Volatiles & Organics in the ISM

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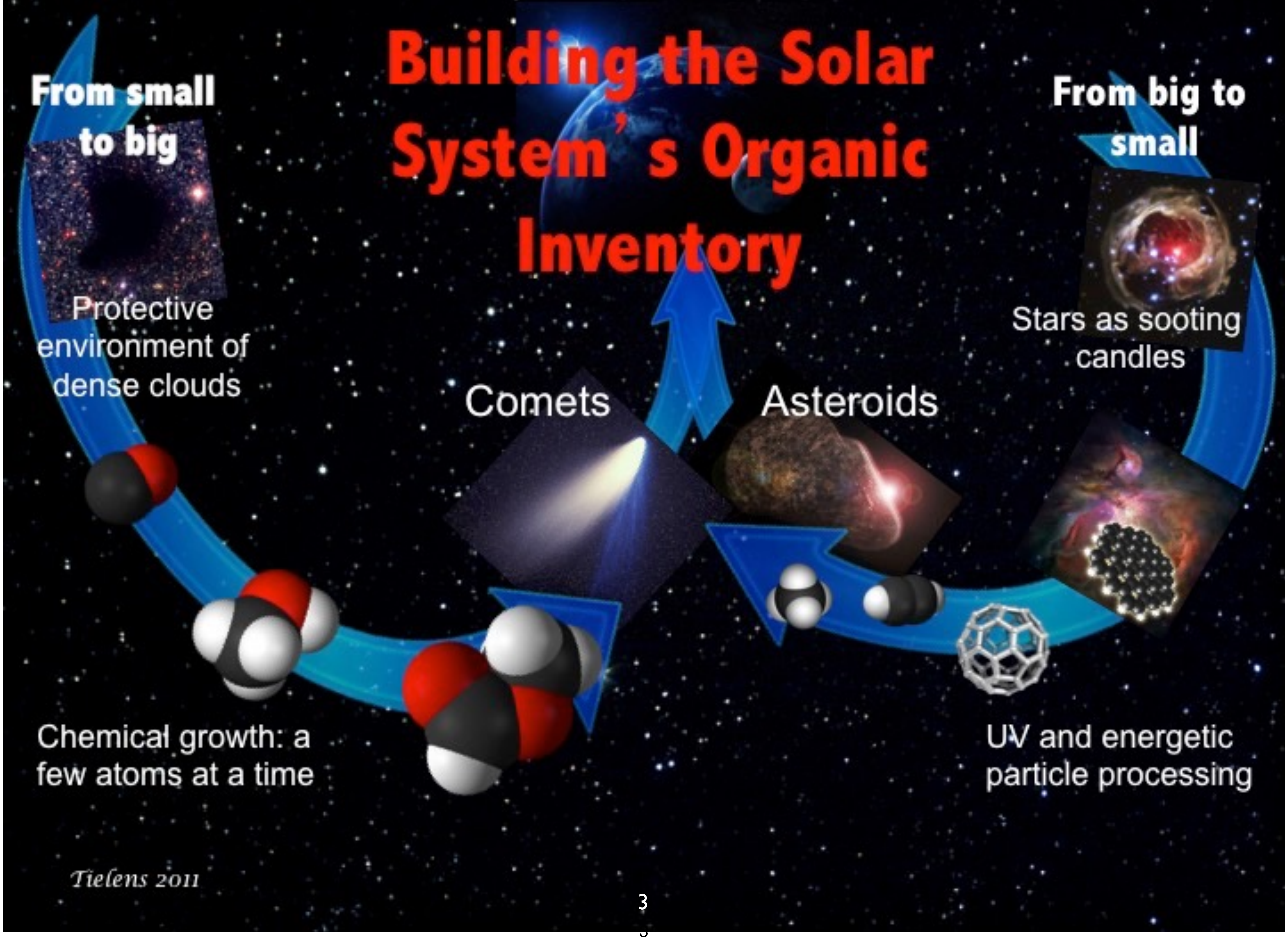
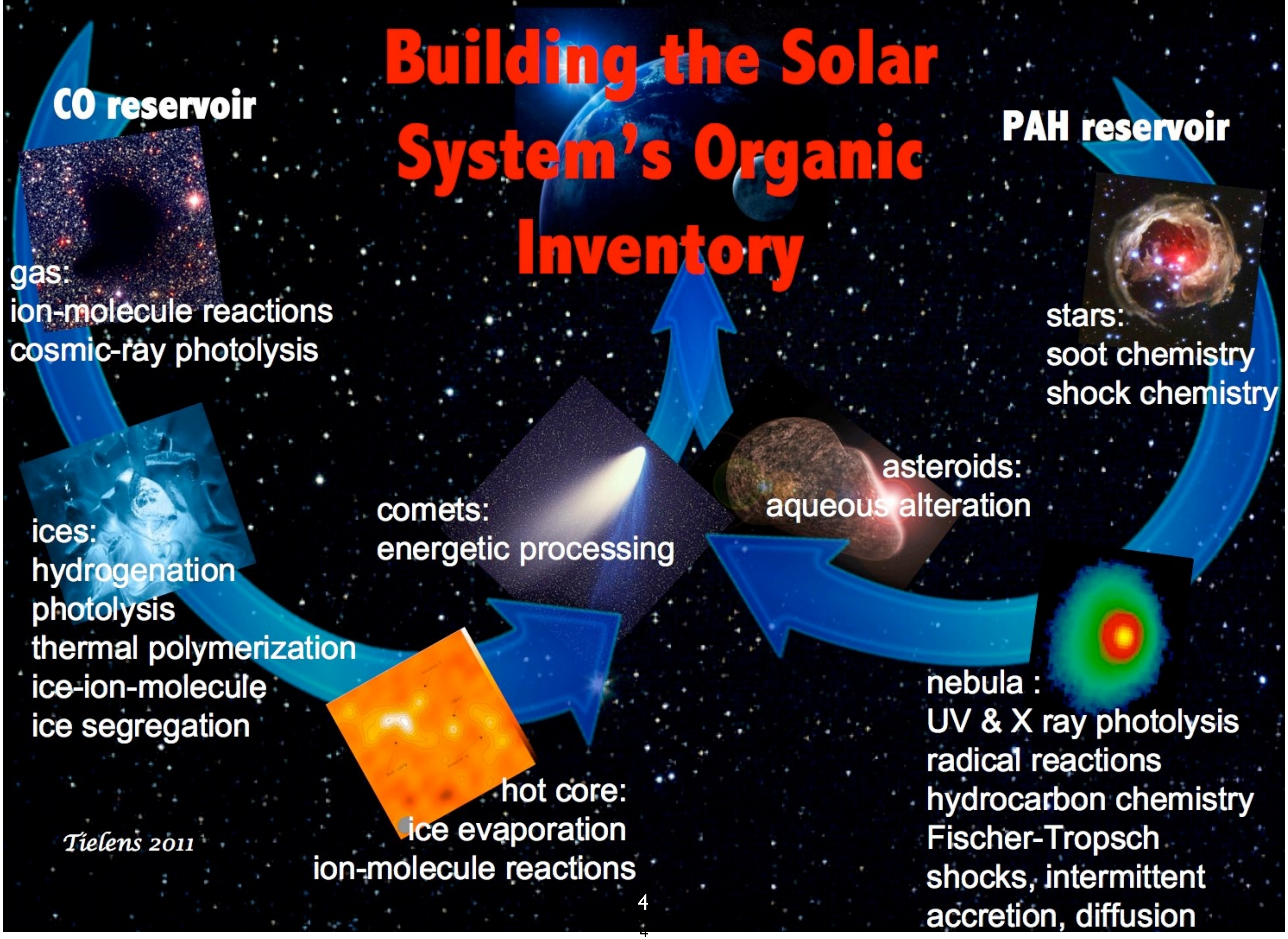
The Grand Challenges of Astrochemistry

- What is the organic inventory of space, in particular in regions of star and planet formation and how does that relate to the prebiotic origin of life ?
- What is the role of molecules in the evolution of the Universe ?
- How can we use molecules to study the Universe ?



Building the Solar System's Organic Inventory
From small to big
From big to small
Protective environment of dense clouds
Comets
Asteroids
Stars as sooting candles
Chemical growth: a few atoms at a time
UV and energetic particle processing
Tielens 2011


Building the Solar System's Organic Inventory
CO reservoir
PAH reservoir
gas:
ion-molecule reactions
cosmic-ray photolysis
stars:
soot chemistry
shock chemistry
asteroids:
aqueous alteration
comets:
energetic processing
ices:
hydrogenation
photolysis
thermal polymerization
ice-ion-molecule
ice segregation
nebula :
UV & X ray photolysis
radical reactions
hydrocarbon chemistry
Fischer-Tropsch
shocks, intermittent
accretion, diffusion
hot core:
ice evaporation
ion-molecule reactions
Tielens 2011

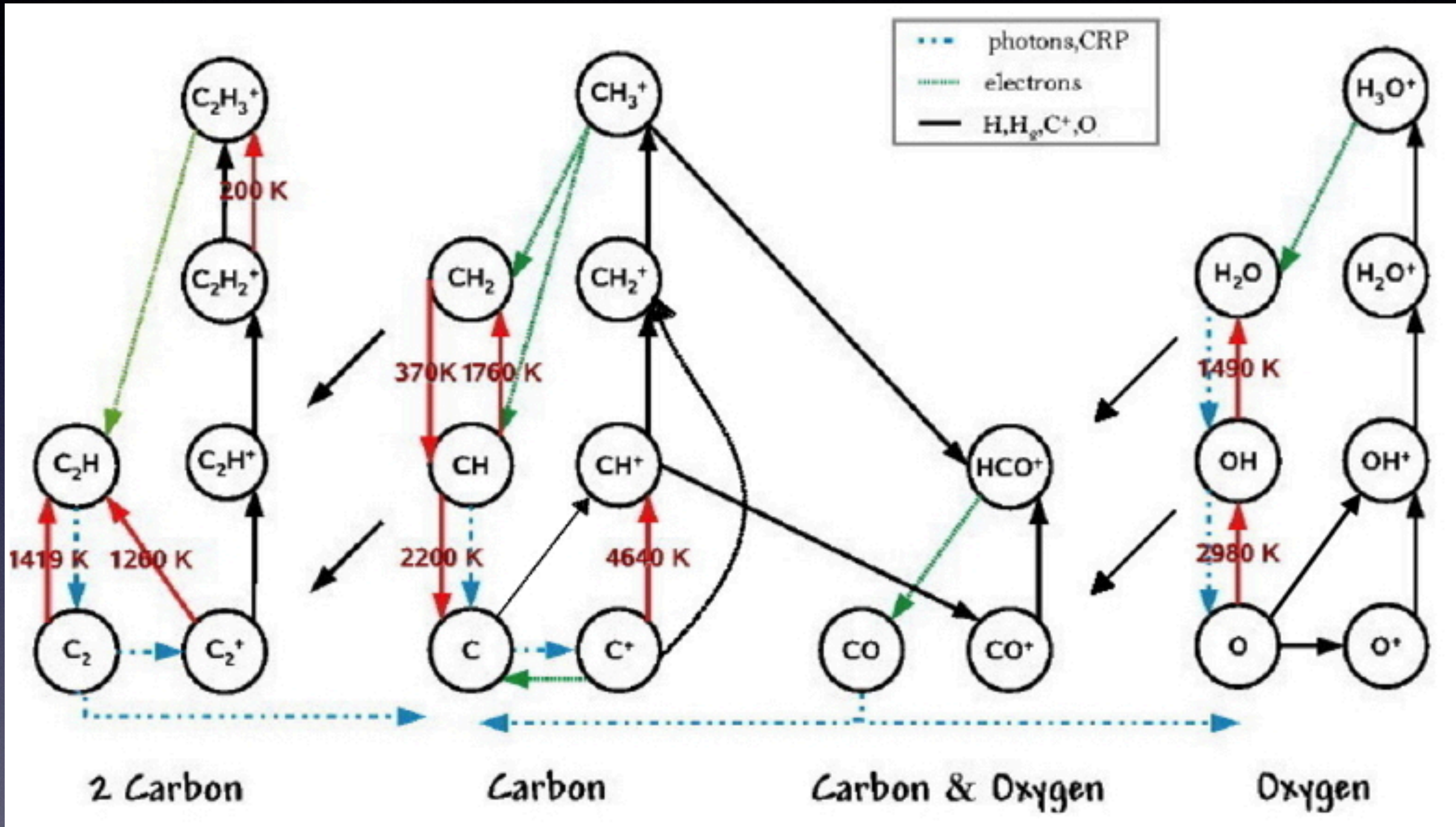
Gas Phase Composition of Dark Clouds

Table 9.2: The composition of dark clouds

Species	TMC1	L134N	Species	TMC1	L134N	Species	TMC1	L134N
H_2	(1)[b]	1						
CO	8 (-5)	8.7 (-5)	CS	4.0 (-9)	1.7 (-9)	CN	3 (-10)	4.8 (-10)
HCO^+	8.0 (-9)	1.2 (-8)	HCS^+	4.0 (-10)		C_3N	6.0 (-10)	< 2.0 (-10)
HOC^+		< 7.0 (-13)	H_2CS	7.0 (-10)		C_5N	3.1 (-11)	
HCO			OCS	2.0 (-9)		HCN	2 (-8)	4.0 (-9)
H_2CO	5.0 (-8)	2.0 (-8)	C_2S	8.0 (-9)		HNC	2 (-8)	6.0 (-9)
CH_3OH	3.0 (-9)	3.0 (-9)	C_3S	1.0 (-9)		$HCNH^+$	2.0 (-9)	
HCOOH	2.0 (-10)	3.0 (-10)	H_2S	5.0 (-10)		HC_3N	1.6 (-8)	
CH3CHO	6.0 (-10)	6.0 (-10)	SO	2.0 (-9)		HC_5N	4.0 (-9)	1.0 (-10)
H_2CCO	6.0 (-10)		SO_2	1.0 (-9)		HC_7N	1.1 (-9)	< 2.0 (-11)
C_2O	6.0(-11)		NH	3 (-10)[g]		HC_9N	4.5 (-10)	
C_3O	1.0(-10)	< 5.0 (-11)	NH_2	6 (-11)[g]		NO	2.7 (-8)	2.0(-8)
O_2	< 7.7 (-8)	<1.7 (-7)	NH_3	2.0 (-8)[g]		C_4H^-	3.0 (-13)	< 4.0 (-12)
OH	3.0 (-7)	7.5 (-8)	N_2	3 (-5)[d]		C_6H^-	1.2 (-11)	
H_2O	< 7.0 (-8)	5.0 (-9)[i]	N_2H^+	4.0 (-10)		C_8H^-	2.1 (-12)	
H_2O_2	2.5 (-11)[m]		C_4H	7.1 (-8)	1.8 (-9)	C_3N^-	< 7.0 (-11)	
CH	1.6 (-8)	1.0 (-8)	C_5H	5.1 (-10)	< 5.0 (-11)	CH_2CN	5.0 (-9)	
C_2	5.0 (-8)		C_6H	7.5 (-10)	< 4.3 (-10)	CH_3CN	6.0 (-10)	
C_2H	6.0 (-8)	2.3 (-9)	C_8H	4.6 (-11)		CH_3C_2H	6.0 (-9)	
c-C_3H	1.0 (-9)	4.3 (-10)	CH_3C_4H	4.0 (-10)		HC_2NC	5.0 (-10)	
l-C_3H	8.4 (-11)	1.3 (-10)	CH_3C_3N	8.0 (-11)		HNC_3	6.0 (-11)	
c-C_3H_2	5.8 (-9)	2.1 (-9))	C_2CHCN	4.0 (-9)		HNC_3	6.0 (-11)	
l-C_3H_2	2.1 (-10)	4.2 (-11)						

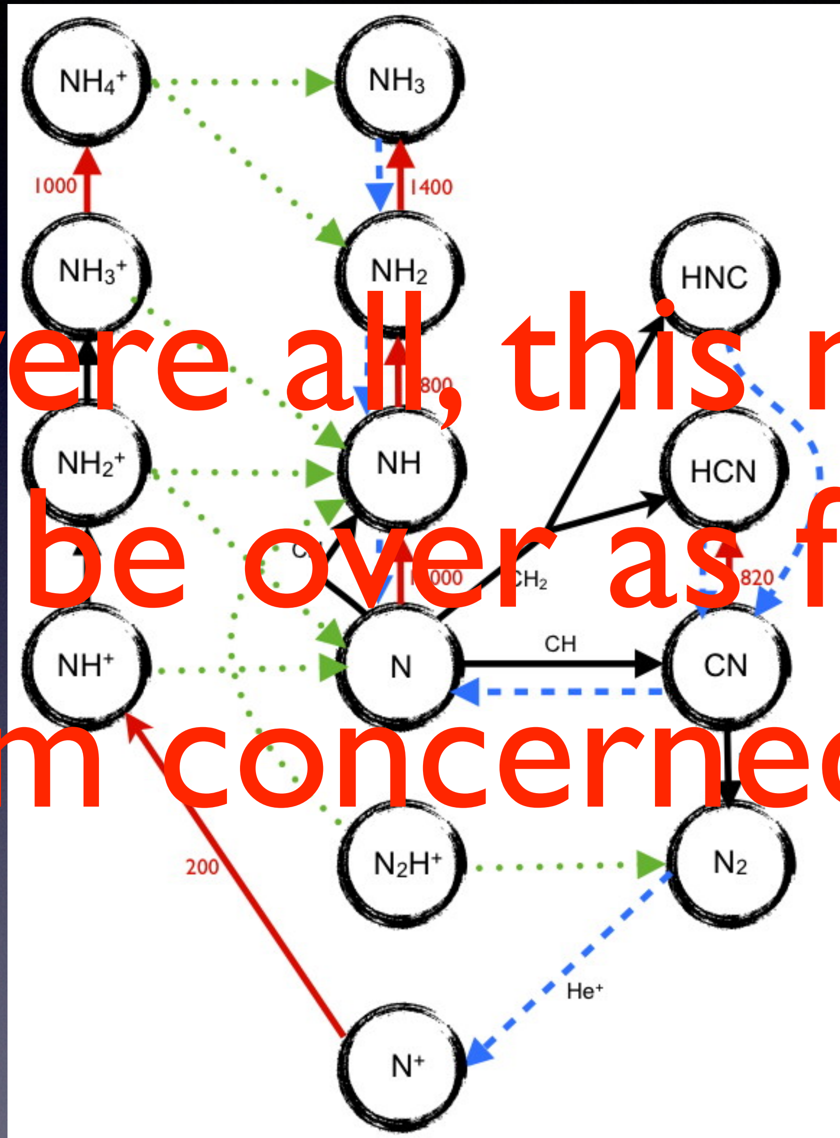
[a] Abundance relative to H_2. Taken from the compilation of [?], which should be consulted for the original references, and the studies by [?, ?, ?]. [m] Measured in the warm carbon chain source L1527 [?]

