Astrochemistry
I. Basic processes

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Leiden/MPE

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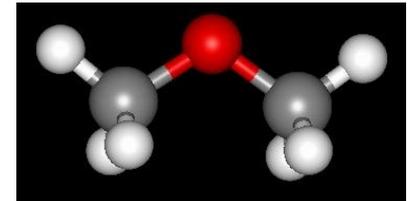
What is astrochemistry?
(or molecular astrophysics)

- 'Formation, destruction and excitation of molecules in astronomical environments and their influence on the structure, dynamics and evolution of astronomical objects'

- 'Blending of astronomy and chemistry in which each area enriches the other in a *mutually stimulating* interaction'

- 'Astrophysics is almost entirely applied atomic, molecular and optical physics'

'

Dalgarno 2008, ARA&A

1.1 Introduction

- Molecules are found throughout the universe
  - Molecular clouds, evolved stars, planetary nebulae, protoplanetary disks, stellar and (exo-) planetary atmospheres, solar photosphere, comets, galaxies (nearby to high z), …..
- Some typical conditions
  - Diffuse clouds: T_{kin}~100 K, n~100 cm^{-3}
  - Dense clouds: T_{kin}~10-100 K, n~10^4-10^8 cm^{-3}
  - Hot cores: T_{kin}~100-1000 K, n~10^6-10^8 cm^{-3}
  - Disk midplane: T_{kin}~10-1000 K, n~10^8-10^{13} cm^{-3}

  - Compare atmosphere at sea level: T_{kin}~300 K, n~3 10^{19} cm^{-3}

=> Conditions very different from those normally encountered in lab on Earth: *molecular physics*

Intro (cont'd)

- Interstellar clouds are birthplaces of new stars
  - Evolution abundances molecules: *astrochemistry*
  - Molecules as physical diagnostics: *astrophysics*
- Progress strongly driven by observations: *technology*

=> *Very interdisplinary topic!*

Birth and death of stars: astrochemical evolution
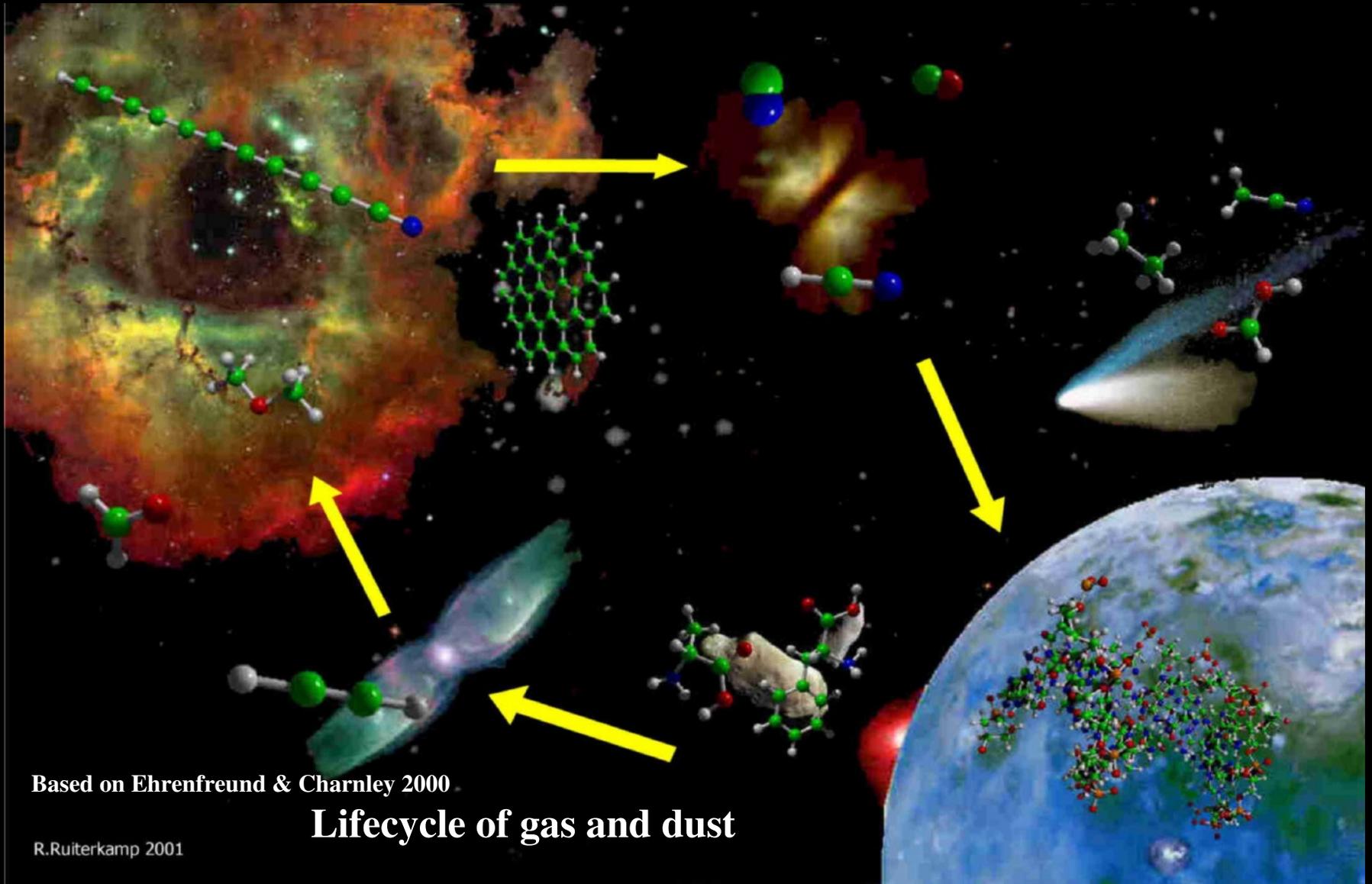
Based on Ehrenfreund & Charnley 2000

Lifecycle of gas and dust

R.Ruiterkamp 2001

1.2 Composition clouds
Cosmic (solar) abundances elements

Element	Abundance	Element	Abundance
H	1.00	Mg	4.2×10^{-5}
He	0.075	Al	3.1×10^{-6}
C	3.5×10^{-4}	Si	4.3×10^{-5}
N	8.5×10^{-5}	S	1.7×10^{-5}
O	5.5×10^{-4}	Ca	2.2×10^{-6}
Na	2.1×10^{-6}	Fe	4.3×10^{-5}

- Precise values for C, N and O under discussion because of revision of solar abundances

The Astronomers' Periodic Table

H

He

0.1

1.0 **by number**

4 **1** **6** 10^{-4}

□ □ □ □

C N O Ne

· · · ·

Mg Si S Ar

4 10^{-5} **4** **1** 10^{-5}

·

Fe **4** 10^{-5}

B. McCall 2001
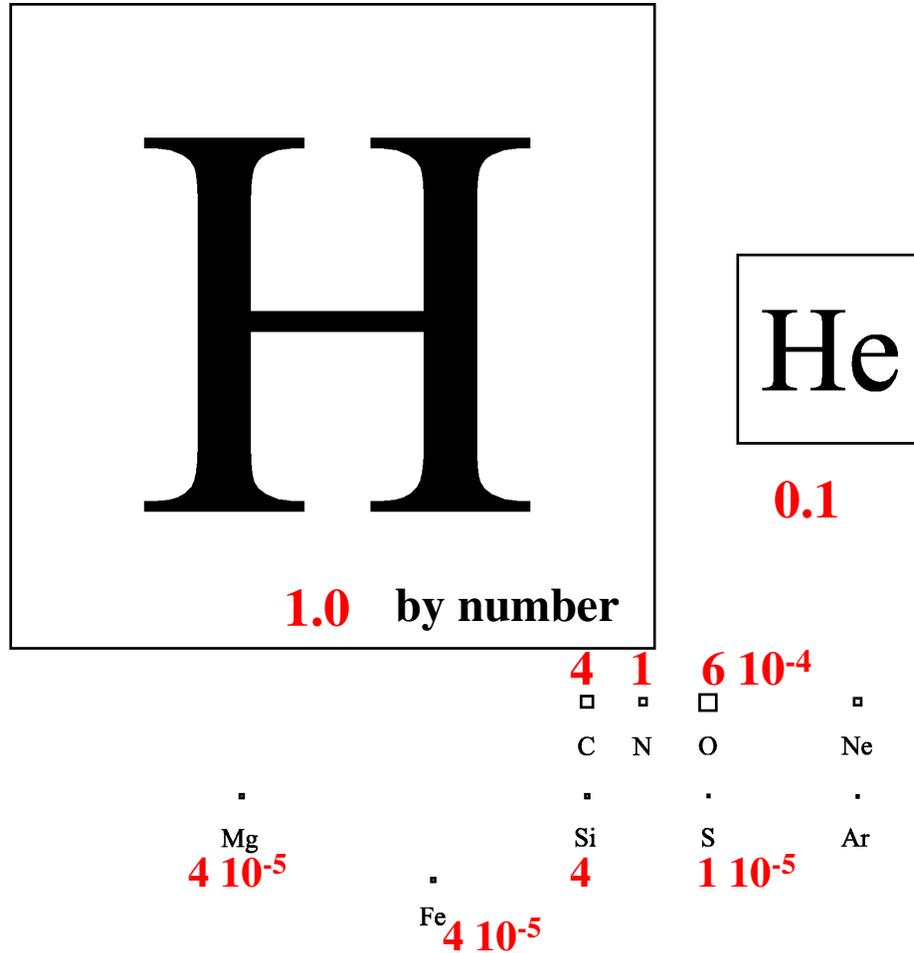
Interstellar grains
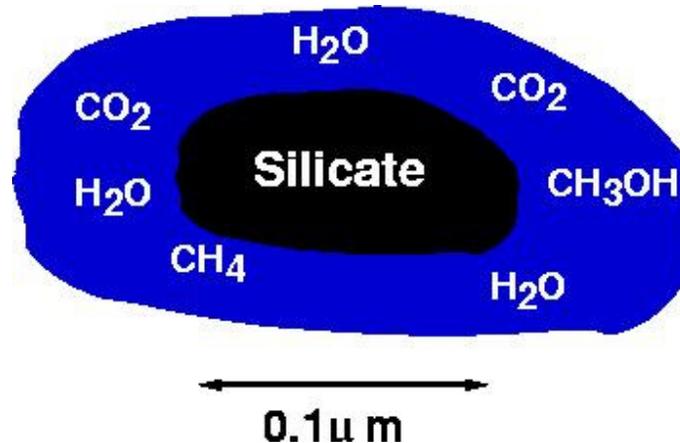
- Small solid particles ~0.01-0.5 μm in size consisting of
  silicates and carbonaceous material; ~10^{-12} by number w.r.t. H
- Most of Si, Mg, Fe incorporated in silicate cores;
  ~30% of O; ~60% of C in carbonaceous material
- Cold dense clouds (T_{dust}~10 K): gas-phase species condense on
  grains forming an icy mantle

1.3. How do we observe molecules?

$$E = E^{el} + E^{vib} + E^{rot}$$
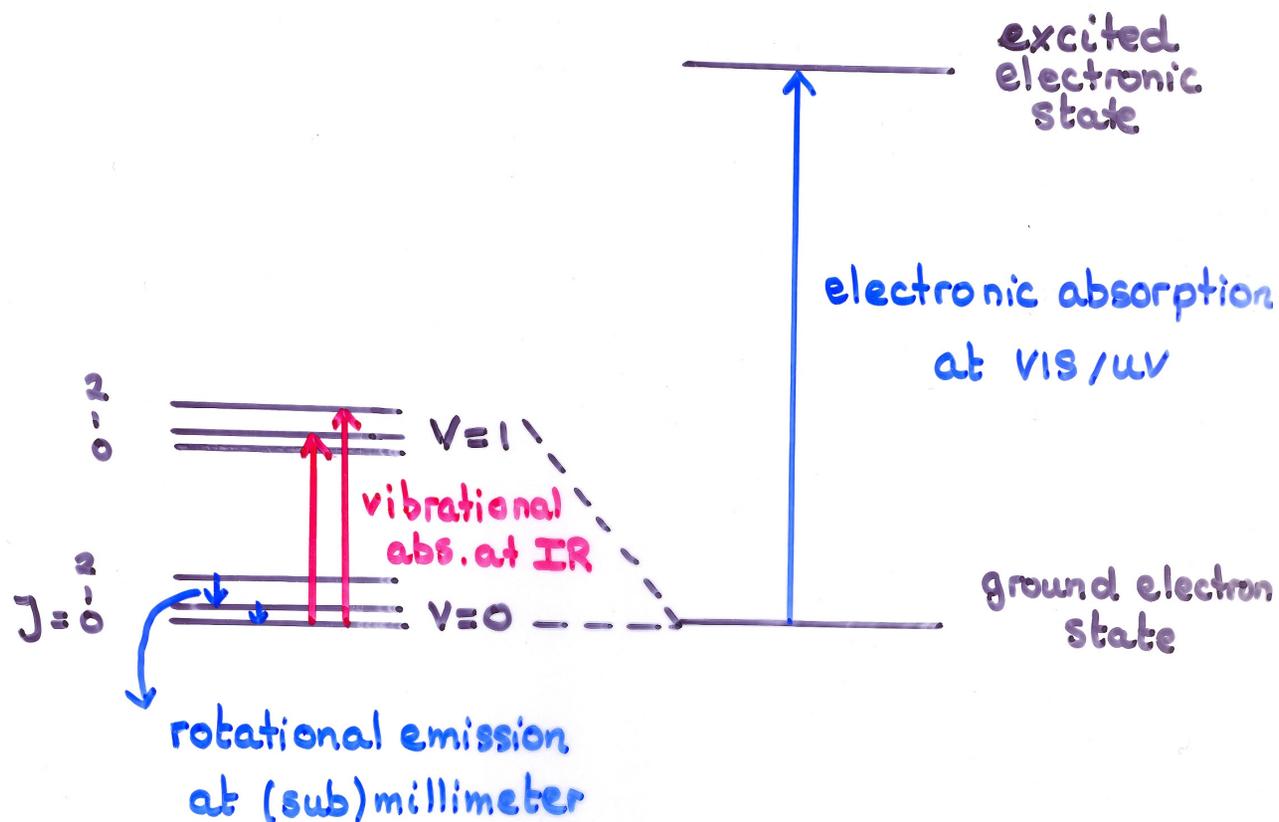
Cold dense clouds

- Opaque at visible and UV wavelengths => molecules shielded from dissociating UV radiation
- Millimeter emission: *rotational* transitions
  - *Limitation*: molecule must have permanent dipole moment => cannot observe H_2, C_2, N_2, CH_4, C_2H_2, …
  - *Advantage*: many molecules down to low abundances; lines in emission => map
- Infrared absorption: *vibrational* transitions
  - *Limitation*: need background IR source => only info along line of sight
  - *Advantage:* symmetric molecules + solid state
- Earth's atmosphere prevents observations of key molecules from ground: H_2O, O_2, CO_2

