Lecture 5: "Gas-phase Chemical Processes and First Molecules"

$$CH_4 \quad + \quad 2O_2 \quad \longrightarrow \quad CO_2 \quad + \quad 2H_2O$$
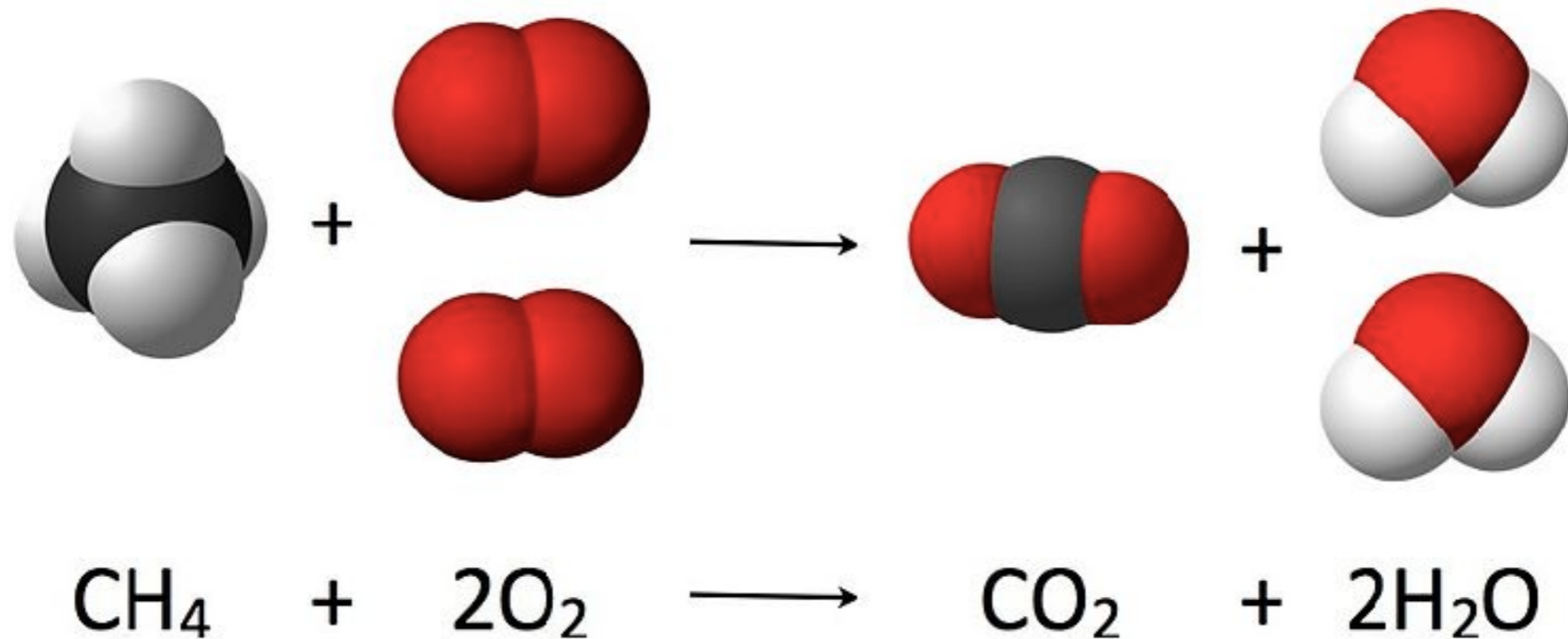
Outline

- Atomic structure and periodic table

- Molecules and chemical bonds

- Gas-phase chemical reactions

- Example: first molecules in the Universe

Modern atomic theory

• John Dalton (1808) used experimental works to provide the empirical evidence: „…every particle of hydrogen is like every other particle of hydrogen, etc."

• Each element has an unique atom

• Chemical reactions: separation, redistribution of and reunion of particles

• Atoms cannot be destroyed by chemical reactions

• First relative atomic weights: $H_2O = H + O$ (masses are 1:7), $NH_3 = H + N$ (masses are 1:5)

J. Dalton

(1766 – 1844)

John Dalton: *A New System of Chemical Philosophy* (1808)

ELEMENTS.

Simple

Binary
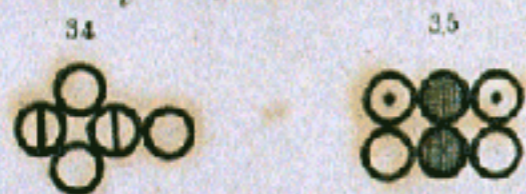
Ternary

Quaternary
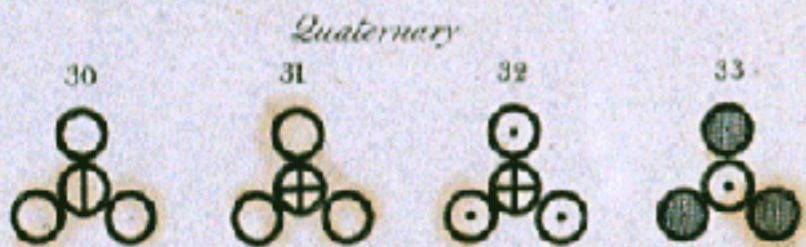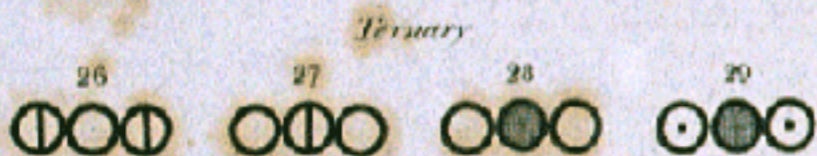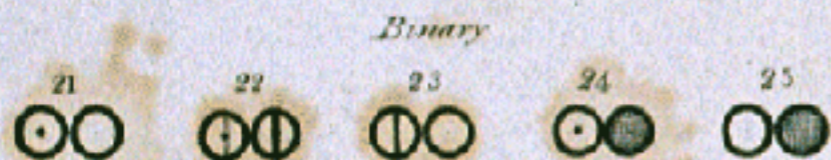
Quinquenary & Sextenary

Septenary

PLATE IV. This plate contains the arbitrary marks or signs chosen to represent the several chemical elements or ultimate particles.

Fig.			Fig.		
1	Hydrog. its rel. weight	1	11	Strontites	46
2	Azote,	5	12	Barytes	68
3	Carbone or charcoal,	5	13	Iron	38
4	Oxygen,	7	14	Zinc	56
5	Phosphorus,	9	15	Copper	56
6	Sulphur,	13	16	Lead	95
7	Magnesia,	20	17	Silver	100
8	Lime,	23	18	Platina	100
9	Soda,	28	19	Gold	140
10	Potash,	42	20	Mercury	167

21. An atom of water or steam, composed of 1 of oxygen and 1 of hydrogen, retained in physical contact by a strong affinity, and supposed to be surrounded by a common atmosphere of heat; its relative weight = ... 8

22. An atom of ammonia, composed of 1 of azote and 1 of hydrogen 6

23. An atom of nitrous gas, composed of 1 of azote and 1 of oxygen 12

24. An atom of olefiant gas, composed of 1 of carbone and 1 of hydrogen 6

25 An atom of carbonic oxide composed of 1 of carbone and 1 of oxygen 12

26. An atom of nitrous oxide, 2 azote + 1 oxygen - 17

27. An atom of nitric acid, 1 azote + 2 oxygen - 19

28. An atom of carbonic acid, 1 carbone + 2 oxygen 19

29. An atom of carburetted hydrogen, 1 carbone + 2 hydrogen 7

30. An atom of oxynitric acid, 1 azote + 3 oxygen 26

31. An atom of sulphuric acid, 1 sulphur + 3 oxygen 34

32. An atom of sulphuretted hydrogen, 1 sulphur + 3 hydrogen 16

33. An atom of alcohol, 3 carbone + 1 hydrogen - 16

34. An atom of nitrous acid, 1 nitric acid + 1 nitrous gas 31

35. An atom of acetous acid, 2 carbone + 2 water - 26

36. An atom of nitrate of ammonia, 1 nitric acid + 1 ammonia + 1 water 33

37. An atom of sugar, 1 alcohol + 1 carbonic acid - 35

Modern atomic theory

- Amedeo Avogadro (1811): diatomic nature of gases (N_2, O_2, etc.)

- Joseph J. Thompson (1897): discovery of e-, m_H/m_{e-} ~1800 => plum pudding model

- Ernest Rutherford (1909): discovery of nucleus (Geiger-Marsden experiment) => planetary model

- Niels Bohr (1913): Bohr model => specific e- orbits with fixed energy and angular momentum

- E. Rutherford (1917): hydrogens in the nuclei (protons)

