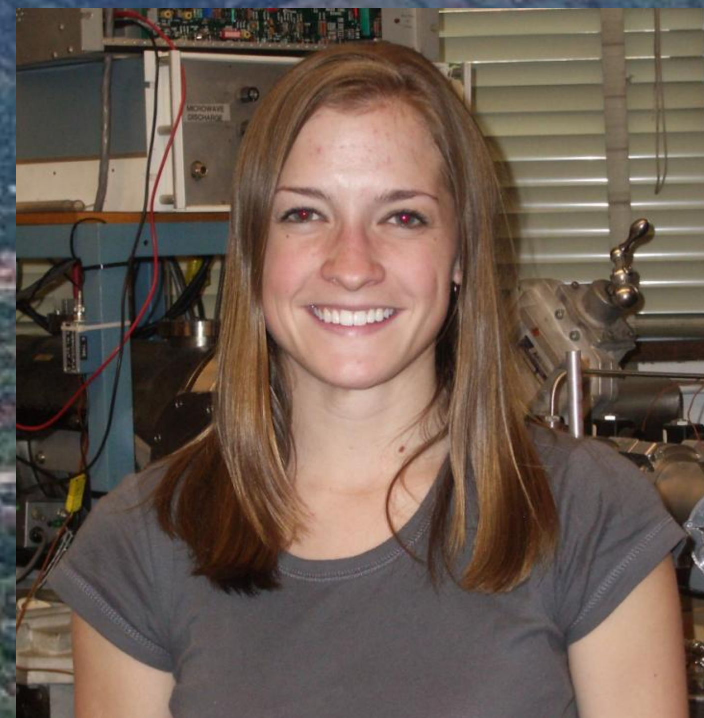
Nick Demarais



Callie Cole

Reactions of Organic Anions with H atoms