Infrared: absorption gas and solids

hot dust
300–1000 K
10^7 cm^{-3}

gas–phase molecules
20–200 K

cold dust
(ice mantles)
10–100 K
10^4 cm^{-3}

Flux

Continuum due to hot dust

Absorption by cold dust

Wavelength
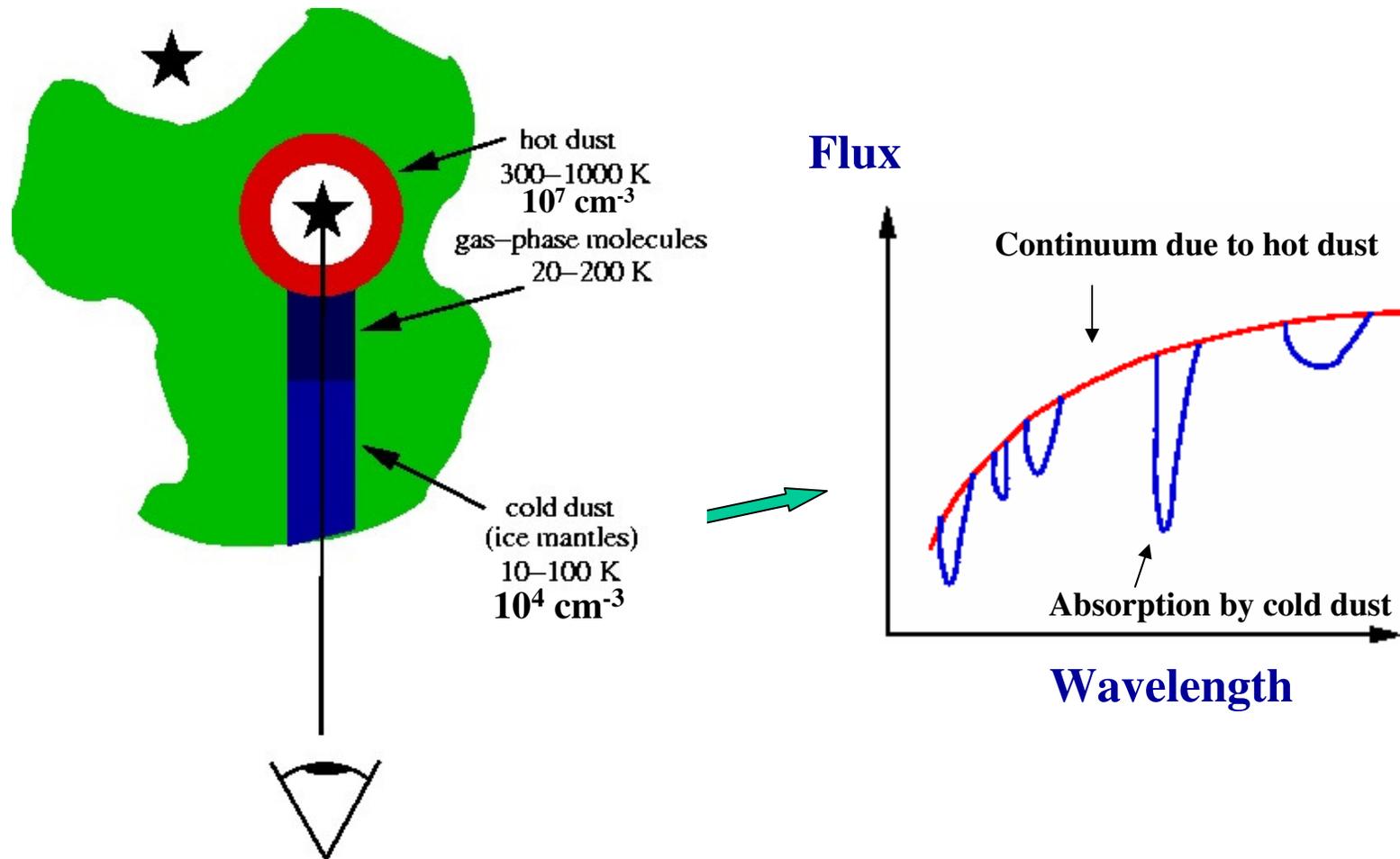
Vibrational transitions of gases *and* solids

1.4 Identified interstellar molecules

N=2		N=3		N=4	N = 5	N = 6	N = 7	N = 8	N = 9	N = 10
H_2	AlCl	CH_2	C_2S	NH_3	CH_4	CH_3OH	CH_3NH_2	$HCOOCH_3$	$(CH_3)_2O$	$(CH_3)_2CO$
CH	PN	H_2S	OCS	H_2CO	SiH_4	CH_3SH	CH_3CCH	CH_3C_2CN	C_2H_5OH	CH_3C_4CN
NH	SiN	NH_2	MgCN	H_2CS	CH_2NH	C_2H_4	CH_3CHO	HC_6H	C_2H_5CN	CH_3CH_2CHO
OH	SiO	H_2O	MgNC	H_2CN	C_5	H_2C_4	c-CH_2OCH_2	C_7H	CH_3C_4H	$(CH_2OH)_2$
O_2(?)	SiS	HNO	NaCN	l-C_3H	l-C_3H_2	CH_3CN	CH_2CHCN	$HOCH_2CHO$	C_8H	
HF	PO	C_2H	SO_2	c-C_3H	c-C_3H_2	CH_3NC	HC_4CN	CH_3COOH	HC_6CN	
C_2	SH	HCN	N_2O	HCCH	H_2CCN	NH_2CHO	C_6H	$H_2CCCHCN$	CH_3CONH_2	N = 11
CN	AlF	HNC	SiCN	HNCO	H_2NCN	H_2CCHO	H_2CCHOH	H_2C_6	CH_2CHCH_3	HC_8CN
CO	FeO	HCO	SiNC	HNCS	CH_2CO	C_5H		CH_2CHCHO		CH_3C_6H
CS	SiC	c-SiC_2		HCCN	HCOOH	C_5N		C_2H_6		
CP		MgCN		C_3CN	C_4H	HC_4N				
NO		MgNC		C_3O	HC_2CN	C_5S(?)				N = 12
NS		AlNC		C_3S	HC_2NC	HC_4H				C_6H_6
SO		HCP	H_3^+	c-SiC_3	C_4Si	CH_2CNH				
HCl	CH^+	C_3	HCO^+	C_3N^-	HNCCC	HC_2CHO				
NaCl	CO^+	C_2O	HOC^+	H_3O^+		c-C_3H_2O				N = 13
KCl	SO^+	CO_2	N_2H^+	HCNH$^+$	H_2COH^+					$HC_{10}CN$
N_2(?)	CF^+		HCS^+	$HOCO^+$	C_4H^-	HC_3NH^+	C_6H^-		C_8H^-	

Herbst, priv. comm.

- ~150 total, not including isotopologues
- number of new molecules still increasing by ~3 per year

Diversity of molecules

- About 150 different molecules firmly identified
- Ordinary molecules

  NH_3, H_2O, H_2CO, CH_3CH_2OH, ….
- Exotic molecules

  HCO^+, N_2H^+, $HCCCCCCCN$, ….

$\Rightarrow$ *Unusual molecules*
(rare on Earth but not in space)

Millimeter spectra: myriads of lines!

- Ultra-high precision spectroscopy (accuracy > 1:10⁶)
- Not all lines identified

Some (recent) detections

- H_3^+, H_2D^+, D_2H^+: cornerstones ion-molecule chemistry
- C_4, C_6H_2, CH_3CHCH_2: new carbon chains
- Cyclic C_2H_4O: fifth ring
- C_6H_6: benzene: simplest PAH
- C_6H^-, C_8H^-, C_4H^-: first negative ions!
- D_2CO, ND_3, CD_3OH: doubly + triply deuterated molecules
- NaCN, AlCN, SiN: metal-containing species

Not convincingly detected: O_2, glycine, ….

Negative ions

Negative ions

C_6H^-

TMC-1

$5 \rightarrow 4$ $4 \rightarrow 3$

10 mK

Laboratory

Relative Intensity

$v - v_0$ (kHz) $v - v_0$ (kHz)
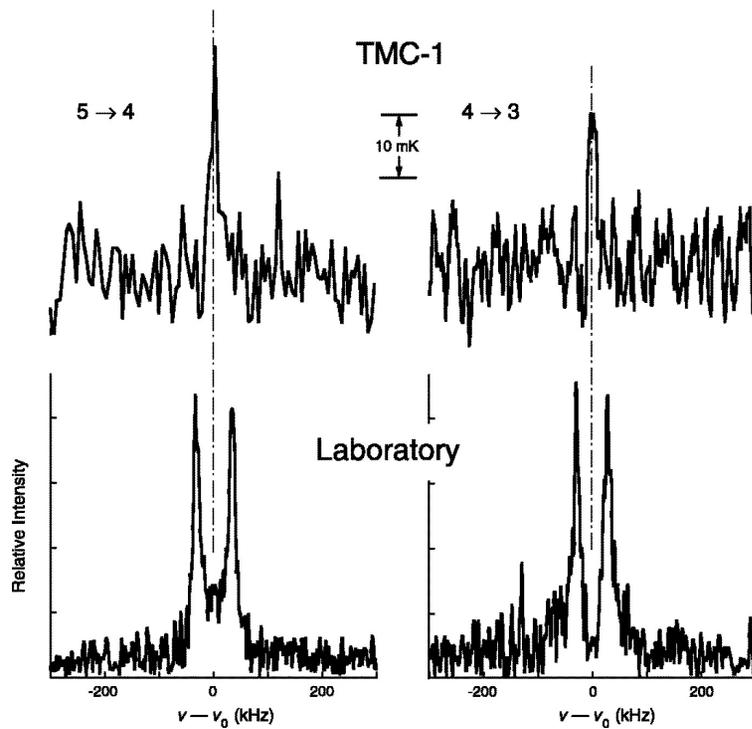
McCarthy et al. 2006

Larger chains have large electron affinity (binding energy)
Herbst & Osamura 2008

Propene in TMC-1
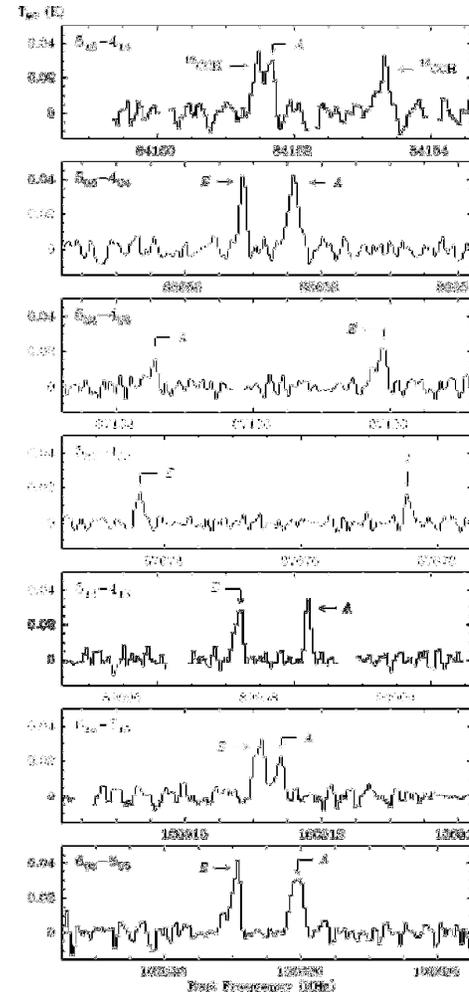
Marcelino et al. 2007
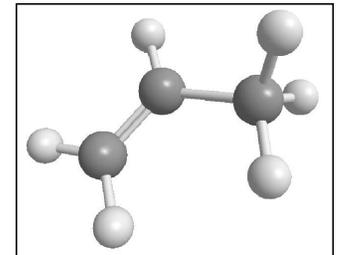
Molecules at high redshift: z=6.4!
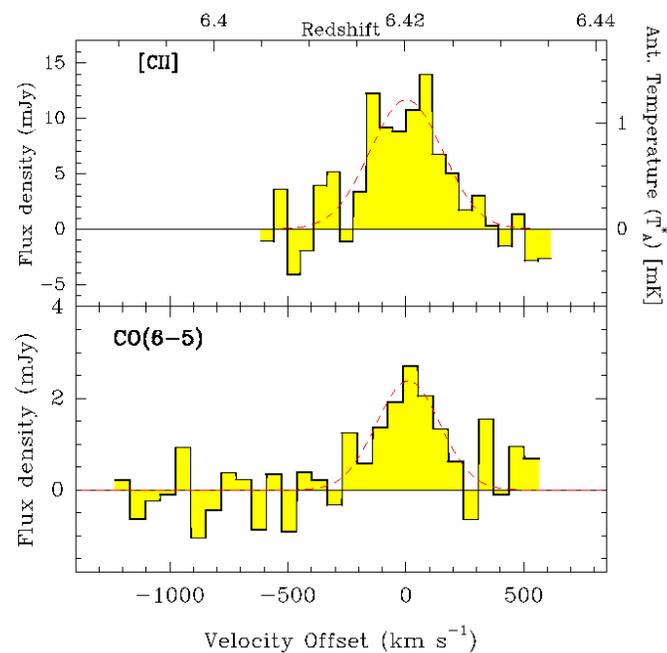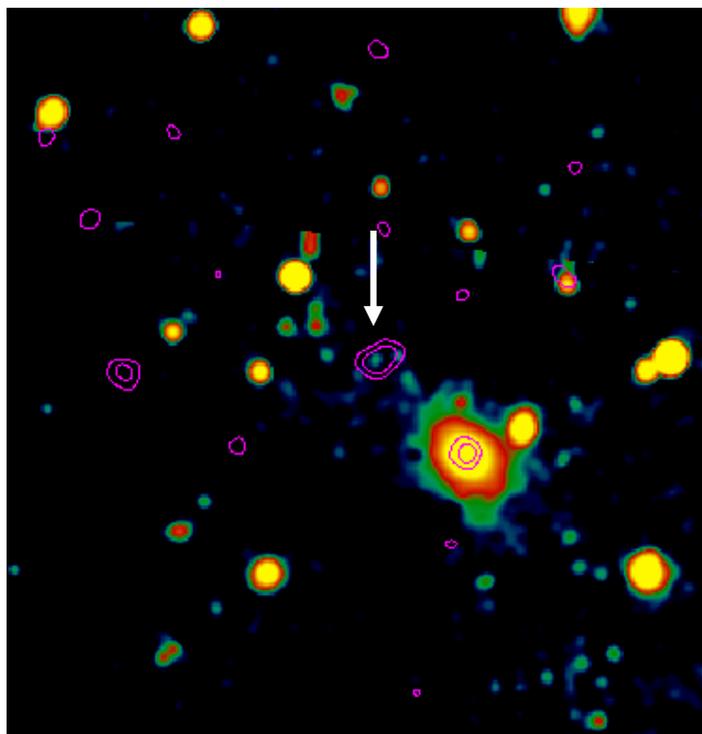
CO and [C II] in quasar SDSS J1148+5251 at z=6.4

