LECTURE 2.1

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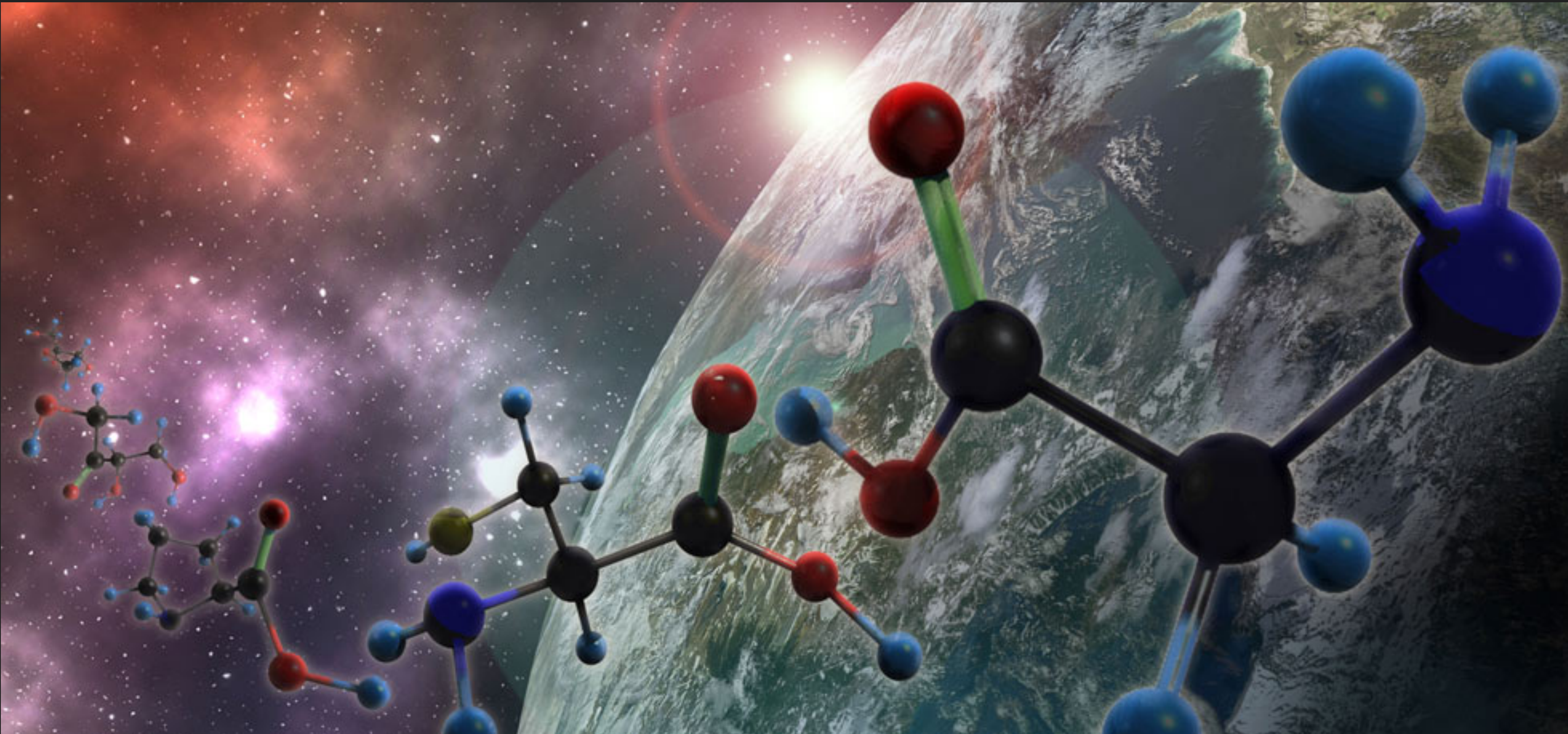
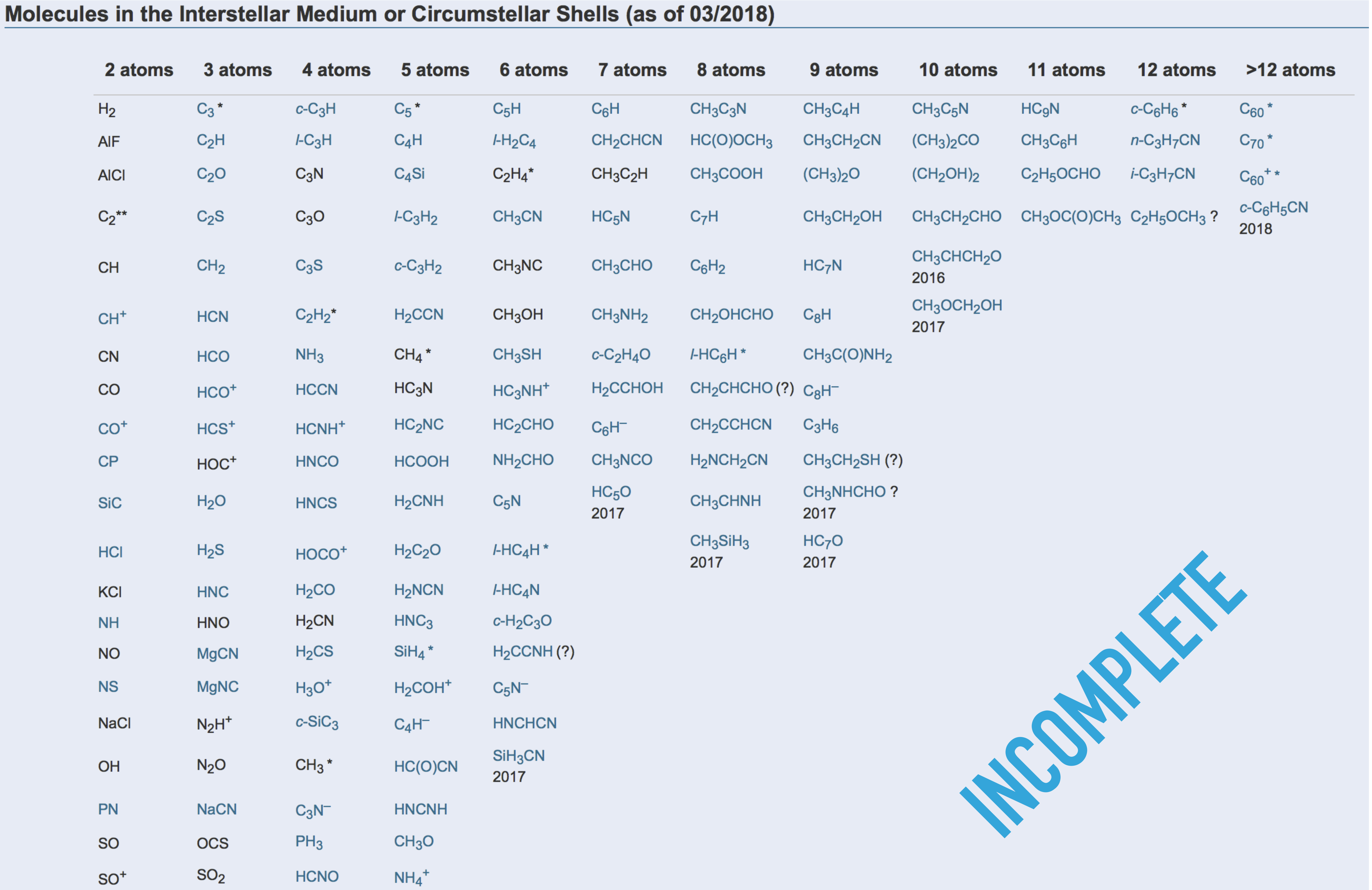


BASICS

- Astrochemistry field evolved over the years together with the technological development (computing + observations)
- Astrochemistry is the study of the chemical processes under ISM conditions
- It is an incredible powerful tool to interpret observations and provide hints on the physics of the observed regions

In 80 years molecules have been observed throughout the Universe: from evolved stars to PPD, galaxies, and comets!



Molecules in the Interstellar Medium or Circumstellar Shells (as of 03/2018)

2 atoms	3 atoms	4 atoms	5 atoms	6 atoms	7 atoms	8 atoms	9 atoms	10 atoms	11 atoms	12 atoms	>12 atoms
H_2	C_3 *	*c*-C_3H	C_5 *	C_5H	C_6H	CH_3C_3N	CH_3C_4H	CH_3C_5N	HC_9N	*c*-C_6H_6 *	C_{60} *
AlF	C_2H	*l*-C_3H	C_4H	*l*-H_2C_4	CH_2CHCN	$HC(O)OCH_3$	CH_3CH_2CN	$(CH_3)_2CO$	CH_3C_6H	*n*-C_3H_7CN	C_{70} *
AlCl	C_2O	C_3N	C_4Si	C_2H_4*	CH_3C_2H	CH_3COOH	$(CH_3)_2O$	$(CH_2OH)_2$	C_2H_5OCHO	*i*-C_3H_7CN	C_{60}^+ *
C_2**	C_2S	C_3O	*l*-C_3H_2	CH_3CN	HC_5N	C_7H	CH_3CH_2OH	CH_3CH_2CHO	$CH_3OC(O)CH_3$	$C_2H_5OCH_3$?	*c*-C_6H_5CN 2018
CH	CH_2	C_3S	*c*-C_3H_2	CH_3NC	CH_3CHO	C_6H_2	HC_7N	CH_3CHCH_2O 2016			
CH^+	HCN	C_2H_2*	H_2CCN	CH_3OH	CH_3NH_2	CH_2OHCHO	C_8H	CH_3OCH_2OH 2017			
CN	HCO	NH_3	CH_4 *	CH_3SH	*c*-C_2H_4O	*l*-HC_6H *	$CH_3C(O)NH_2$				
CO	HCO^+	HCCN	HC_3N	HC_3NH^+	H_2CCHOH	CH_2CHCHO (?)	C_8H^-				
CO^+	HCS^+	$HCNH^+$	HC_2NC	HC_2CHO	C_6H^-	CH_2CCHCN	C_3H_6				
CP	HOC^+	HNCO	HCOOH	NH_2CHO	CH_3NCO	H_2NCH_2CN	CH_3CH_2SH (?)				
SiC	H_2O	HNCS	H_2CNH	C_5N	HC_5O 2017	CH_3CHNH	CH_3NHCHO ? 2017				
HCl	H_2S	$HOCO^+$	H_2C_2O	*l*-HC_4H *		CH_3SiH_3 2017	HC_7O 2017				
KCl	HNC	H_2CO	H_2NCN	*l*-HC_4N							
NH	HNO	H_2CN	HNC_3	*c*-H_2C_3O							
NO	MgCN	H_2CS	SiH_4 *	H_2CCNH (?)							
NS	MgNC	H_3O^+	H_2COH^+	C_5N^-							
NaCl	N_2H^+	*c*-SiC_3	C_4H^-	HNCHCN							
OH	N_2O	CH_3 *	HC(O)CN	SiH_3CN 2017							
PN	NaCN	C_3N^-	HNCNH								
SO	OCS	PH_3	CH_3O								
SO^+	SO_2	HCNO	NH_4^+								