- James Chadwick (1932): discovery of a neutron

xkcd.com/2100/

MODELS OF THE ATOM
OVER TIME

1810 — SMALL HARD BALL MODEL

1904 — PLUM PUDDING MODEL

1907 — TINY BIRD MODEL

1911 — RUTHERFORD MODEL

1913 — BOHR MODEL

1928 — NUNCHUCK MODEL

1932 — CHADWICK MODEL

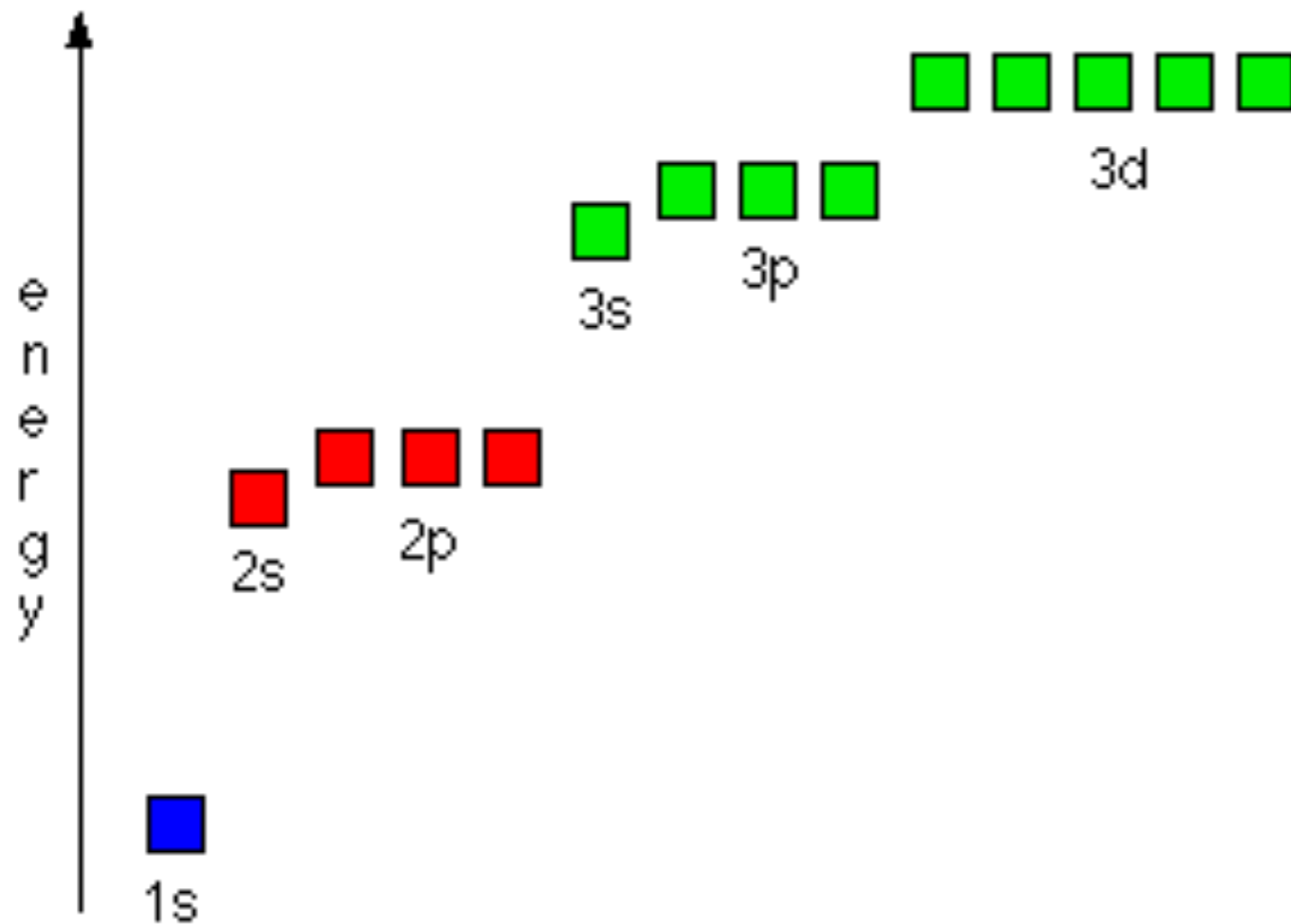2008 — 538 MODEL (38%, 31%, 31%)

TODAY — QUANTUM MODEL

FUTURE — "SMALL HARD BALL SURROUNDED BY MATH" MODEL

Electron configuration (each e- moves in an orbital)

- Electronic shells: n = 1, 2, 3, …   (K, L, M, N)

- Sub-shells: ℓ = 0, 1, 2, 3   (s-, p-, d-, f-)

- Orbitals: m = -ℓ, …0,… +ℓ

- Max e- per orbital: 4ℓ + 2

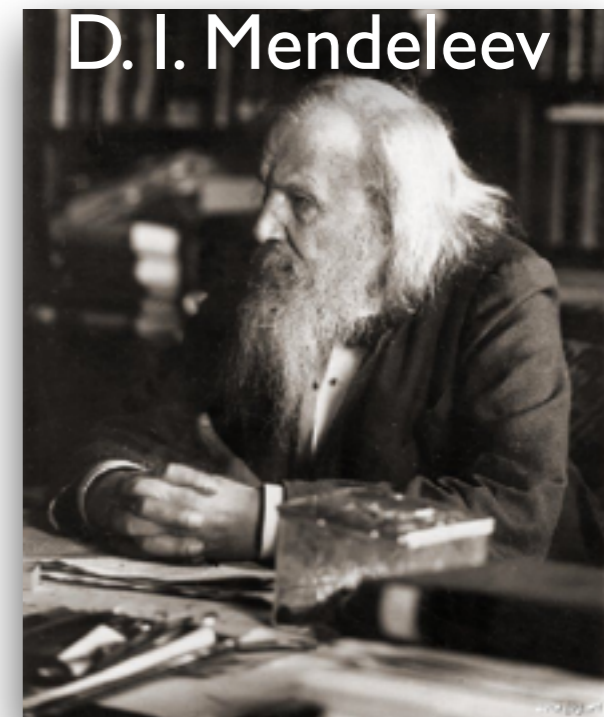| Shell name	Subshell name	Subshell max electrons
K	1s	2
L	2s	2
	2p	6
M	3s	2
	3P	6
	3d	10
N	4s	2
	4p	6
	4d	10
	4f	14

Periodic table

(1780 – 1849)

- Johann Wolfgang Döbereiner (1817): trends in element' properties, 4 groups x 3 = 12 elements

- Dmitri Mendeleev (1869): first periodic table arranged by atomic mass, 8 groups
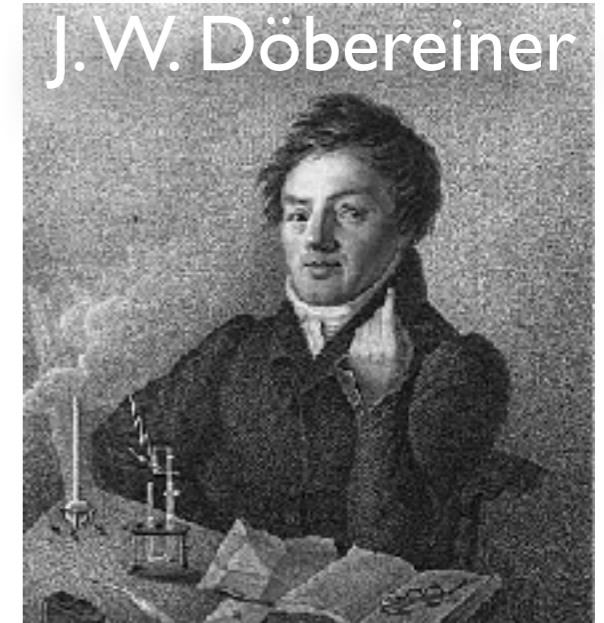
Ueber die Beziehungen der Eigenschaften zu den Atomgewichten der Elemente. Von D. Mendelejeff. — Ordnet man Elemente nach zunehmenden Atomgewichten in verticale Reihen so, dass die Horizontal-reihen analoge Elemente enthalten, wieder nach zunehmendem Atomge-wicht geordnet, so erhält man folgende Zusammenstellung, aus der sich einige allgemeinere Folgerungen ableiten lassen.

D. I. Mendeleev

(1834 – 1907)

		Ti = 50	Zr = 90	? = 180
		V = 51	Nb = 94	Ta = 182
		Cr = 52	Mo = 96	W = 186
		Mn = 55	Rh = 104,4	Pt = 197,4
		Fe = 56	Ru = 104,4	Ir = 198
	Ni = Co = 59		Pd = 106,6	Os = 199
		Cu = 63,4	Ag = 108	Hg = 200
H = 1				
Be = 9,4	Mg = 24	Zn = 65,2	Cd = 112	
B = 11	Al = 27,4	? = 68	Ur = 116	Au = 197 ?
C = 12	Si = 28	? = 70	Sn = 118	
N = 14	P = 31	As = 75	Sb = 122	Bi = 210 ?
O = 16	S = 32	Se = 79,4	Te = 128 ?	
F = 19	Cl = 35,5	Br = 80	J = 127	
Li = 7 Na = 23	K = 39	Rb = 85,4	Cs = 133	Tl = 204
	Ca = 40	Sr = 87,6	Ba = 137	Pb = 207
	? = 45	Ce = 92		

Zeitschrift für Chemie (1869), pages 405-6

Periodic Table

- Groups: similar arrangement of outer electrons
- Elements in the same group: similar chemical reactions
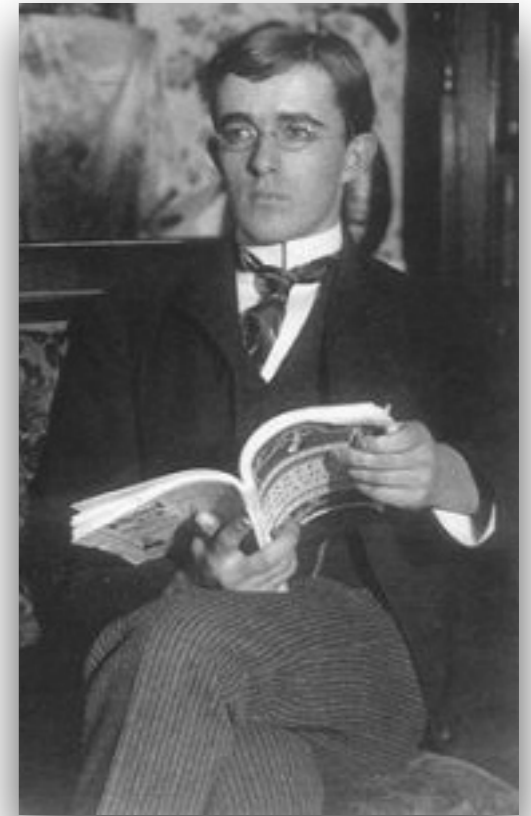- Periods: similar amount of electron shells

Molecules

- Electrically neutral group of atoms held together by chemical bonds

- Homonuclear: one chemical element

- Heteronuclear: two chemical elements or more

- Chemical bonds: covalent and ionic (lengths ~ 1 – 2 Å)

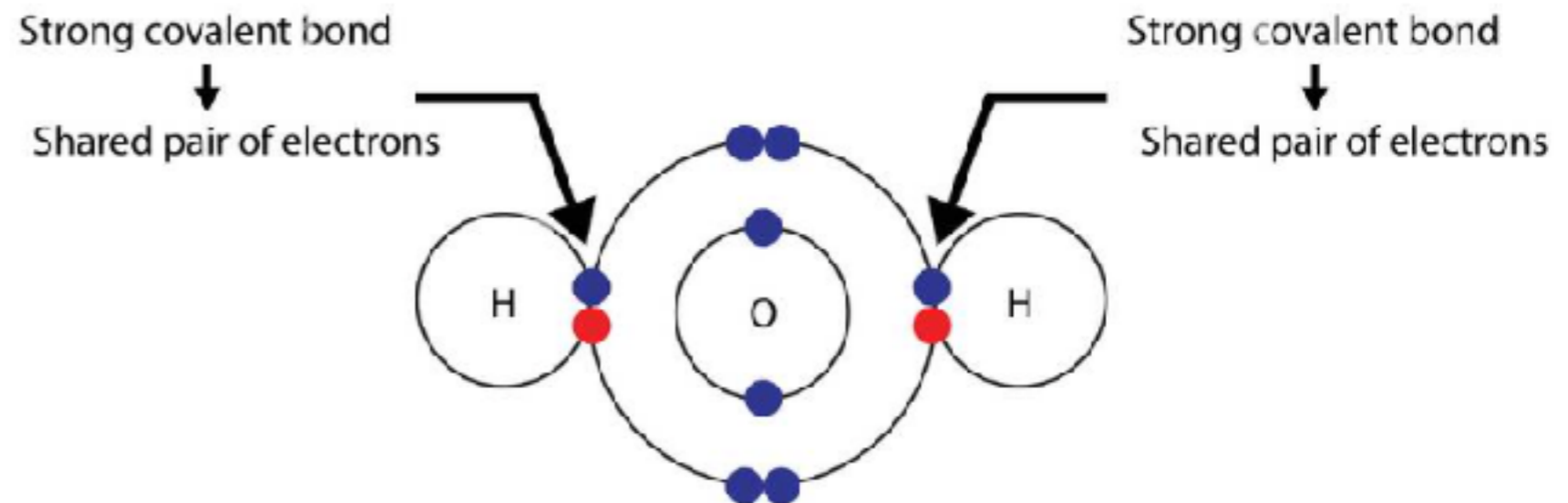- Chemical reactions: bond formation, rearrangement and destruction