Walter et al. 2003, Maiolino et al. 2005

HCO⁺, CN at high z

HCO⁺

CN
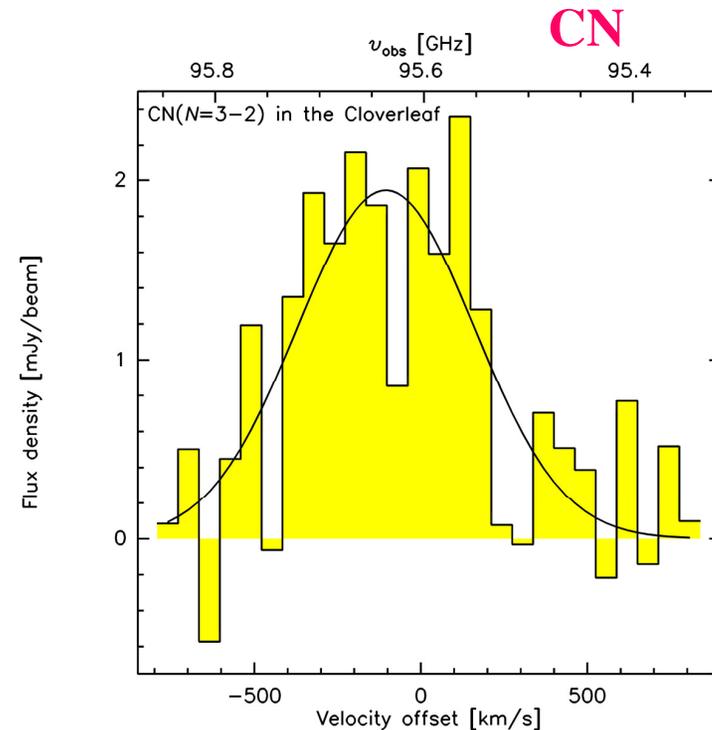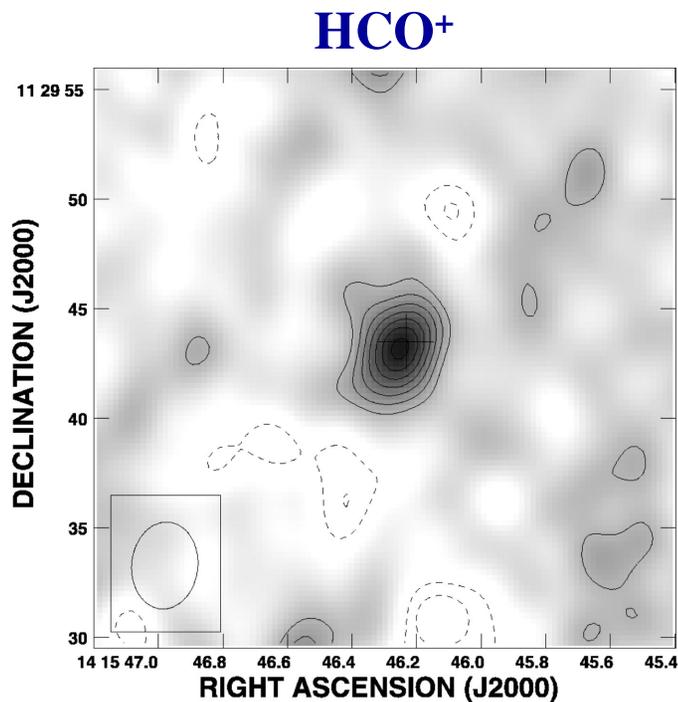
Riechers et al. 2007a,b

- Detection of HCO⁺ and CN toward Clover Leaf quasar at z=2.56 (lensed system => signal enhanced)
- Both lines require high densities 10^5-10^6 cm^{-3} for excitation

1.5 Importance of molecules

- Exotic chemistry: unique laboratory

- Astrochemical evolution

- Molecules as diagnostics of temperature T_{kin}, density n_H, velocity, …

- Molecules as coolants

  - Radiation escapes from cloud => net kinetic energy lost => cloud cools down

  Collisions   **Radiation**

  CO (J=0) $\Longrightarrow$ **CO(J=1)** $\Longrightarrow$ **CO(J=0)**

Questions addressed

- What are chemical processes leading to formation and destruction of molecules?

- How well are basic molecular processes known from experiments or theory

- What is evolution of molecules in the universe, from their creation at high redshifts to interstellar clouds to incorporation in new solar systems

- How can molecules be used as physical and chemical diagnostics of physical structure, evolution, cosmic-ray ionization, …

1.6 Basic molecular processes: gas phase

- Because of low temperatures and densities in clouds, chemistry is ***not*** in thermodynamic equilibrium but controlled by two body reactions => abundances depend on physical conditions (T,n,radiation field), history, …

- Three body reactions do not become important until $n>10^{12}$ cm^{-3}

- Although models contain thousands of reactions, only few different types of processes

- Rate of reaction: $k\ n(X)\ n(Y)$ cm^{-3} s^{-1}

Rate coefficient in cm^3 s^{-1}

Chemical network: example
Carbon chemistry and its coupling with oxygen

These networks look complicated but are built up from only a handful of basic types of reactions

Types of chemical reactions

- ## Formation of bonds
  - Radiative association: $X^+ + Y \rightarrow XY^+ + h\nu$
  - Associative detachment $X^- + Y \rightarrow XY + e$
  - Grain surface: $X + Y{:}g \rightarrow XY + g$
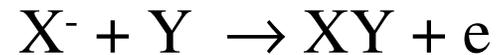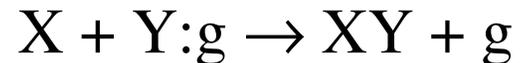
- ## Destruction of bonds
  - Photo-dissociation: $XY + h\nu \rightarrow X + Y$
  - Dissociative recombination: $XY^+ + e \rightarrow X + Y$
  - Collisional dissociation: $XY + M \rightarrow X + Y + M$
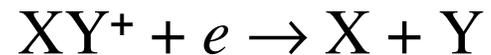
- ## Rearrangement of bonds
  - Ion-molecule reactions: $X^+ + YZ \rightarrow XY^+ + Z$
  - Charge-transfer reactions: $X^+ + YZ \rightarrow X + YZ^+$
  - Neutral-neutral reactions: $X + YZ \rightarrow XY + Z$
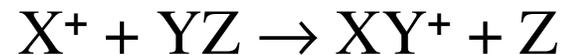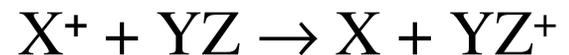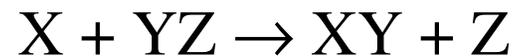
1.7 Radiative association

- $X + Y \underset{\tau_d}{\overset{\tau_c}{\rightleftharpoons}} XY^* \overset{\tau_r}{\rightarrow} XY + h\nu$

- Energy conservation => photon must be emitted, which is a very slow process
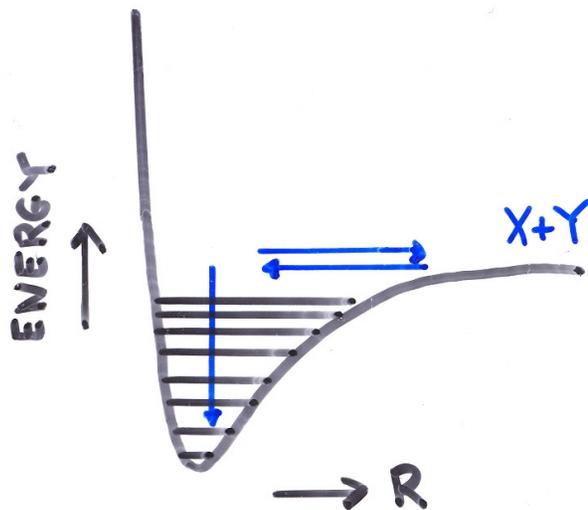
$\tau_r = 10^{-2} - 10^{-3}$ s vibrational transition

$\tau_{c,d} = 10^{-13}$ s   collision time

$\Rightarrow$ *Molecule formation occurs only 1:10^{10} collisions*

Radiative association (cont'd)

- Process becomes more efficient if electronic states available: τ_r smaller
  - $C^+ + H_2$ example
- Also more efficient for larger molecules: τ_d longer
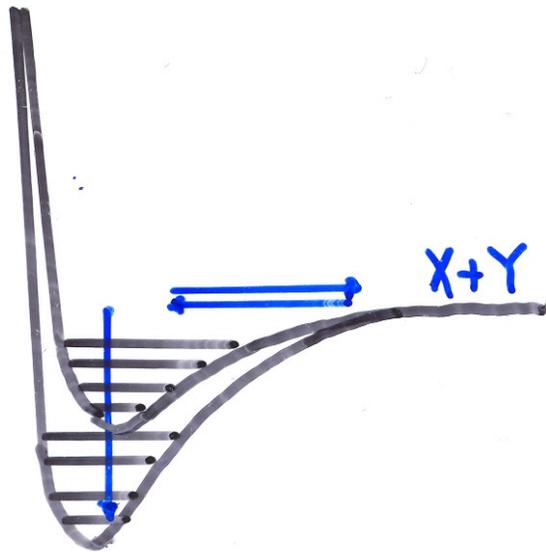
$\tau_r = 10^{-8}$ s   electronic transition

$\tau_{c,d} = 10^{-13}$ s   collision time

=> *Efficiency increased to 1:10^5*

Radiative association (cont'd)

- Radiative association is extremely difficult to measure in laboratory because 3-body processes dominate under most lab conditions.

- Many rate coefficients are based on theory; overall uncertainties 1-2 orders of magnitude

- Exception: $C^+ + H_2 \rightarrow CH_2^+ + h\nu$
  - $k \sim 10^{-15}$ cm^3 s^{-1} within factor of 2-3
  - Initiates carbon chemistry

1.8 Associative detachment

- Usually not important in cold clouds, but can play a role in partly ionized regions and early universe

- Form negative ions by radiative attachment

$$X + e \rightarrow X^- + h\nu \quad \textit{slow} \text{ process}$$

- Form molecule by associative detachment

$$X^- + Y \rightarrow XY + e \quad \textit{fast} \text{ process}$$

Associative detachment

- Examples: $H + e \rightarrow H^- + h\nu$

$$H^- + H \rightarrow H_2 + e \qquad \text{fast}$$
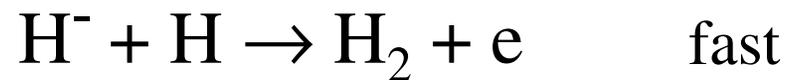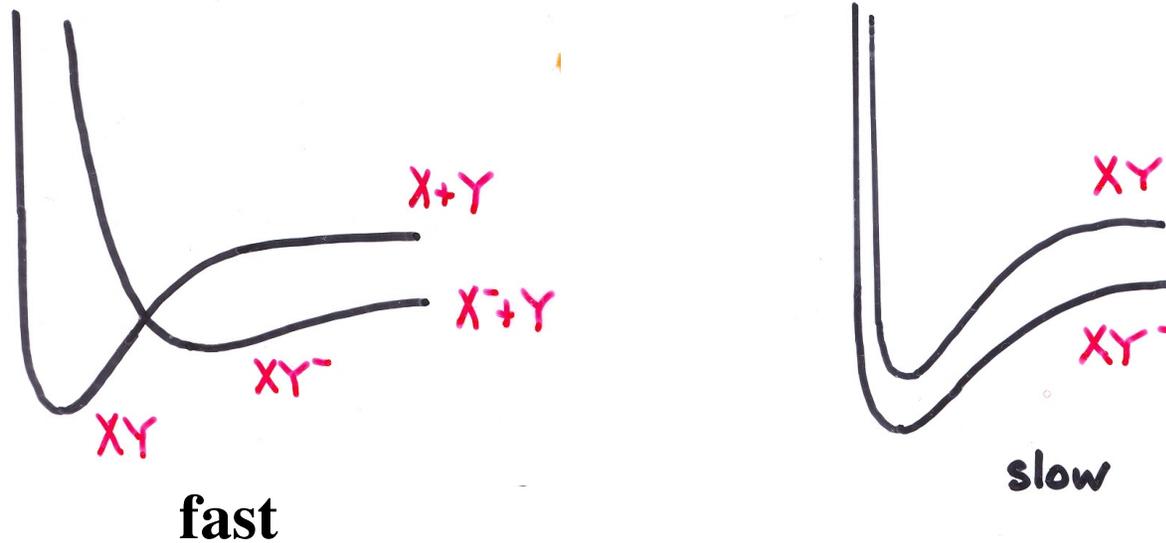
Application: early universe chemistry

Black 1990
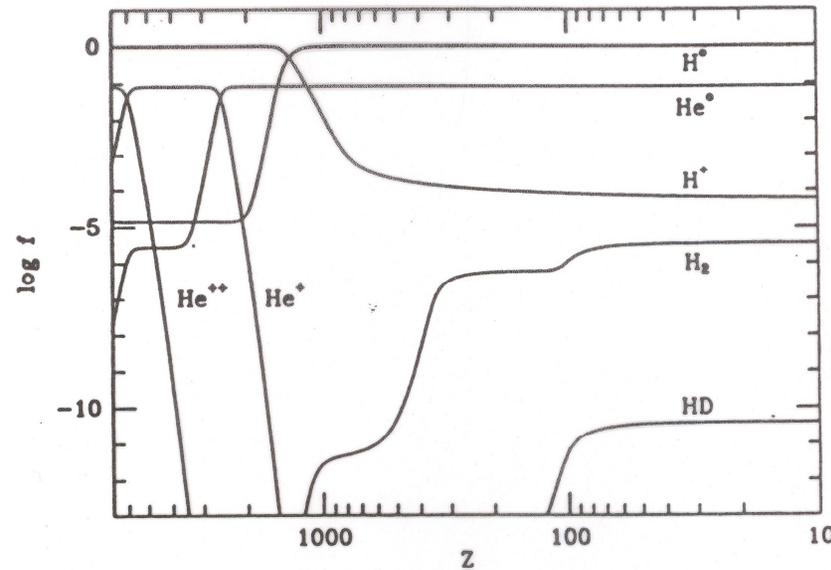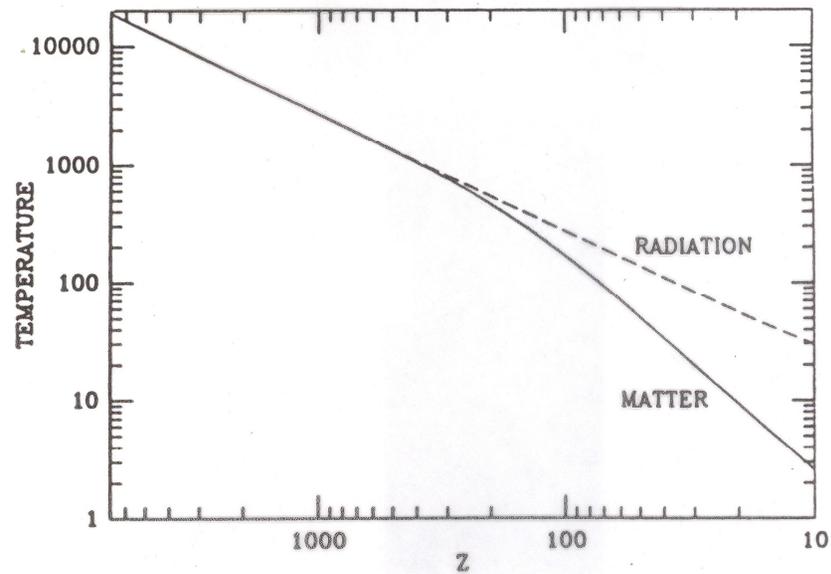
First molecules in universe: He_2^+ and HeH^+
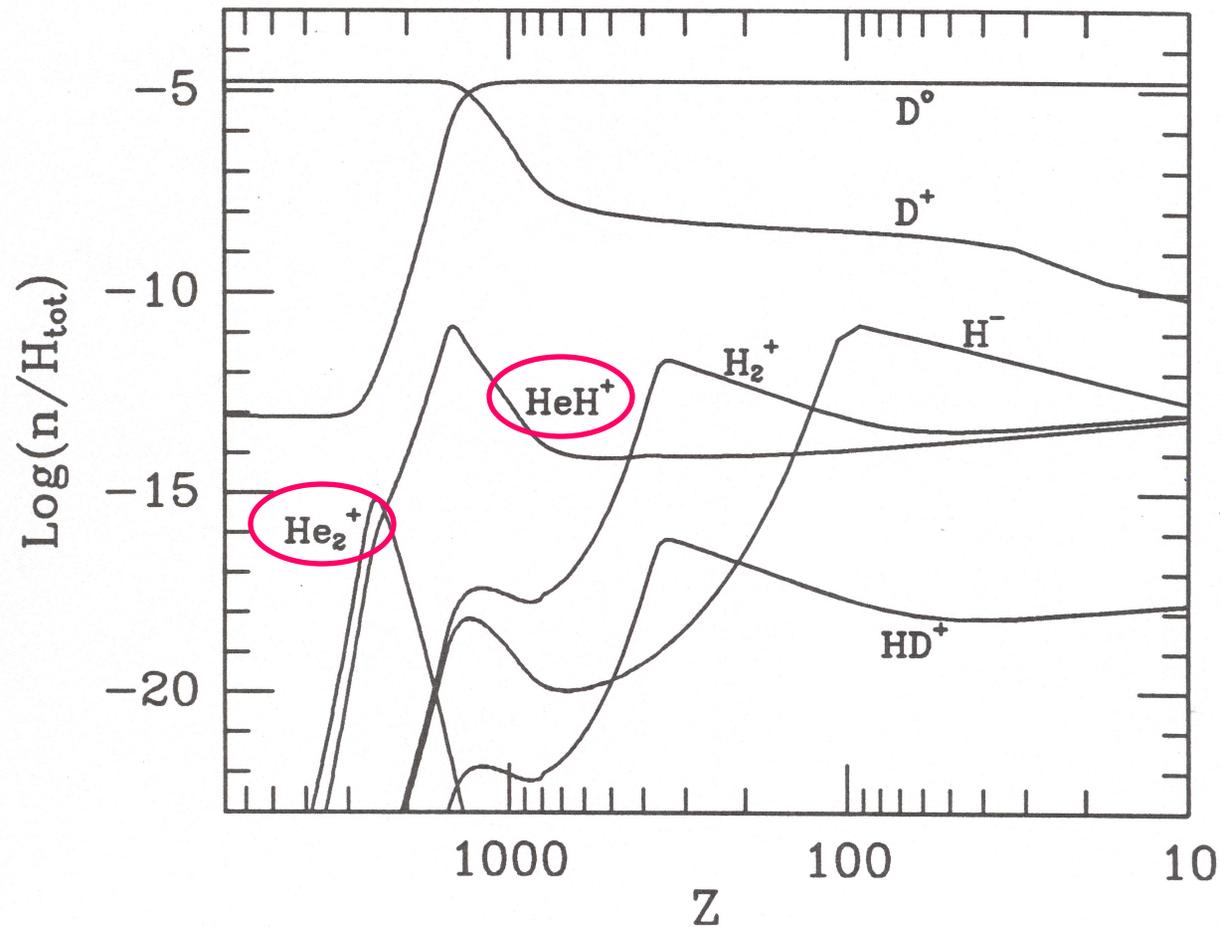
Latter 1989