INCOMPLETE

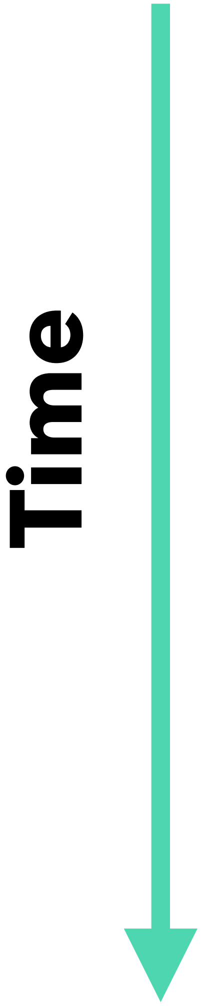
HOW DO THESE MOLECULES FORM? AND WHERE?

The interstellar medium

The interstellar medium

- The stuff between the stars in around galaxies
- ISM is the most important part of a galaxy
- ISM is responsible for forming stars (dominant sources of energy)
- ISM turbulent and out of equilibrium

History of the ISM



Optical - Naked eyes

Optical - Photographic plates / Imaging

Optical - Spectroscopy

Radio

UV / X-ray / IR

mm

Pre-20th-century

1608 - Galileo Galilei: invented the telescope

1610 - Discovery of the Orion Nebula (Nicolas Fabri de Peiresc)

1656 - First detailed description of the Orion Nebula (Christian Huygens)

Pre-20th-century

Phæno-
menon in
Orione
novum.

Unum vero c
currit, à nemine hucuſque,
quidem niſi grandibus hiſce teleſ
In Orionis enſe tres ſtellæ ab Aſtronomis
ſe proximæ. Harum mediam Anno 1656 forte pe
inſpicienti mihi, pro ſtella una duodecim (quod quidem mi-
nimè novum) ſeſe obtulerunt; eo poſitu quem ſubjecta figu-
ra expreſſimus.

Ex his autem tres illæ pene inter ſe contiguæ, cumque
his aliæ quatuor, velut trans nebulam lucebant, ita ut
ſpatium circa ipſas, qua forma hîc conſpicitur, multo illu-
ſtrius appareret reliquo omni cælo; quod cum apprimè ſe-
renum eſſet ac cerneretur nigerrimum, velut hiatu quodam
inter-

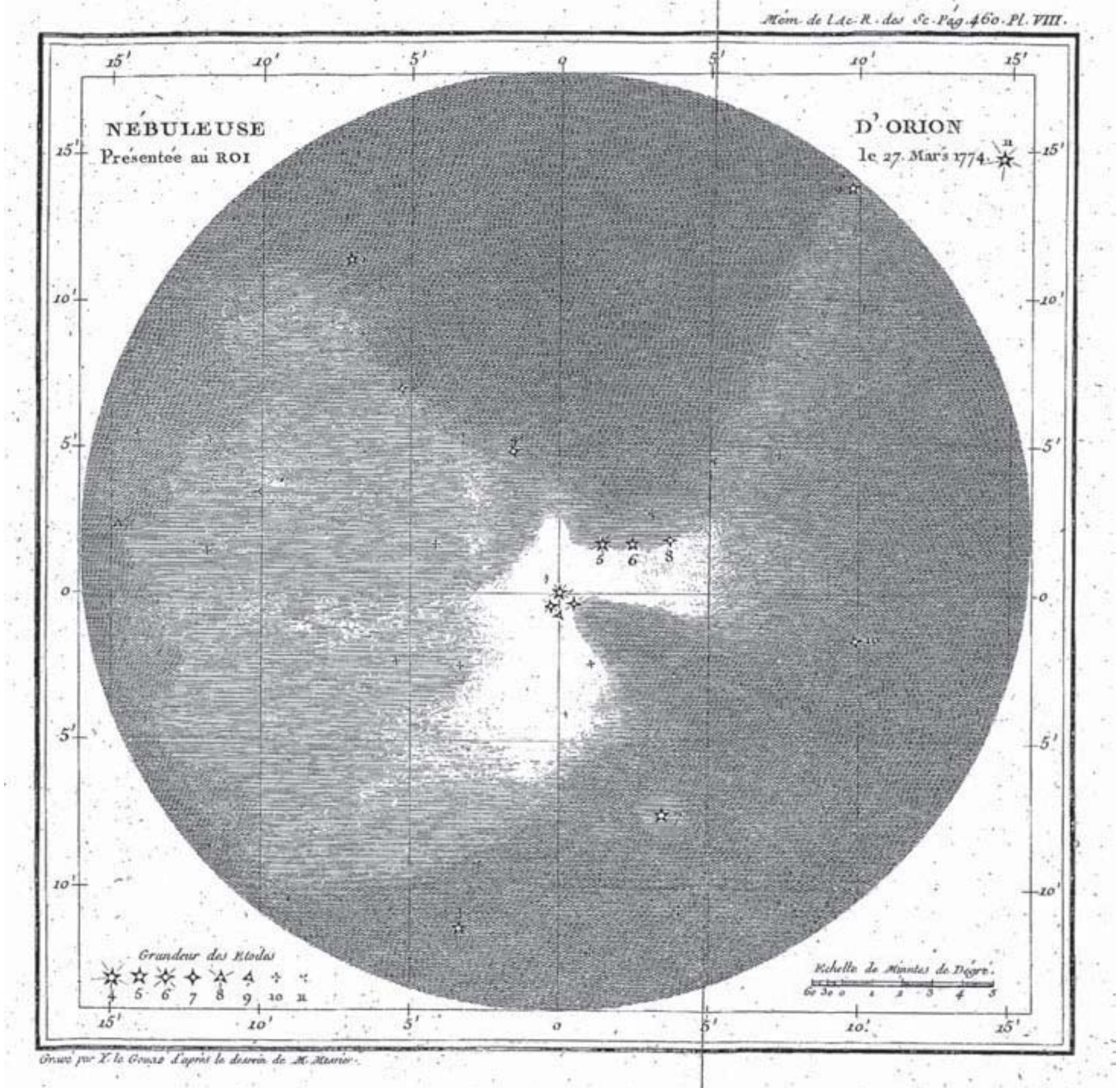
tæ, atque ipſa
habere comperiuntur, neq
habere comperiuntur, neq
larum congeries & frequentia.
In Lunæ facie autem quàn
buſque obſervatoribus præter
tur, non referam; quandoqu
ſcripto opus eſſet, coque a
ctenus non ſuſcepimus, cre
ſum, ſi montium omnium e
titudine nobis videntur, d
turni obſervationes pergo.
omnes, uſque ad eam qu
vimus, tubo 12 pedum
terque autem everſo ſit
mata omnia, non ut pr
mus, ſed ſupera inferis
ra pateret diſpoſitio.

occaſum ve

"Systema Saturniun (book)"

Charles Messier, 1781

M42: Orion Nebula



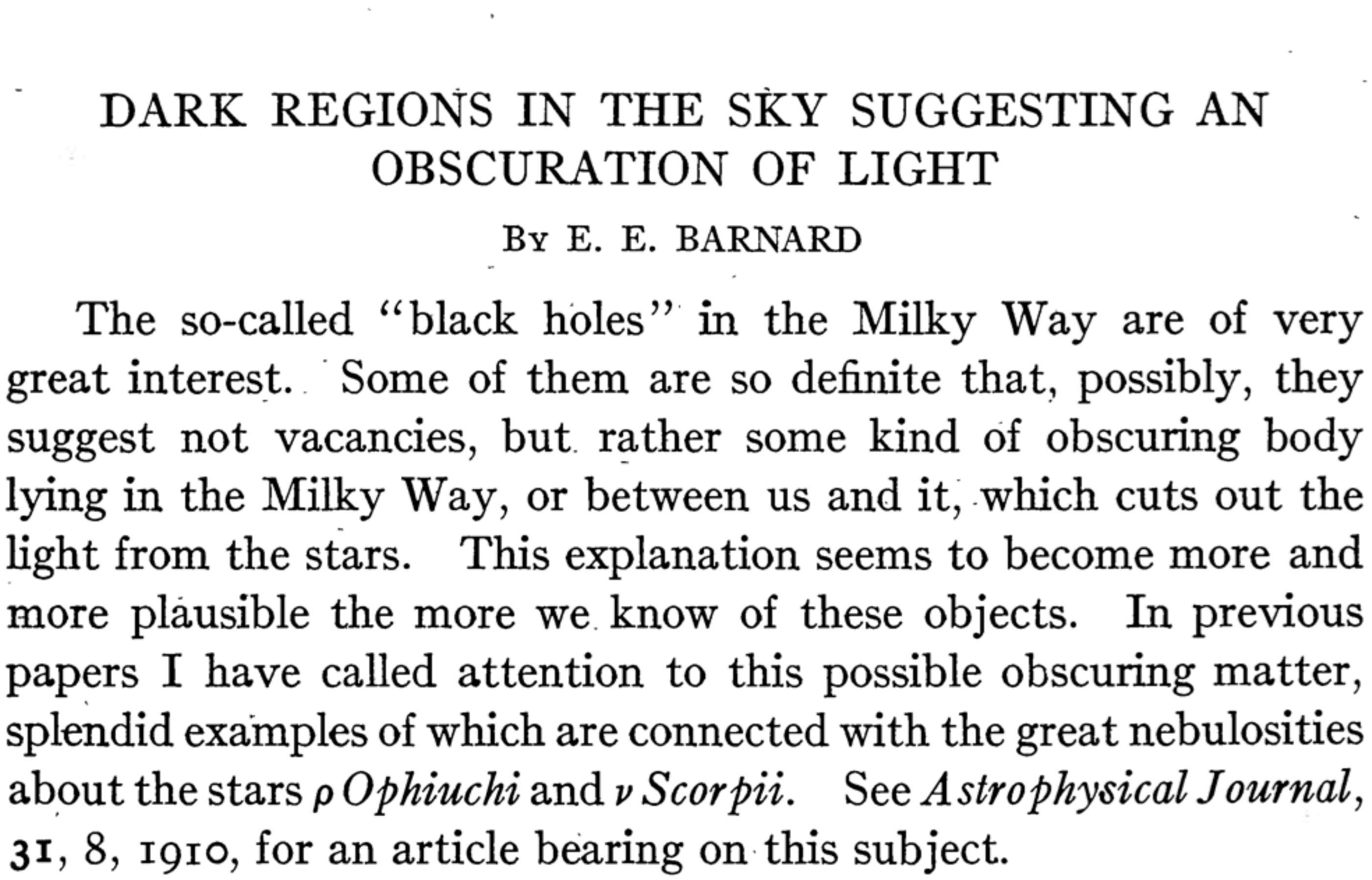
1880 - Henry Draper: First photograph of Orion Nebula