Kinetics of C & O Chemistry



Ion-molecule chemistry: Carbon forms small hydrocarbon radicals but the route to CH_4 is closed. Hence, carbon burns to CO. A small fraction flows to carbon chains through radical reactions.

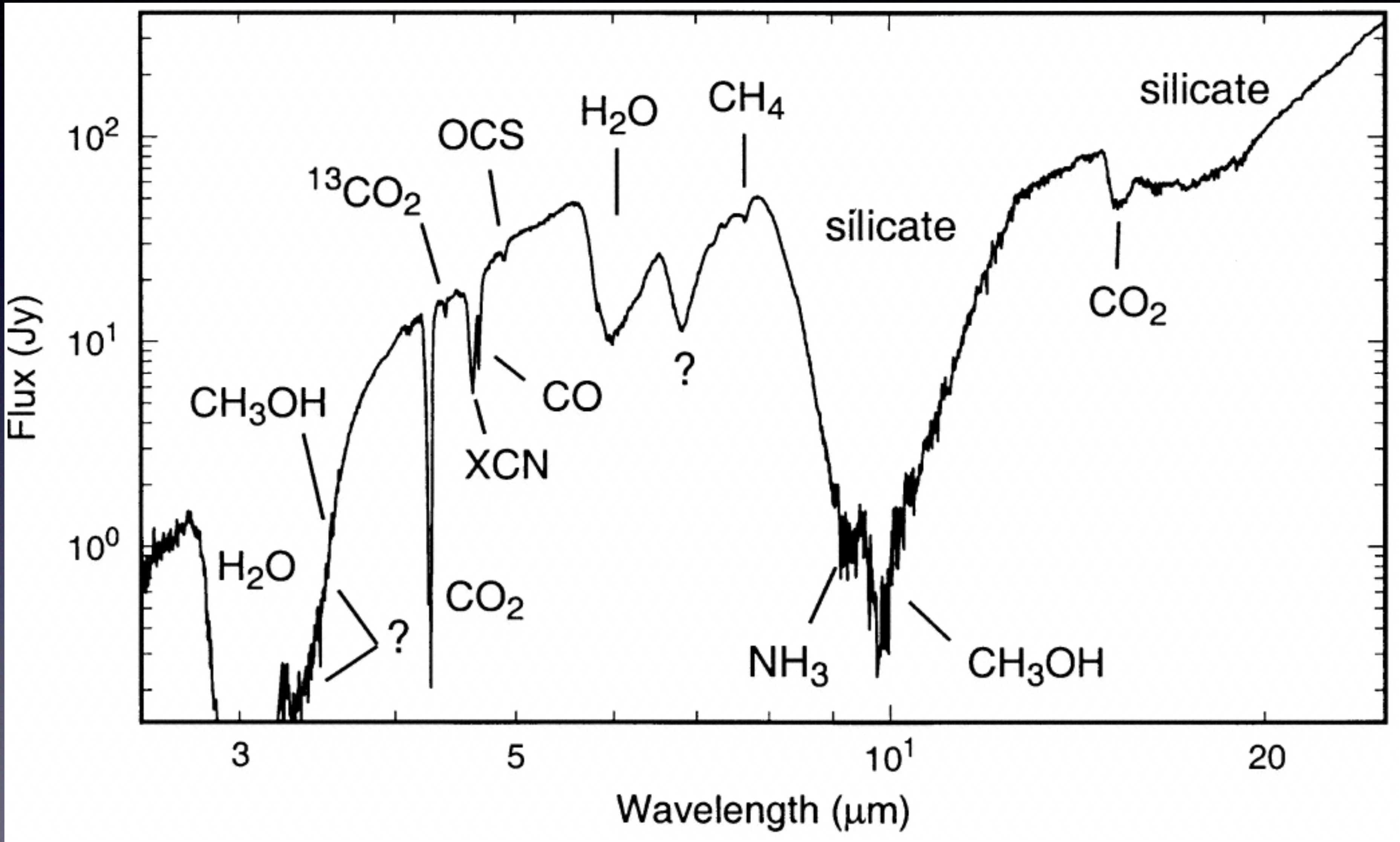
Kinetics of N Chemistry



If this were all, this meeting would be over as far as I am concerned

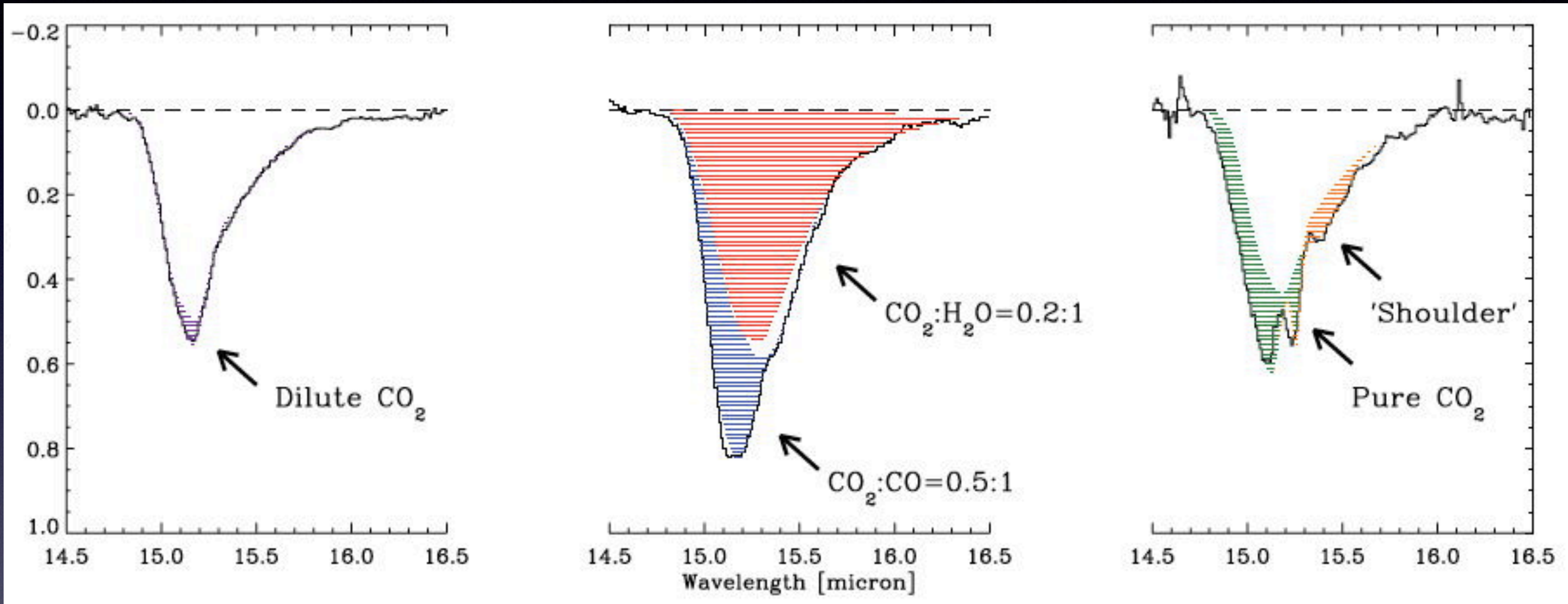
Neutral neutral reactions with radicals flow to N_2. The ion-molecule or neutral routes to NH_3 are really closed.

Interstellar Ices



Gibb et al, 2004, ApJS, 151, 35
Boogert et al 2015, ARAA, 53, 541

(non) Hydrogen-bonding Ice



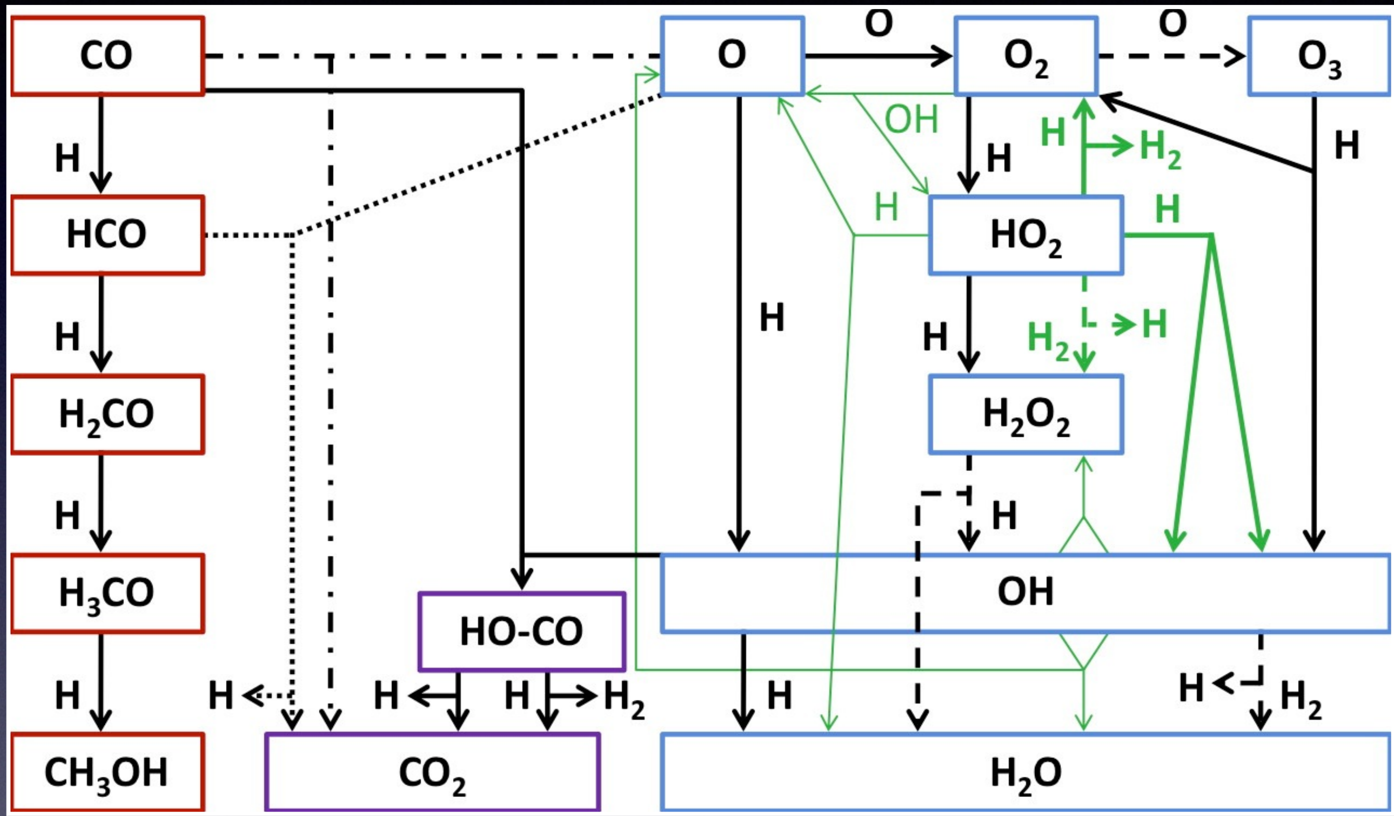
hydrogen bonding ices: H_2O:CO_2:CH_3OH:CO=100:20:10:3
non hydrogen bonding ices: CO_2:CO=3:20

Table 9.4: The composition of interstellar ice[a]

Species	Quiescent cloud[b]	Low mass protostar[c]	High mass protostar[d]	Comets[e]
H_2O	100	100	100	100
CO (total)	25	5	13	23
CO (H_2O-ice)	3	10	6	–
CO (pure CO)	22	4	3	–
CO_2 (total)	21	19	13	6
CO_2 (H_2O-ice)	18	(10)[f]	9	–
CO_2 (CO-mix)	3	(10)[f]	2	–
CO_2-CH_3OH complex	–	–	1.2	–
CO_2 (pure crystalline)	–	–	1.0	–
CH_4	< 3	< 1.4	1.5	0.6
CH_3OH	10	30	18	2.4
H_2CO	–	–	6	1.1
HCOOH	< 1	< 1	7	0.09
OCS	< 0.2	< 0.1	0.2	0.4
NH_3	< 8	< 11	15	0.7
OCN^-	< 0.5	< 0.2	3.5	0.1[g]

Grain Surface Reactions

- Hydrogenation & oxidation
- Tunneling
- Deuteration



$H_2CO/CH_3OH/CO_2/CO$

H_2O

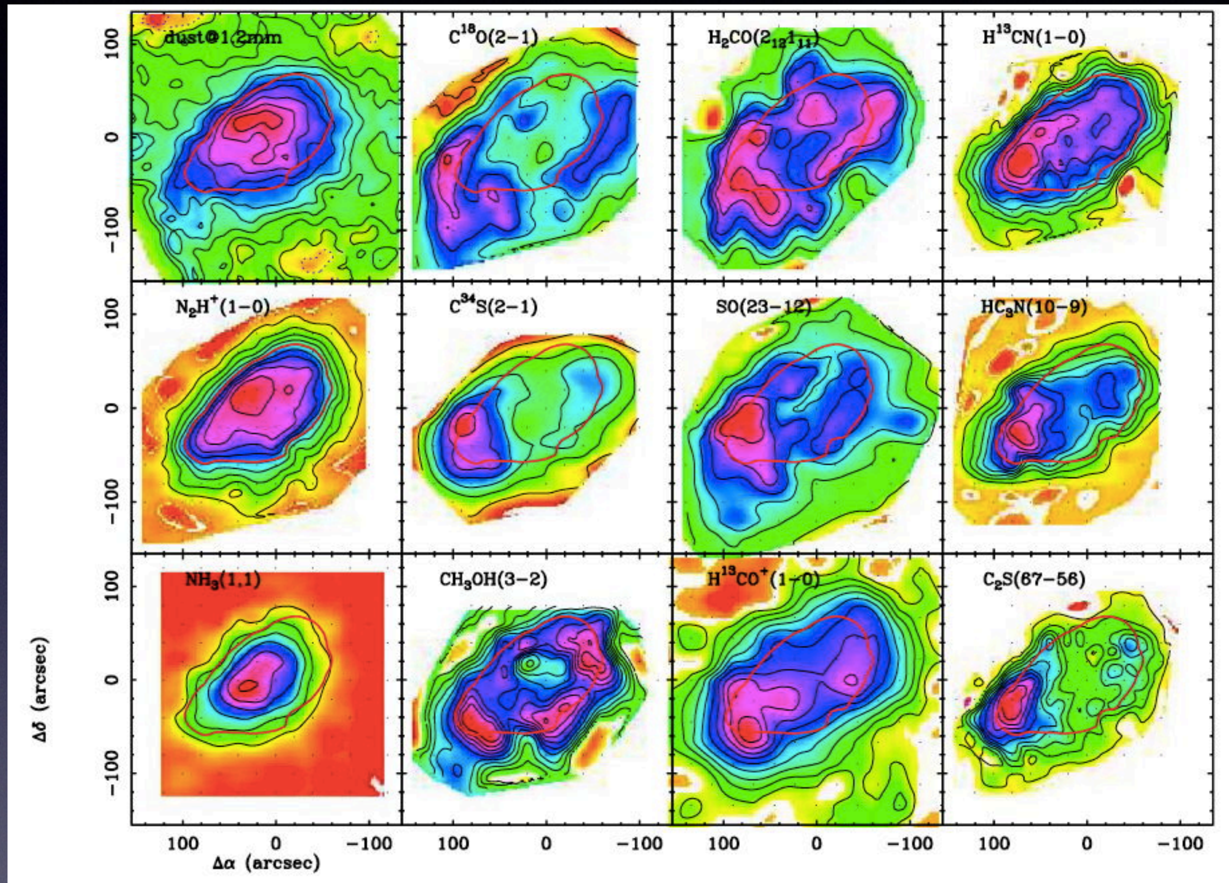
Tielens & Hagen, 1982, A&A, 114, 245

Fuchs et al 2009, A&A, 505, 629; Hidaka et al, 2004, ApJ, 614, 1124; 2009, ApJ, 702, 291; Hiraoka et al 1998, ApJ, 498, 710; Ioppolo et al. , 2008, ApJ, 686, 1474