Covalent bonds

- Irving Langmuir (1919)

- Covalent bond: electron pairs shared between atoms

- Stable balance of attractive and repulsive forces

- Valence electron is an electron in the outermost shell

- Via covalent bonds, atoms may attain full valence shells $\Rightarrow$

stable electronic configurations

(1881 – 1957)

Strong covalent bond
↓
Shared pair of electrons

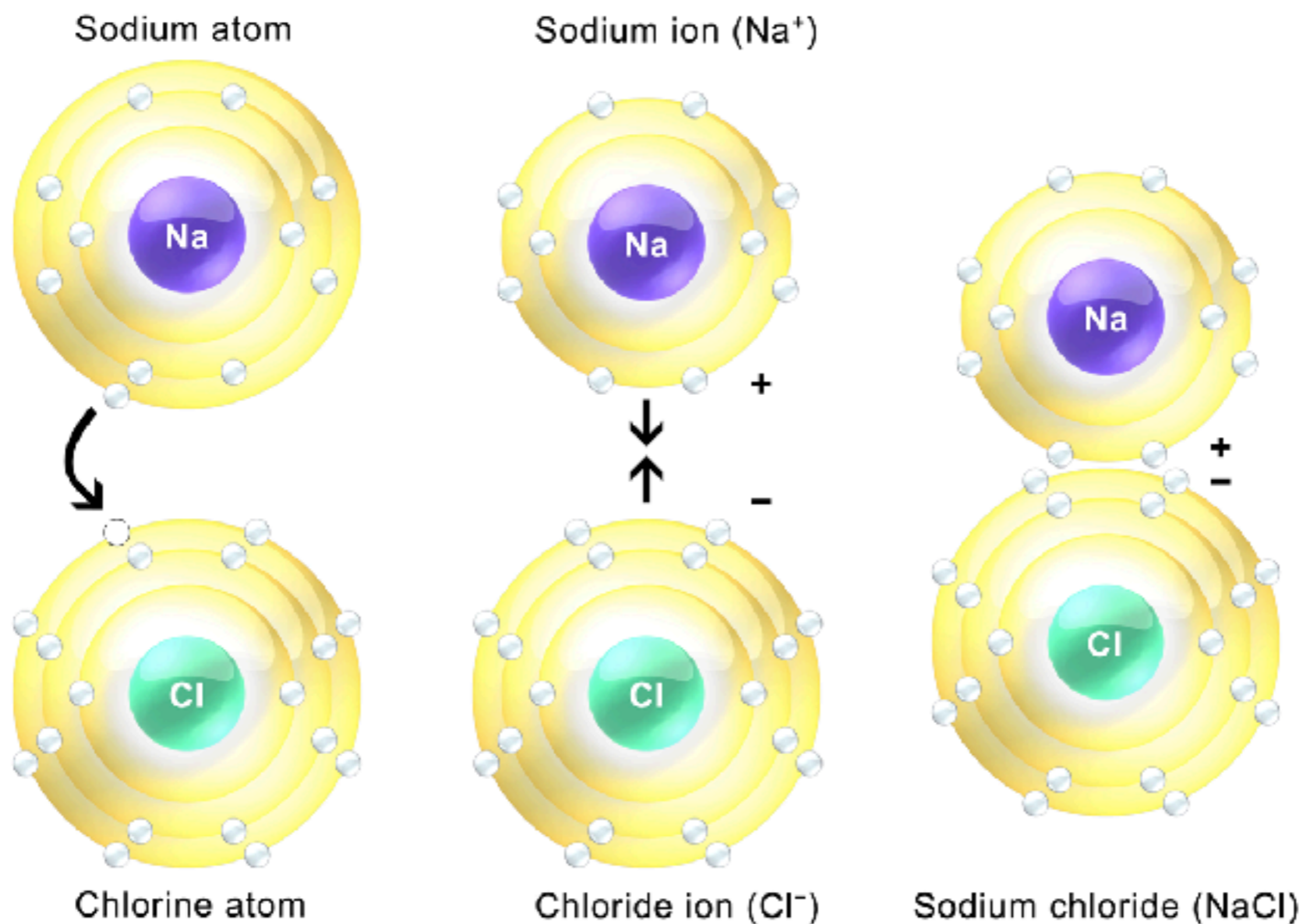Strong covalent bond
↓
Shared pair of electrons

+1   2e   +1

H:H
H – H
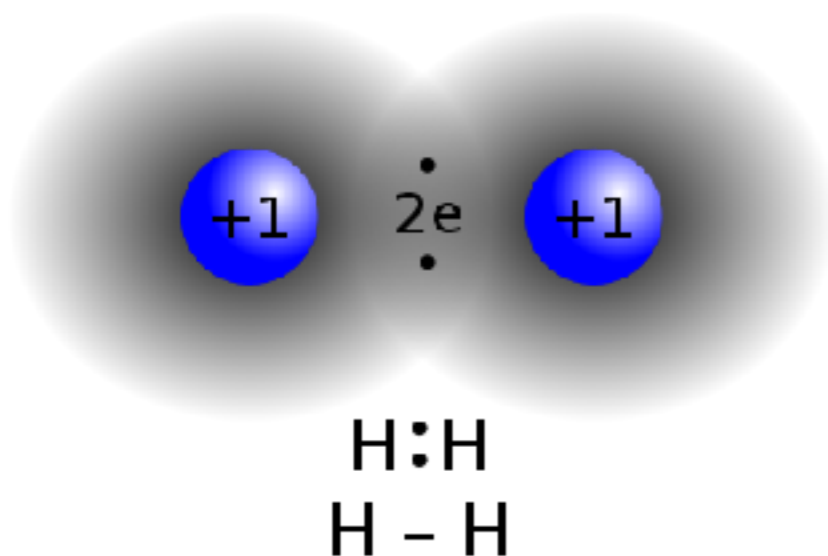
Ionic bonds

- Electrostatic attraction between oppositely charged atomic ions

- Transfer of e- to obtain full valence shells (electrovalence)

- Exists along with covalence bonding (ionic is stronger)

Sodium atom

Sodium ion (Na⁺)

Chlorine atom

Chloride ion (Cl⁻)

Sodium chloride (NaCl)

Typical bond energies

C≡O	**Carbon monoxide**	11.16 eV
H–C≡C–H	Acetylene	10.07 eV
N≡N	Nitrogen	9.71 eV
NaCl	*Sodium chloride*	7.94 eV
C≡N	Cyanogen	7.77 eV
O=C=O	Carbon dioxide	5.50 eV
O=O	Oxygen	5.11 eV
H–O–H	**Water**	5.11 eV
NH_3	Ammonia	4.58 eV
CH_4	Methane	4.49 eV
H–H	**Hydrogen**	4.478 eV
O–H	Hydroxyl	4.41 eV

Chemical reactions

- Transformation of substances by creating, changing or destruction

of chemical bonds

- Rearrangement of outer (valence) electrons

- Collision A + B $\Rightarrow$ Activated complex AB* $\Rightarrow$ Stabilization $\Rightarrow$ C + D
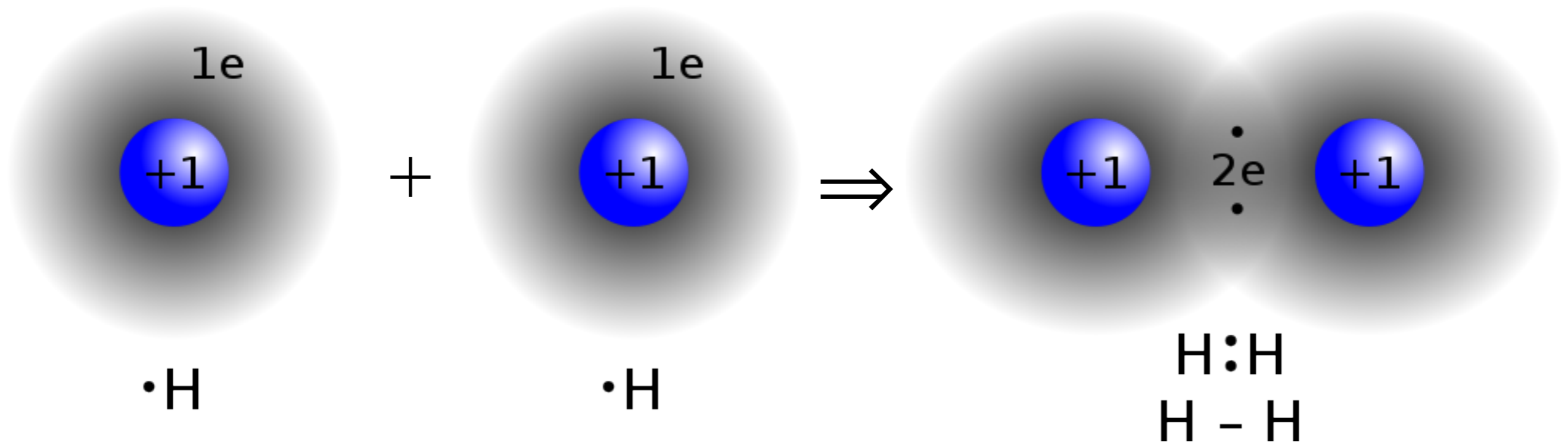
Chemical potential energy (enthalpy)