1883 - Andrew Ainslie Common

45 cm reflector, long exposure time

20th-century

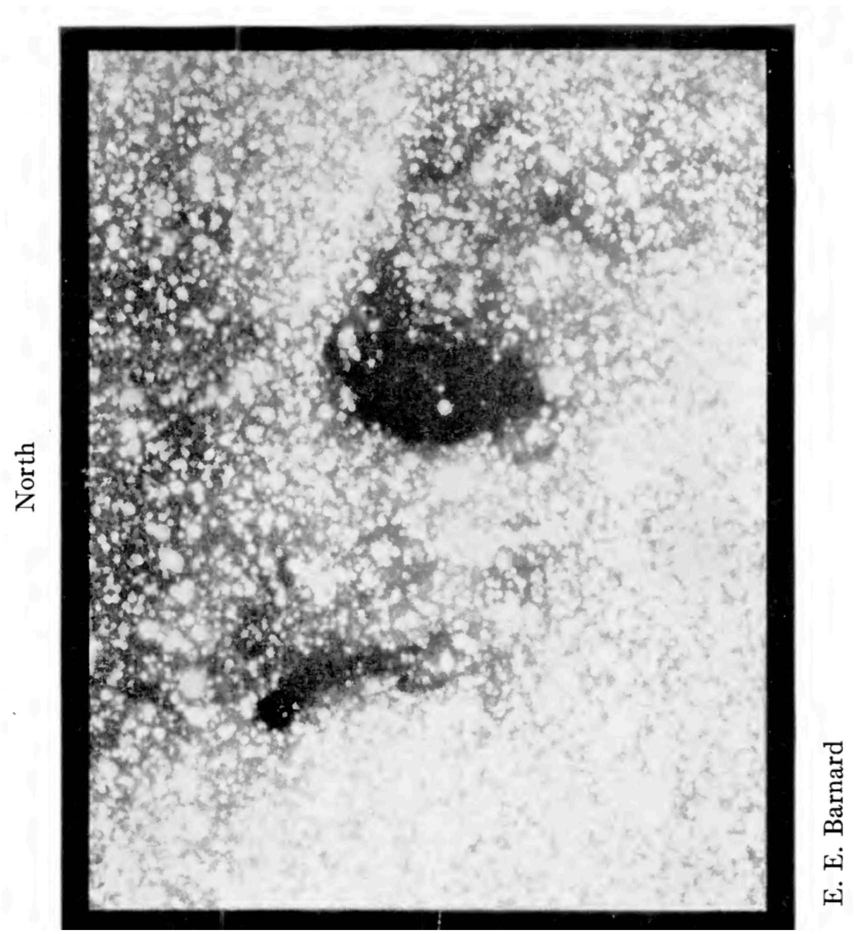
1910-1927 - E. E. Barnard: no hole in the distribution but some obscuring matter, catalog of dark nebulae



DARK REGIONS IN THE SKY SUGGESTING AN OBSCURATION OF LIGHT

By E. E. BARNARD

The so-called "black holes" in the Milky Way are of very great interest. Some of them are so definite that, possibly, they suggest not vacancies, but rather some kind of obscuring body lying in the Milky Way, or between us and it, which cuts out the light from the stars. This explanation seems to become more and more plausible the more we know of these objects. In previous papers I have called attention to this possible obscuring matter, splendid examples of which are connected with the great nebulosities about the stars ρ *Ophiuchi* and ν *Scorpii*. See *Astrophysical Journal*, **31**, 8, 1910, for an article bearing on this subject.



20th-century

- CO shows there are cold, dense regions of gas associated with star formation

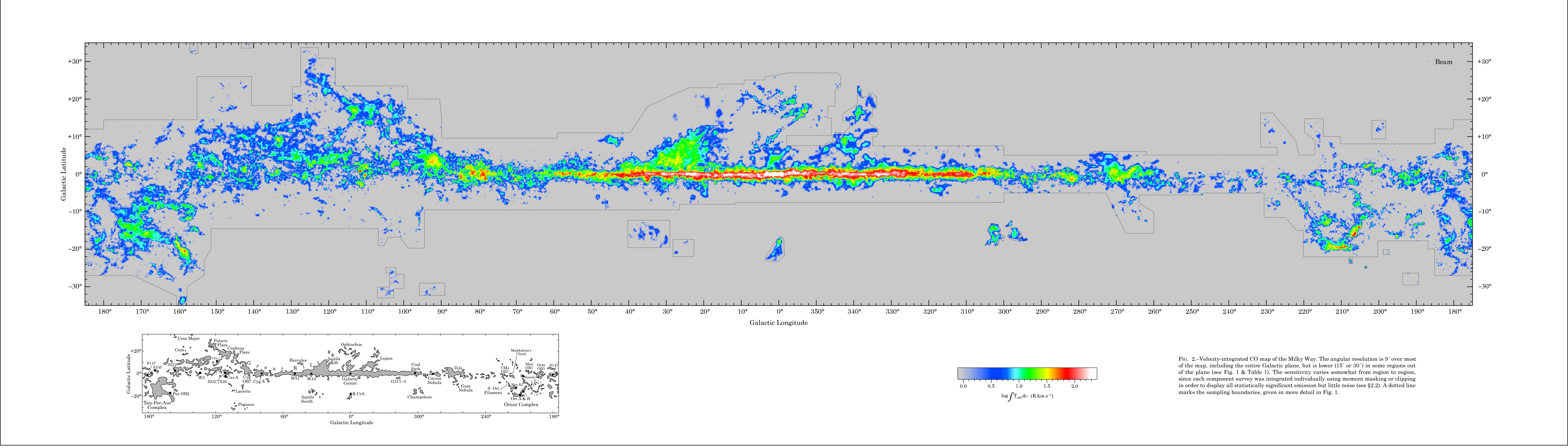
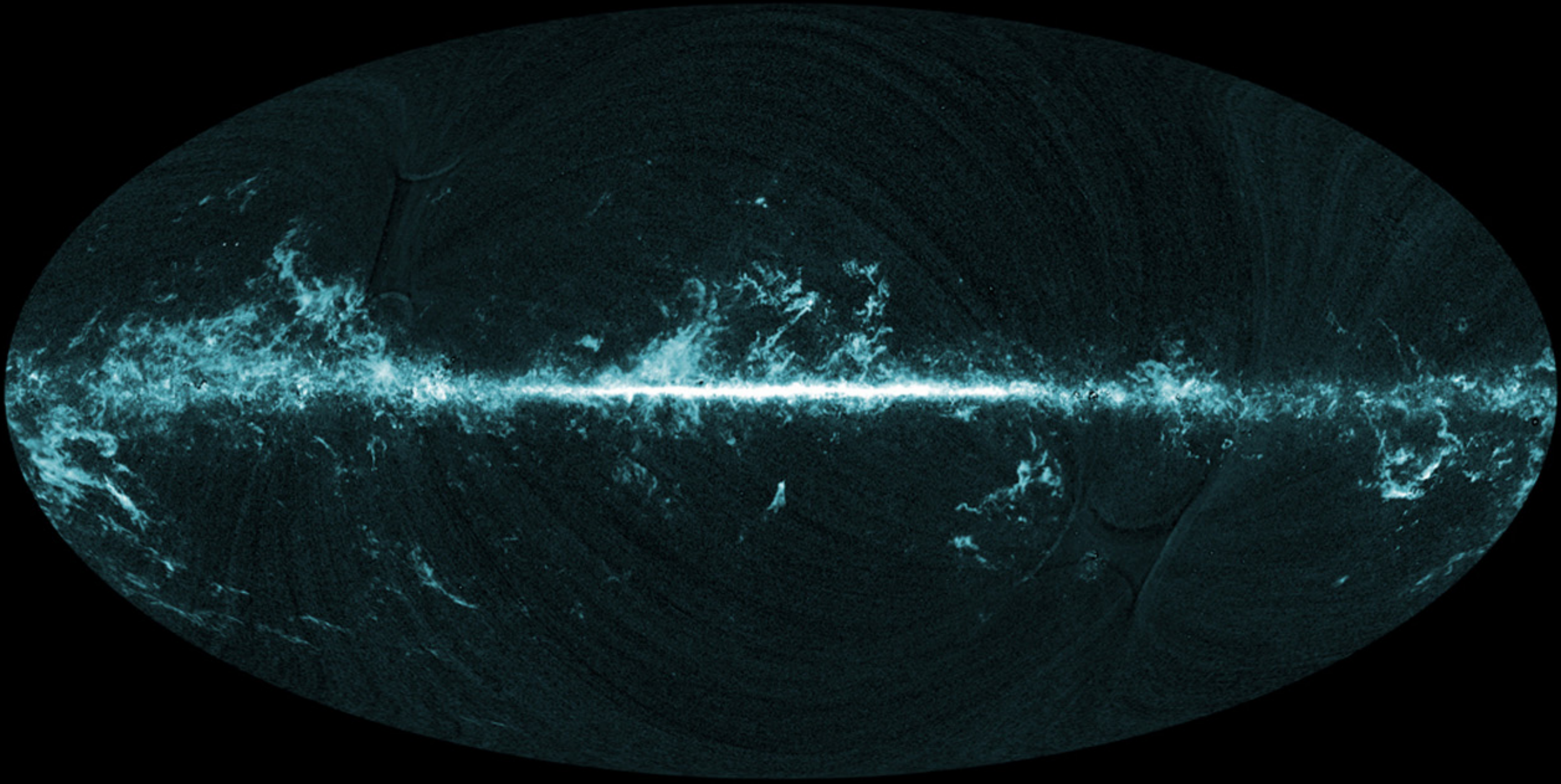


FIG. 2.–Velocity-integrated CO map of the Milky Way. The angular resolution is 9′ over most of the map, including the entire Galactic plane, but is lower (15′ or 30′) in some regions out of the plane (see Fig. 1 & Table 1). The sensitivity varies somewhat from region to region, since each component survey was integrated individually using moment masking or clipping in order to display all statistically significant emission but little noise (see §2.2). A dotted line marks the sampling boundaries, given in more detail in Fig. 1.