Ioppolo et al. , 2008, ApJ, 686, 1474; Dulieu et al 2010, A&A, 512, A30; Hiraoka et al 1998, ApJ, 498, 710; Miyauchi et al 2008, Chem Phys Lett, 456, 27; Mokrane et al, 2009, ApJ, 705, L195

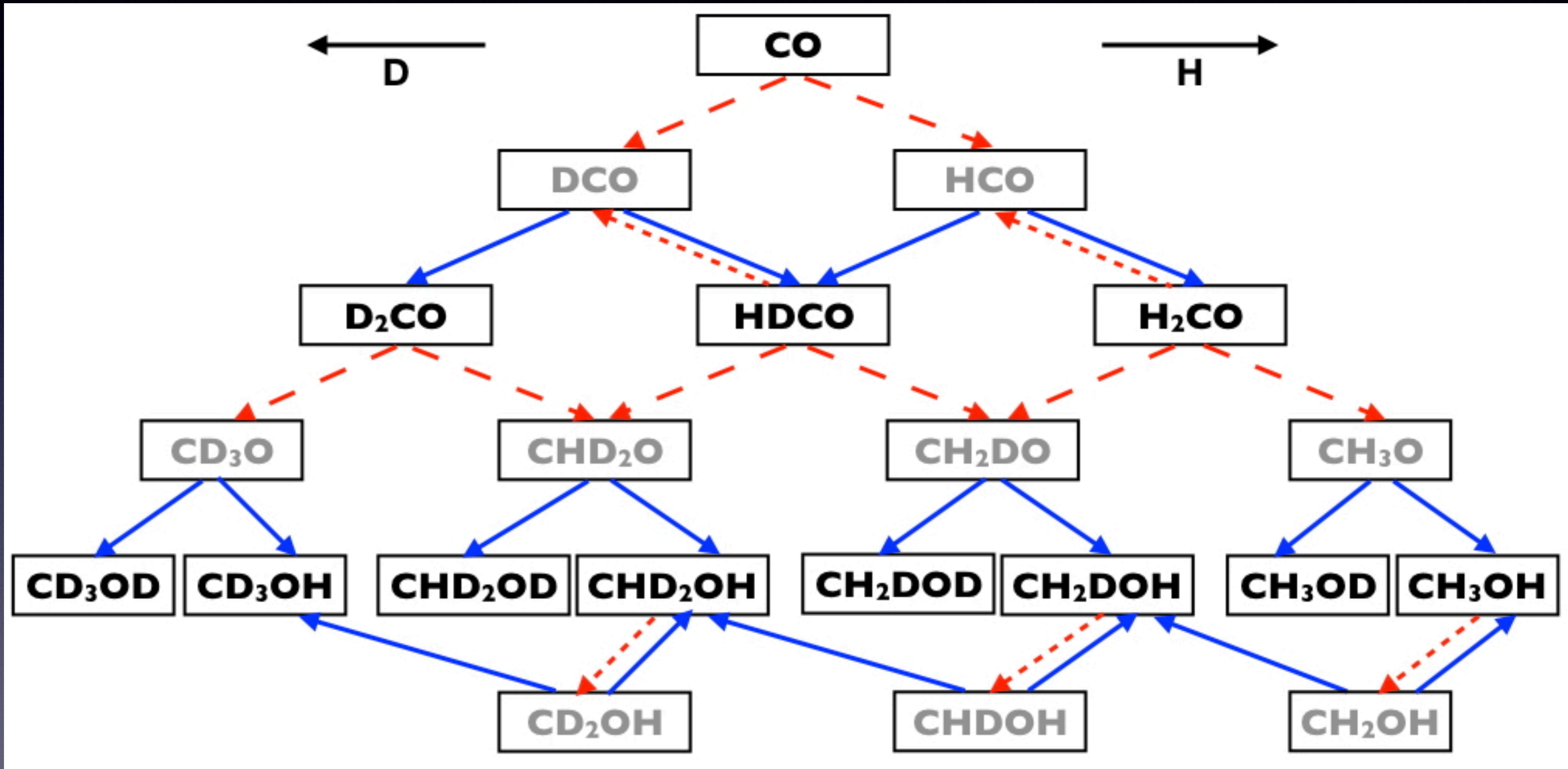
Gas-Grain Interaction is at the core of interstellar chemistry

- Depletion in dense cores (i.e., B68, L1489)
- Interstellar ice
- H_2O & surfaces of molecular clouds
- Gas phase HO_2 & H_2O_2 (i.e., ρ Oph)
- High deuterium abundances of CH_3OH/H_2CO in protostellar envelopes
- Hot Core composition &



Caselli et al, 1999, ApJ, 523, L165 & Bergin et al, ApJ, 2001, 570, L101
Gibb et al, 2004, ApJS, 151, 35; Boogert et al 2015, ARAA, in press
Parise et al 2012
Ceccarelli et al,
Blake et al 1987, ApJ, 315, 621 & Ceccarelli et al, 2007, PPV, 47

Deuterium Chemistry



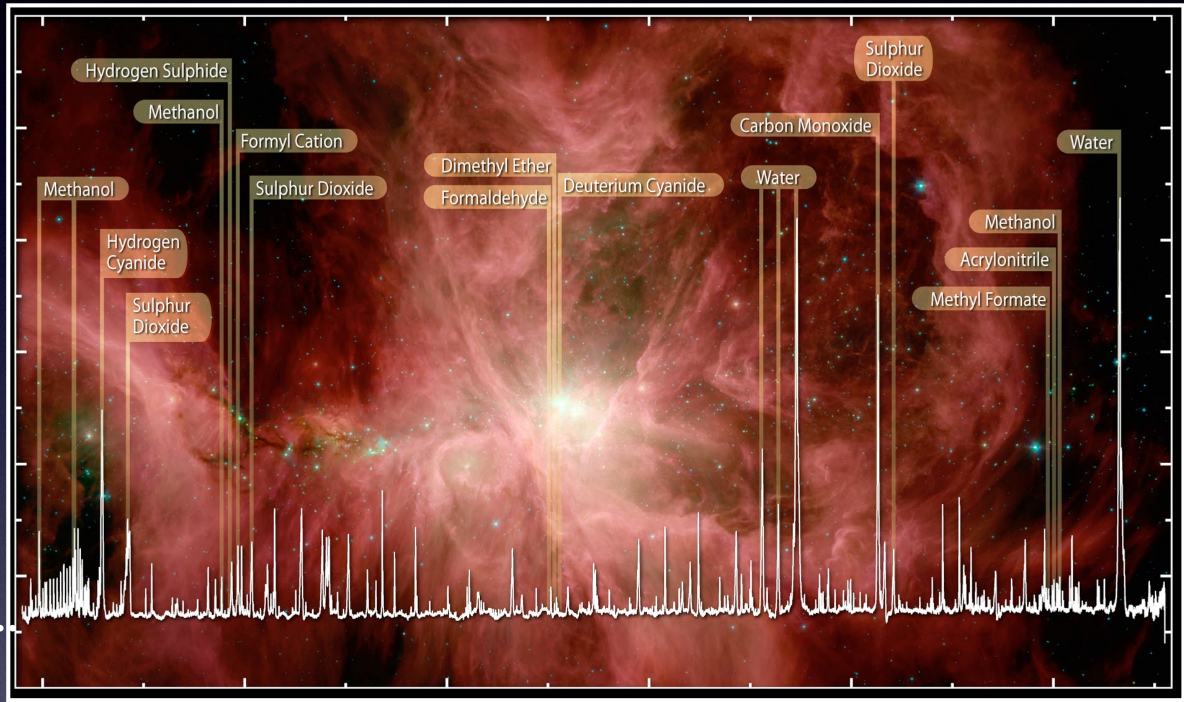
High atomic D/H in the accreting gas

Tunneling abstraction reactions

Tielens 1983, A&A, 119, 177
Charnley et al, 1997, ApJ, 482, L203
Hama & Watanabe, 2013, Chem Rev, 113, 8783

Simple Organic Molecules ("SOM")

- Warm dense gas with rich organic inventory: of relatively simple organic molecules
  - CH_3OH, CH_3CH_2OH, CH_3OCH_3, H_2CO, CH_3CHO, HCOOH, NH_2CHO, ...
  - HCN, CH_3CN, CH_3CH_2CN, ...
- Large deuterium fractionations
- Driven by evaporation of ice mantles formed in cold phase



Blake et al, 1987, ApJ, 315, 621
Ceccarelli et al, 2007, PPV, 47
Bergin et al 2010, A&A, 521, L20

Origin of "SOM"

Deuterium fractionation implies formed from cold-reservoir-progenitors

- Surface chemistry in cold regions
- Photolysis of ices
- Evaporation followed by gas phase reactions
- Ion molecule chemistry in ices

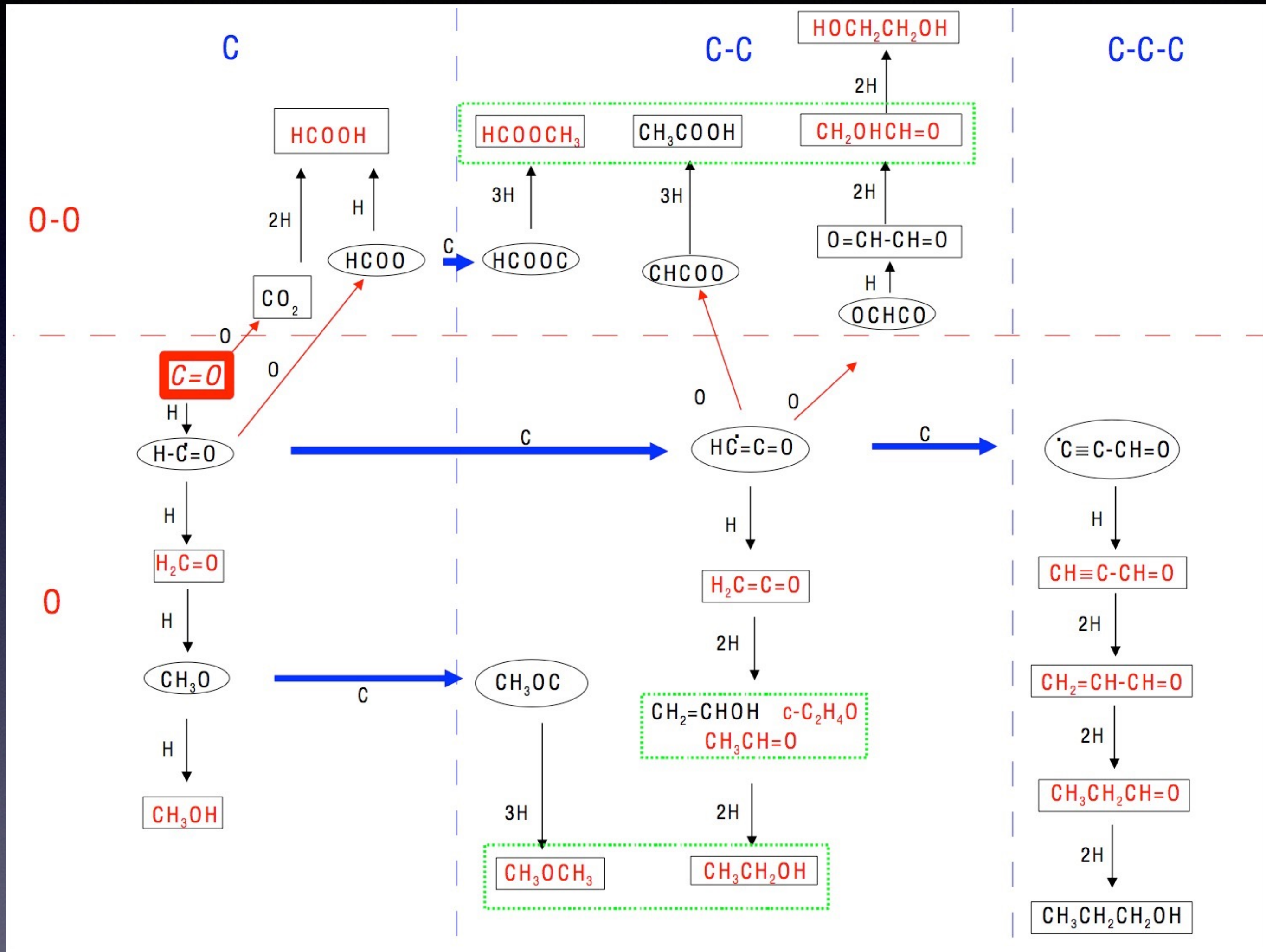
Gas phase chemistry: Charnley et al 1992, ApJ, 399, L71, Caselli et al, 1993, ApJ, 408, 538; Geppert et al, Faraday discussions, 133, 177, Horn et al, 2004, ApJ, 611, 605

Grain surface chemistry: Charnley & Rodgers 2007 Bioastronomy

Charged ices: Bouwman et al, 2011, A&A, 529, 46; Schutte et al, 2003, 398, 1049; Demyk et al, 1998, A&A, 339, 553, Balog et al 2009, Phys Rev Lett, 201, 73003

Photolyzed ices: Garrod et al, 2008, ApJ, 682, 283; Oberg et al, 2010, ApJ, 718, 832

Grain Surface Chemistry



"SOM" molecules require 'free' carbon

Dark clouds: $C/CO \sim 6 \times 10^{-3}$

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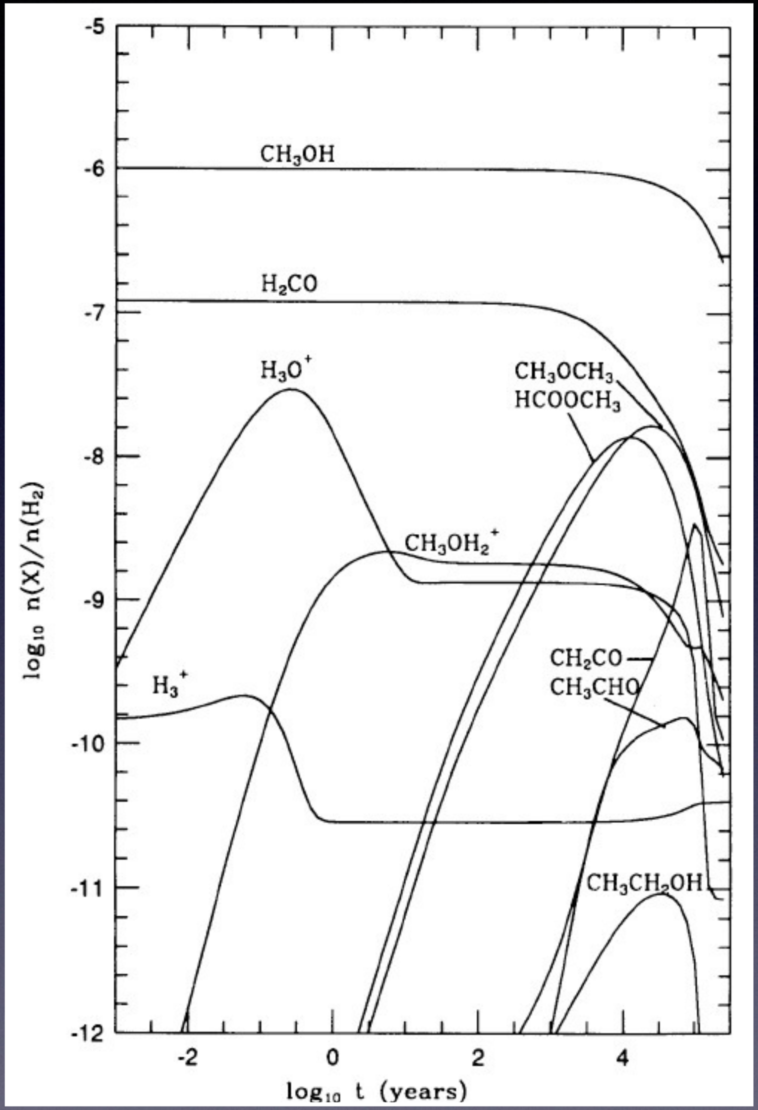
Evaporating Ices

- Evaporating ice molecules drive rich chemistry
- Protonated methanol & methyl transfer
- Issues:
  - Experimental studies disagree
    - formation of intermediaries inhibited
    - Recombination leads to fragmentation
    - Role of ammonia as proton scavenger
  - Chemical clock ~3×10^4 yr incompatible with hot corinos ?