Collision A + B $\Rightarrow$ Activated complex AB* $\Rightarrow$ Stabilization $\Rightarrow$ C + D
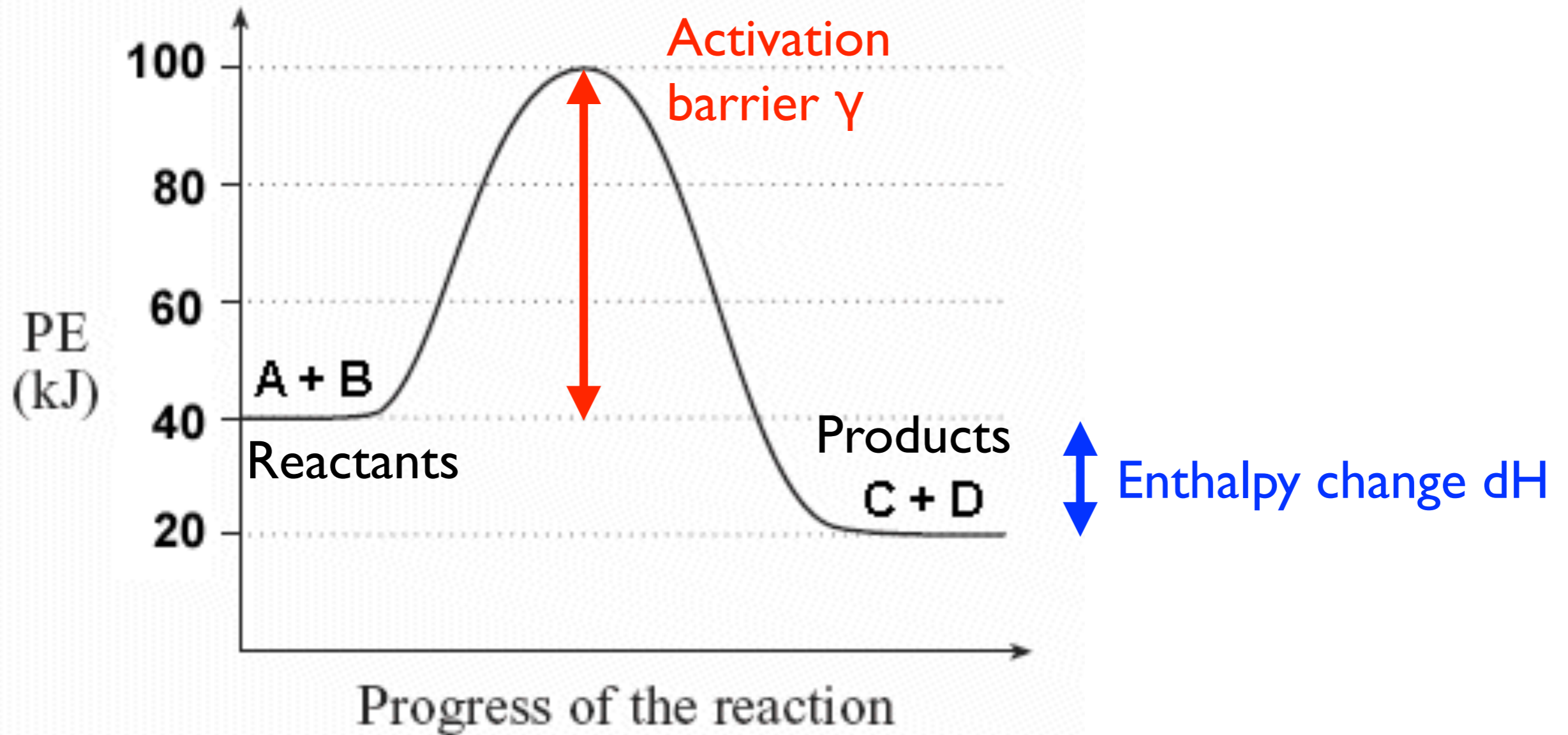
- Exothermic reaction: dH < 0 (energy is released)
- Endothermic reaction: dH > 0 (energy is absorbed)

Reaction rates and rate constants

$$aA + bB \Rightarrow cC + dD$$

- Abundances [A] and [B] and a reaction rate k

- Net abundance change: $k(T)[A]^m[B]^n$, where m and n are partial orders of reaction (m, n ≠ a, b)

- $k(T)$ contains pre-exponential factor (collisional cross section, Coulomb attraction, etc.), T-dependence, and barrier γ

- Arrhenius equation with only 3 coefficients (works in a limited temperature range):

$$k = \alpha \left(\frac{T}{300} \right)^{\beta} \exp\left(-\gamma/T \right)$$

Radiative association: bond formation
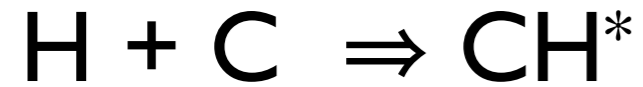
$H + C \Rightarrow CH^*$ Formation of a excited collisional complex

$CH^* \Rightarrow CH + h\nu$ Stabilization $\Rightarrow$ Emission of photon
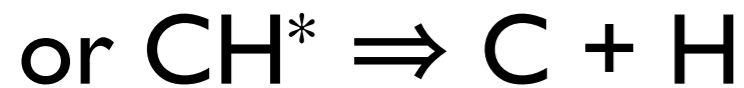
or $CH^* \Rightarrow C + H$ Or break-up back to atoms

- No barriers

- Slow rates: $k_{RA} \approx 10^{-17} - 10^{-12}$ cm³s⁻¹

- A key process to form first molecules (early Universe)

(Courtesy of Tom Millar, David Williams, Eric Herbst)

Radiative association: bond formation

Timescales in interstellar medium:

- $t_{vib} \sim 10^{-2}$ s (vibrational transition)

- $t_{el} \sim 10^{-9}$ s (electronic transition)

- $t_{coll} \sim 10^{-13}$ s (collisional timescale)

Probability of molecule formation per collision:

- Either $t_{coll}/t_{vib} \sim 10^{-11}$

- Or $t_{coll}/t_{el} \sim 10^{-4}$

- Slow for small reactants, rapid for more complex species

- Hard to measure in laboratory (3-body processes dominate)

- Hard to calculate for complex species (too many atoms & e-)

Photodissociation: bond destruction

dissociation limit

A

X

(a)

cross section

Wavelength
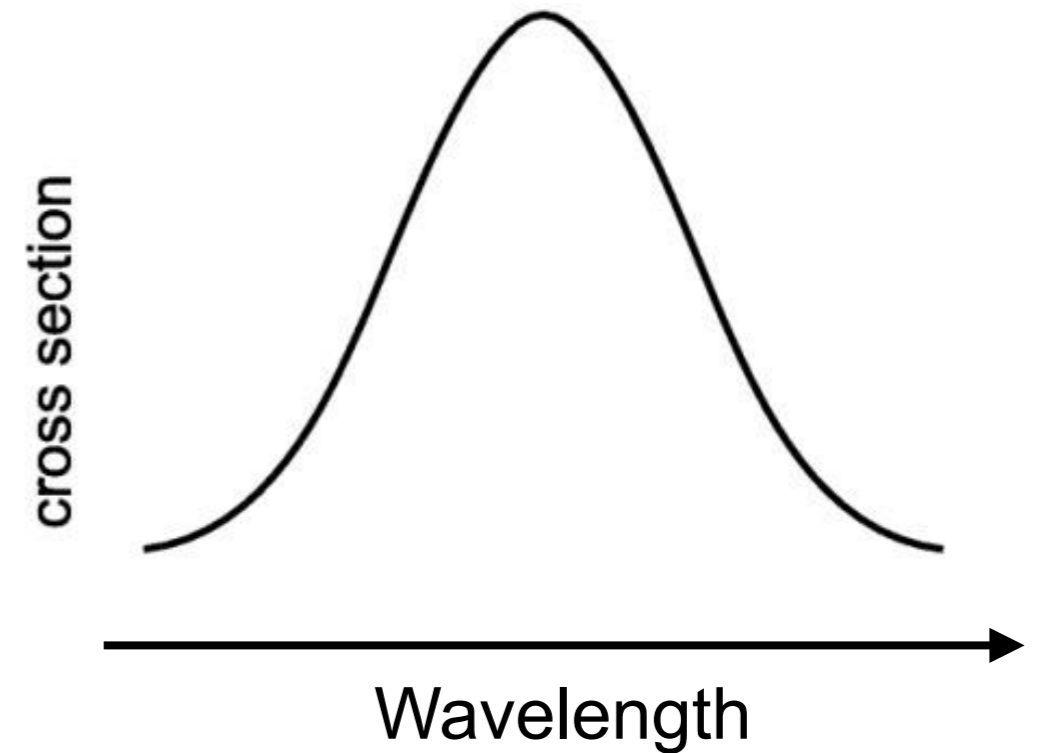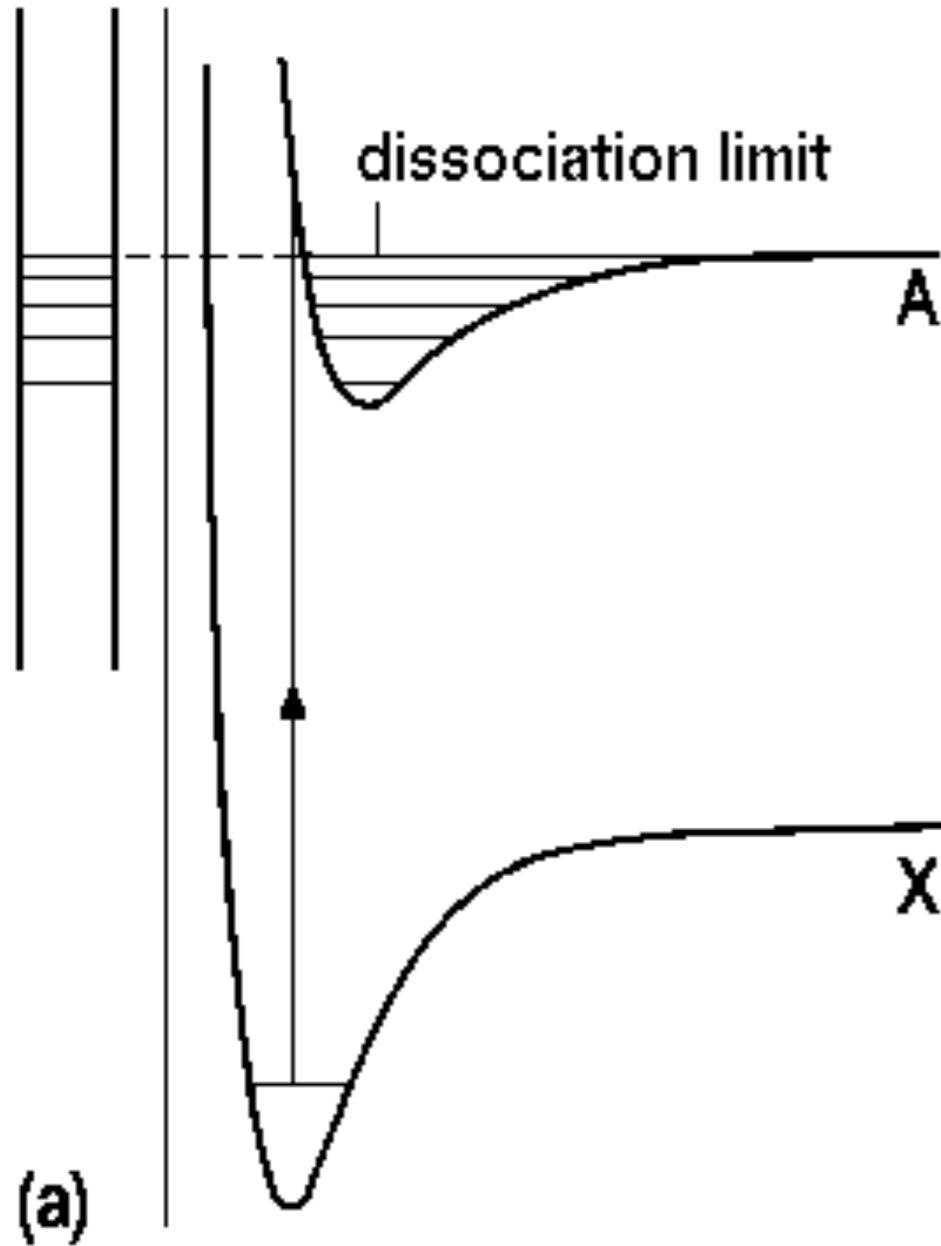
- Bonding energies: $4 - 10$ eV $\Rightarrow$ FUV

- Direct dissociation: transition to a continuum of excited electronic state

- Example: H_2O, OH, ...