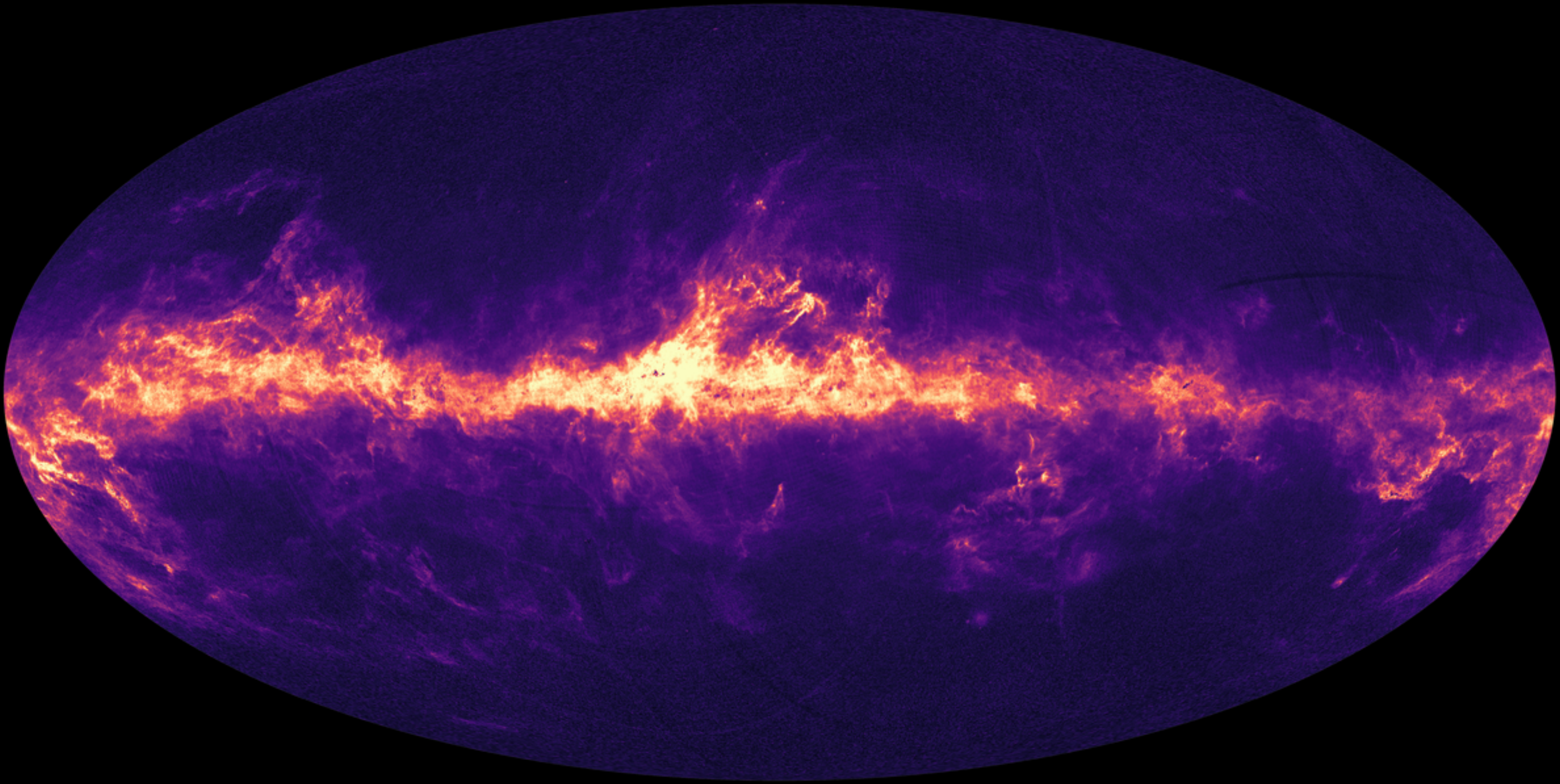
Dame 2000 CO-survey of the galaxy

Our Galaxy: molecular gas in CO

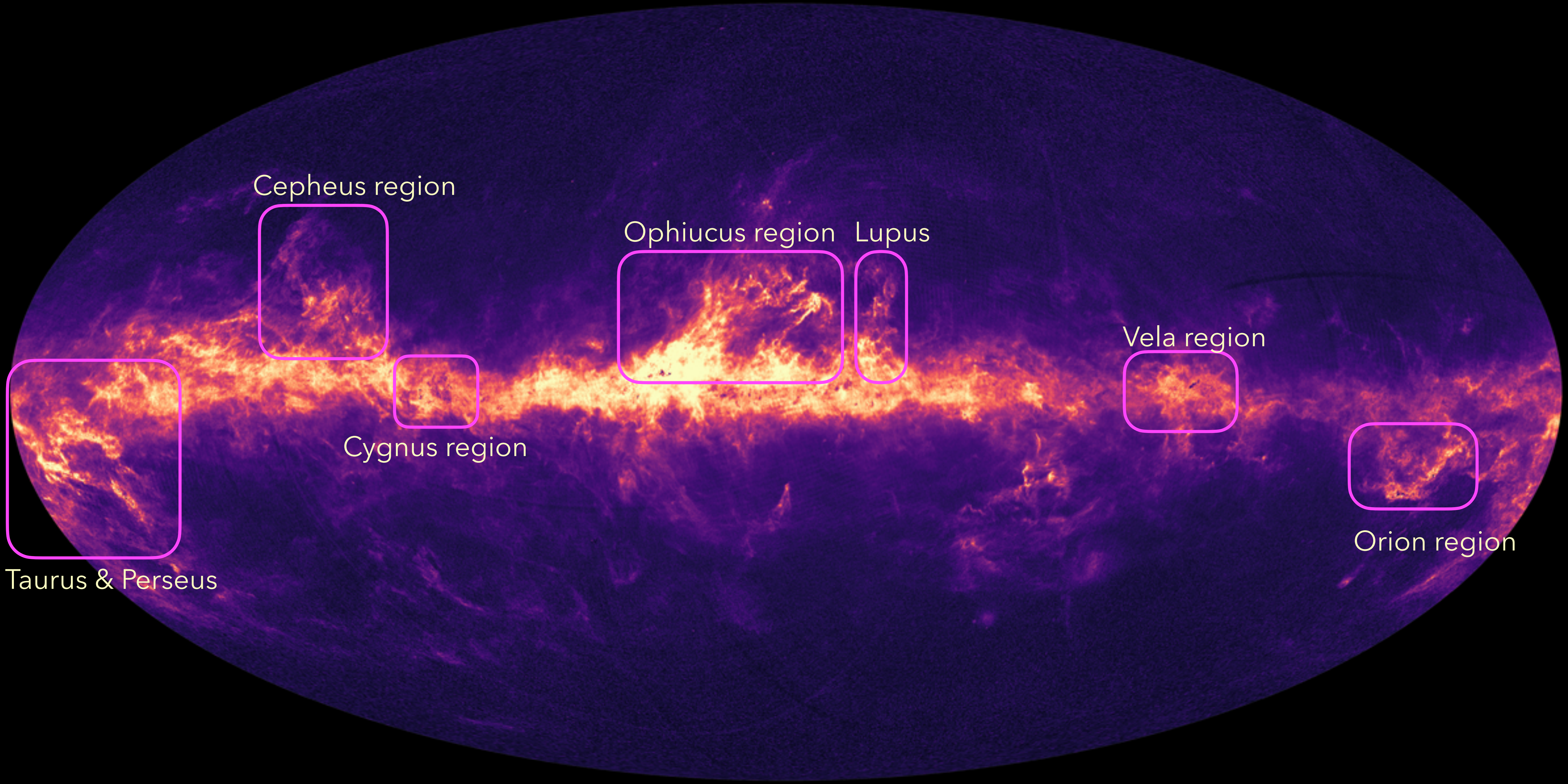


Credit: ESA/NASA/Planck Collaboration

Our Galaxy: dust



Credit:ESA/Gaia/DPAC, CC BY-SA 3.0 IGO



Credit:ESA/Gaia/DPAC, CC BY-SA 3.0 IGO

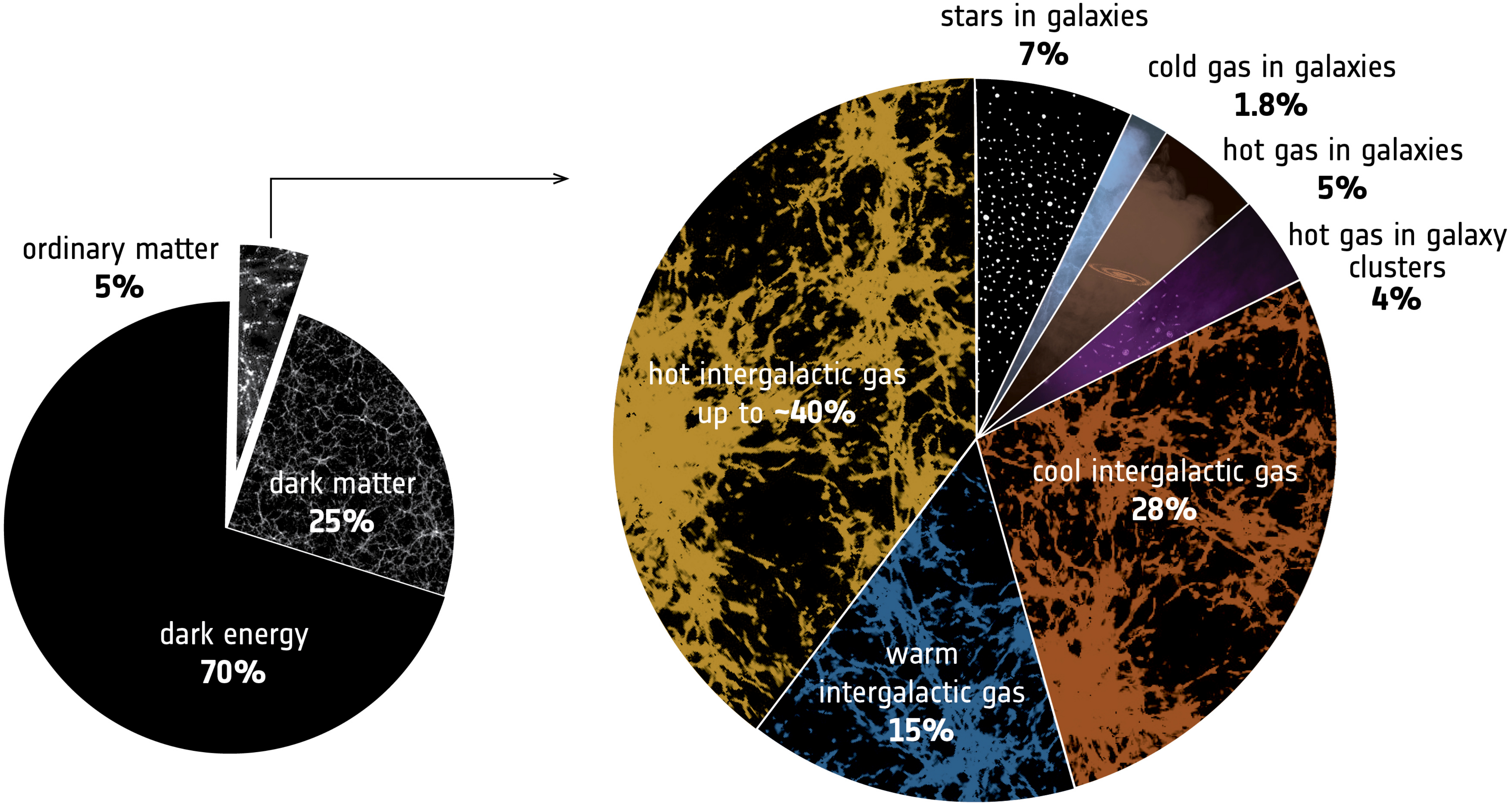
Late 20th-century

- CO shows there are cold, dense regions of gas associated with star formation

- Interstellar chemistry complex