Charnley et al 1992, ApJ, 399, L71
Caselli et al, 1993, ApJ, 408, 538
Geppert et al, Faraday discussions, 133, 177
Horn et al, 2004, ApJ, 611, 605

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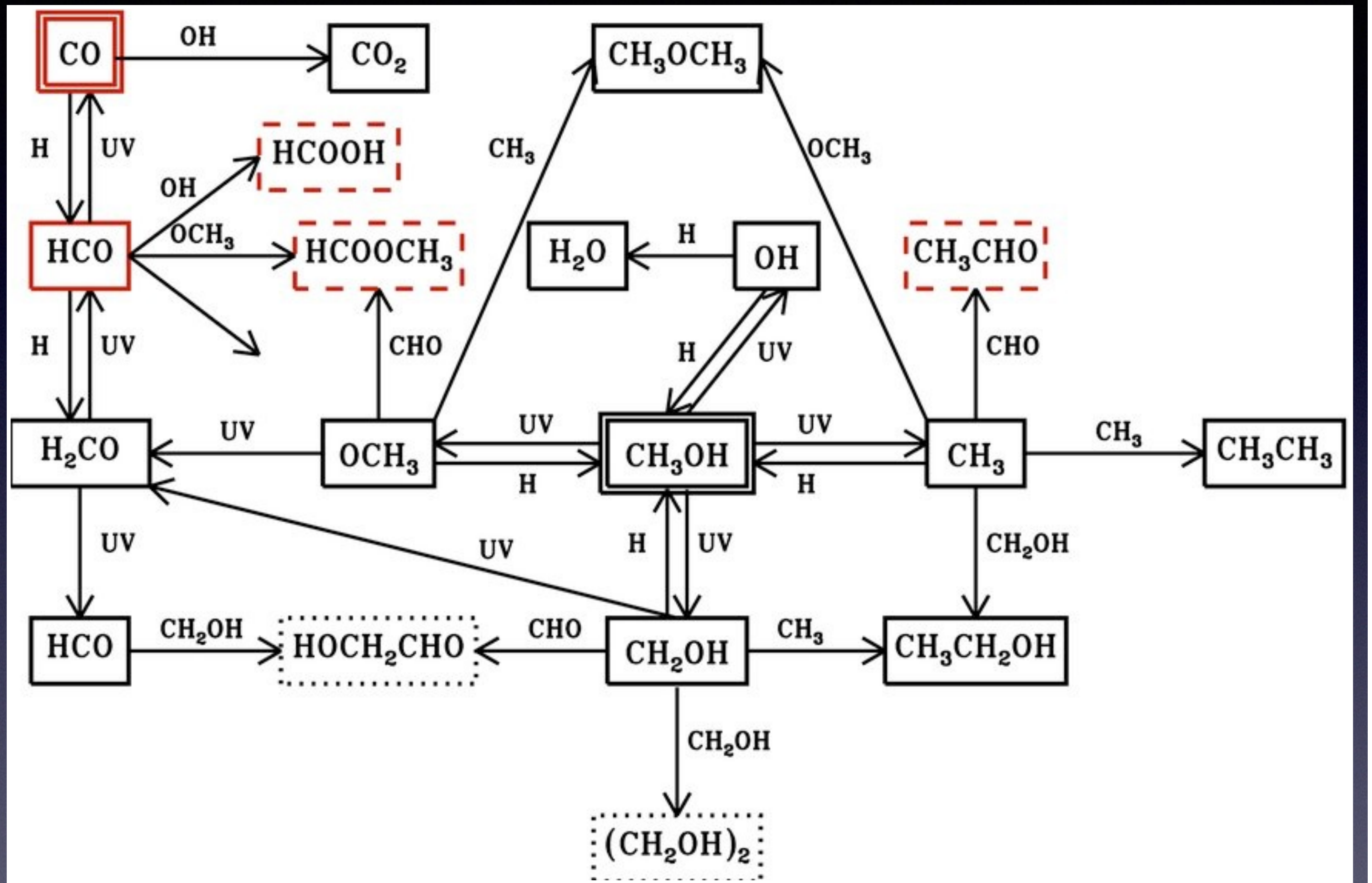
Photolyzed Ices

UV photolysis/ion bombardment & warm up

- Radical production (CH_3 & others)
- Recombination
- Issues:
  - Polymerization
  - Chemical specificity
  - Simple photolysis products (HCO) not observed



Garrod et al, 2008, ApJ, 682, 283
Oberg et al, 2010, ApJ, 718, 832

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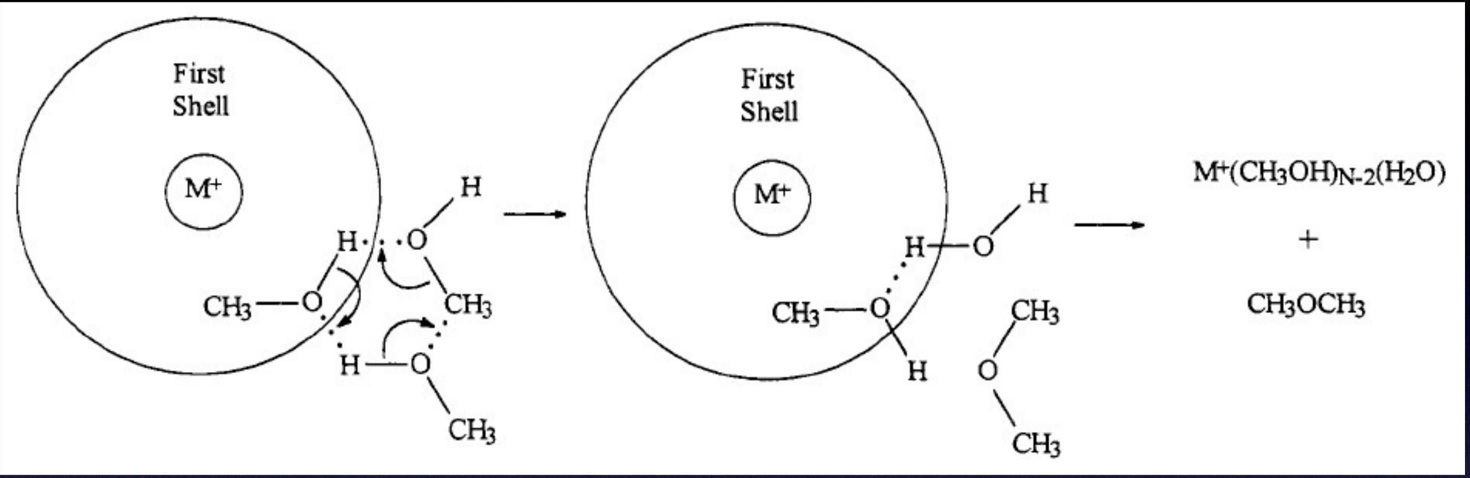
Charged Ices



Ion-molecule Chemistry in Ices

- Ices are charged & charges are localized:
  - Na, PAHs
  - OCN^-
  - Polarization charge
- Warm-up leads to segregation
- H-bonding
- Stereochemistry
- Methanol drives chemistry
- Near evaporation, "droplets" may conduce methyl transfer without fragmentation

charged ices: Bouwman et al, 2011, A&A, 529, 46; Schutte et al, 2003, 398, 1049; Demyk et al, 1998, A&A, 339, 553, Balog et al 2009, Phys Rev Lett, 201, 73003

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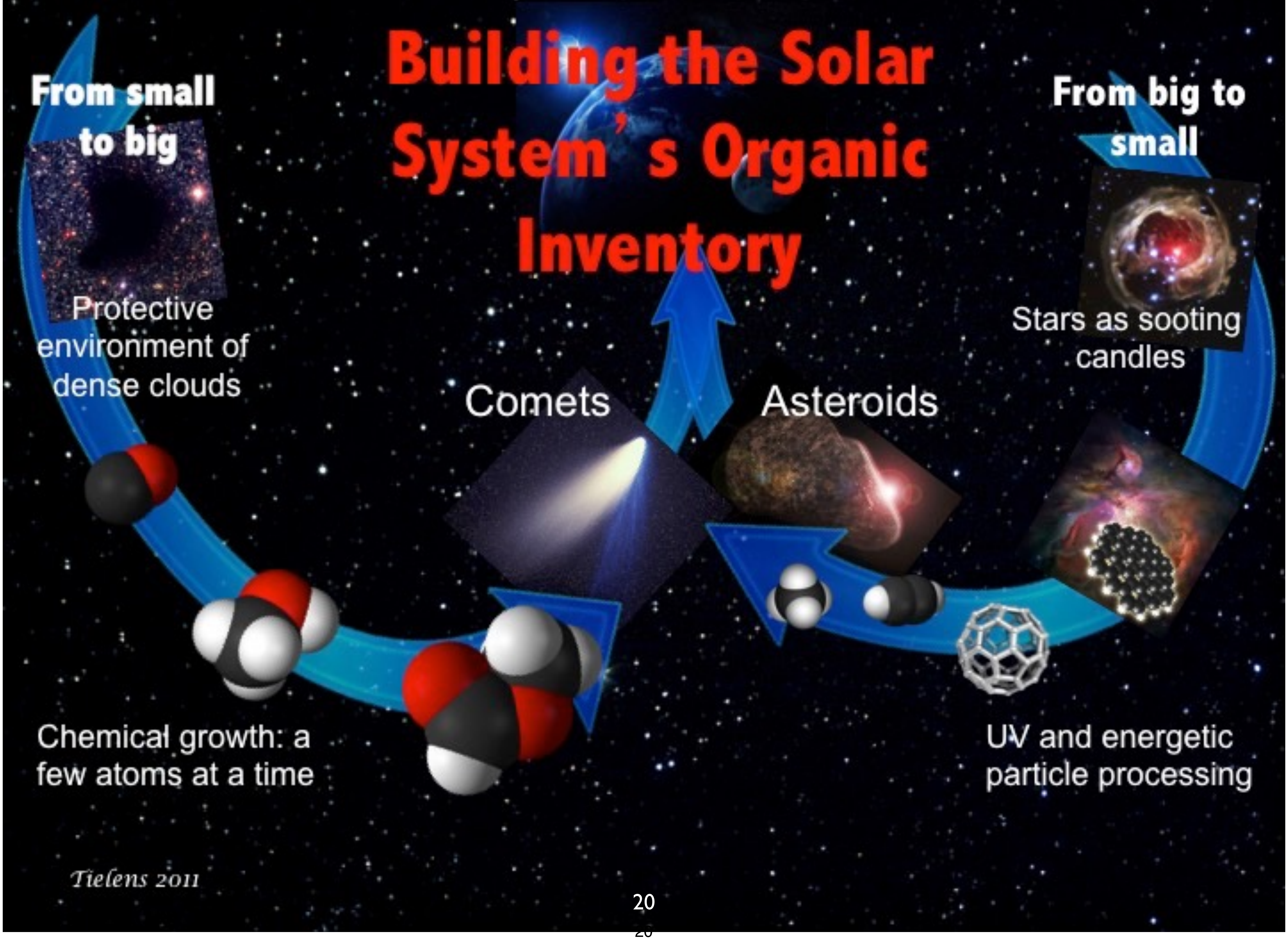
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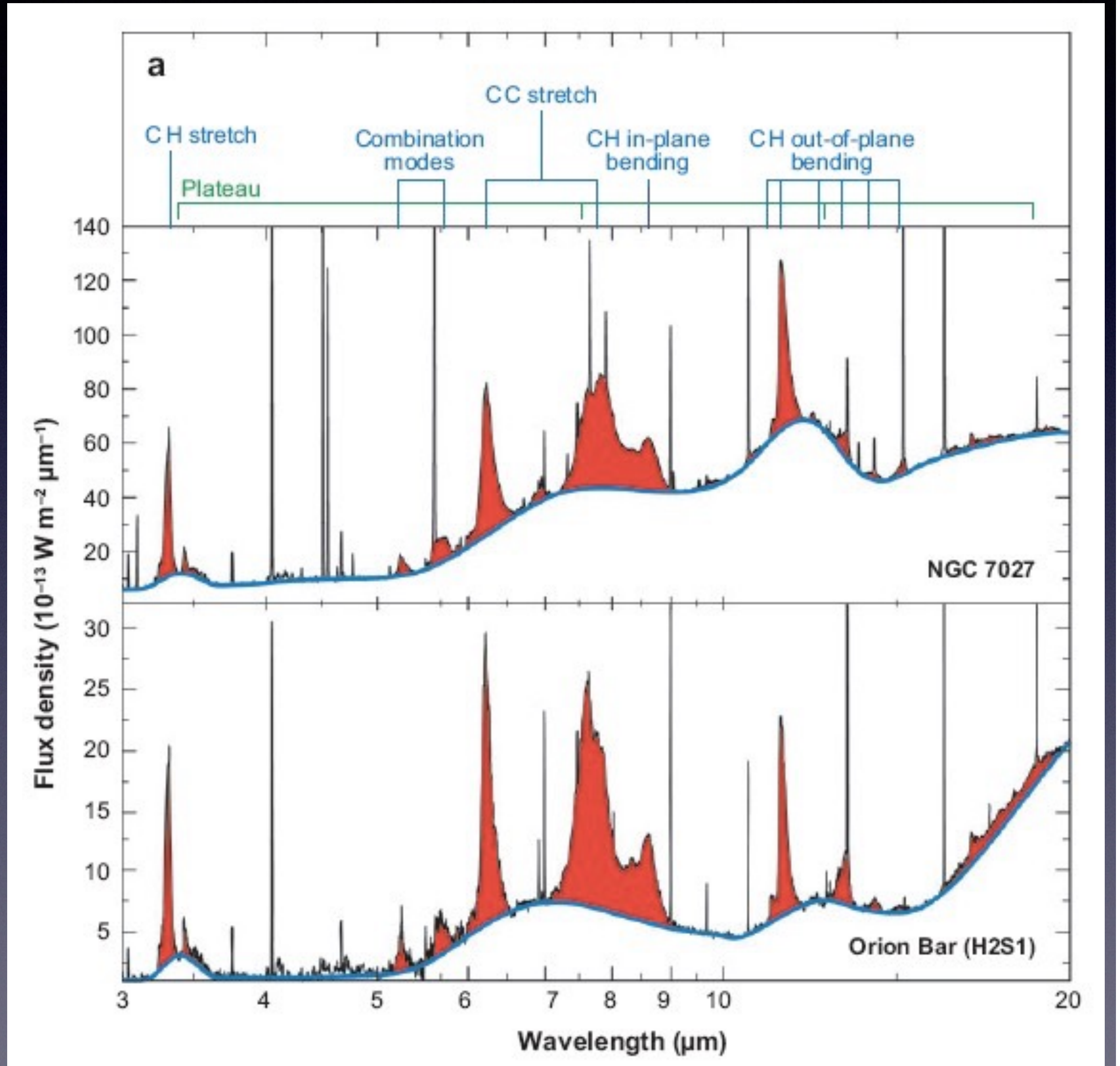
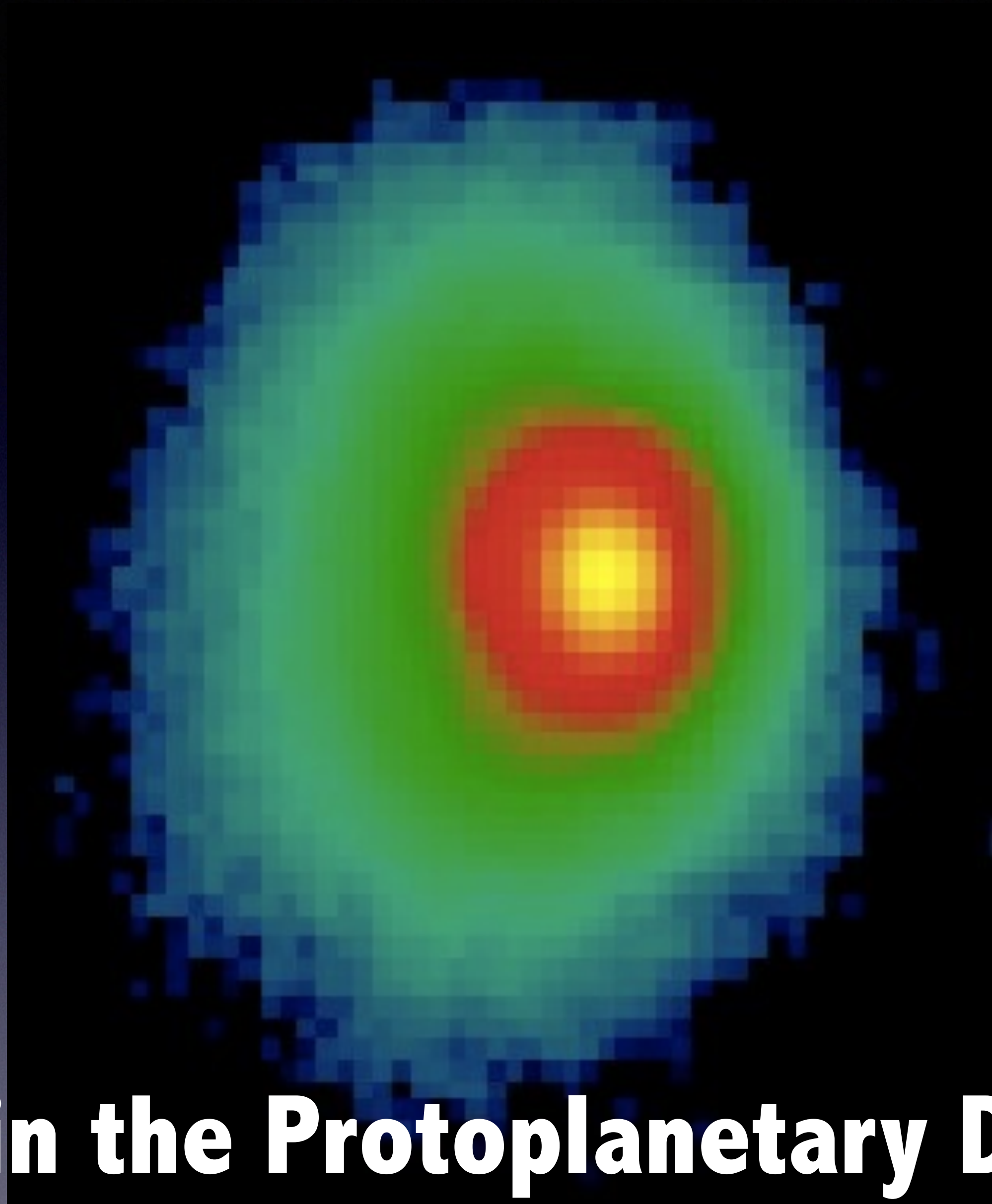
The incredibly rich spectrum of interstellar PAHs