He_2^+ and HeH^+ formed by radiative association

H chemistry in early universe

- Hydrogen chemistry in early universe is very different from that in the current era due to the absence of dust => H_2 must be formed by slow gas-phase reactions

- Direct formation by radiative association $H + H \rightarrow H_2 + h\nu$ is much too slow since H_2 does not have a dipole moment => consider other routes

H$^+$ route

- H$_2$ formation:
  - H + H$^+$ → H$_2^+$ + $h\nu$
  - H$_2^+$ + H → H$_2$ + H$^+$
- H$_2^+$ can be destroyed by photodissociation and dissociative recombination
  - H$_2^+$ + $h\nu$ → H + H$^+$
  - H$_2^+$ + e → H + H
  => Formation of H$_2$ only becomes effective when T_R<4000 K and photodissociation of H$_2^+$ ceases

H⁻ route

- At later times (z~100), H_2 can be formed through H⁻
  - $H + e \rightarrow H^- + h\nu$
  - $H^- + H \rightarrow H_2 + e$
- H⁻ is destroyed by photodetachment
  - $H^- + h\nu \rightarrow H + e$

  with threshold of 0.75 eV => need T_R < 1000 K before route becomes effective

H$_2$ chemistry

- Both H$^+$ and H$^-$ routes are catalytic, since H$^+$ and e returned
- H$_2$ destroyed by
  - H$_2$ + H$^+$ → H$_2^+$ + H
  - H$_2$ + e → H + H$^-$
- Net result: $f(\mathbf{H_2}) = n(\mathbf{H_2})/n_{\mathrm{H}} \sim 10^{-6}$ as $z \rightarrow 0$

Small molecular fraction in early universe

(but very important as coolants, allowing clouds to collapse and setting the mass of the first stars)

H$_2$ formation in early universe by H$^+$ and H$^-$ routes

Latter 1989
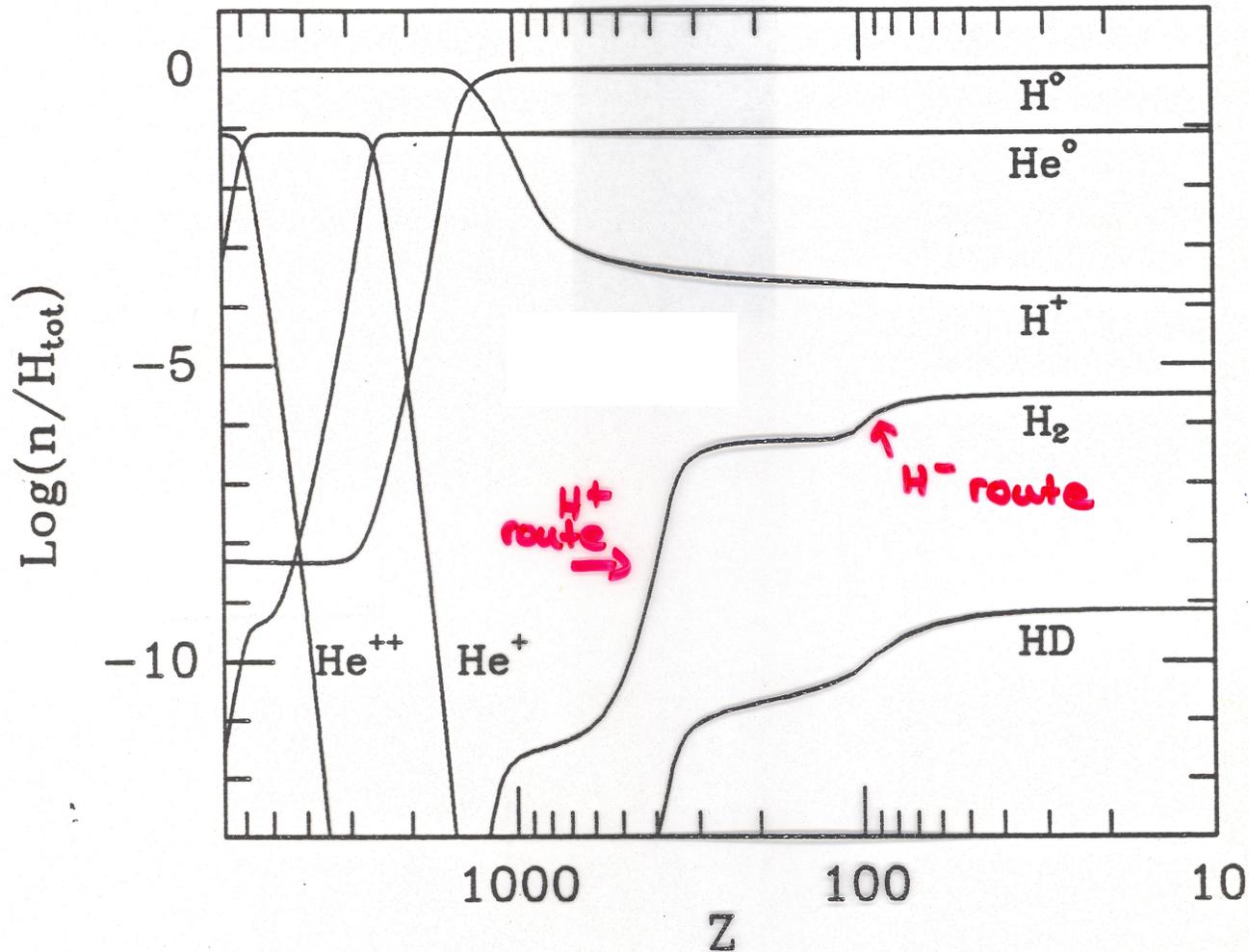
Sensitivity to cosmological parameters
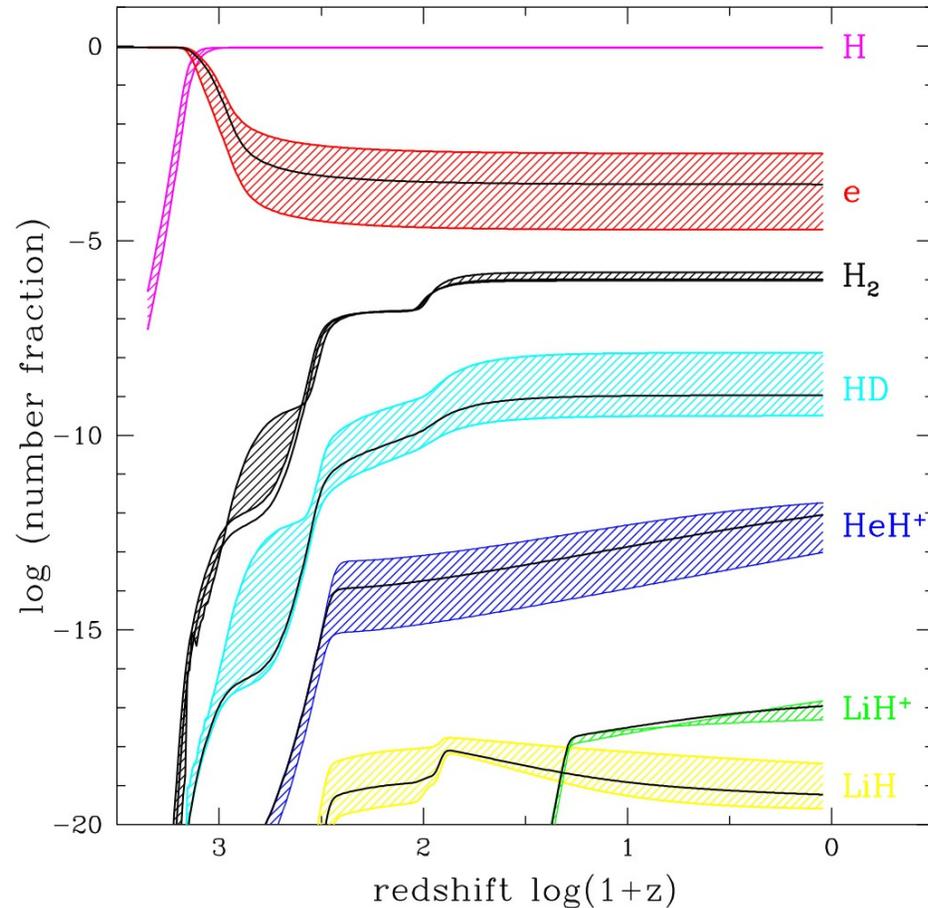
Hatched area covers range of variation of Ω_0=0.1-1, $h=H_0/100$=0.3-1 and η_{10}=baryon/photon=1-10

1.9 Photodissociation

- $XY + h\nu \rightarrow X + Y$
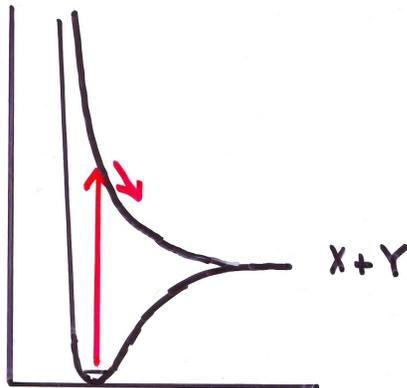
Direct photodissociation
OH, H_2O, CH, CH_2, …
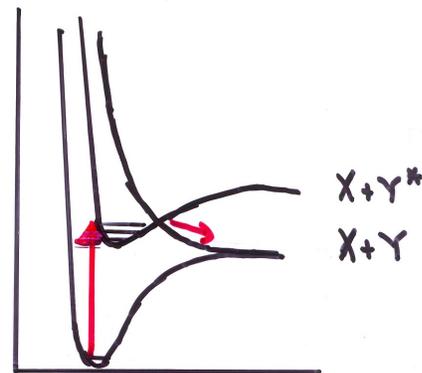
Predissociation
CO, NO, …..

- Experiments available for stable molecules, but not for radicals or ions
- Small molecules: theory works well: quantum chemical calculations of potential surfaces of excited states + transition dipole moments, followed by nuclear dynamics to obtain cross sections

Examples experiments
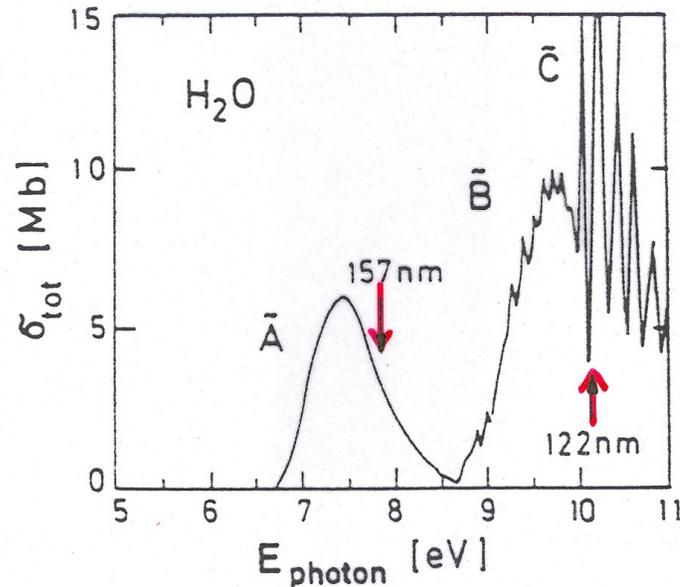
H_2O absorption followed by direct dissociation: accurate cross sections within 20%
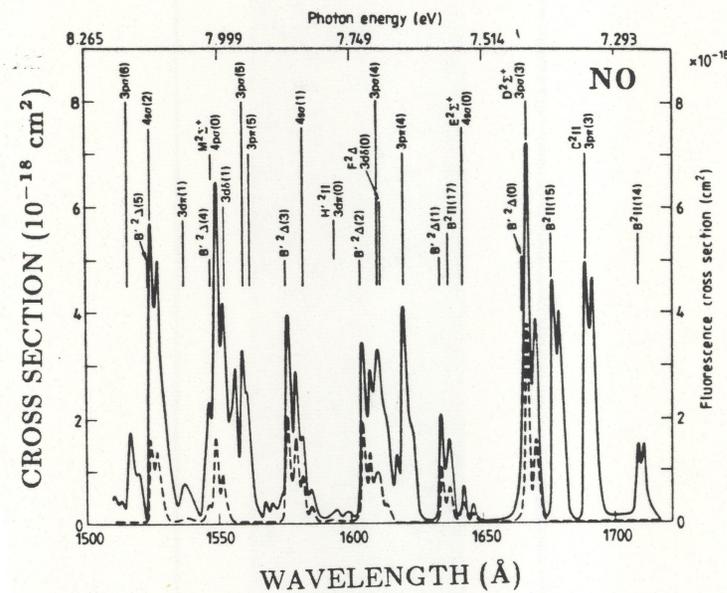
NO absorption (full) and fluorescence (dashed); mostly predissociation through discrete transitions; large uncertainties (order of magnitude)