Photodissociation: bond destruction
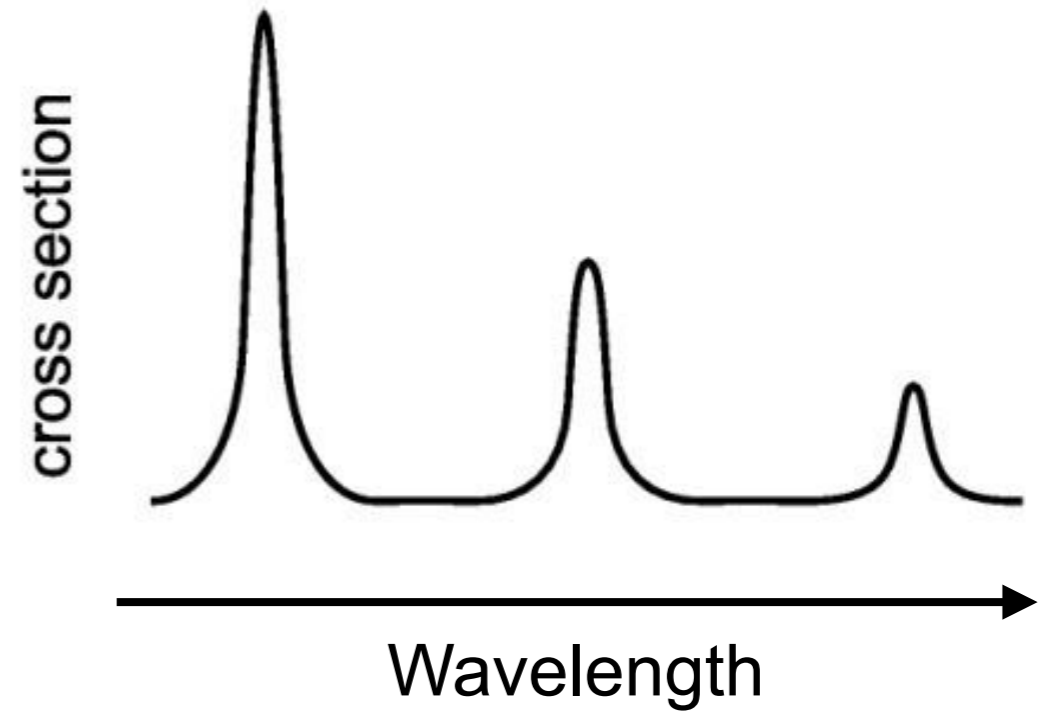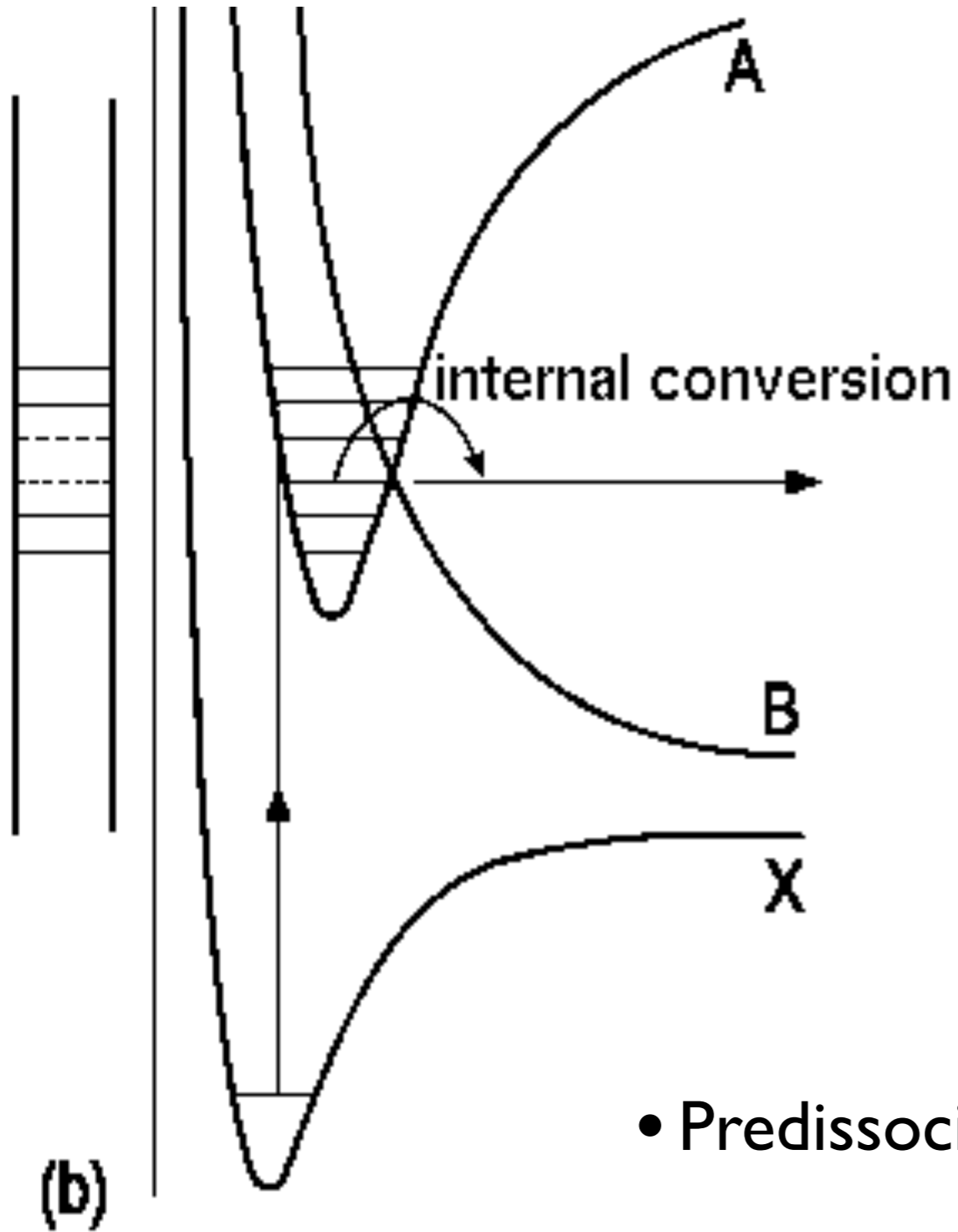
- Predissociation: excited electronic state is mixed with dissociative state

- Example: CO

Photodissociation: bond destruction
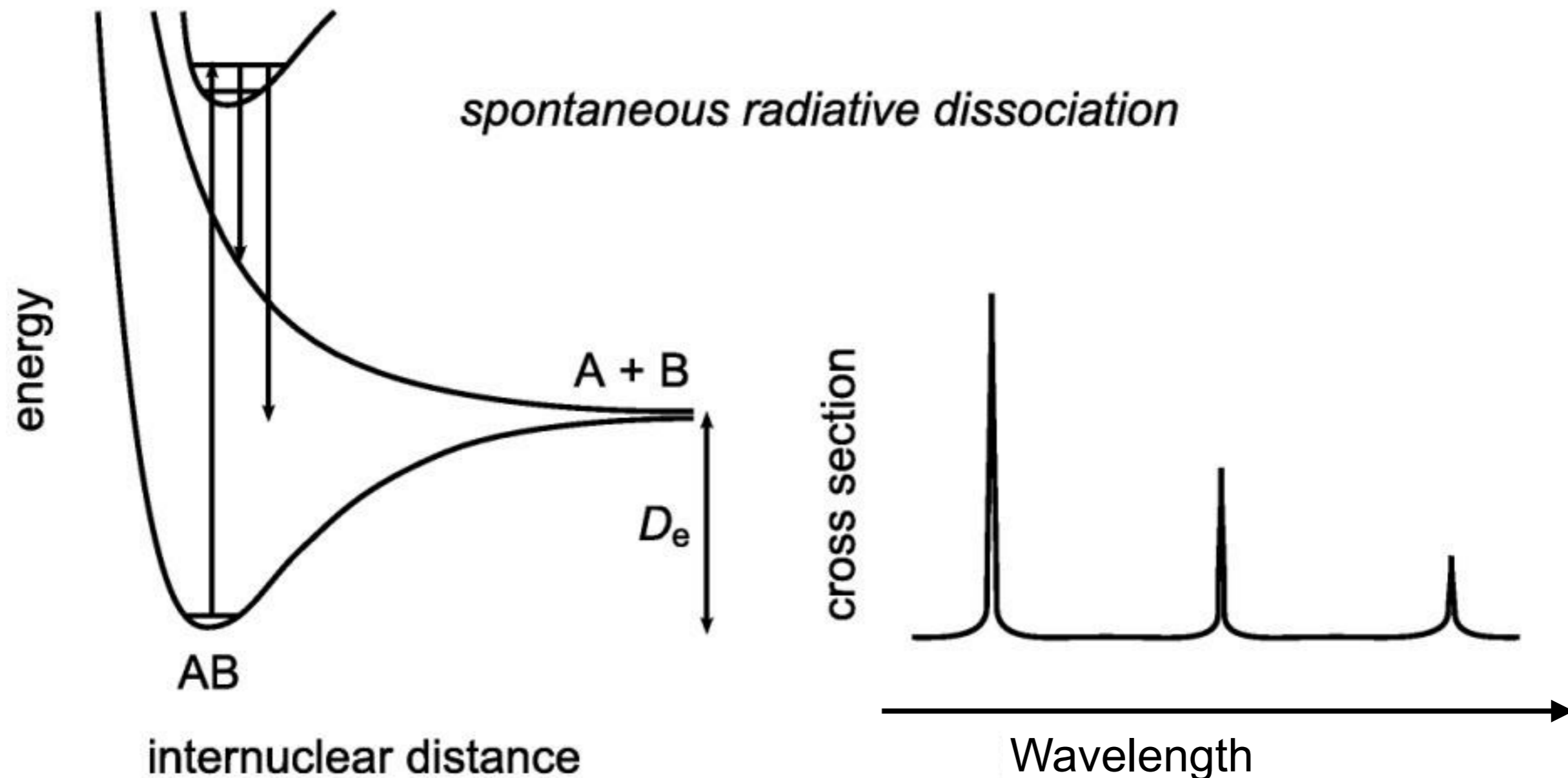
- Electronic excited state decays into diss. continuum of the ground state or repulsive state
- H_2