- 1980-until now: many complex molecules have been discovered

The interstellar medium



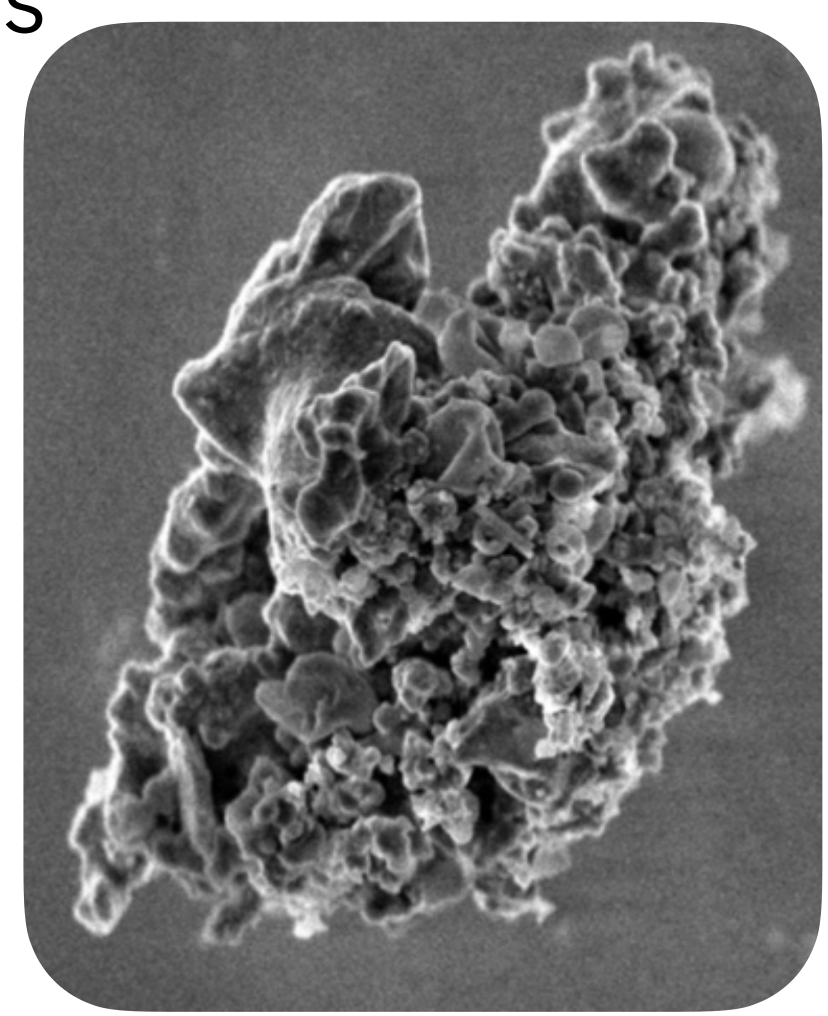
This 5% allows structures to form (galaxies, stars, and planets)

What is in between the stars?

- Interstellar gas
- Interstellar dust
- Cosmic rays
- Electromagnetic radiation
- Magnetic field

Interstellar dust grains (solid)

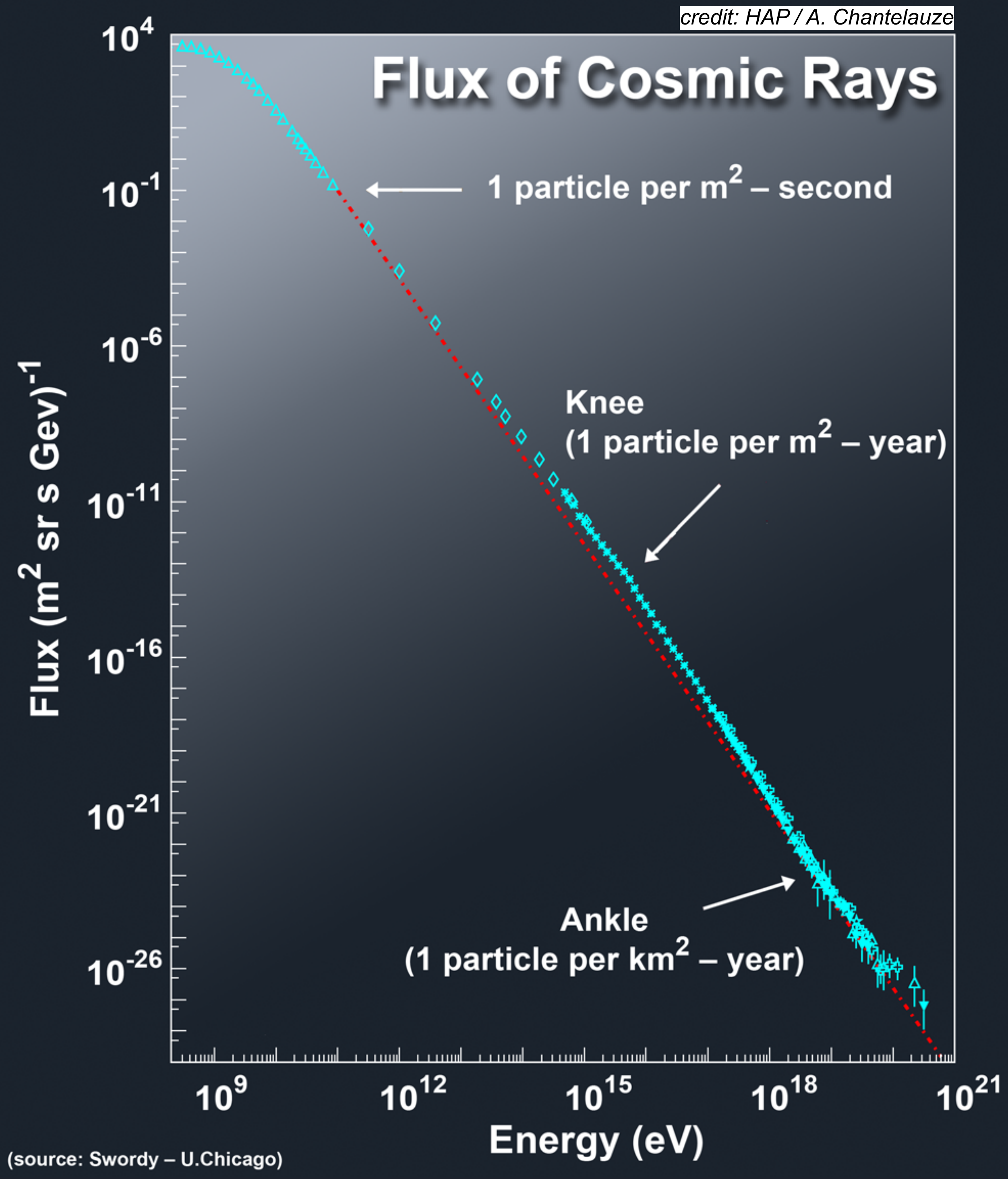
- Small solid particles, mainly less than 1 micron in size, mixed with the interstellar gas