H$_2$ spontaneous radiative dissociation
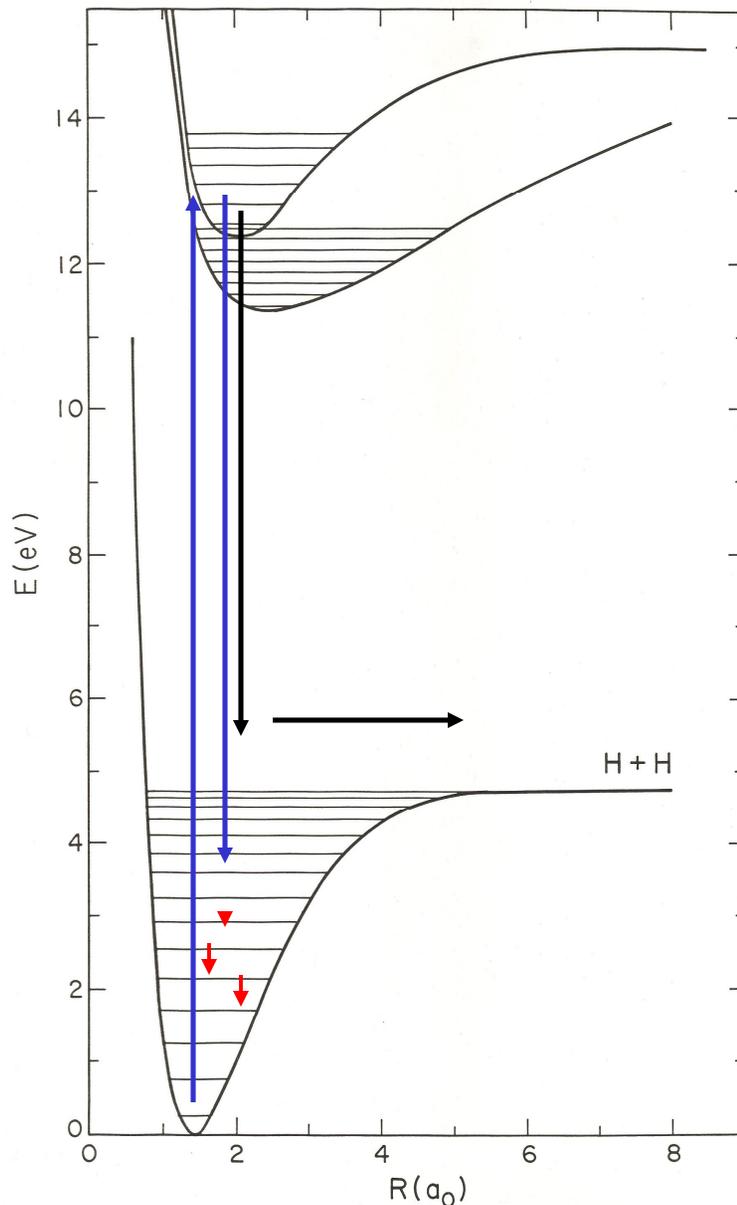
- 90% of absorptions into B and C states are followed by emission back into <u>bound</u> vibrational levels of the X state
- 10% of the absorptions are followed by emission into the <u>unbound</u> vibrational continuum, leading to dissociation

Both H$_2$ and CO p.d. initiated by line absorptions => self-shielding

Interstellar radiation field

$$k = \int \sigma(\lambda) I(\lambda) d\lambda$$

cross section · radiation field

CO, H$_2$

CH, OH
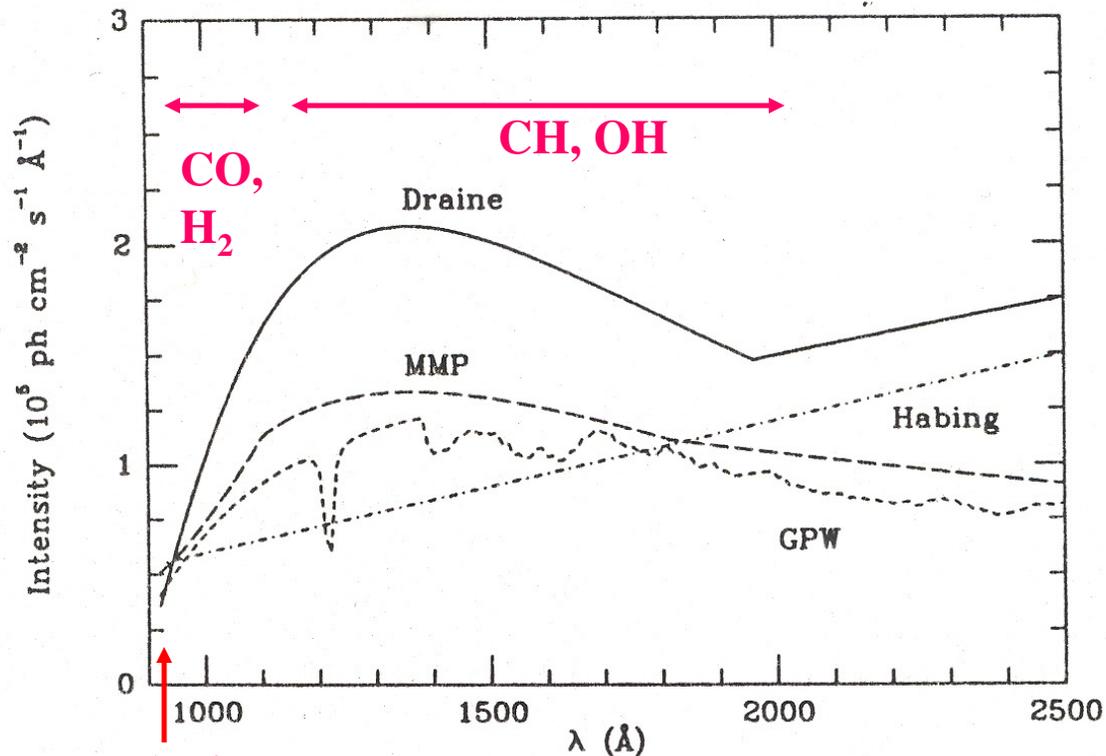
912 Å = 13.6 eV cutoff

Figure 5. *The intensity of the interstellar radiation field as a function of wavelength cf. Draine (1978) (full line), Mathis et al. (1983) (long–dashed line), Gondhalekar et al. (1980) (short–dashed line) and Habing (1968) (dash–dotted line).*

Average radiation provided by early-type stars in solar neighborhood

Note that H$_2$ and CO p.d. and C photoioniation only occur at 912-1100 Å
C can be photoionized by ISRF, but not O and N

Cosmic-ray induced radiation:
UV radiation inside dense clouds

$$H_2 + CR \Rightarrow H_2^+ + e^*$$

$$H_2 + e^* \Rightarrow H_2^* + e$$

$$H_2^* \Rightarrow H_2 + h\nu$$
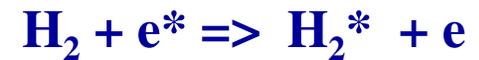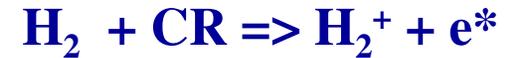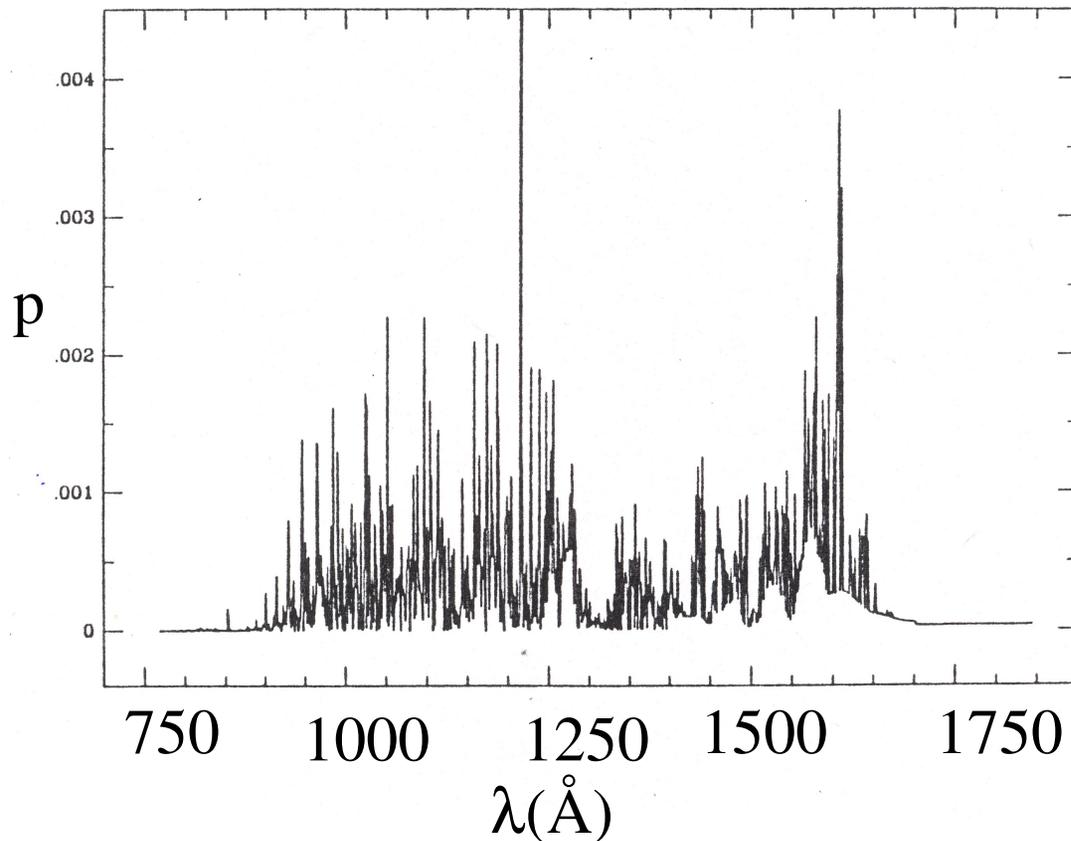
Prasad & Tarafdar 1983
Gredel et al. 1987

-Detailed line + continuum spectrum peaking around 1600 Å and continuing below
  912 Å

Other radiation fields

- Ly-α dominated
  - Shocks, …..
- Stellar blackbodies T_{eff}=4000-10000 K
  - Disks, (exo-)planets, cool PDRs, …
- Solar radiation T_{eff}=5500 K + Ly α
  - Comets

http://www.strw.leidenuniv.nl/~ewine/photo

See van Dishoeck et al. 2006

1.10 Dissociative recombination

- Atomic ions: $X^+ + e \rightarrow X + h\nu$ **Radiative: slow**
- Molecular ions: $XY^+ + e \rightarrow XY + h\nu$ **Radiative: slow**

$$\rightarrow X + Y$$ **Dissociative: rapid at low T**

slow   rapid
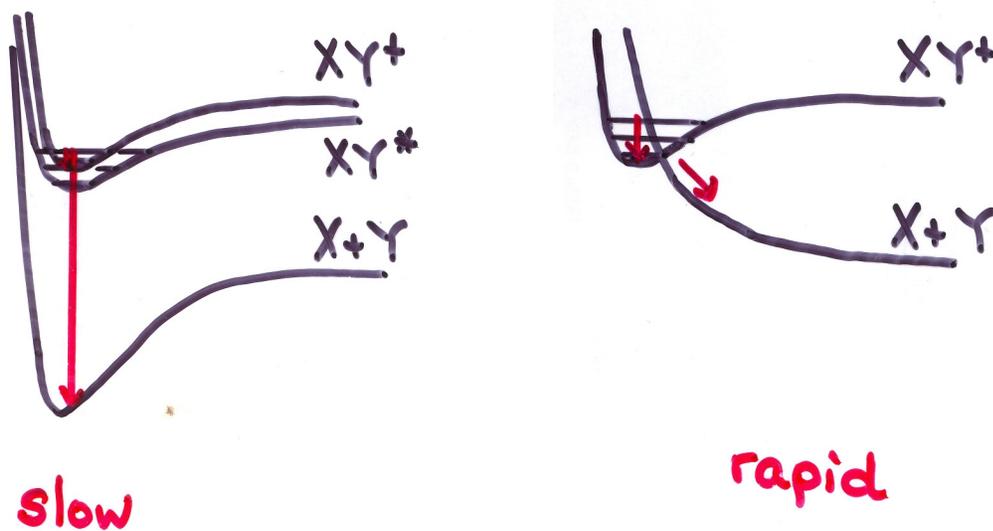
- Need curve crossing between XY^+ and repulsive XY potential for reaction to proceed fast
- Most rates well known; branching ratios products major uncertainty

Storage ring experiments
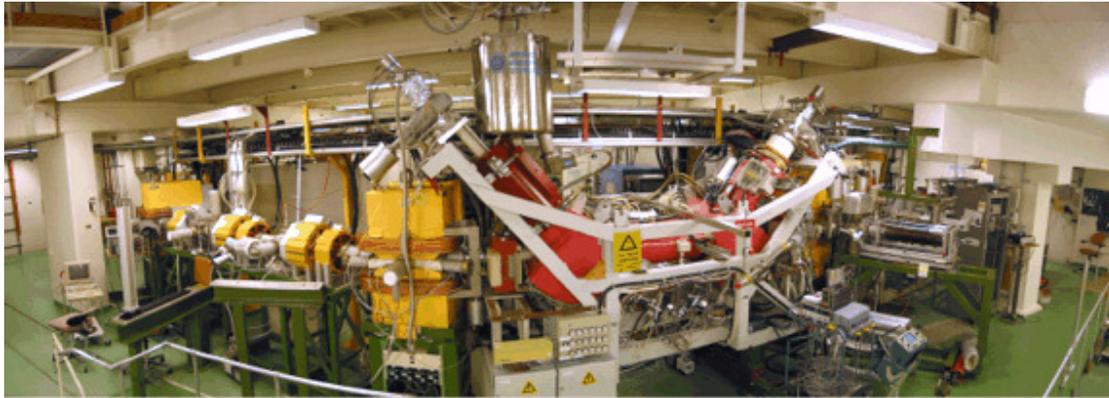
CRYRING, Stockholm