Photodissociation: bond destruction

$$CO + h\nu \Rightarrow C + O$$
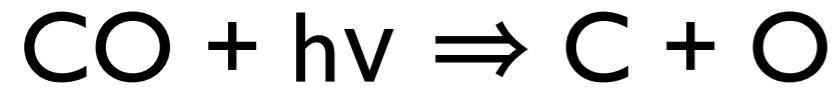
- Line dissociation: H_2, CO

- Continuum dissociation: OH, H_2O, CH_4

- Measured cross-sections: ~ 30 molecules

- Need to know UV spectrum

- $k \sim 10^{-10}$ x radiation intensity [s^{-1}]

Cosmic ray ionization

$H_2 + CRP \Rightarrow H_2^+ + e^-$

or

$He + CRP \Rightarrow He^+ + e^-$
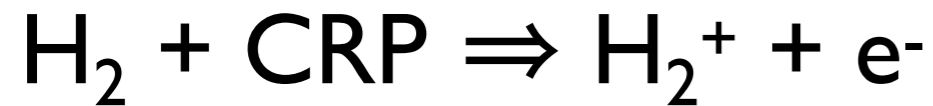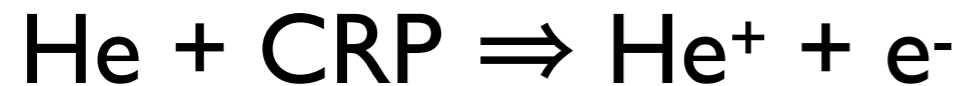
From observations:

$k_{CRP} \approx 10^{-17} - 10^{-15} \text{ s}^{-1}$

- Relativistic energy particles: 89% p, 10% ^{4}He, 1% heavy elements
- Penetrate a large gas columns
- Direct ionization + secondary e^-
- Or via He$^+$: I.P. of He is 24.6 eV $\Rightarrow$ He$^+$ breaks chemical bonds
- Example: $He^+ + CO \Rightarrow C^+ + O + He$
- CR ionization rates: hard to measure accurately within the solar system's heliosphere

Ion-molecule reactions: bond rearrangement

$H_2^+ + H_2 \Rightarrow H_3^+ + H$

$H_3^+ + CO \Rightarrow$

$H_2 + HCO^+$
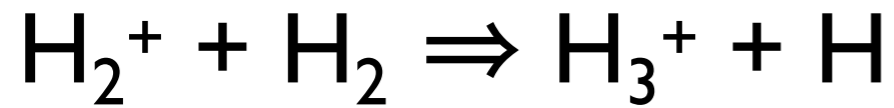
Fast rates:

$k_{IM} \approx 10^{-9}\text{-}10^{-7} \text{ cm}^3\text{s}^{-1}$

- Long-range Coloumb attraction

- No activation barriers

- Fast at very low T (~10-20 K)

- Key process to form molecules in space

- ~50% of all processes in astrochemical

  models

Neutral-neutral reactions: bond rearrangement

$N + CH \Rightarrow CN + H$

$N + CH_3 \Rightarrow HCN + H_2$
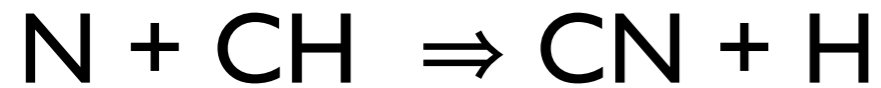
- Long-range attraction is weak

- Usually have barriers ~100-1000 K

- Many barriers are 'guessed' values

- Some are rapid at ~ 10 K

- Competitive at high temperatures, >100 K

$k_{NN} \approx {<}10^{-11}\text{-}10^{-9} \text{ cm}^3\text{s}^{-1}$

Dissociative recombination: bond destruction

$HCO^+ + e^- \Rightarrow CO + H$

$H_3O^+ + e^- \Rightarrow H_2O + H$

$$OH + 2H$$
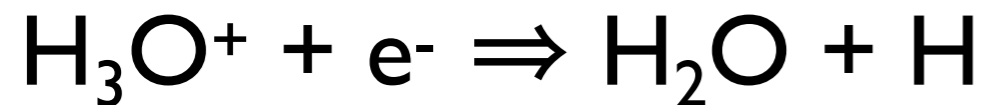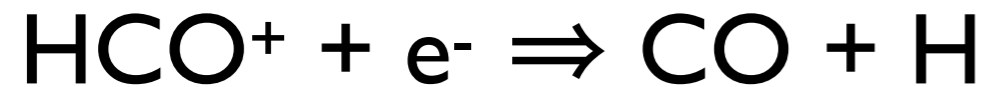
- Capture of e- by an ion $\Rightarrow$ dissociation

- Rapid processes

- Increased rates at low T

- If radiative, then slow

- Branching ratios and products are not

  well known

$k_{DR} \approx 10^{-7} \text{ cm}^3\text{s}^{-1}$

Radiative attachment

$$C_6H + e^- \Rightarrow C_6H^- + h\nu$$
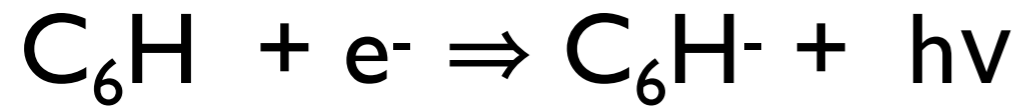
$$k_{RAt} < 10^{-7} \text{ cm}^3\text{s}^{-1}$$

- Effective for molecules with large e- affinities

- ~10% of anion/neutral for large hydrocarbons (Herbst 1981)

- Discovered in ISM with predicted abundances (McCarthy et al. 2006, Bruencken et al. 2007, etc.)

Chemical reaction databases

- **Ohio State University (OSU):**
  4300 reactions, 430 species, 12 elements

- **Manchester University (UMIST/UDFA):**
  Rate06: 4600 reactions, 420 species, 12 elements

- **NIST Chemical Kinetics Database**:
  ~30,000 neutral-neutral reactions (T>300K)

- **KIDA (KInetic Database for Astrochemistry)**:
  most up-to-date, 6000 reactions, 450 species, 12 elements

Only ~10-20% of accurate rates!

KInetic Database for Astrochemistry (KIDA): kida.astrophy.u-bordeaux.fr

Computational chemistry

$$\frac{\partial n_i}{\partial t} = \sum_{j,k \neq i} k_{jk} n_j n_k - n_i \sum_l k_l n_l$$

- Physical conditions

- Initial abundances

- Chemical network

- ODE solver

- Public astrochemical codes
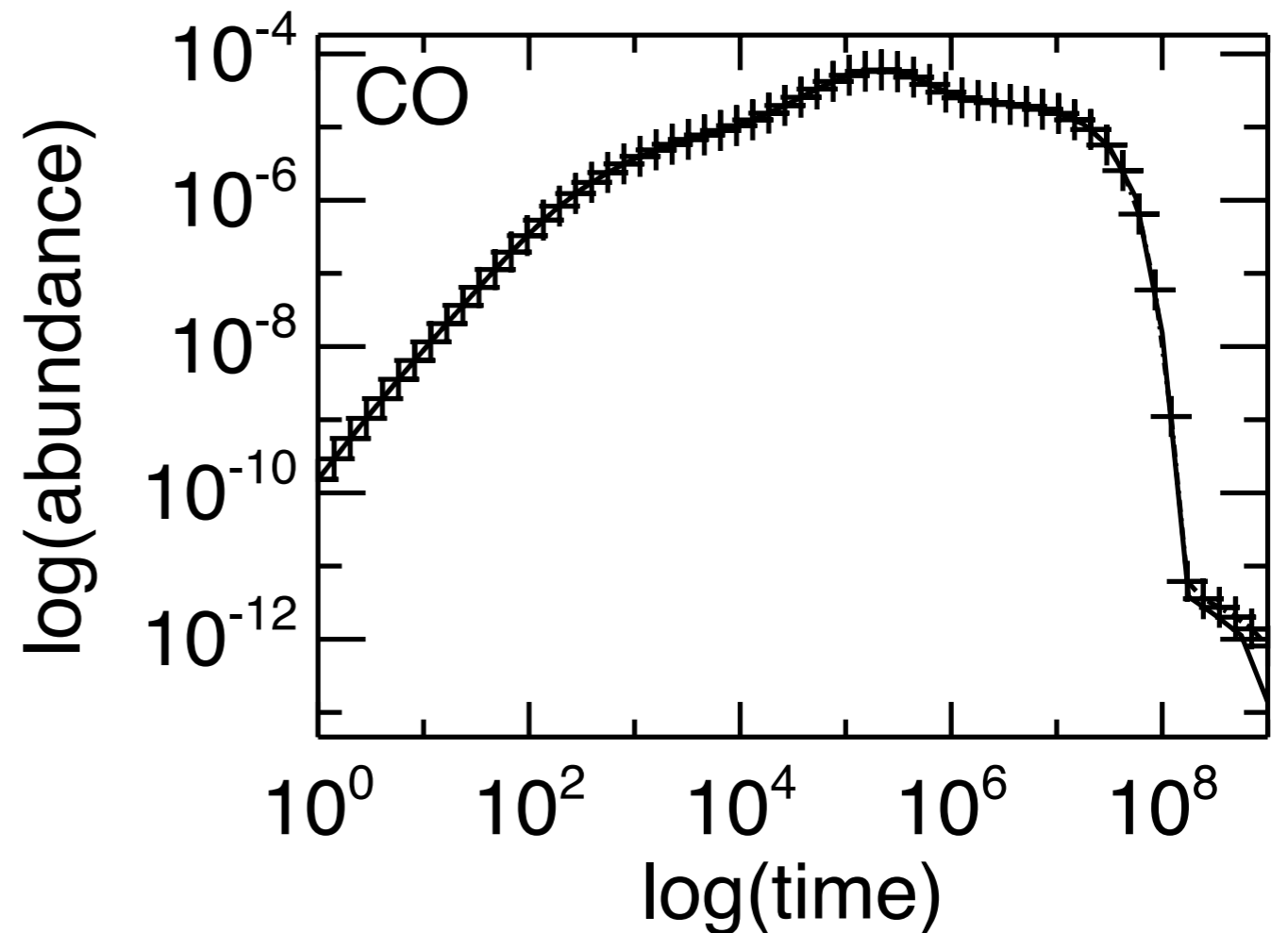
I run takes ~1-10 s on a modern CPU