- Dust contains most of the heavy elements
- Are produced in the shells around stars
- Reprocessed in the ISM

Cosmic rays

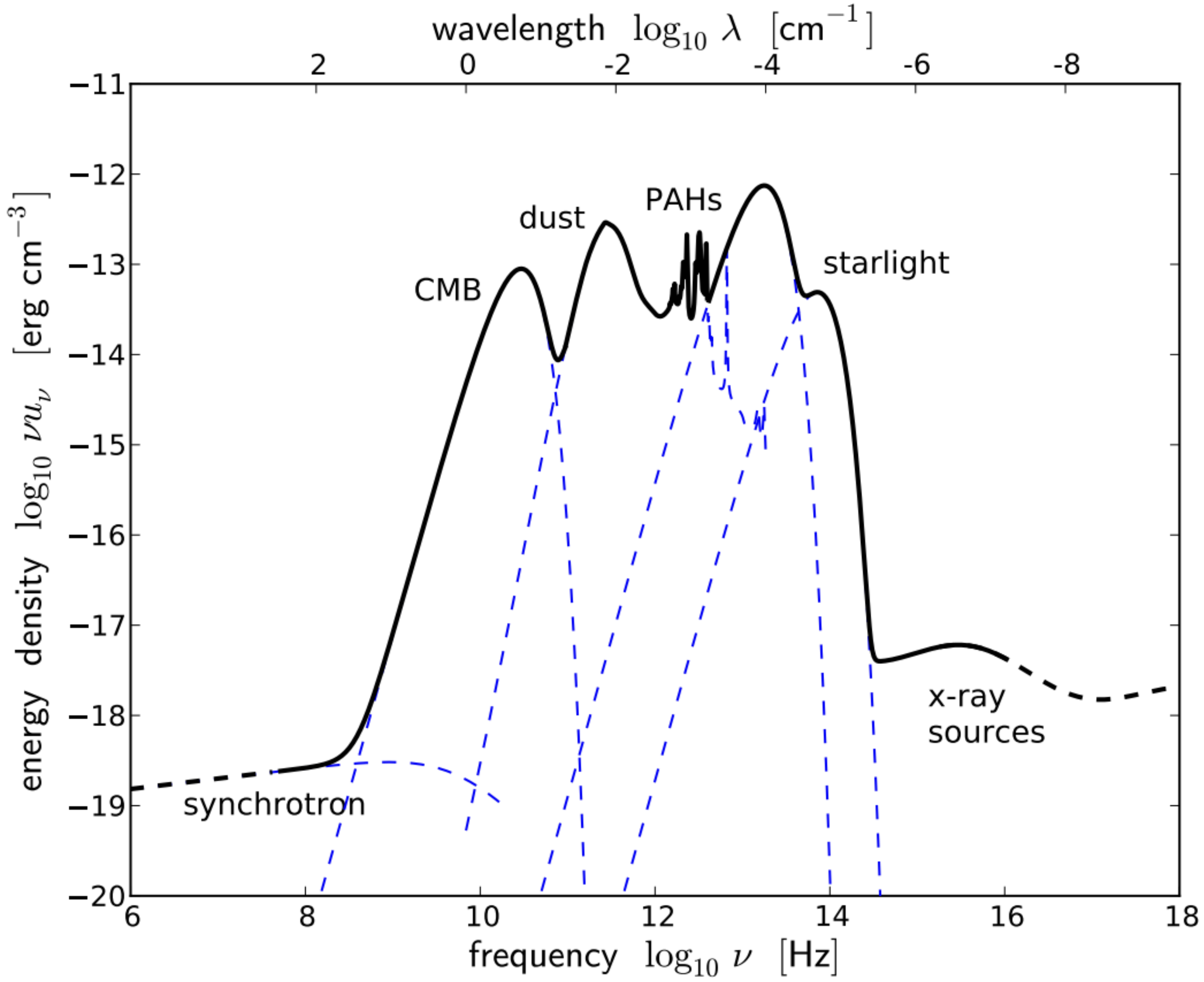
- Ions and electrons with high kinetic energies, much larger than thermal, often relativistic



(source: Swordy – U.Chicago)

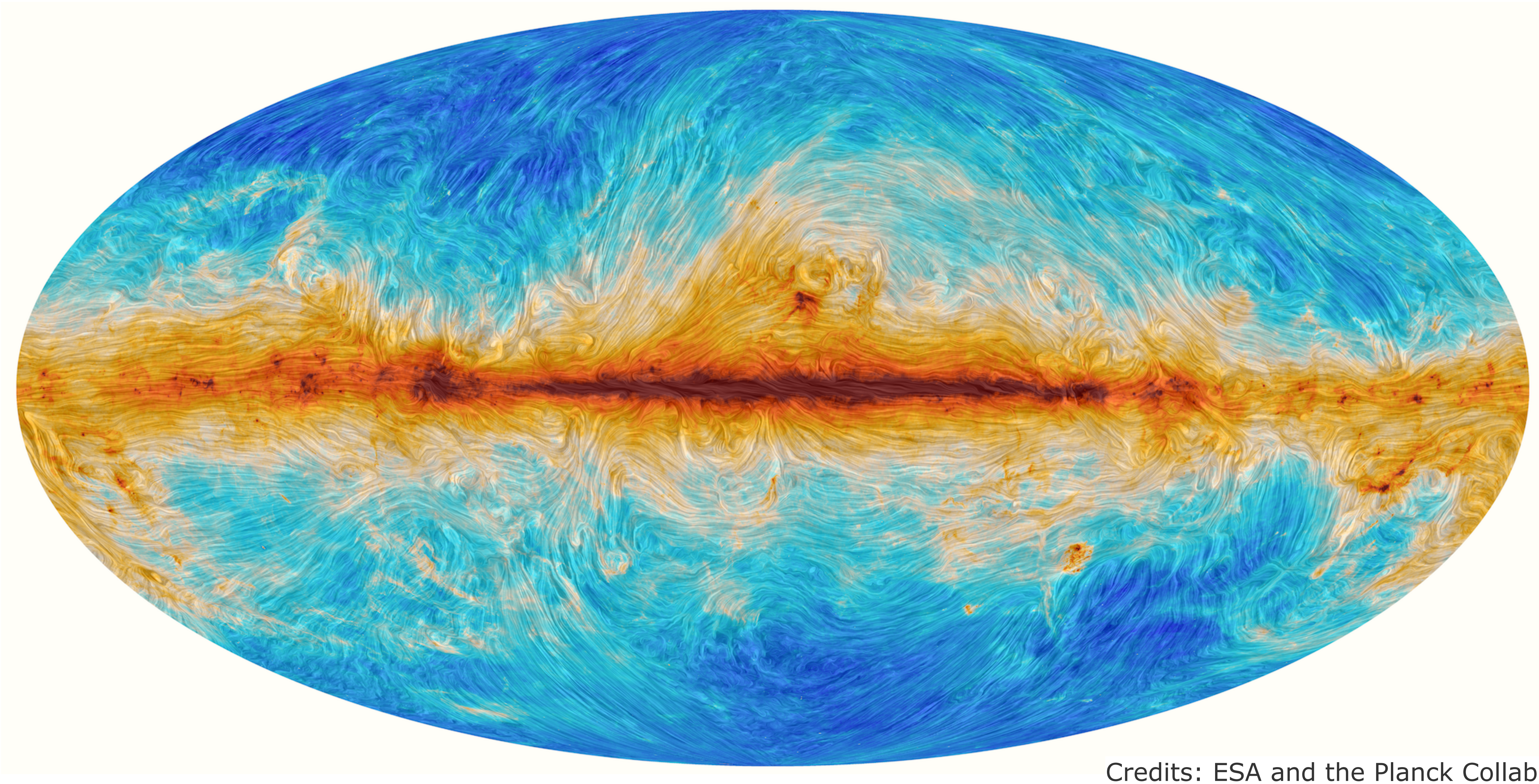
Interstellar radiation field

- Photons from many sources, including the CMB; starlight; radiation emitted by ions, atoms and molecules; thermal emission from interstellar grains heated by starlight; bremsstrahlung from plasma; synchrotron radiation from relativistic electrons; gamma rays



Magnetic fields

- Resulting from electric currents in the ISM. Guide the CRs, and they are dynamical important