- Also Aarhus, Heidelberg
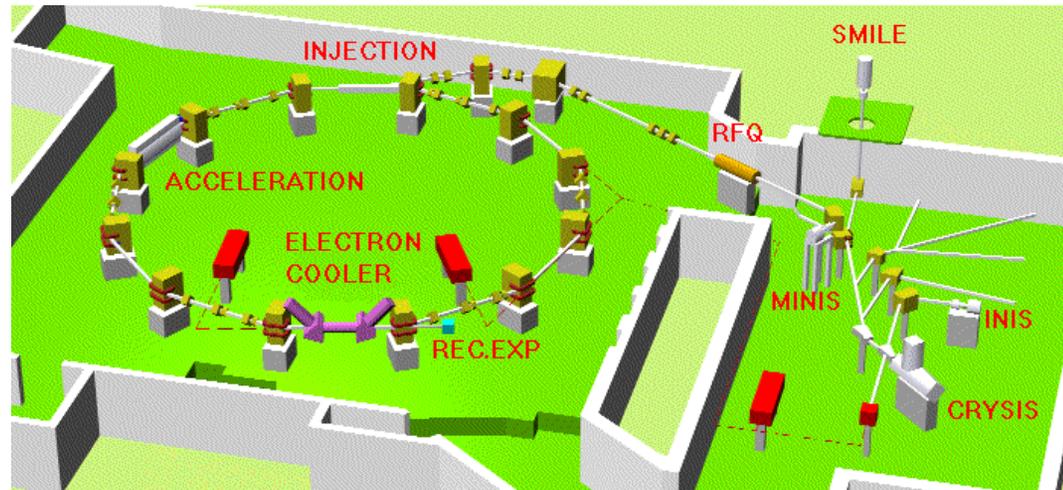
H$_3^+$ + e DR rate
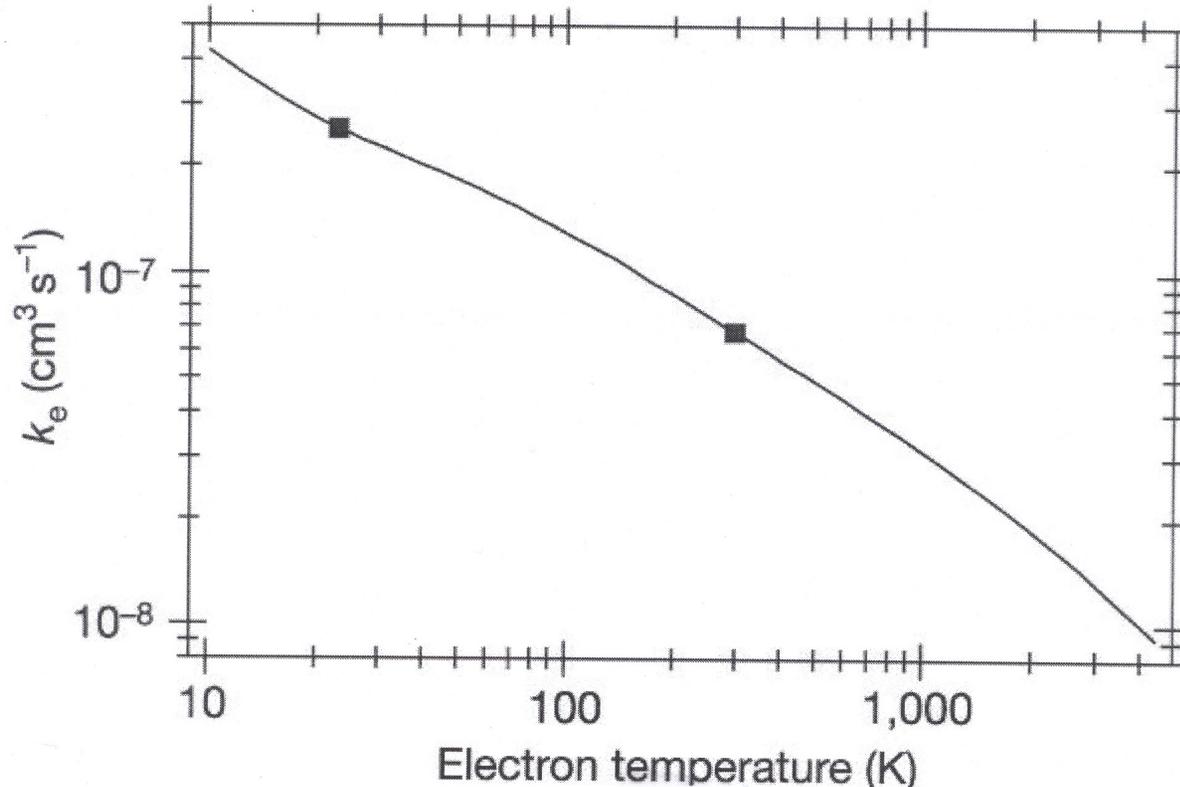
McCall et al.
2003

- Literature values range from $<10^{-12}$ to 10^{-7} cm^3 s^{-1} at 300 K over
  last 25 years
- High rate coefficients now also reproduced by theory, even
  without curve crossing
- Affects determination cosmic ray ionization rates in diffuse clouds

1.11 Ion-molecule reactions

- Ion induces dipole moment in molecule when it approaches it => long-range attraction which goes as $\propto 1/R^4$

- Reaction is rapid even at low T *if* the reaction is exothermic; rate can be readily computed by classical capture theory developed by Langevin 1905

Classical capture theory

k independent of T

$$k = \sqrt{\alpha e^2}/\mu$$
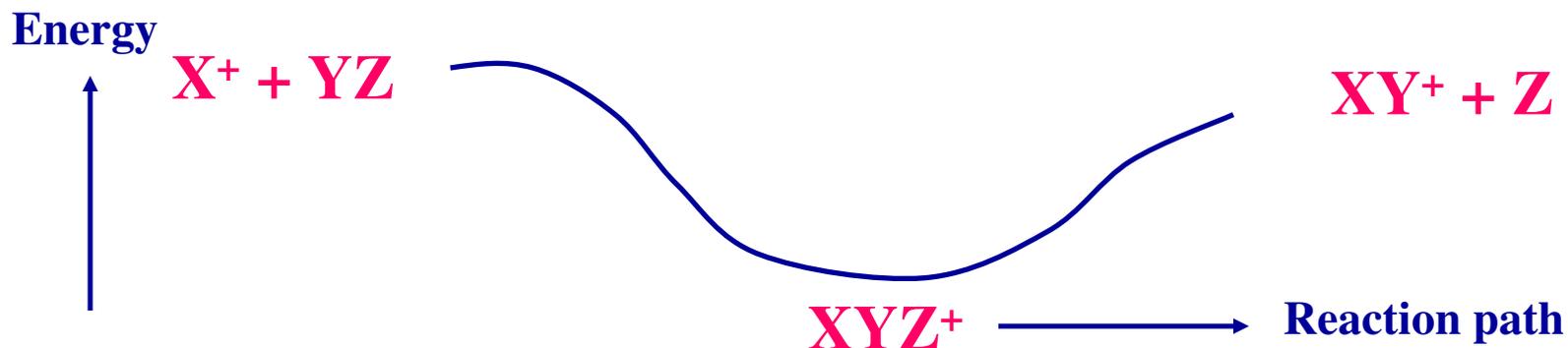
↑
polarizability
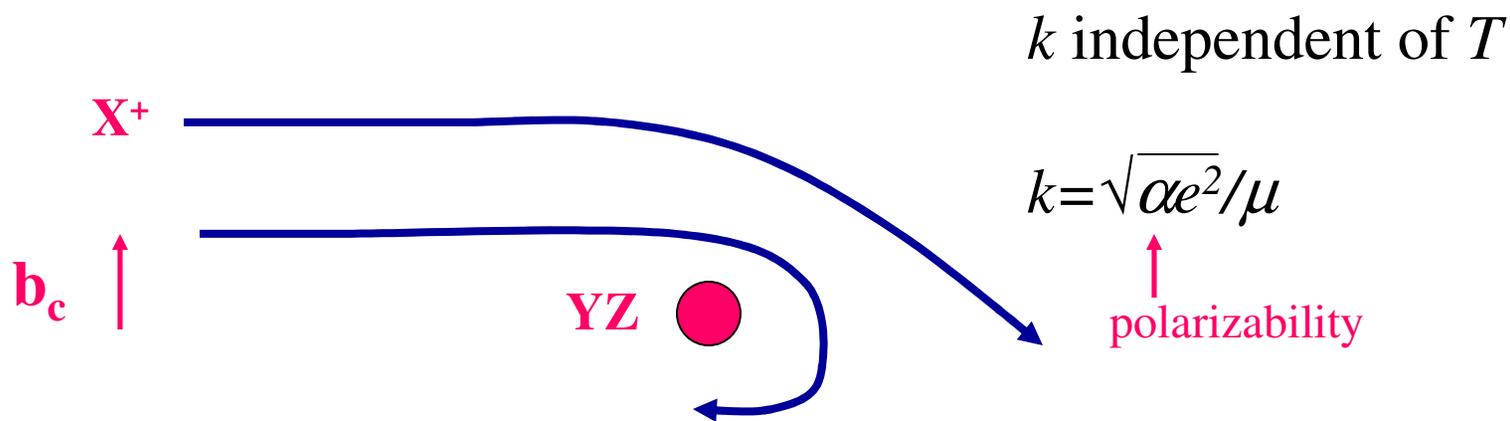
- Reaction only occurs if impact parameter b small enough that X^+ is 'captured', i.e., spends enough time near YZ for reaction to take place
- Gas-phase reaction networks built on ion-molecule reactions; initial ionization provided by cosmic rays (H^+ and H_3^+) or photons (C^+)

Ion-molecule processes

- $X^+ + YZ \rightarrow XY^+ + Z$ exchange

  $\rightarrow X + YZ^+$ charge transfer

- Many experiments performed at room T, some at low T. Most reactions (>90%) indeed proceed at Langevin rate, but some exceptions known

$NH_3^+ + H_2 \rightarrow NH_4^+ + H$
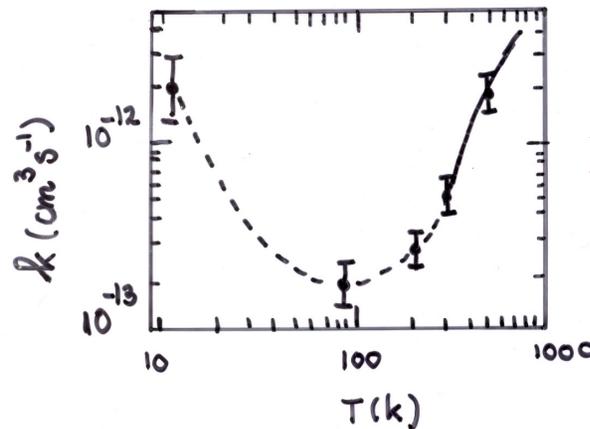
Experiments
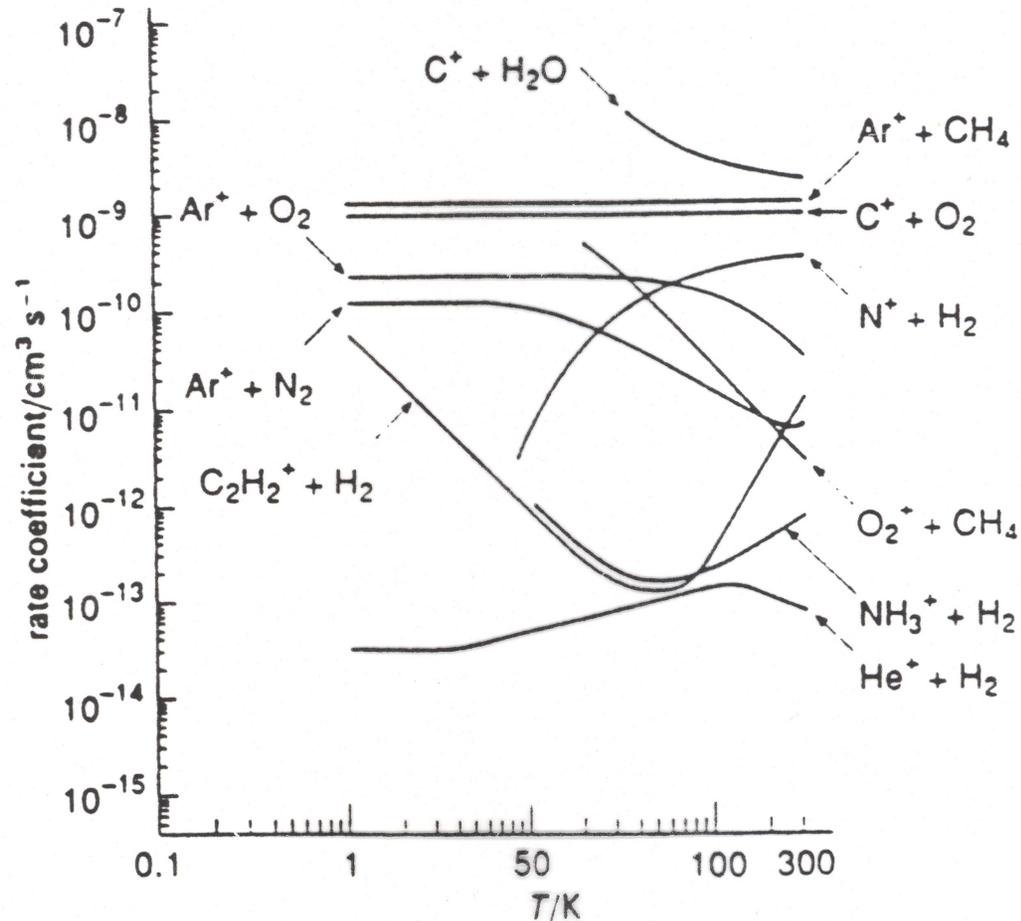
M. Smith 1993

-Rate coefficients for ion-polar reactions may be factors of 10-100 larger than Langevin values at low T, because $V(R) \propto R^{-2}$
Example: $C^+ + OH \rightarrow CO^+ + H$

1.12 Neutral-neutral reactions

- Long-range attraction weak: van der Waals interaction $\propto 1/R^6$

- Potential barriers may occur in entrance and exit channels => reactions thought to be slow at low T

- Experiments: *reactions can be fast at low T!*
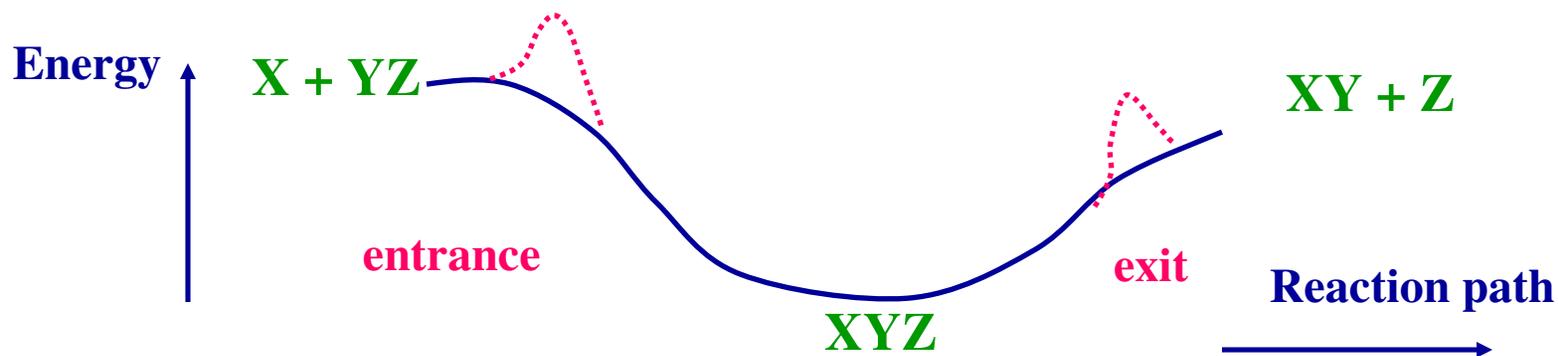
CN + C₂H₆: or why extrapolation is unreliable
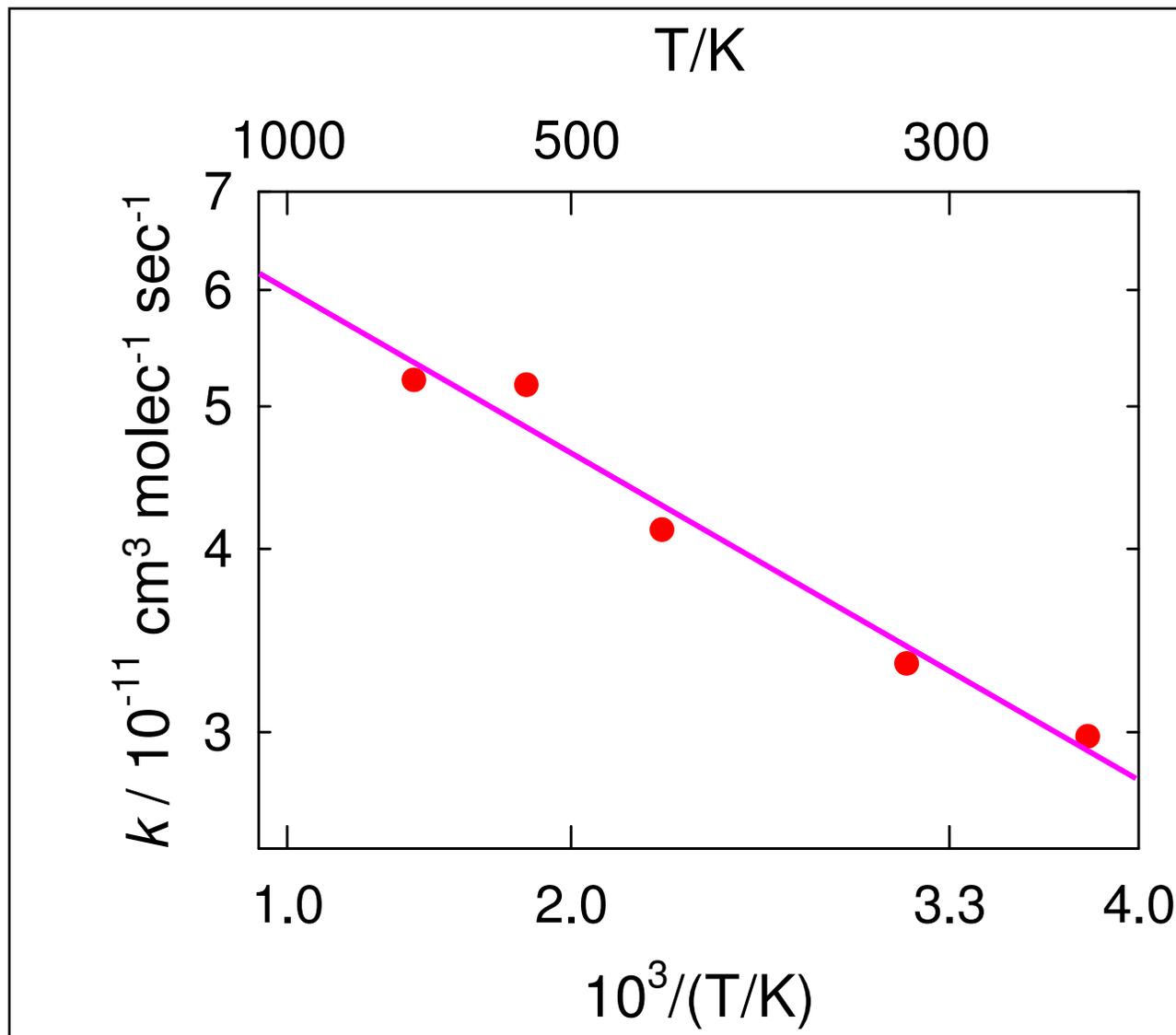
I. Sims et al. Rennes/Birmingham