Chemical models

- ALCHEMIC (MPIA Heidelberg): gas-grain

- GADGET (ITA Heidelberg): gas-phase, early Universe

- NAHOON (Bordeaux Obs.): gas-grain, uncertainties

- MONACO (MPE Garching): gas-grain, Monte Carlo

- ASTROCHEM (Grenoble): gas-grain

- OSU codes (Univ. of Virginia): gas-grain, warm-up

- CLOUDY (Meudon, Leiden, etc.,)

Chemistry in the Early Universe

- Light elements: H, D, He, Li

- Isotropic physical conditions

- High-z molecules are detected (z ~ 7)

- First molecules: cooling of gas ⇒ formation of first stars (Pop III)

Standard Cosmological Model

Composition at the beginning of the matter-dominated era:

H   = 1

D   = 2.6×10^{-5}

^{3}He = 1.0×10^{-5}

^{4}He = 0.2467-0.2576

^{7}Li = $4.6\text{-}5.4 \times 10^{-10}$

^{6}Li = $1.1\text{-}1.2 \times 10^{-14}$

Ionization potentials [in eV]

	1st	2nd	3rd
H	13.6		
He	**24.6**	54.4	
Li	5.4	75.6	122.5

Chemistry of He

- He$^+$ radiatively recombines:

He^{2+} + e- $\rightarrow$ He$^+$ + hν z ~ 6000   (k_{RR} ~ 10^{-10} cm^3/s)

He$^+$ + e- $\rightarrow$ He + hν z ~ 2500   (k_{RR} ~ 4.5x10^{-12} cm^3/s)

- First molecules formed by slow radiative association:

He$^+$ + He $\rightarrow$ He$_2^+$ + hν (k_{RA} ~ 4x10^{-20} cm^3/s)

He + H$^+$ $\rightarrow$ HeH$^+$ + hν (k_{RA} ~ 5x10^{-21} cm^3/s)

- Destroyed by photodissociation & dissociative recombination:

He$_2^+$ + hν $\rightarrow$ He$^+$ + He   fast

HeH$^+$ + hν $\rightarrow$ He$^+$ + H   fast

He$_2^+$ + e- $\rightarrow$ He$^+$ + He   (k_{DR} ~ 6.1x10^{-11} cm^3/s)

HeH$^+$ + e- $\rightarrow$ He + H   (k_{DR} ~ 3x10^{-9} cm^3/s)

Chemistry in the early Universe: He

Galli, Palla (1998), A&A, 335, 403
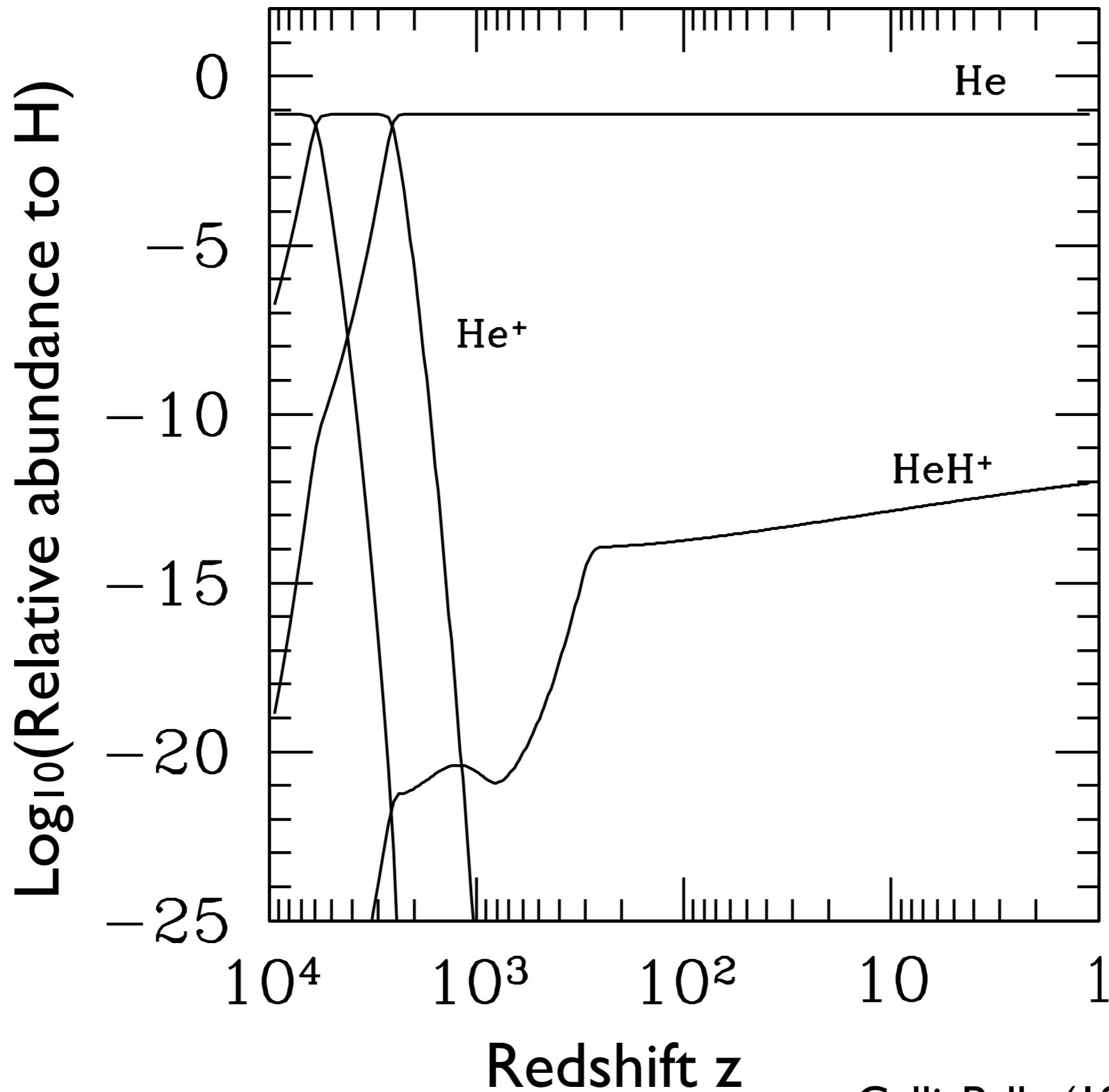
Chemistry of H (z < 1300)

- Molecular hydrogen: only gas-phase reactions

- Radiative association is too slow:

  $H + H \rightarrow H_2 + h\nu \quad (k << 10^{-20} \text{ cm}^3/\text{s})$

- 3-body reactions are ineffective

Formation of H_2 from HeH^+

- H_2 via ion-molecule and charge transfer reactions:

$He + H^+ \rightarrow HeH^+ + h\nu$ $(k_{RA} \sim 5 \times 10^{-21}\ cm^3/s)$

$HeH^+ + H \rightarrow H_2^+ + He$ $(k_{IM} \sim 10^{-9}\ cm^3/s)$

$H_2^+ + H \rightarrow H_2 + H^+$ $(k_{CT} \sim 6 \times 10^{-10}\ cm^3/s)$

Formation of H$_2$ from H$^+$

- Later, formation H$_2$ involves H via RA & charge transfer:

H + H$^+$ → H$_2^+$ + hν   (k_{RA}~ 4x10^{-20} cm^3/s)

H$_2^+$ + H → H$_2$ + H$^+$ (k_{CT} ~ 6x10^{-10} cm^3/s)

- H$_2^+$ is destroyed by photodissociation and DR:

H$_2^+$ + hν → H + H$^+$ fast

H$_2^+$ + e- → H + H   (k_{DR}~ 10^{-8} cm^3/s)

- Photodissociation of H$_2^+$ when T$_R$ > 4000 K ⇒ no H$_2$ at earlier times

Formation of H_2 from H^-

- At z ~100, H_2 can be formed through H^-:

$H + e- \rightarrow H^- + h\nu$ (radiative attachment)   ($k_{RAtt} \sim 3 \times 10^{-16}$ cm^3/s)

$H^- + H \rightarrow H_2 + e-$ (associative detachment)   ($k_{AD} \sim 10^{-9}$ cm^3/s)

- H^- is destroyed by photodetachment:

$H^- + h\nu \rightarrow H + e-$ fast

Barrier is 0.75 eV $\Rightarrow T_R < 1000$ K is needed

New experiments on H⁻ + H

Kreckel et al. (2010), Science
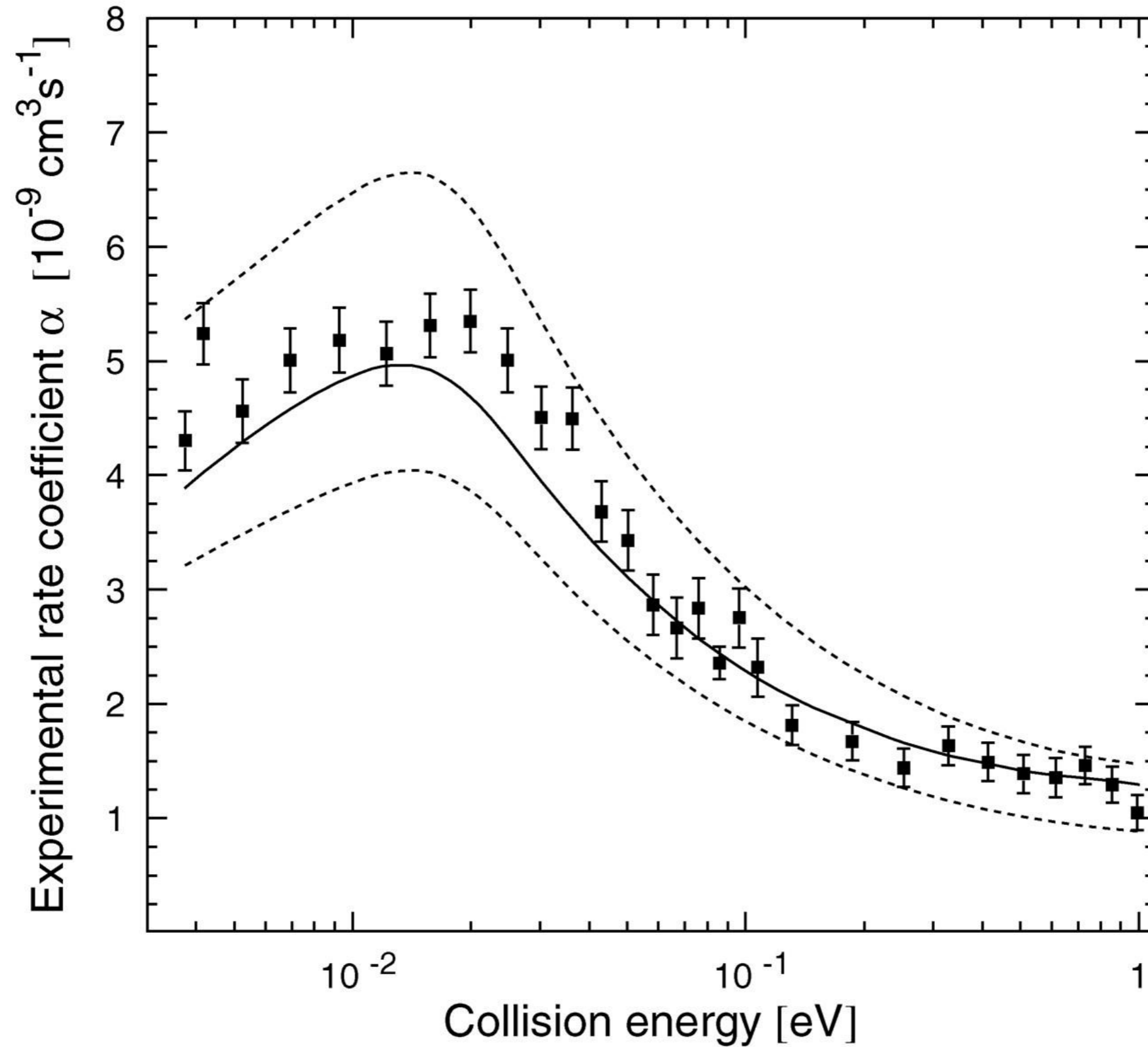
Destruction of H$_2$