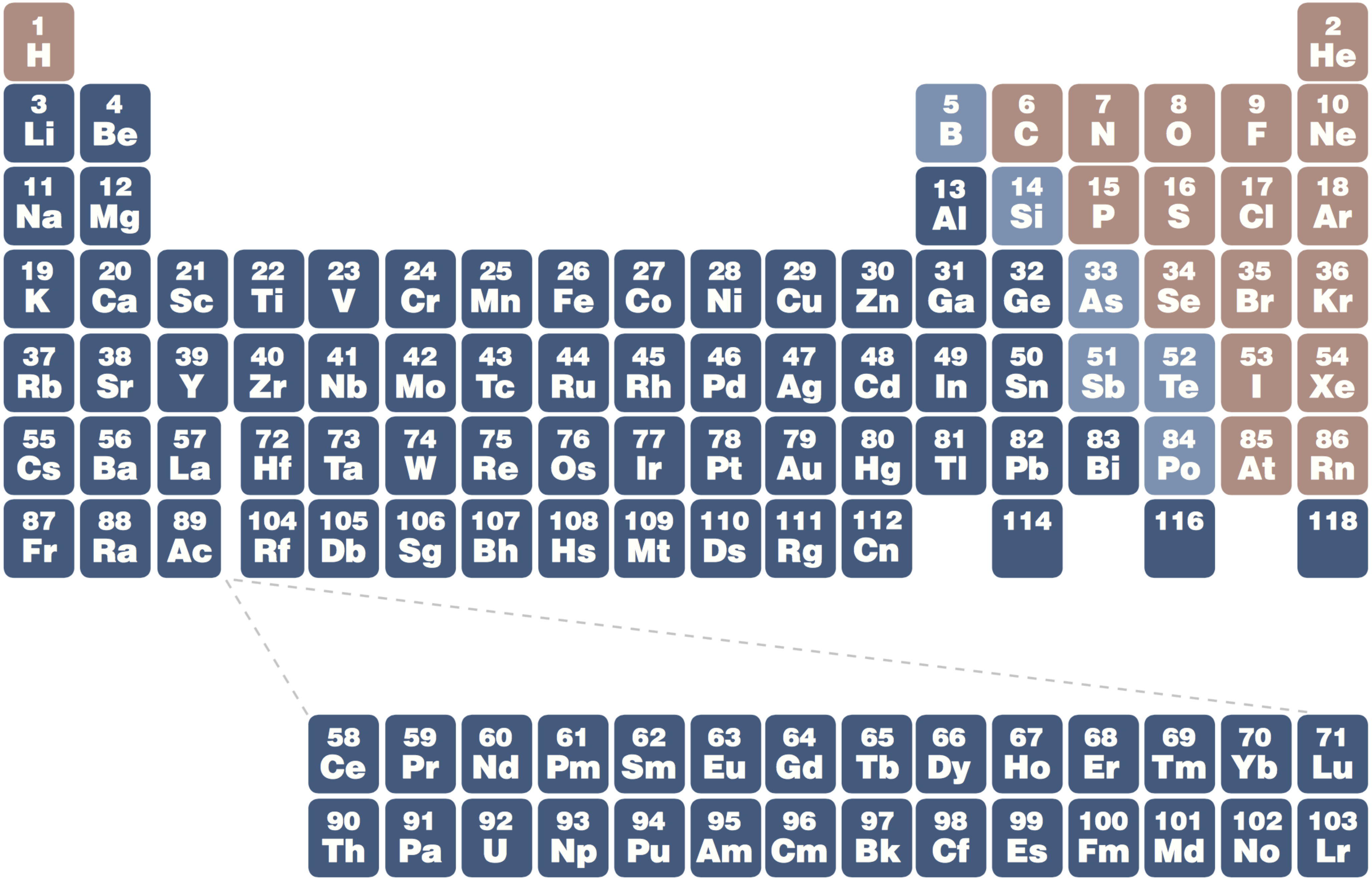


Credits: ESA and the Planck Collaboration

Interstellar gas

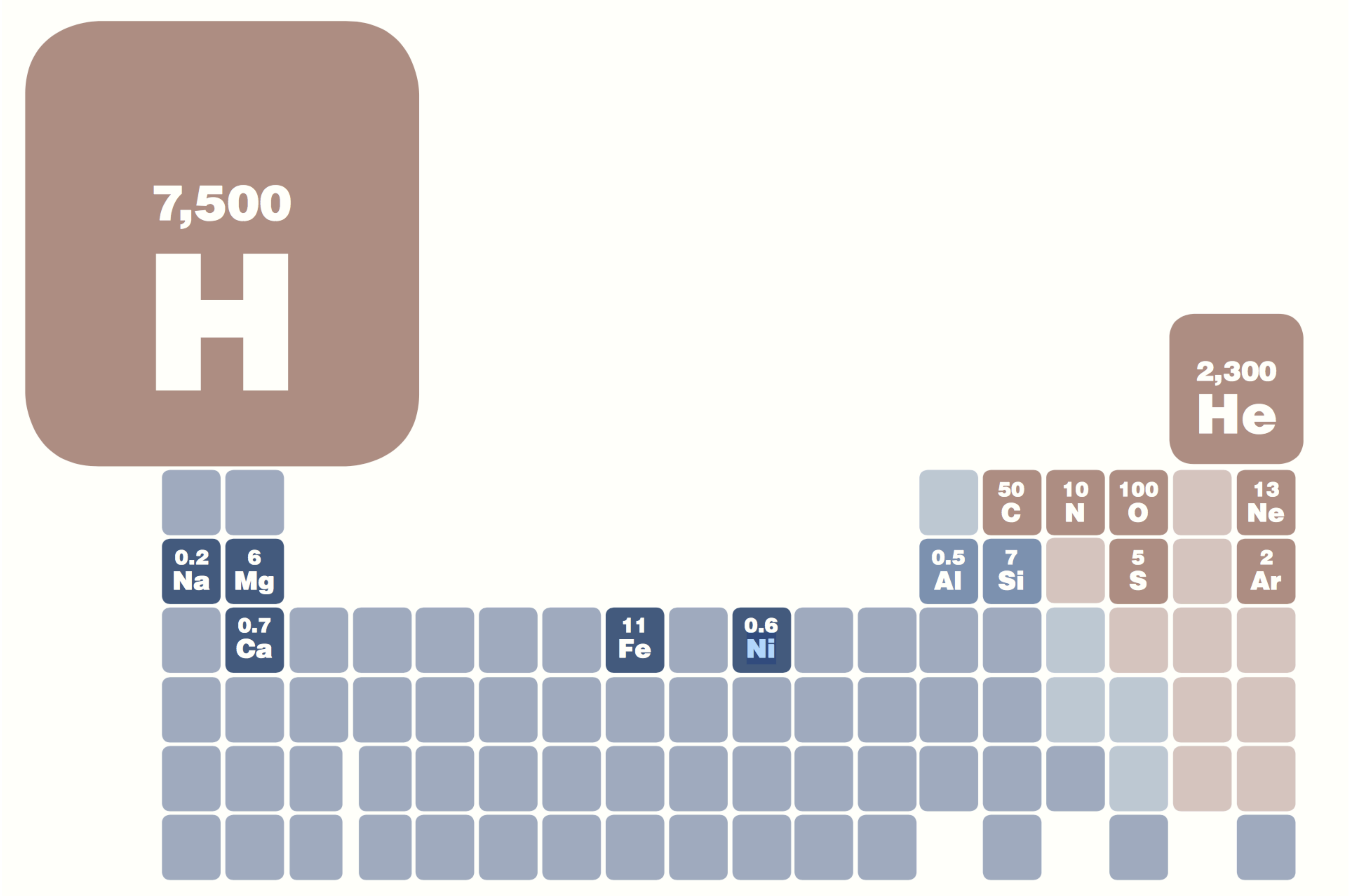
- Ions, molecules, atoms in the gas phase, velocity distributions very nearly thermal

COMPOSITION OF THE 5% OF UNIVERSE? VERY DIFFERENT FROM EARTH!



1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn		114		116		118
				58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
				90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

98% IS MADE BY HYDROGEN AND HELIUM, 2% BY METALS + DUST



Solar system and the local interstellar medium

			solar system		local ISM*	
element		Z	[X]/[H]	mass fraction	gas, [X]/[H]	dust, [X]/[H]
^{1}**H**	hydrogen	1	1	0.71		
^{4}**He**	helium	2	0.098	0.28		
^{16}**O**	oxygen	8	$4.9\,10^{-4}$	$5.6\,10^{-3}$	$2.8\,10^{-4}$	$2.6\,10^{-4}$
^{12}**C**	carbon	6	$2.5\,10^{-4}$	$2.1\,10^{-3}$	$1.8\,10^{-4}$	$2.1\,10^{-4}$
^{20}**Ne**	neon	10	$1.0\,10^{-4}$	$1.4\,10^{-3}$		
^{56}**Fe**	iron	26	$2.8\,10^{-5}$	$1.1\,10^{-3}$	$1.4\,10^{-6}$	$2.7\,10^{-5}$
^{14}**N**	nitrogen	7	$8.5\,10^{-5}$	$8.5\,10^{-4}$	$5.0\,10^{-5}$	$3.6\,10^{-5}$
^{28}**Si**	silicon	14	$3.5\,10^{-5}$	$6.9\,10^{-4}$	$5.0\,10^{-6}$	$2.9\,10^{-5}$
^{24}**Mg**	magnesium	12	$3.5\,10^{-5}$	$5.9\,10^{-4}$	$2.9\,10^{-6}$	$3.2\,10^{-5}$
^{32}**S**	sulfur	16	$2.1\,10^{-5}$	$4.9\,10^{-4}$	$1.1\,10^{-5}$	$1.0\,10^{-5}$