CN + C$_2$H$_6$: or why extrapolation is unreliable
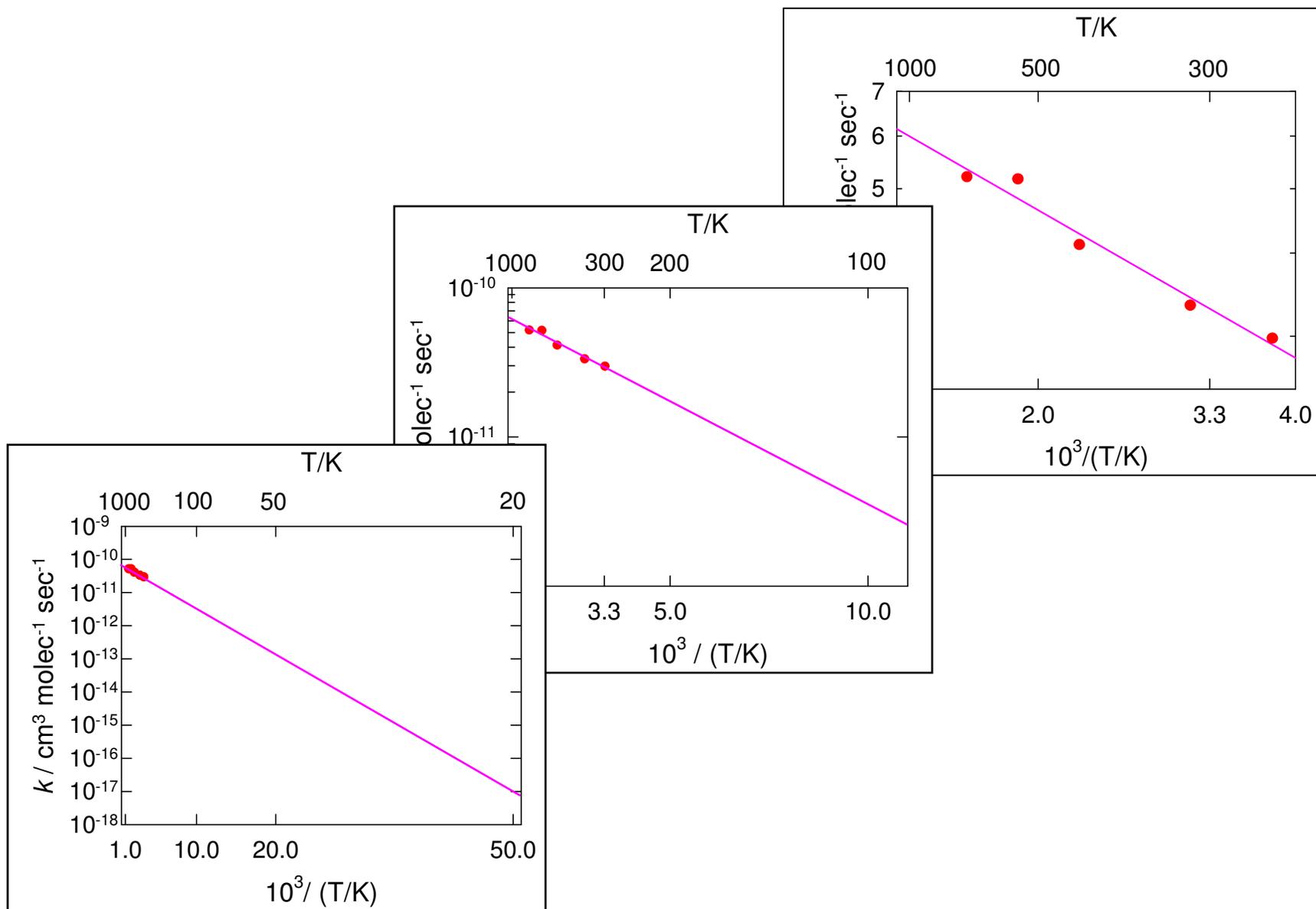
CN + C₂H₆: or why extrapolation is unreliable
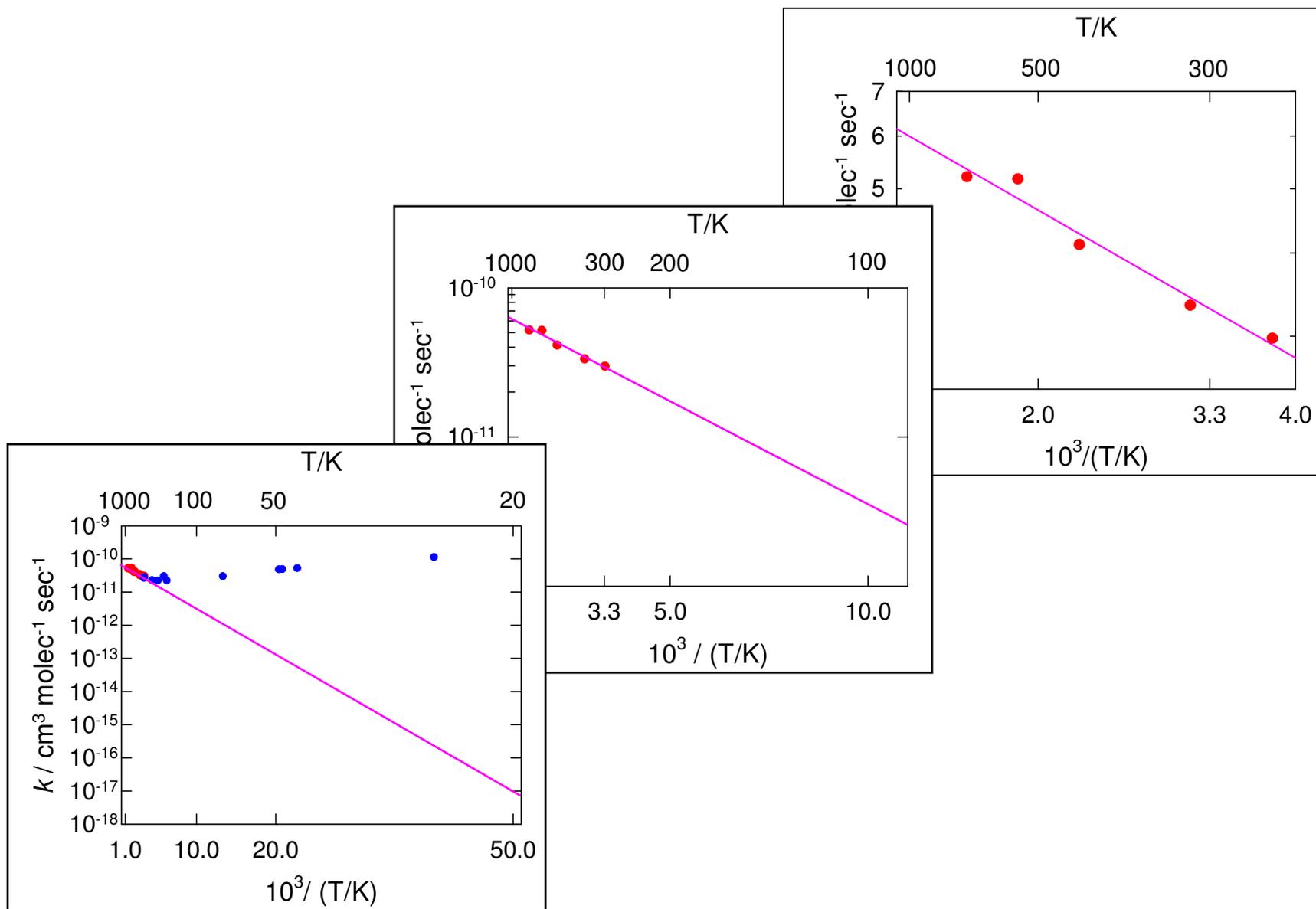
CN + C$_2$H$_6$: reaction stays rapid at low T!

I. R. Sims, J. L. Queffelec, D. Travers, B. R. Rowe, L. B. Herbert, J. Karthäuser, and I. W. M. Smith, Chem. Phys. Lett. **211** (4-5), 461 (1993).
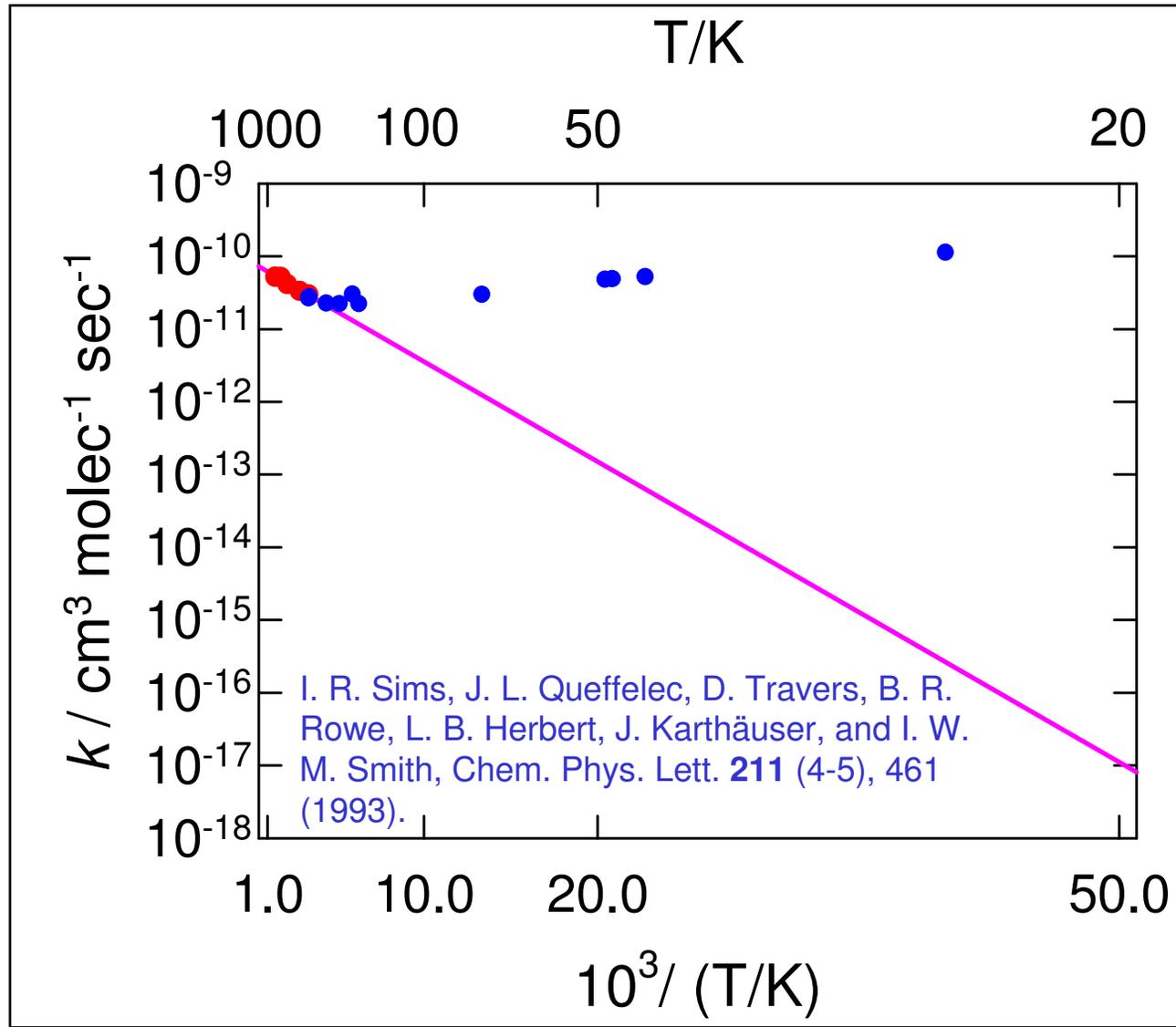
CRESU technique