- H$_2$ is destroyed by background radiation:

$$H_2 + h\nu \rightarrow H + H \qquad\qquad \text{fast (if } \lambda < 1150\text{Å)}$$

- H$_2$ is destroyed by collisions with H$^+$ and e$^-$:

$$H_2 + H^+ \rightarrow H + H_2^+ \qquad\qquad (k_{CT} \sim 5\times10^{-13} \text{ cm}^3\text{/s})$$

$$H_2^+ + e^- \rightarrow e^- + 2H \qquad\qquad (k_{CD} \sim 2\times10^{-9} \text{ cm}^3\text{/s})$$

- Small molecular fraction in the early Universe: $X(H_2) \lesssim 10^{-6}$

Chemistry in the early Universe: H
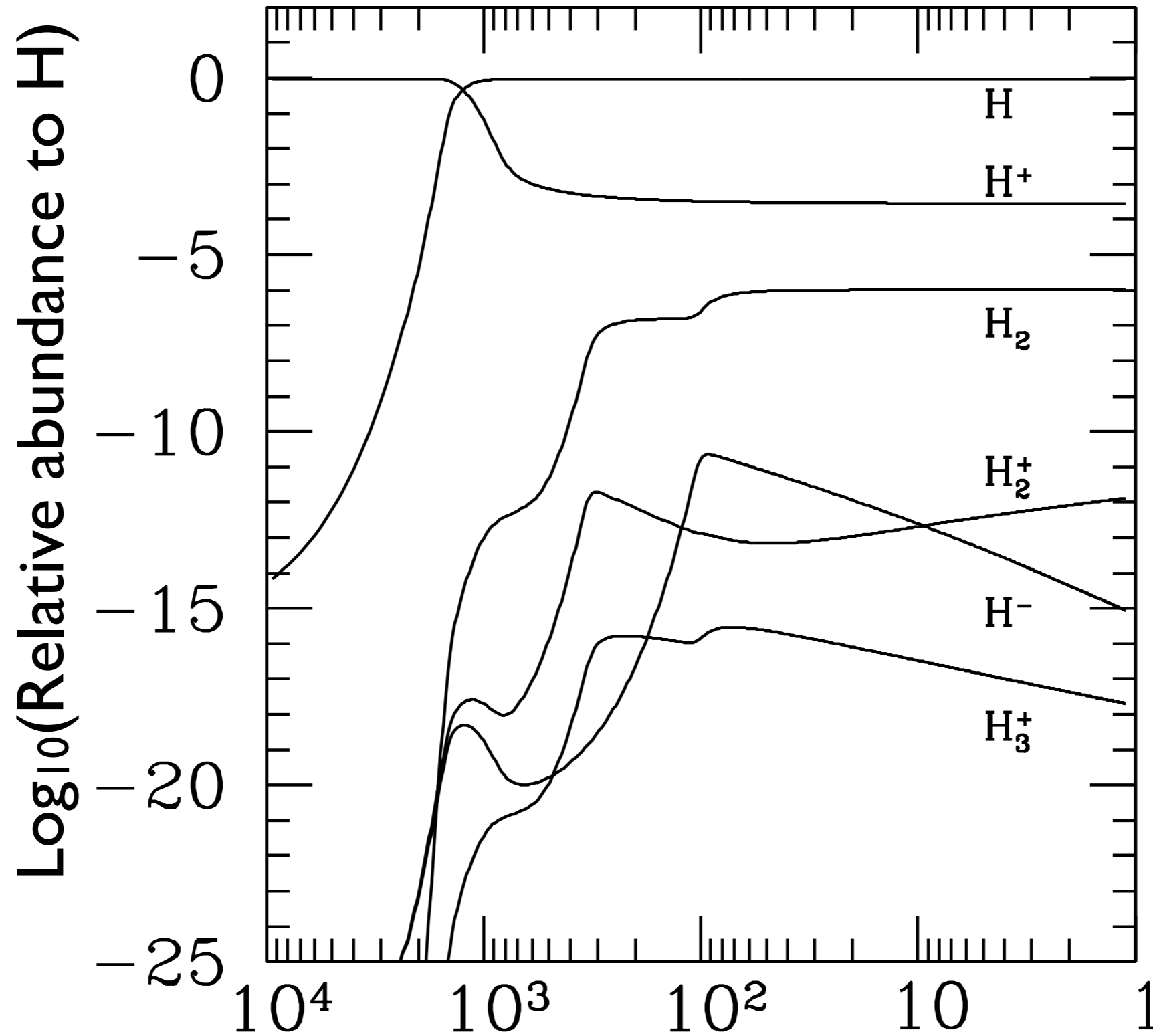
Chemistry of D

- Formation of HD is dominated by ion-molecule and charge transfer processes:

  $H^+ + D \rightarrow H + D^+$ $\qquad\qquad$ ($k_{CT} \sim 10^{-9}$ cm^3/s)

  $D^+ + H_2 \rightarrow HD + H^+$ $\qquad\qquad$ ($k_{IM} \sim 3\text{x}10^{-9}$ cm^3/s)

- HD is destroyed by similar processes as H_2

- $X(HD) \sim 10^{-11} - 10^{-9}$

Chemistry in the early Universe: D
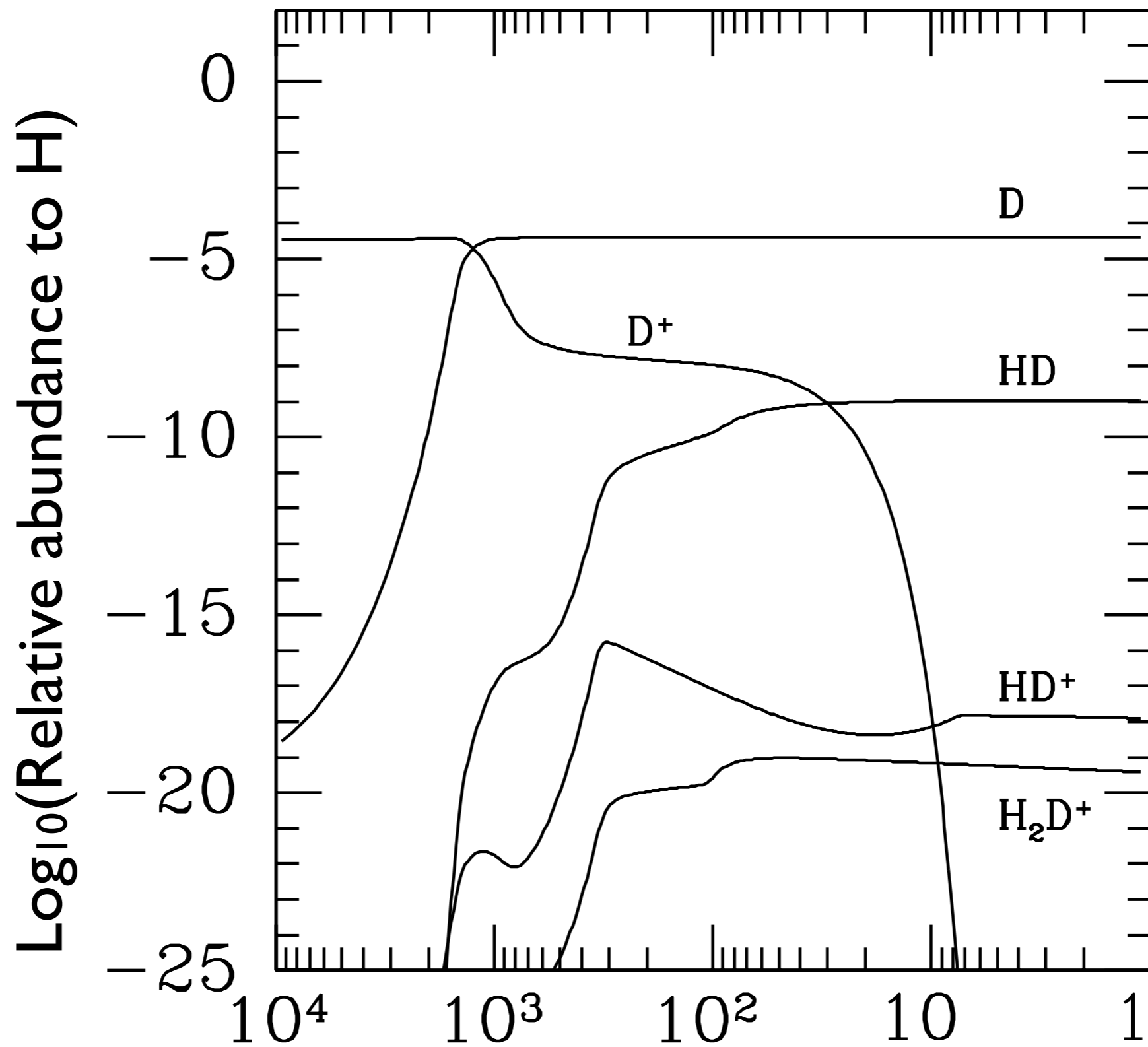
Suggested literature

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Thank you!