Peeters et al, 2002, A&A,390, 1089

Orion

PAHs in Orion



PAHs in the Protoplanetary Disk of HD 97048

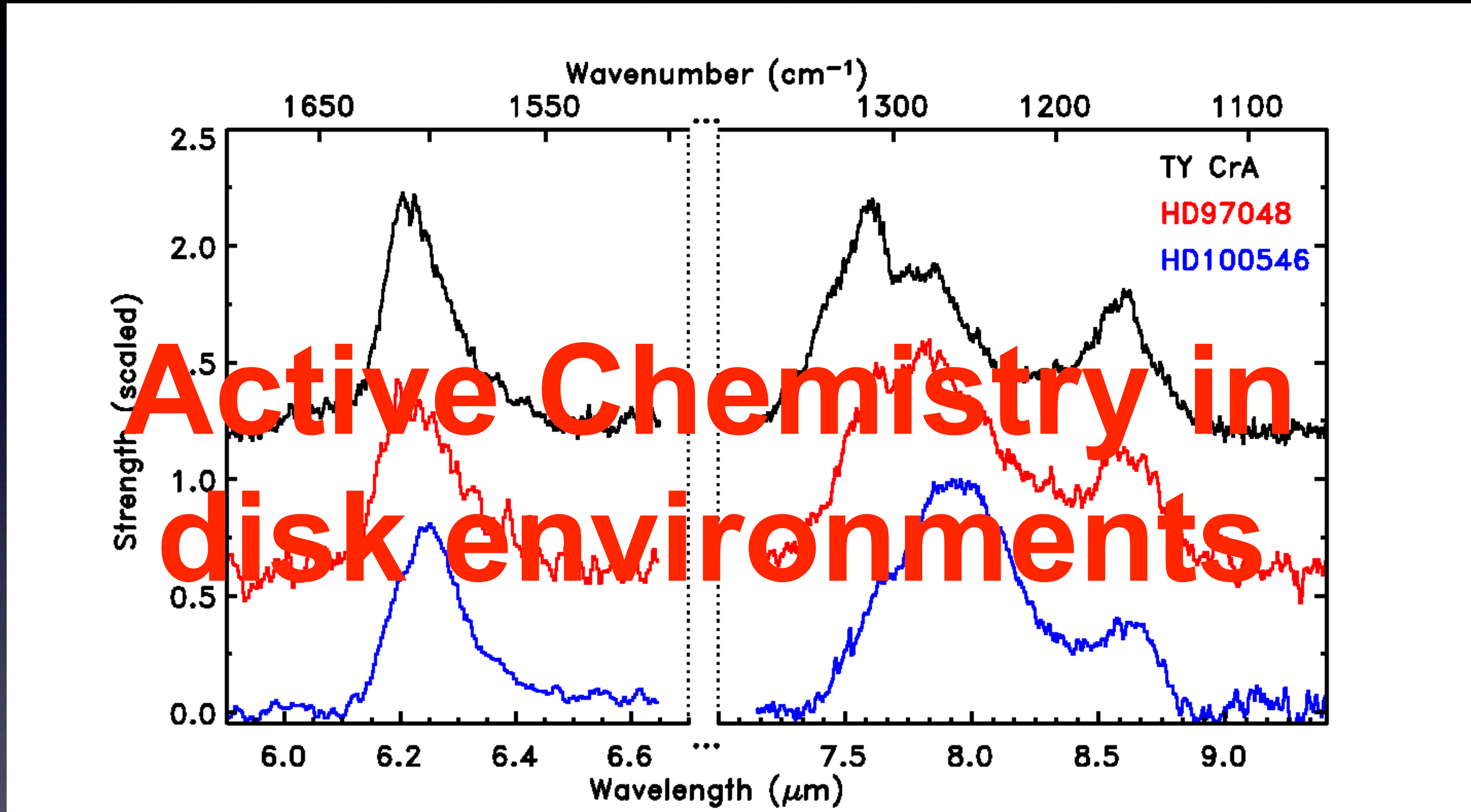
Doucet et al 2007, A&A, 470, 625

PAHs and Herbig Stars

Interstellar

↓

Disk



Active Chemistry in disk environments

Source	Sp T	Size	Location
TY Cra	B7-B9	~2000 AU	HAeBe in cloud
HD 97048	B9-A0	~100-1000 AU	HAeBe cloud edge
HD 100546	B9	~150 AU	isolated HAeBe star

Boersma et al, 2008, A & A, 484, 241

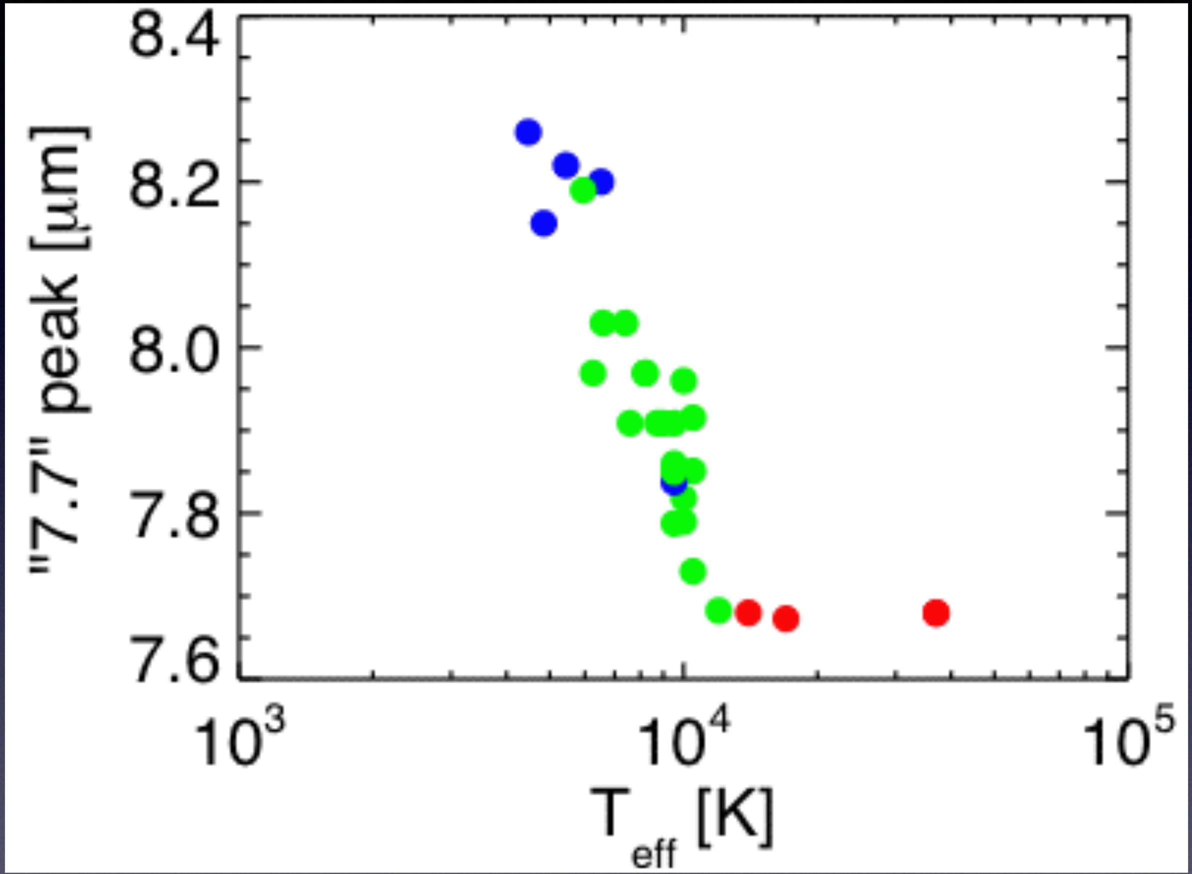
PAH Variations in Regions of Star Formation

- Peak position of the 6.2 & 7.7 µm bands vary depending on local characteristics

- Aromatic versus aliphatic hydrocarbons

- N-incorporation

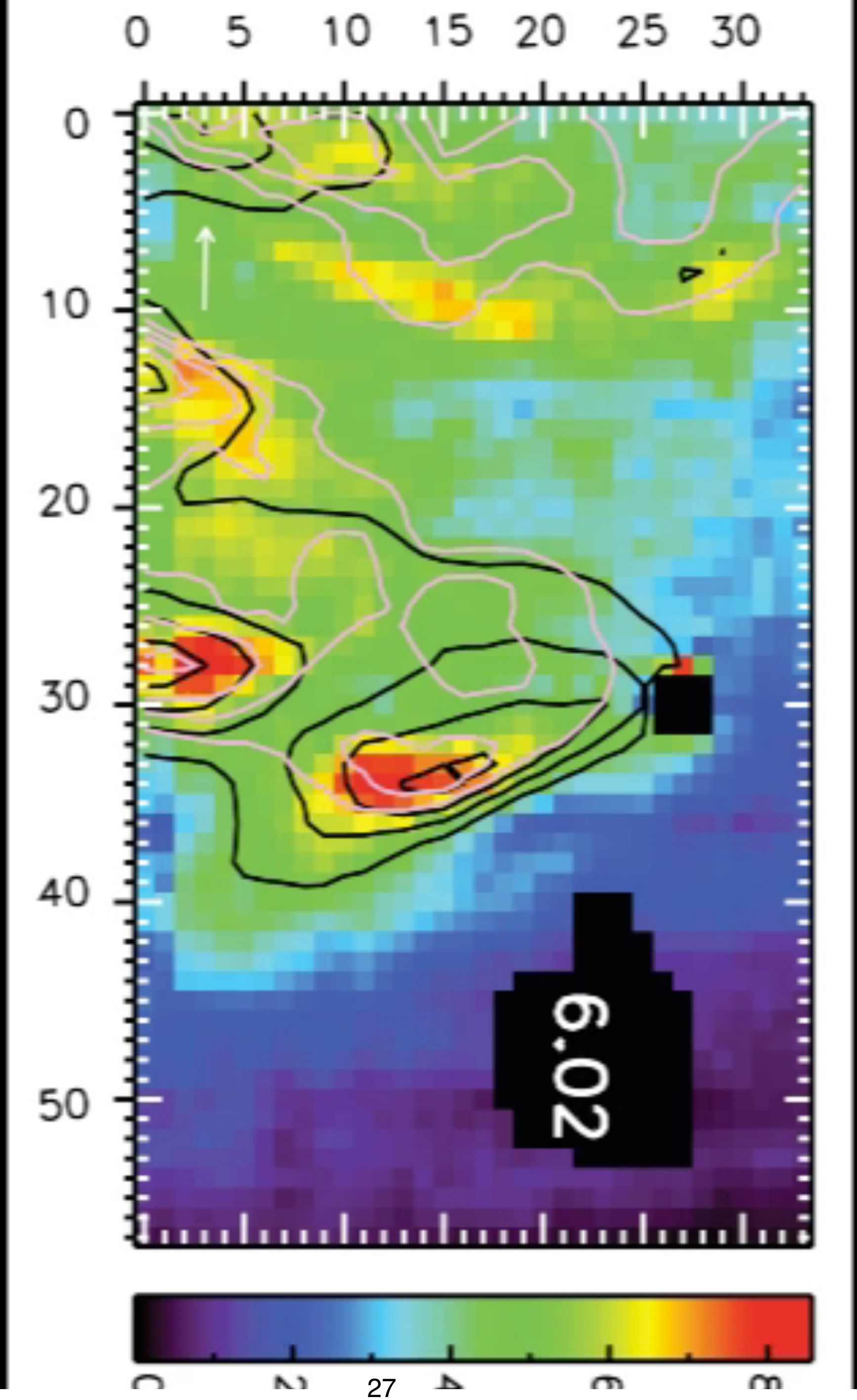
- PAH size



Active chemistry:
Key is strength of the radiation field
Key is stability

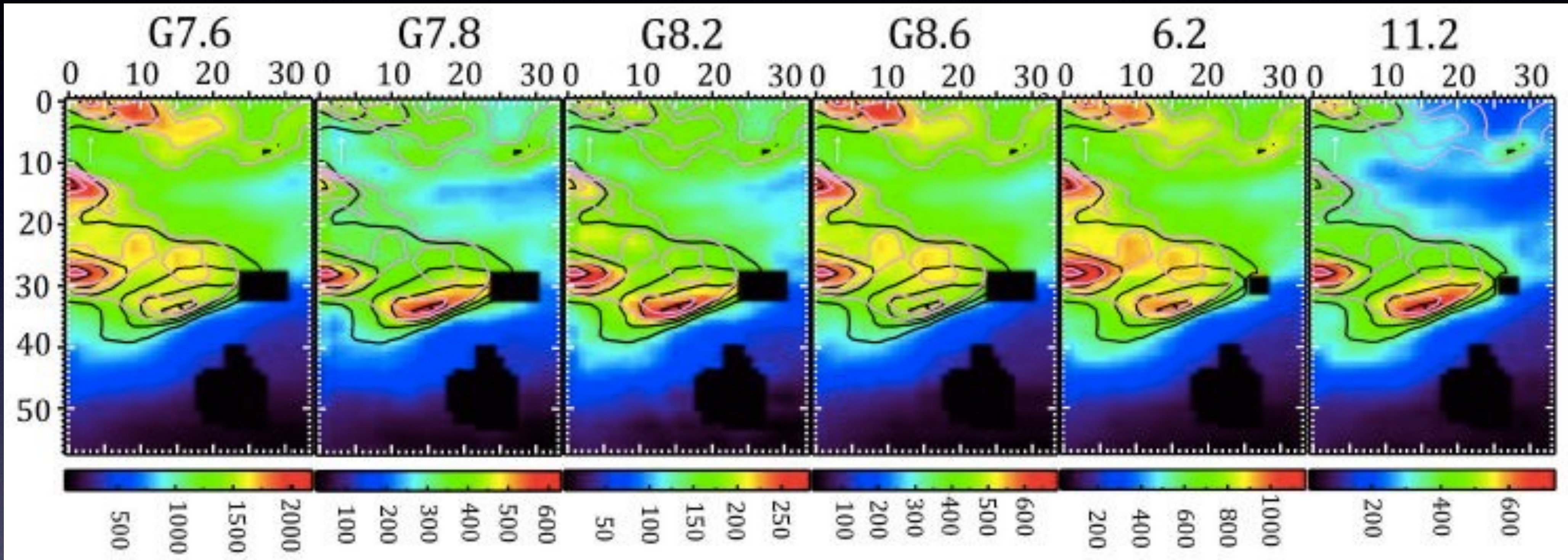
Sloan et al 2007, ApJ, 664, 1144
Boersma et al, 2008, A & A, 484, 241