50-100 slm carrier gas (He, Ar or N_2) + precursor + reagent

axisymmetric Laval nozzle

boundary layer sets scale of apparatus

nozzle throat diameter 3 mm – 5 cm

uniform supersonic flow
$T = 7 - 220$ K
$\rho = 10^{16} - 10^{18}$ cm^{-3}

chamber pressure 0.1 – 0.25 mbar
pumping speed ~ 30000 m^3 hr^{-1}
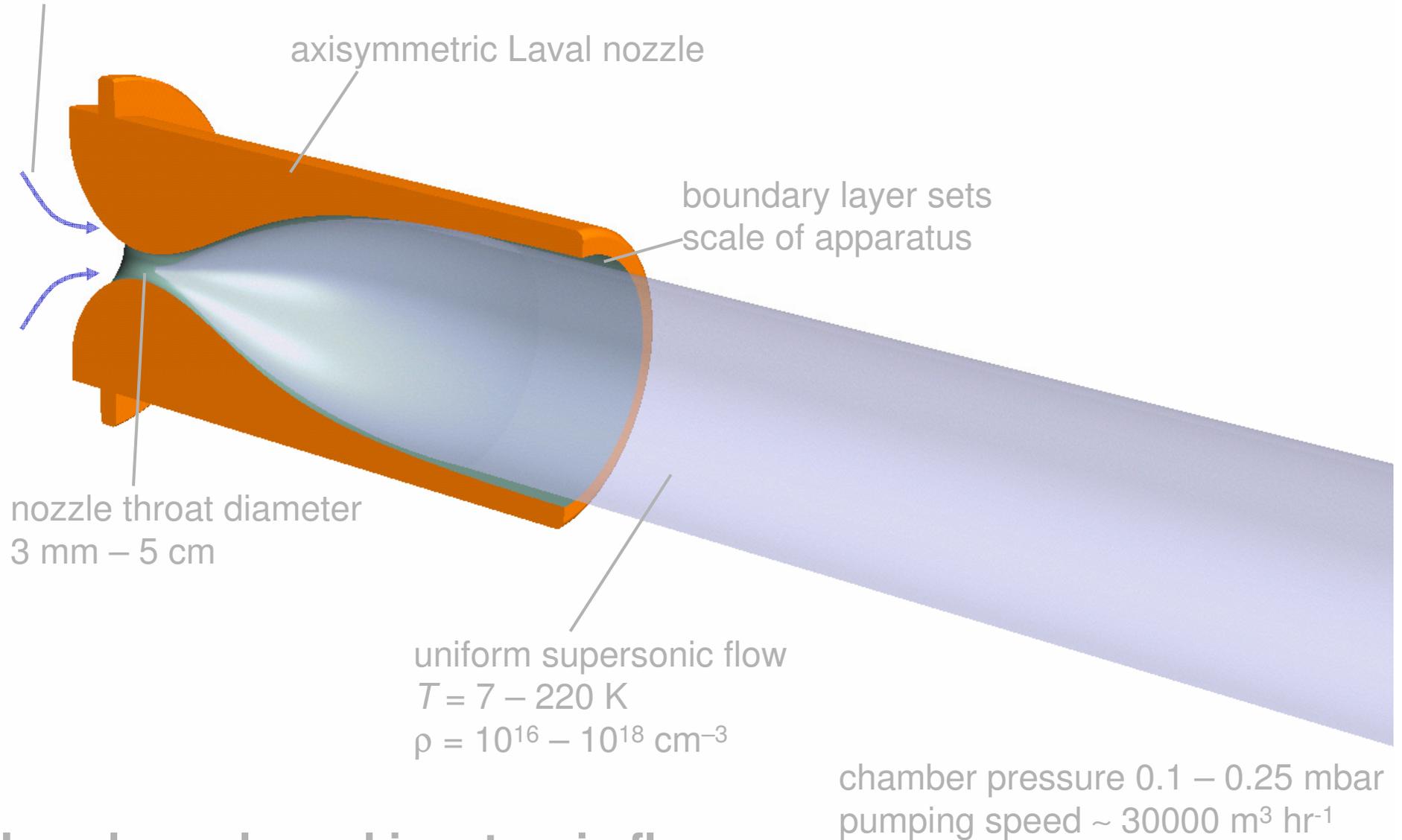
Laval nozzle and isentropic flow

Types of neutral-neutral reactions

	E_A/k	$V(R)$

- **Molecule-molecule** — $>10^4$ K
  - E.g., $H_2 + D_2 \rightarrow 2HD$
- **Radical-saturated mol** — ~ 2000
  - E.g., $OH + H_2 \rightarrow H_2O + H$
- **Radical-unsaturated mol** — ~ 0
  - E.g., $OH + CO \rightarrow CO_2 + H$
- **Radical-radical** — -100
  - E.g., $O + OH \rightarrow O_2 + H$
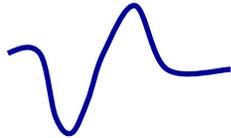
Not all neutral-neutral reactions are rapid

See also Smith 2006, Faraday Disc

1.13 Pure gas-phase models

- Most recent models contain nearly ~4500 gas-phase reactions between ~450 species containing up to 13 atoms. Publicly available on web
  - UMIST code
    - http://www.udfa.net/
  - Ohio state code
    - http://www.physics.ohiostate.edu/~eric/research.html
- Most dark cloud models ignore depth dependence $\Rightarrow$ solve chemical networks for given T, n at single position and assume

$$x(\text{AB}) = \frac{N(\text{AB})}{N(\text{H}_2)} = \frac{n(\text{AB})}{n(\text{H}_2)}$$

observed   **calculated**

How important are reactions?
Sensitivity analysis gas-phase networks
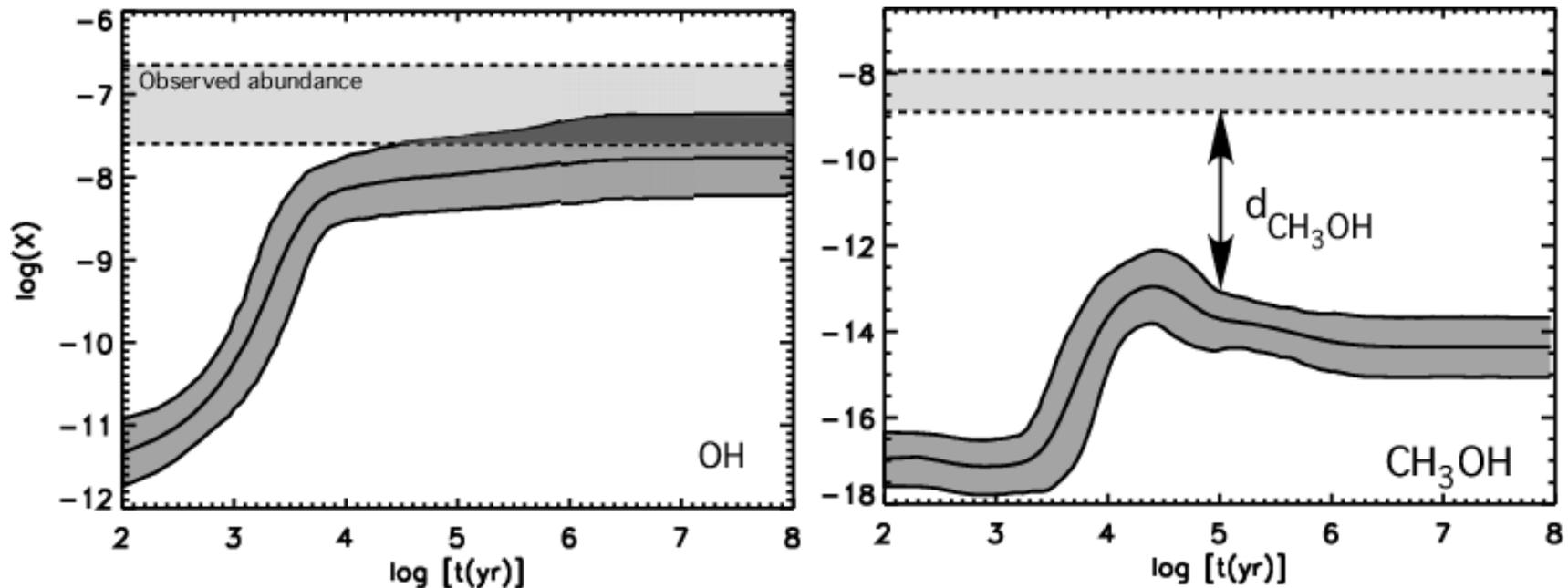
- Take estimated uncertainties in rate coefficients into account
- Uncertainties become larger for large molecules
- Observed CH_3OH cannot be produced by pure gas-phase reactions
- Use analysis to identify critical reactions for which rates need to be better determined

Wakelam et al. 2005

1.14 Gas-grain chemistry

- Evidence for gas-grain chemistry
  - H_2 in interstellar clouds
  - NH in diffuse clouds
  - Abundances H_2O, CO_2, CH_3OH, … in ices higher than expected from freeze-out of gas phase
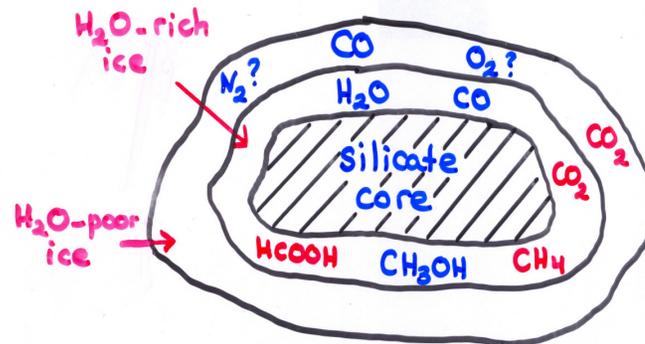
Formation mechanisms

- ***Diffusive mechanism*** (Langmuir-Hinshelwood)
  - X + g:Y → X:g:Y → X-Y:g → XY + g
    - sticking
    - diffusion + molecule formation
    - desorption
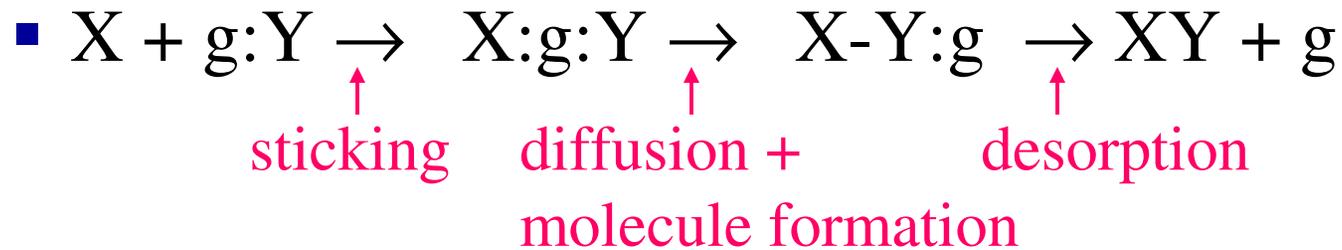
- ***Direct mechanism*** (Eley-Rideal)
  - X + Y:g → X-Y:g → XY + g
    - direct reaction
    - desorption
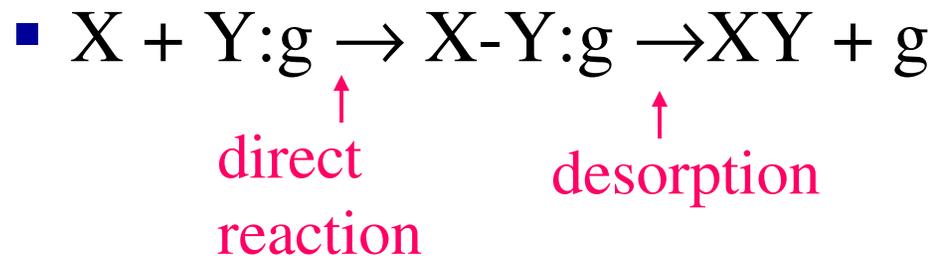
- Surface can be silicates, carbonaceous, ice, …

    See Lecture 2 for more on grain surface processes

Simulations diffuse mechanism

Takahashi et al. 1998
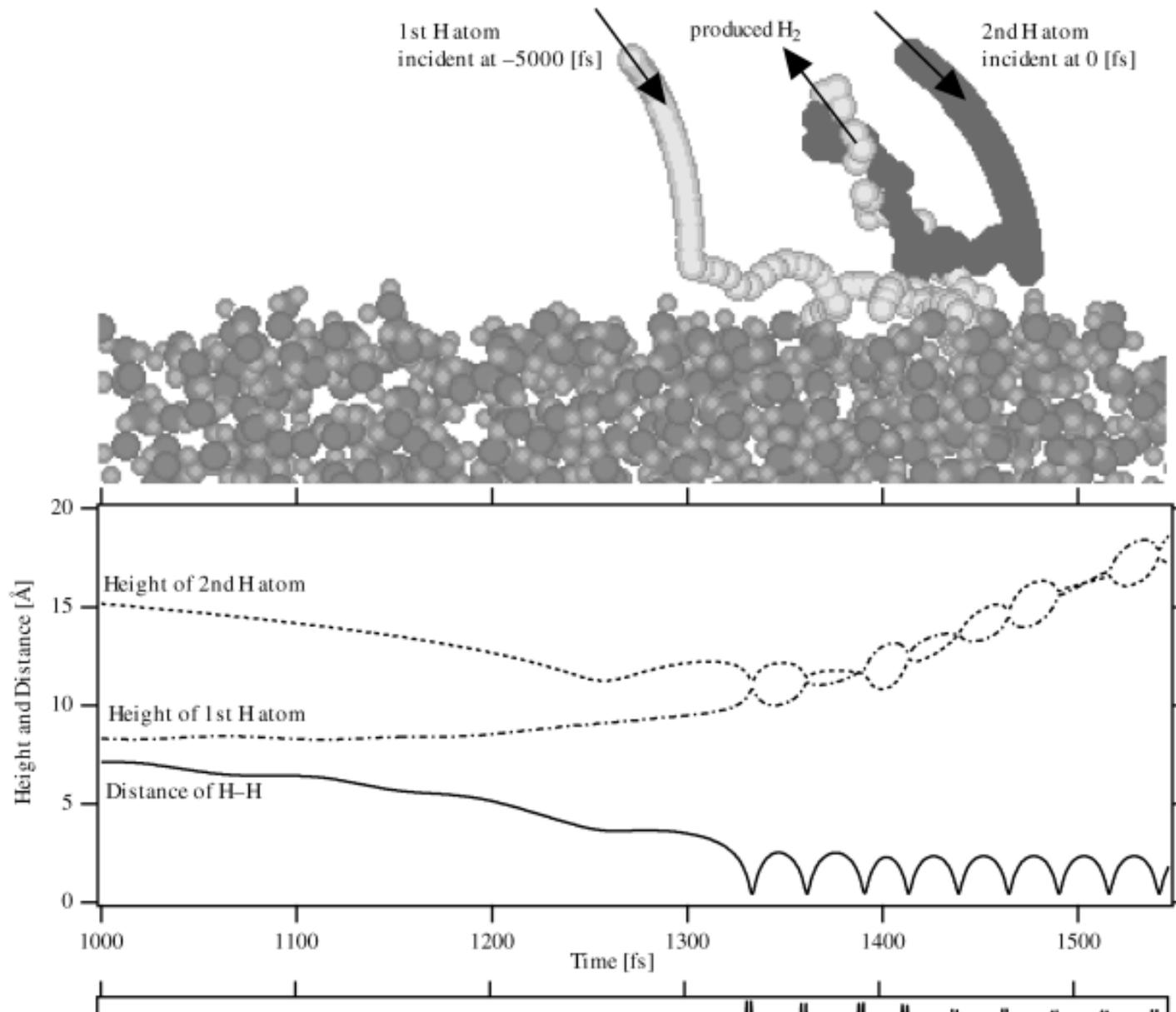
Summary lecture 1

- Large variety of molecules observed in ISM
- Basic processes for formation and destruction identified
- Networks built for explaining abundances
- Results completely dependent on thousands of input rates
  - Many not known under astrophysical conditions (but for many accurate rates not needed)
  - Key: identify those reactions which are important to study well
- Many experiments and theory on basic processes over last 30 years
  - Good, new chemical physics questions!
  - Significant progress in neutral-neutral reactions, surface reactions
- Some processes now well understood, others take decades of hard work to make just a little progress
  - Funding of lab astrophysics groups becoming major problem
  - Note: photoionization codes like CLOUDY got atomic input data thanks to huge efforts in atomic and plasma physics