NGC 2023: The Movie



Peeters, et al, 2017, ApJ, 836, 198

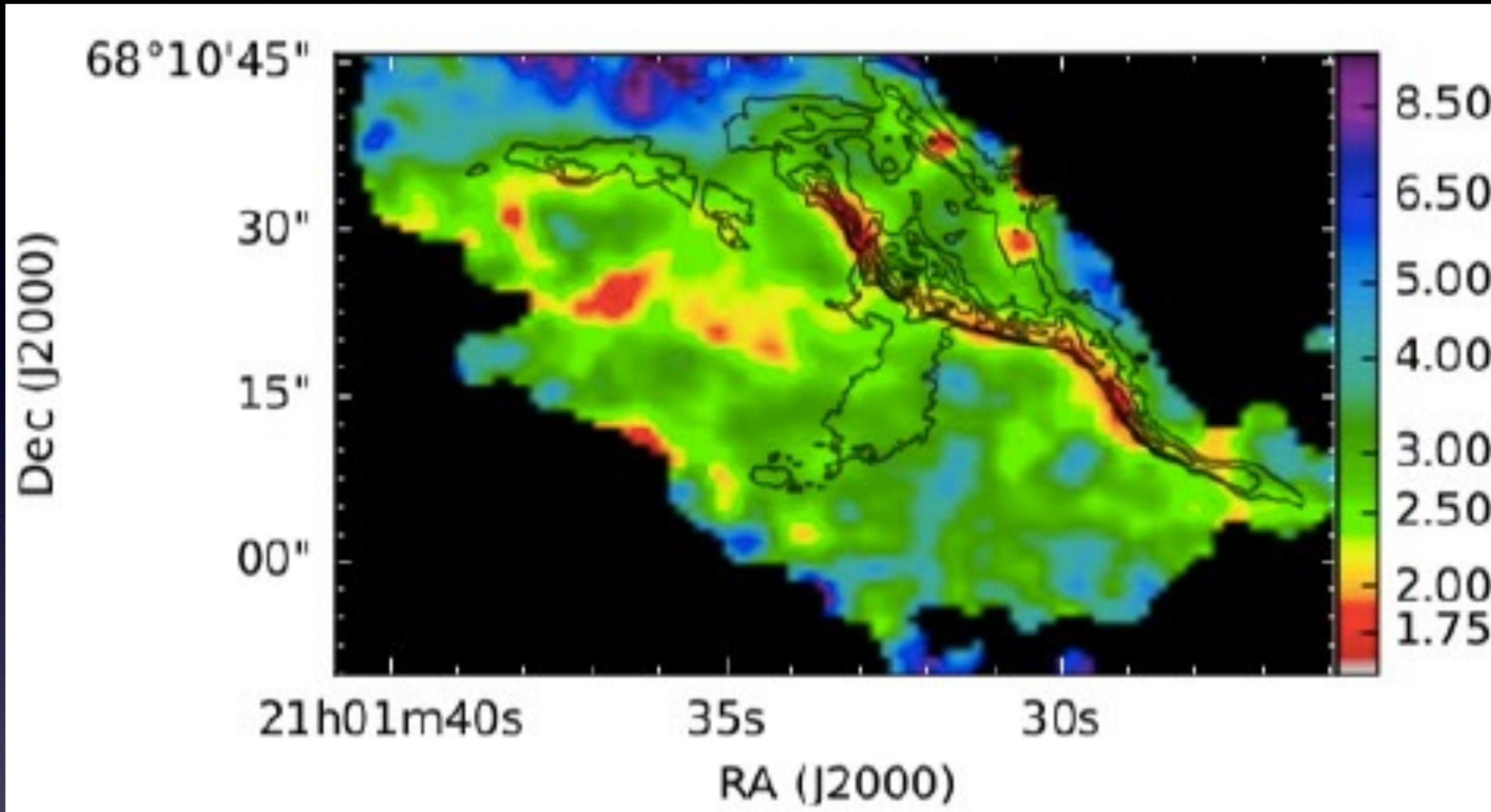
Stills from the Movie



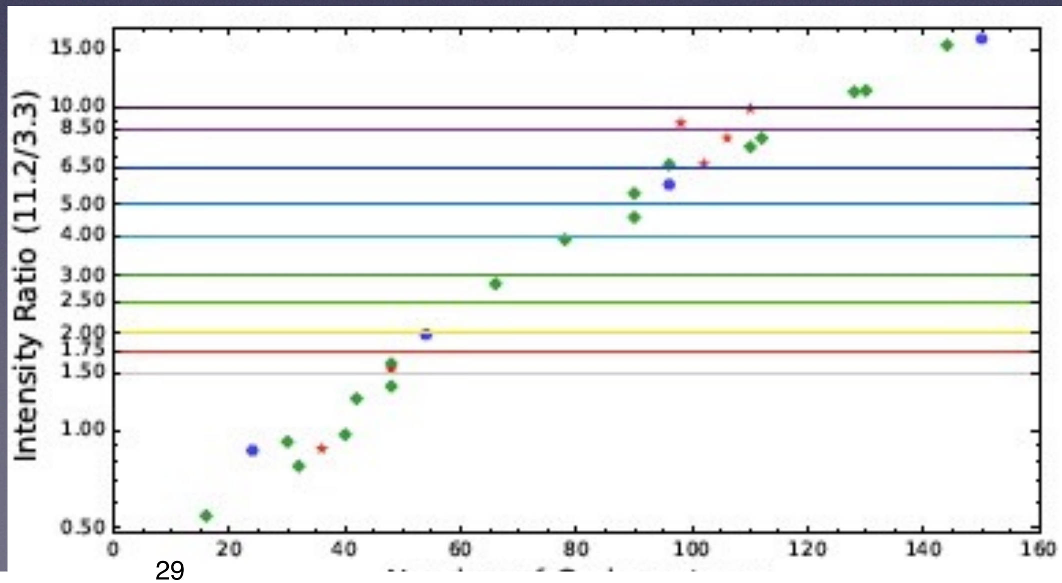
Two Components:
6.2, G7.6, & G8.6 versus G7.8, G8.2 & 11.2

Peeters, et al, 2017, ApJ, 836, 198

Interstellar PAH Sizes



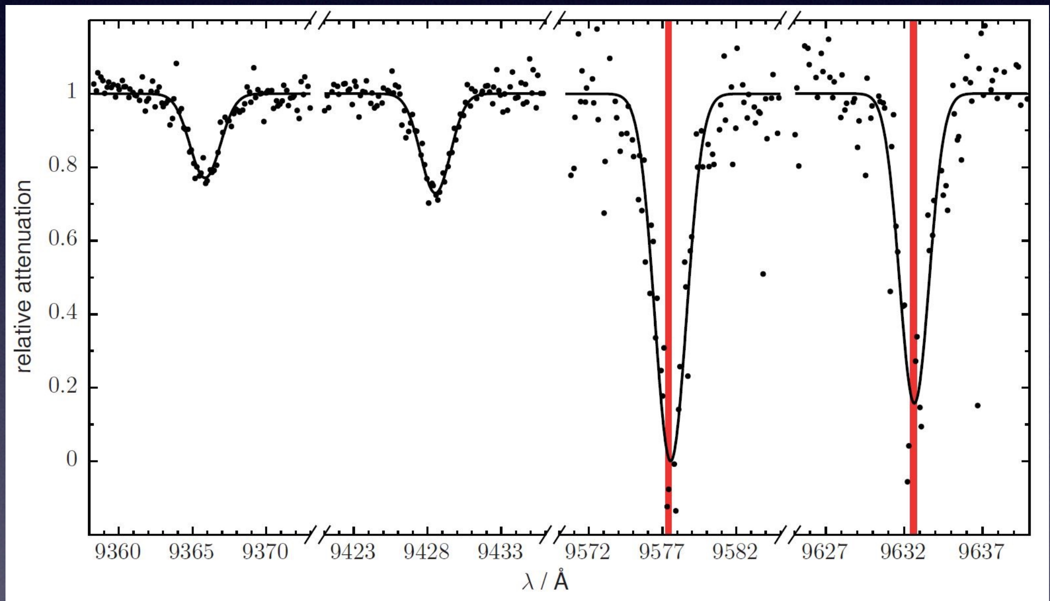
The 11.2/3.3 μm ratio



Croiset et al, 2016, A&A, 590, A26

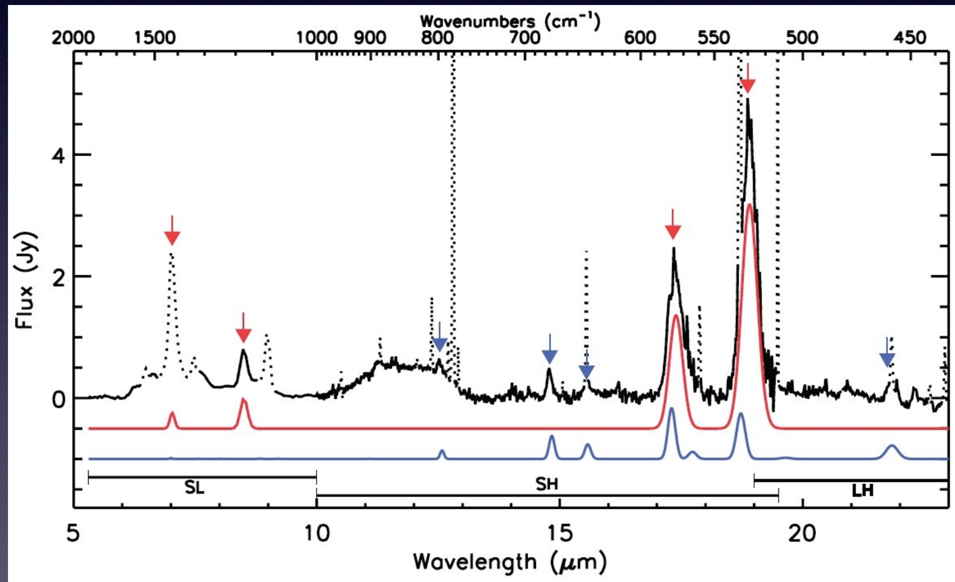
The Largest Molecule in Space: C_{60}

C_{60}^{+} & the DIBs



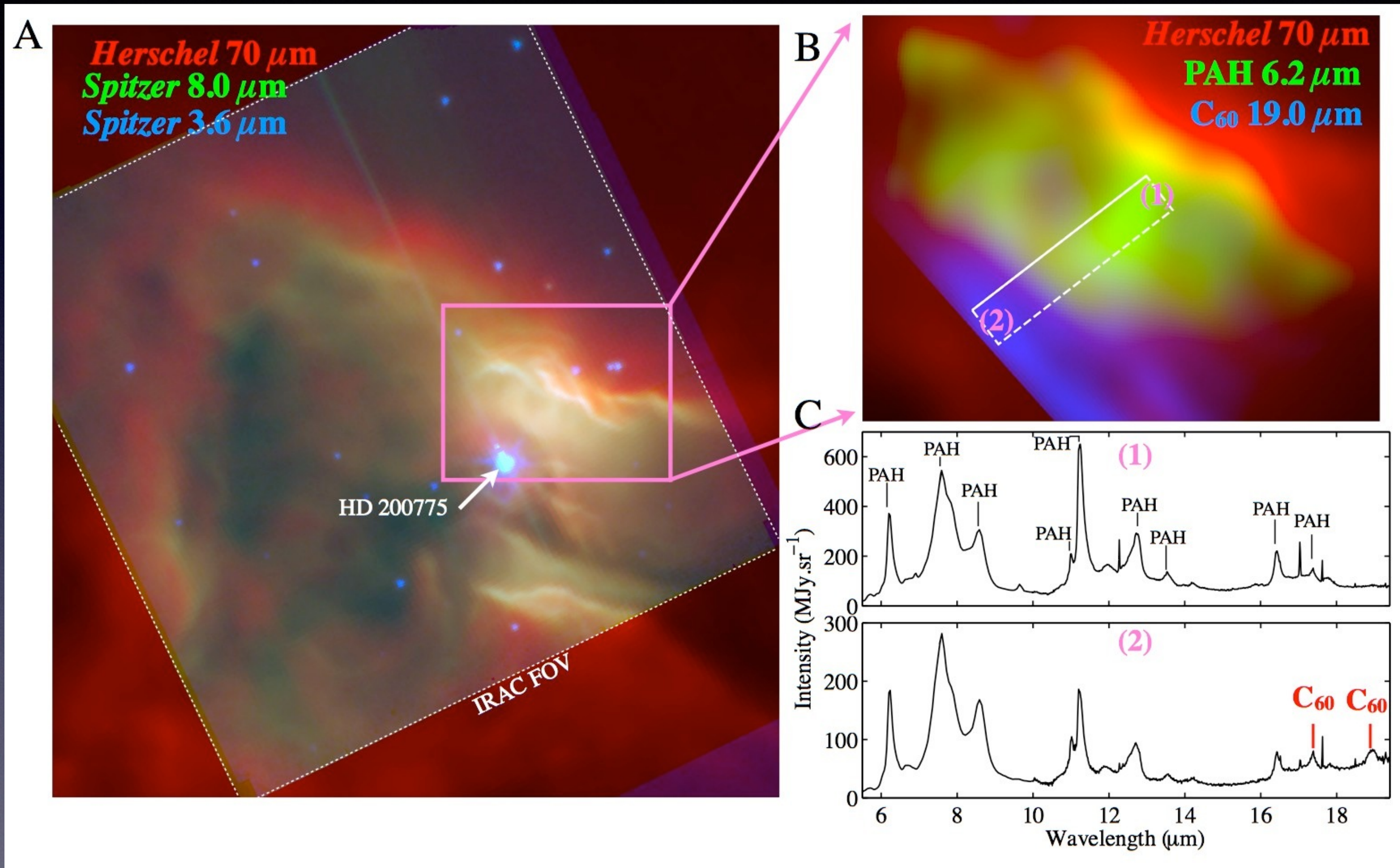
Campbell et al, 2015, Nature, 523, 322

C_{60} in the PNe, TC1



Cami et al, 2010, Science, 329, 1180

PAHs & C_{60} in NGC 7023



Berne & Tielens, 2012, PNAS, 109, 401

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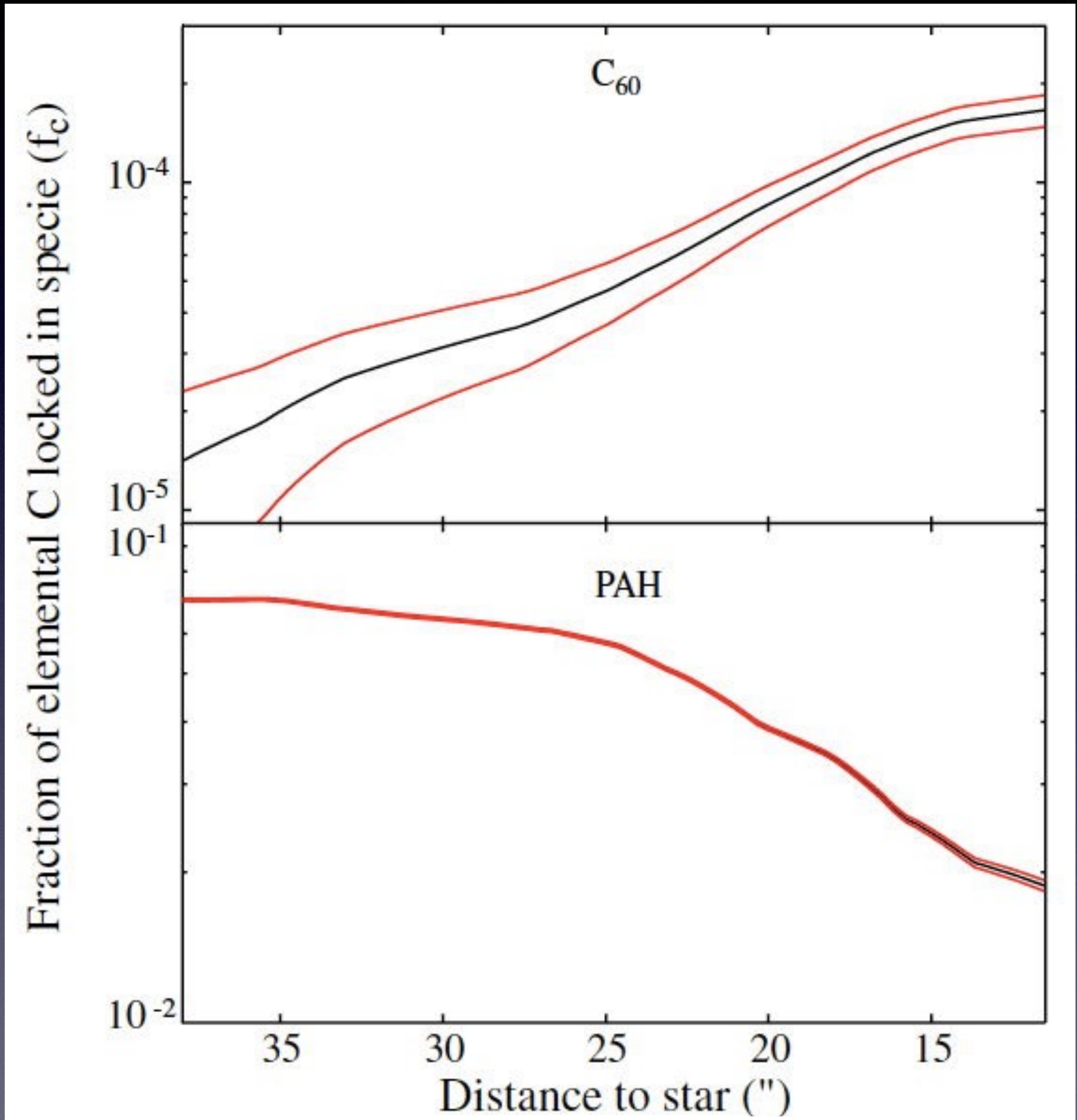
PAHs & C_{60} abundance



Berne & Tielens, 2012, PNAS, 109, 401

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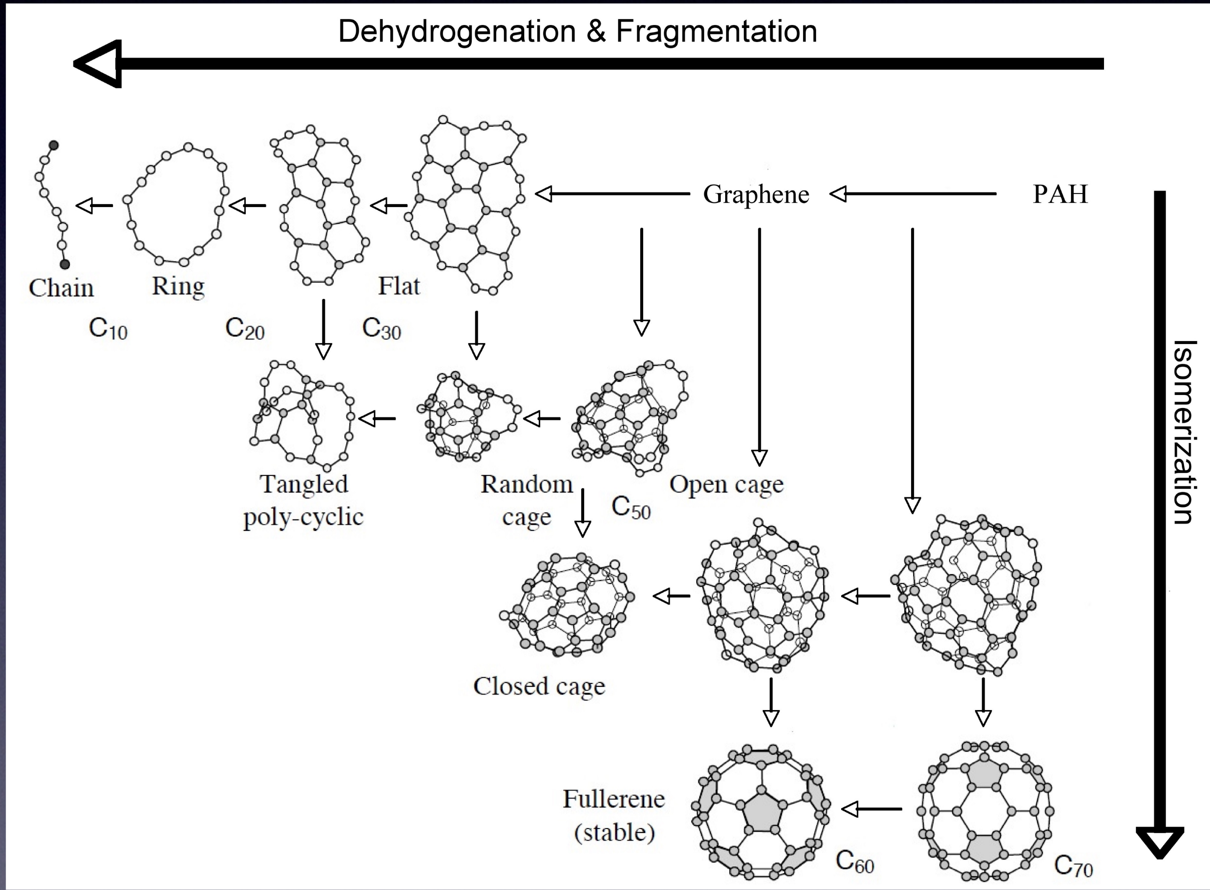
PAH photolysis

- Dehydrogenation & isomerization
- Stable intermediaries: cages & fullerenes
- Fragmentation products: hydrocarbon chains & radicals
- Relevant for hydrocarbon reservoir in PDRs ?

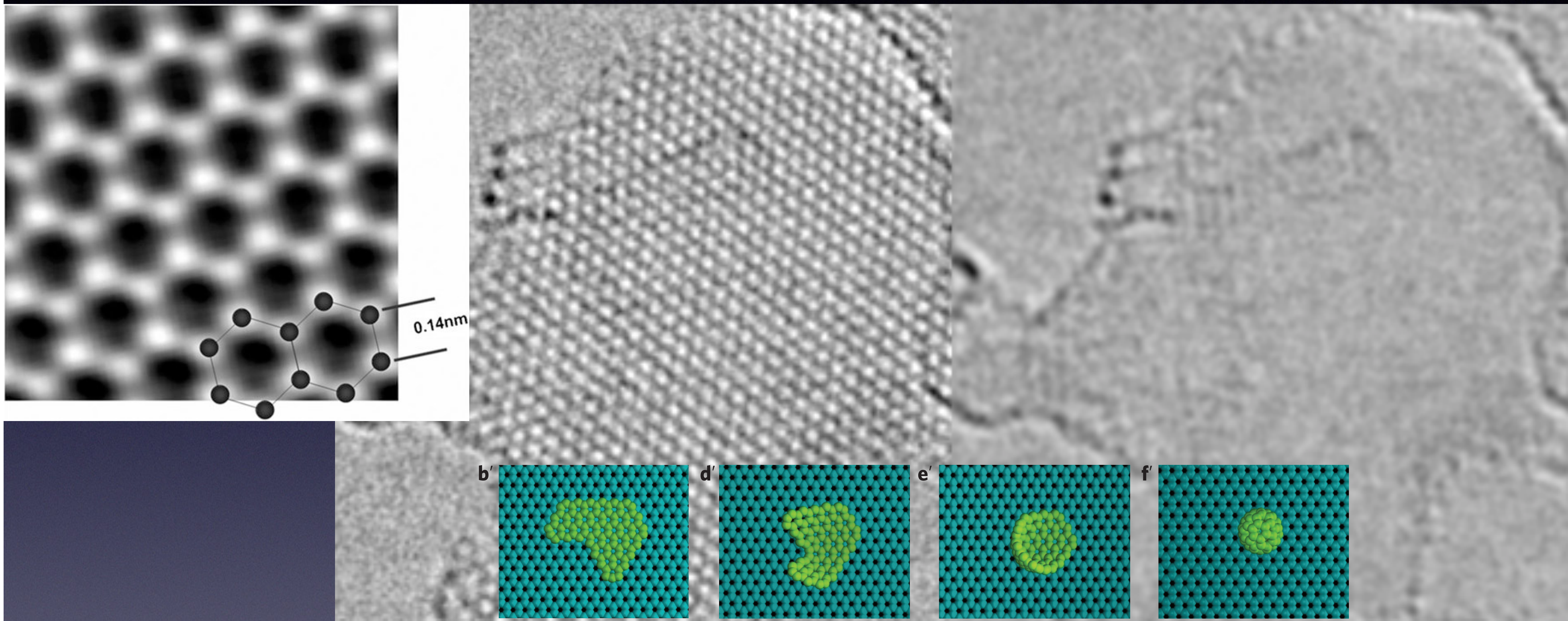


Berne & Tielens, 2012, PNAS, 109, 401
Pety et al, 2005, A&A, 435, 885
Wehres et al, 2010, A&A, 518, 36

33

From Graphene to C_{60}

[National Center for electron microscopy]



[Chuvilin et al. Nature Chem. 2010]

Transformation of graphene to C_{60}, driven by electron irradiation

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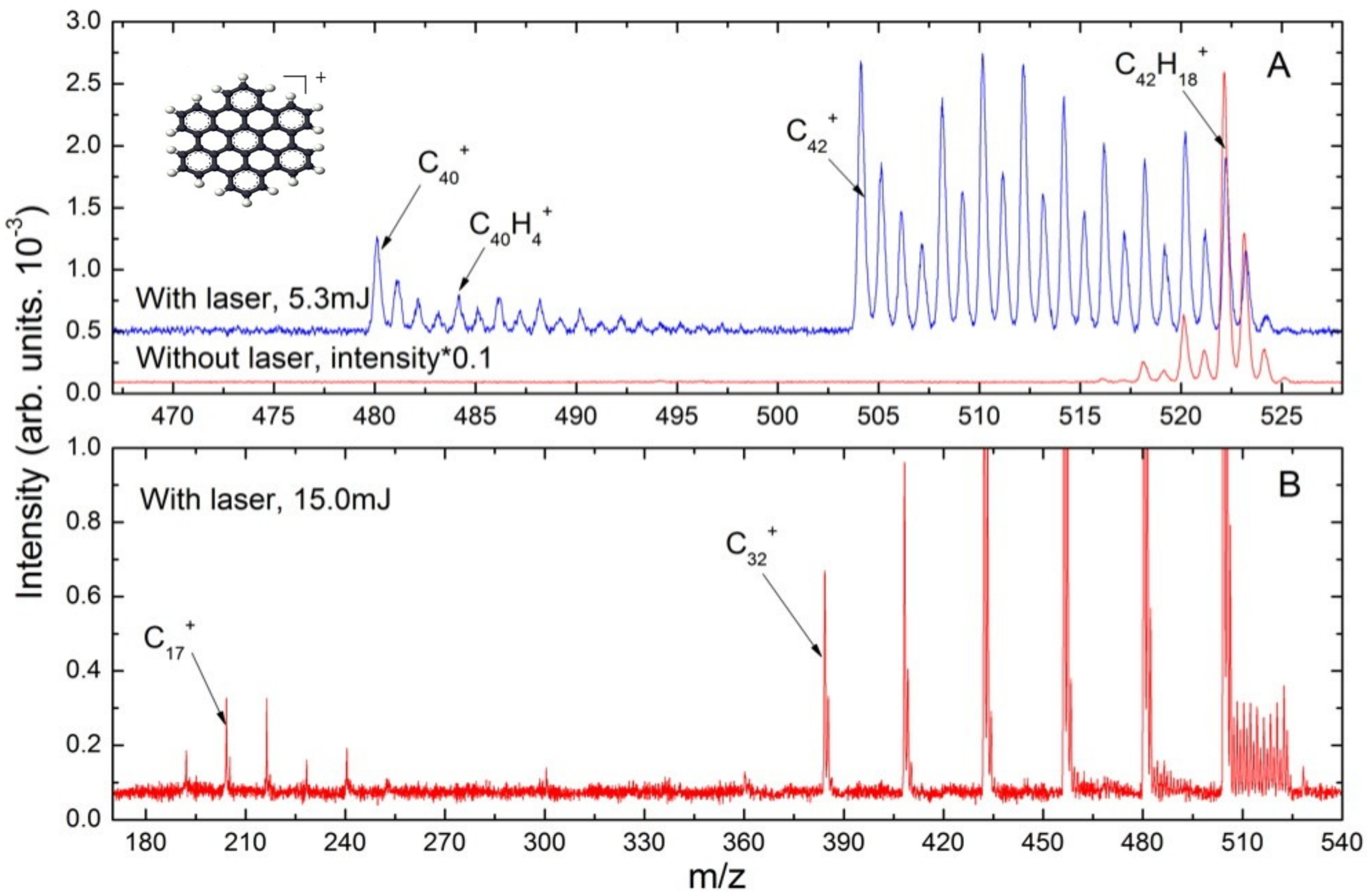
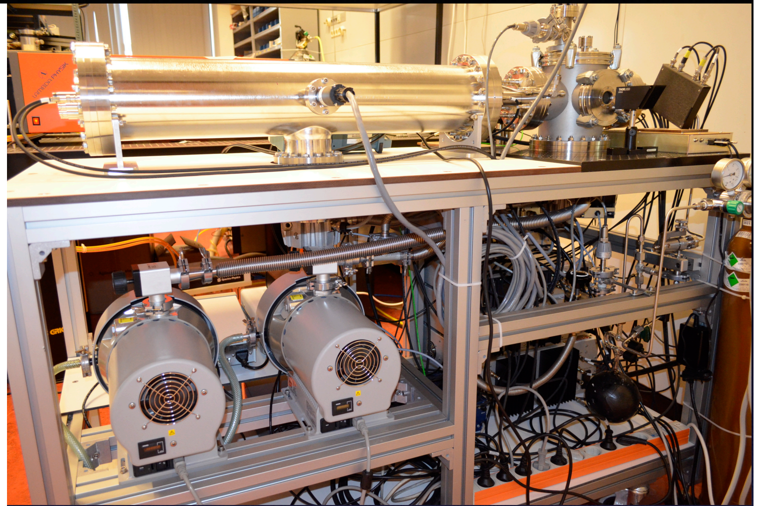
PAHs Photolysis

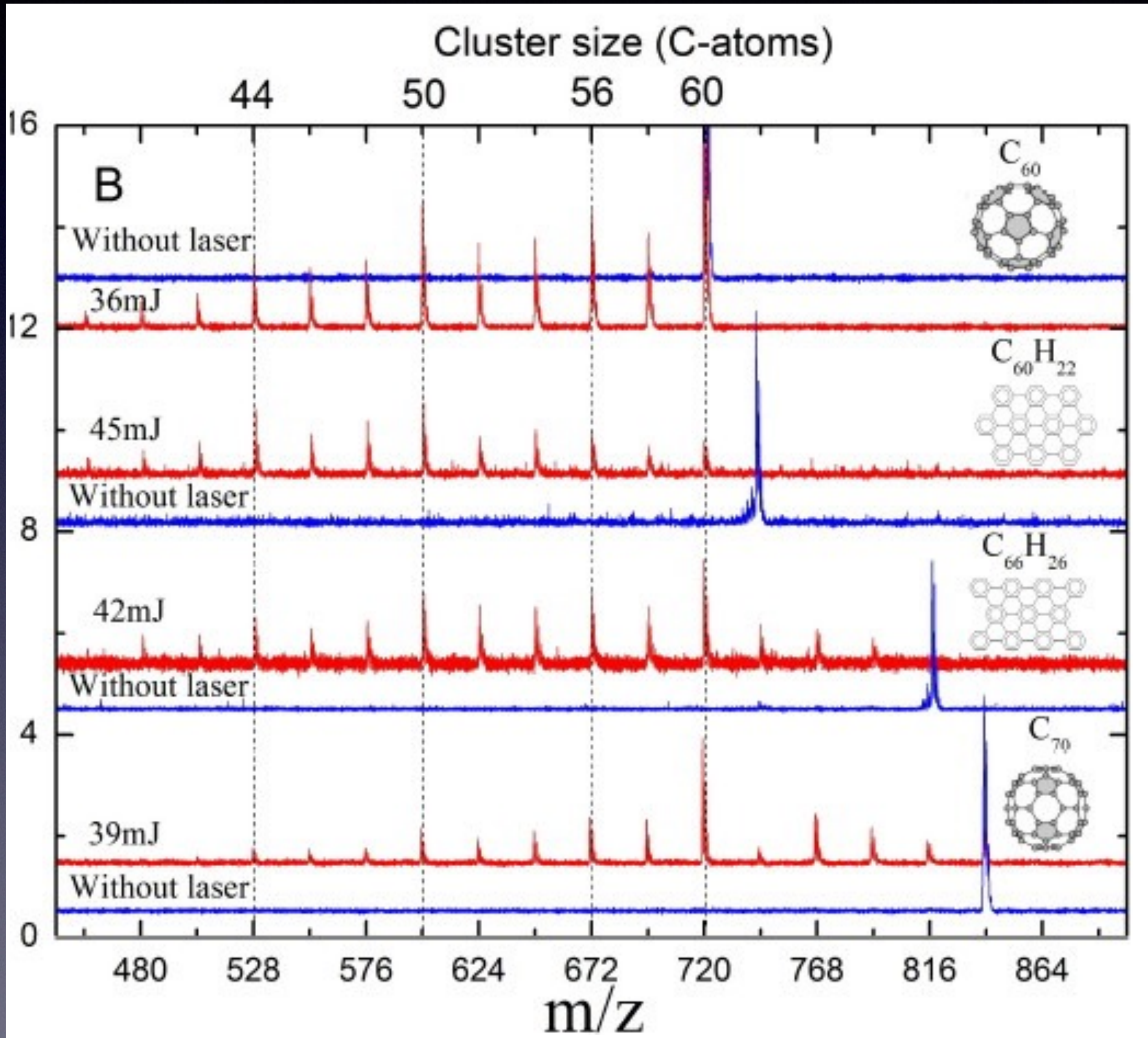




Ekern et al, 1997, ApJ, 488 L39
Joblin et al, 2003, Edp. Sci. Conf. Ser. 175
Zhen et al, 2014, Chem Phys Lett, 592, 211

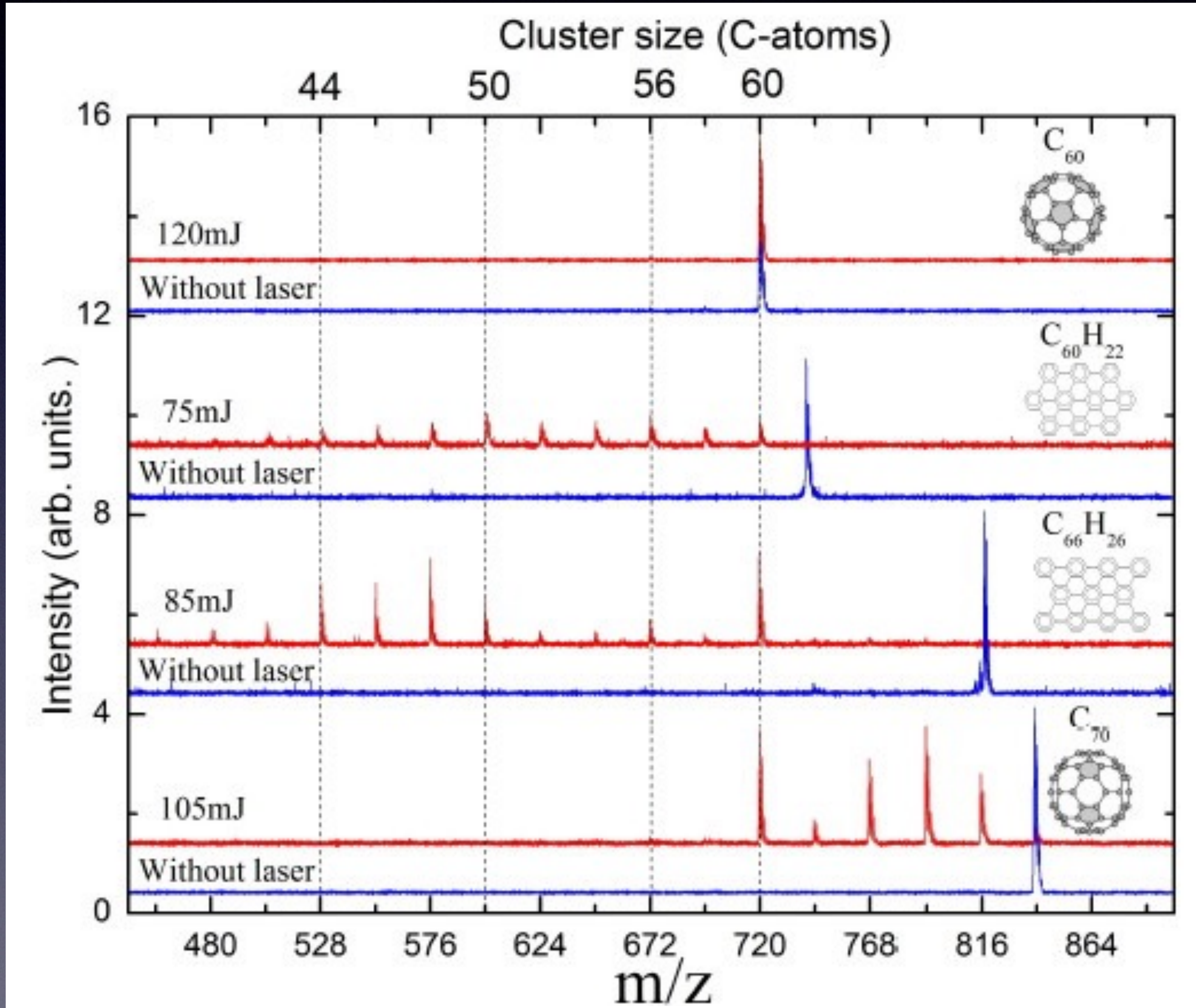
- Multiphoton absorption leads to fragmentation in a laser pulse
- Many pulses strip the molecule down
- Loss of all H followed by loss of C_2 and C units (magic numbers)

From PAHs to C_{60}



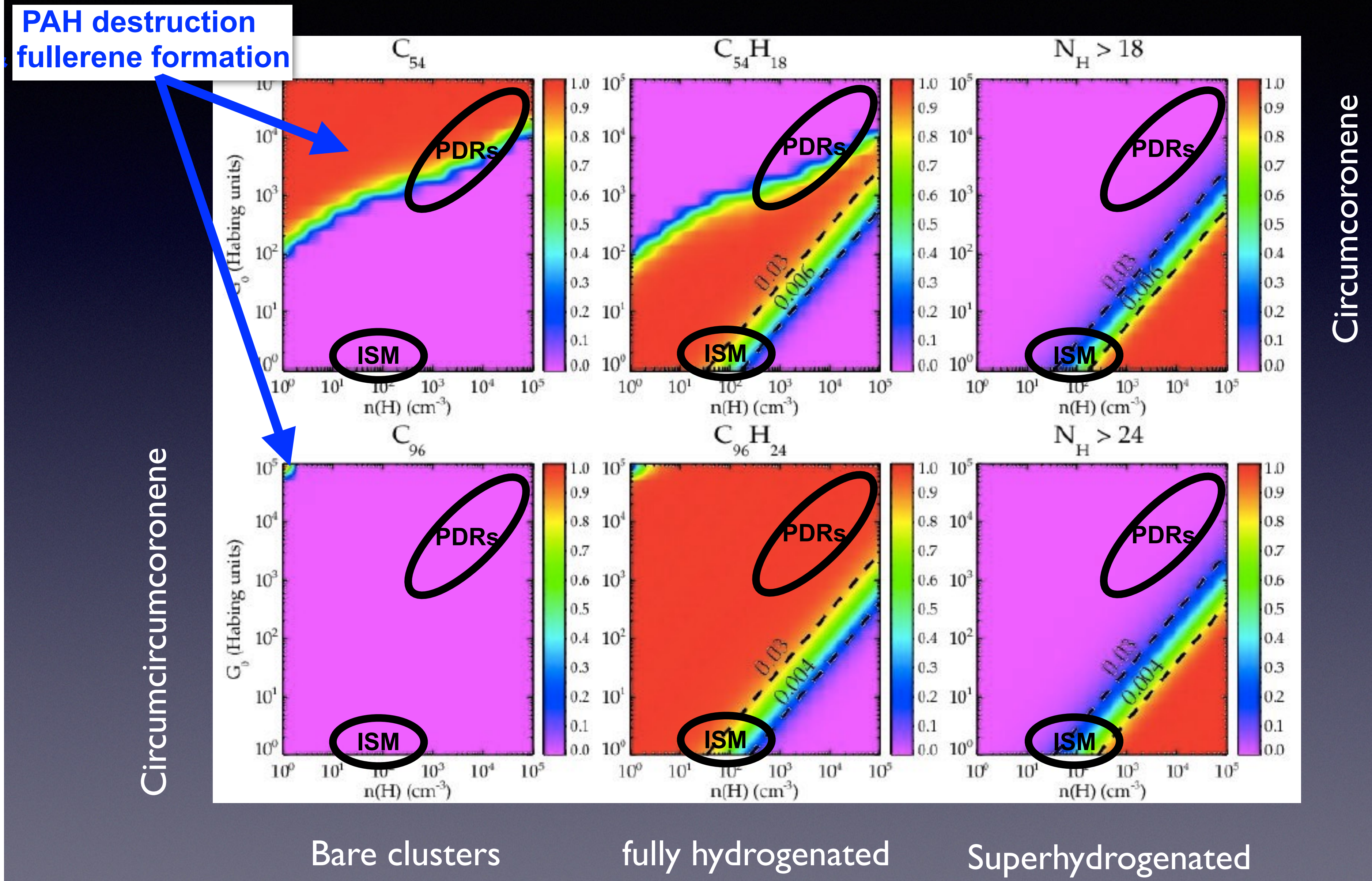
λ=356nm

From PAHs to C_{60}



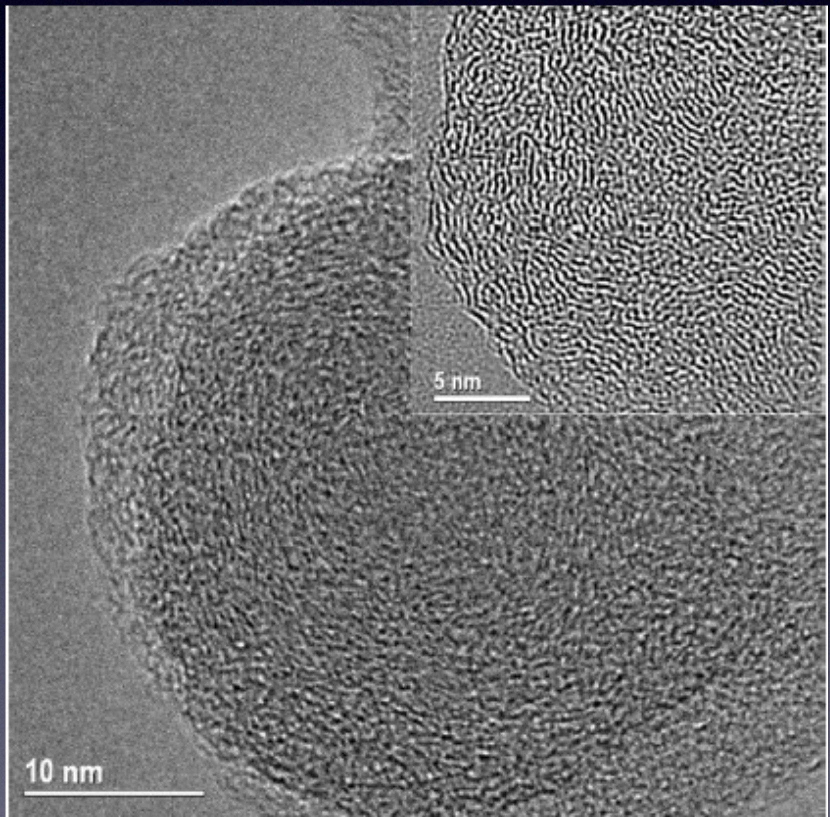
λ=532nm

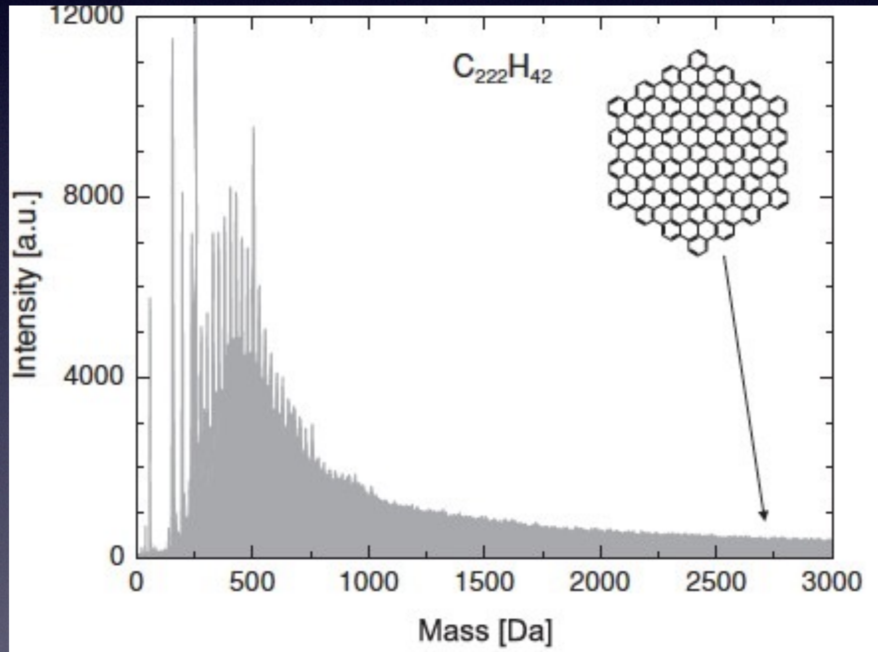
UV Processing in Space



Andrews et al, 2016, A&A, 595, A23
Montillaud et al, 2013, A&A, 552, A15

PAHs & Soot



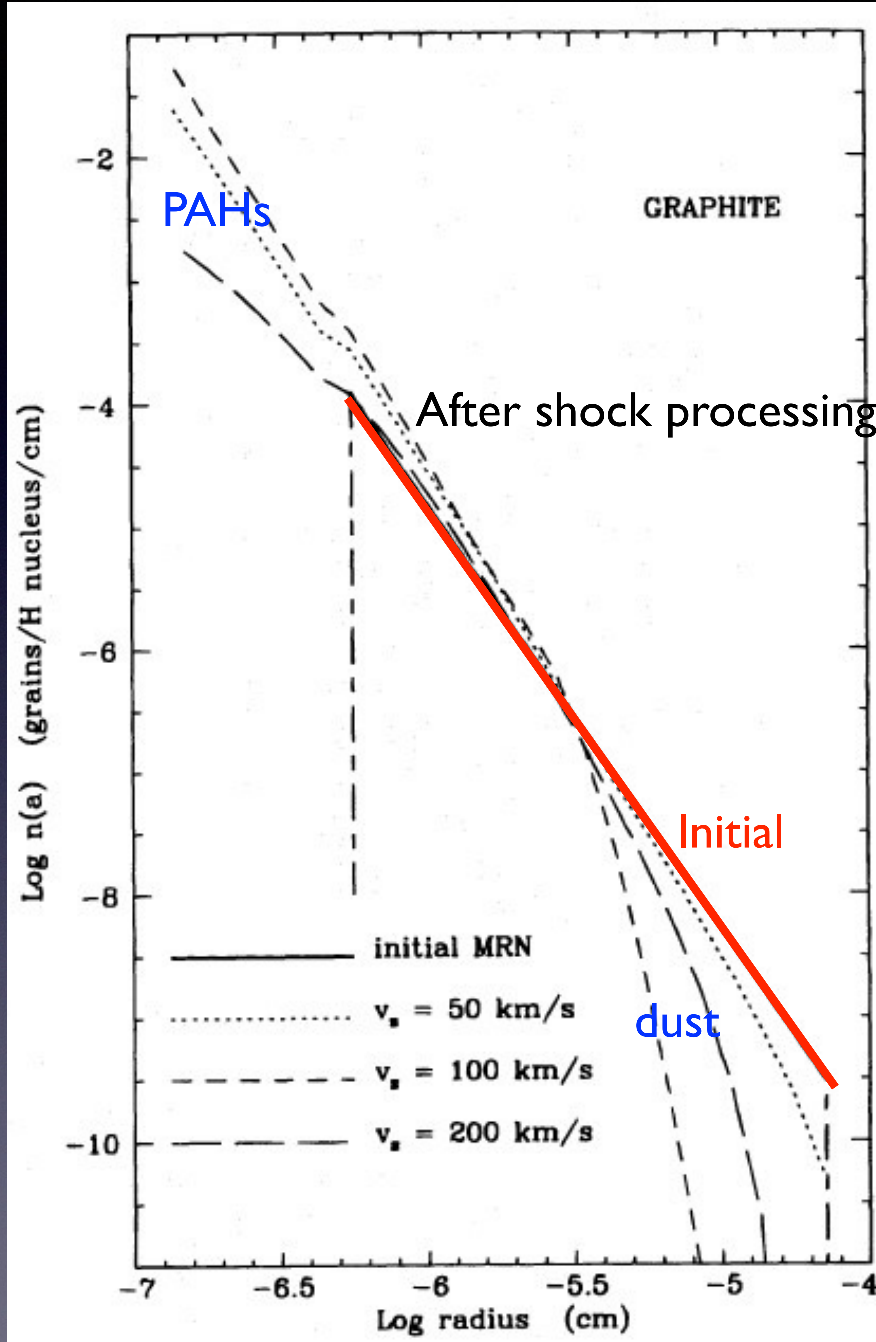


Jaeger et al, 2009, ApJ, 696, 706

PAH "Formation" in (Interstellar) Shocks

Shattering of carbon soot produces PAHs galore

Jones et al, 1996, ApJ, 469, 740



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Summary

- Bottom-up chemistry (~10% of elemental C)
  - Gas inventory: Largely CO (~99.5%), small amounts of hydrocarbon chains: ion-molecule & neutral-neutral radical chemistry
  - Icy inventory: H_2O dominated with CO, CO_2 & CH_3OH at 10-25%: Hydrogenation "activates" CO
  - Hot Cores Inventory: Largely CO (~98%), small amounts of methanol and its "daughter" products; Origin of SOM: methanol ice released to the gas
- Top-down chemistry (~10% of elemental C)
  - Largely aromatic
  - Produced in stellar outflows & shattering in interstellar shocks
  - Photochemistry: PAHs —>GrandPAHs—>Graphene—>C_{60}