* according to Kimura et al. 2003, ApJ 582, 846

From Jorma Harju lectures

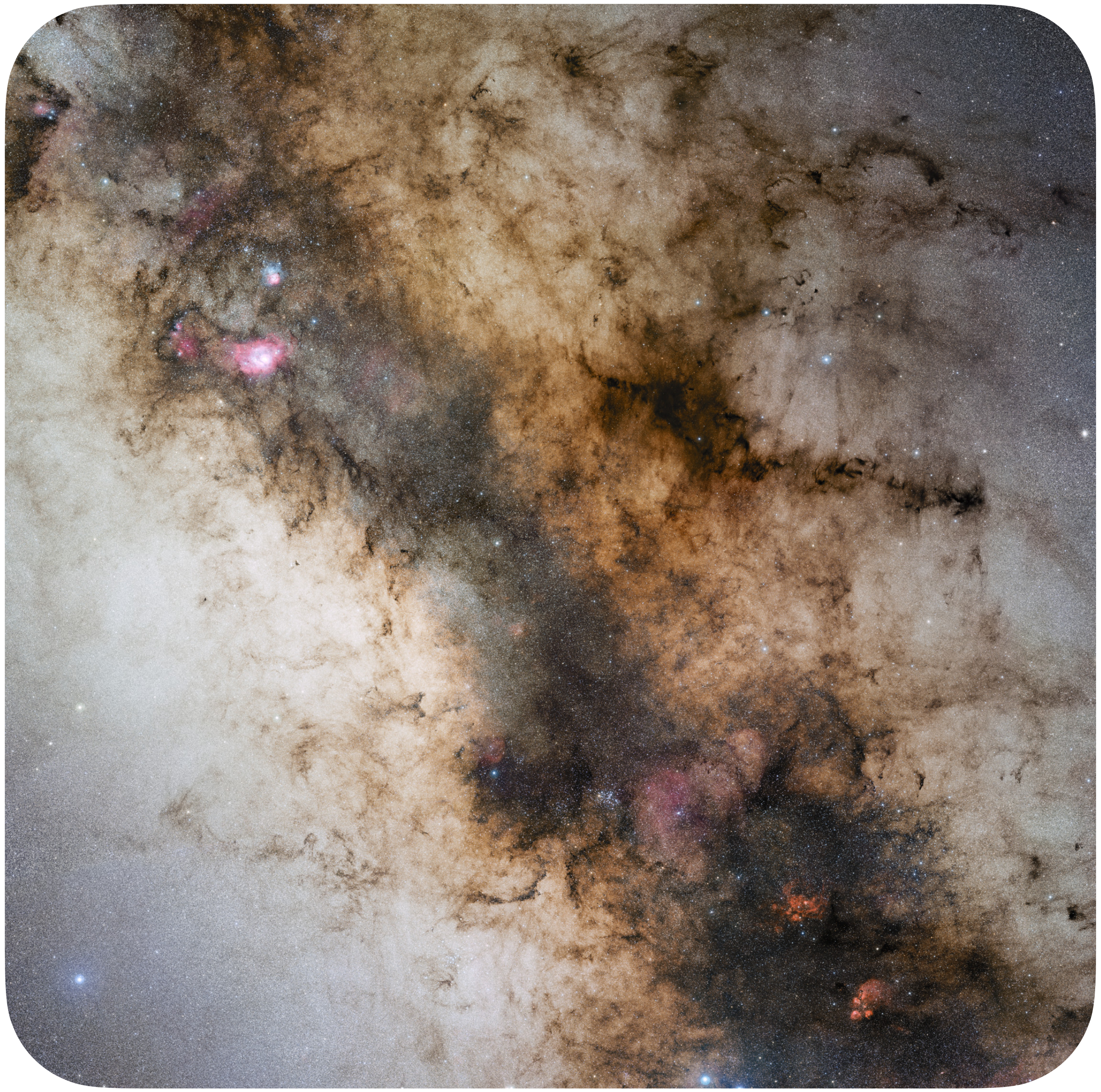
Chemistry under different conditions

Density: 10^{19} cm^{-3}

Temperature: 300 K

Density: 10^{4}-10^{6} cm^{-3}

Temperature: 10 K



General properties of the ISM

- Large range in temperature & density

  $T \sim 10\text{-}10^6$ K $\qquad$ $n \sim 10^{-3} - 10^6$ cm^{-3}

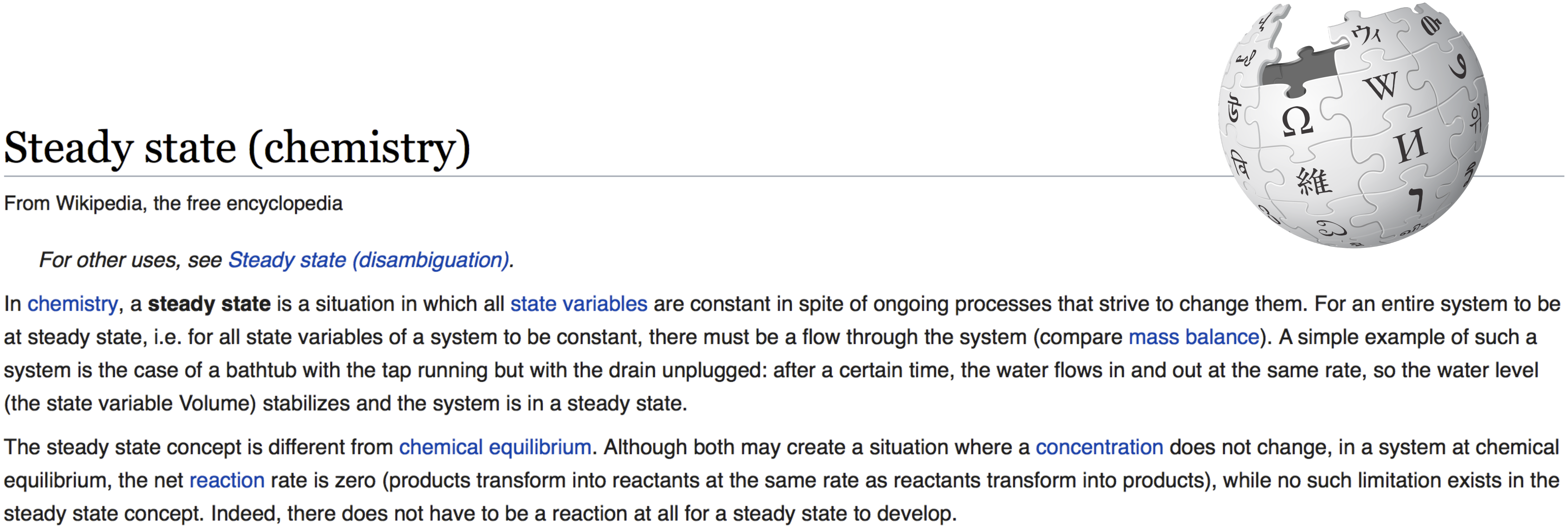
- Even dense regions are “ultra-high vacuum”

  Lab UHV: 10^{-10} Torr ($n \sim 4 \times 10^6$ cm^{-3})

- Multiphase / multicomponent medium

- Far from equilibrium and steady state

  Complex processes & Challenging physics



Steady state (chemistry)

From Wikipedia, the free encyclopedia

For other uses, see Steady state (disambiguation).

In chemistry, a **steady state** is a situation in which all state variables are constant in spite of ongoing processes that strive to change them. For an entire system to be at steady state, i.e. for all state variables of a system to be constant, there must be a flow through the system (compare mass balance). A simple example of such a system is the case of a bathtub with the tap running but with the drain unplugged: after a certain time, the water flows in and out at the same rate, so the water level (the state variable Volume) stabilizes and the system is in a steady state.

The steady state concept is different from chemical equilibrium. Although both may create a situation where a concentration does not change, in a system at chemical equilibrium, the net reaction rate is zero (products transform into reactants at the same rate as reactants transform into products), while no such limitation exists in the steady state concept. Indeed, there does not have to be a reaction at all for a steady state to develop.

UNDER ISM CONDITIONS CHEMISTRY IS IN EQUILIBRIUM OR OUT OF EQUILIBRIUM?

IT DEPENDS ON DYNAMICAL TIMESCALES

CHEMISTRY IN EQUILIBRIUM OR NOT?

EQUILIBRIUM

- Photon-dominated regions (diffuse clouds irradiated by stars)
- Quiescent regions, early stage of gravitational collapse

NON-EQUILIBRIUM

- Regions where physical conditions change rapidly are not in equilibrium: star-forming regions, shocks, stellar outflows, supernovae
- In general galaxies, stars, and planets formation are strongly affected by chemistry

In pills

- The matter in between the stars
- It is a vast medium of extremes
- Lengths from parsec/kparsec
- Density variation 5-6 orders of magnitude (even more in MCs)
- Velocity range: from diffusion to hypersonic
- Temperatures from a few K to 10^7 K

LECTURE 2.2

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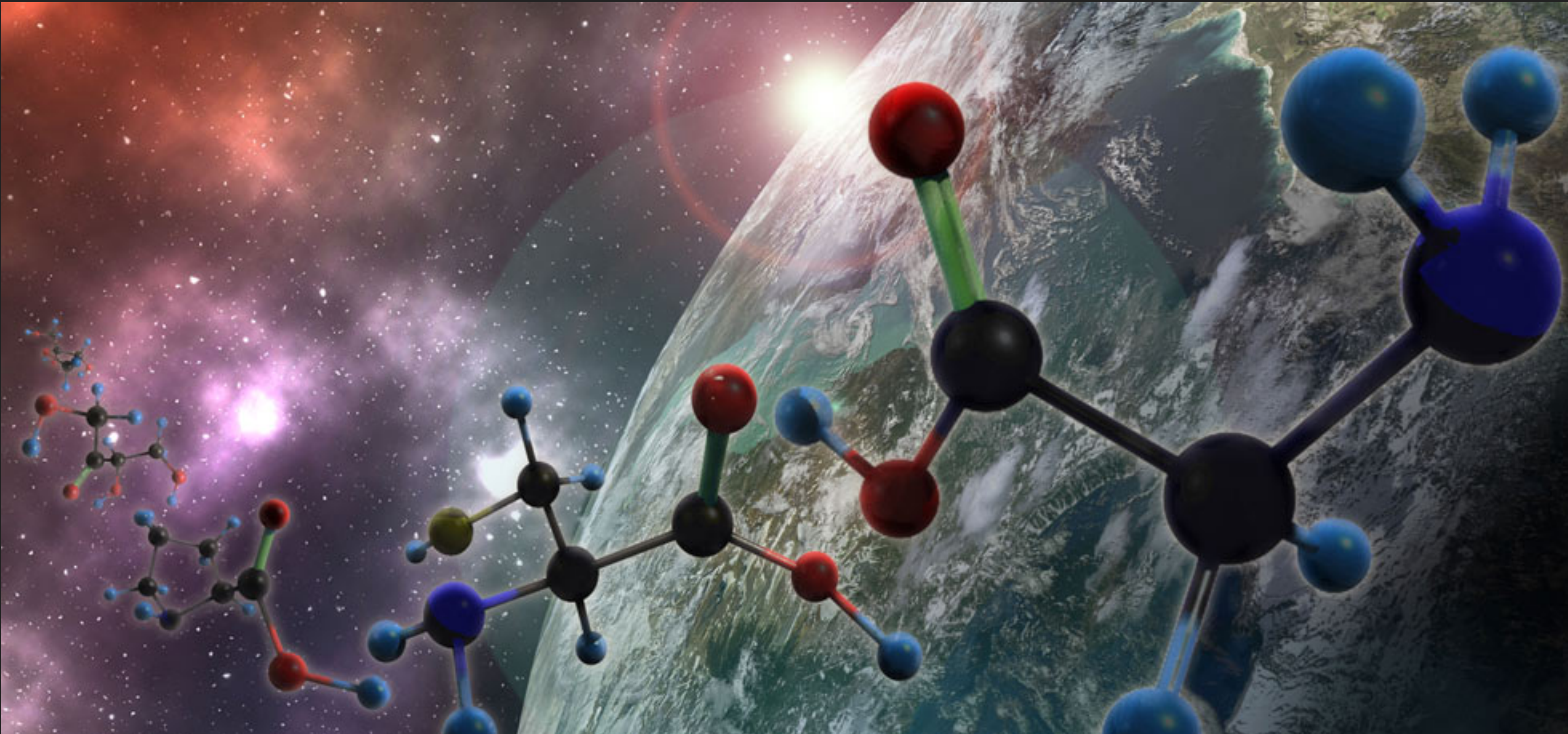
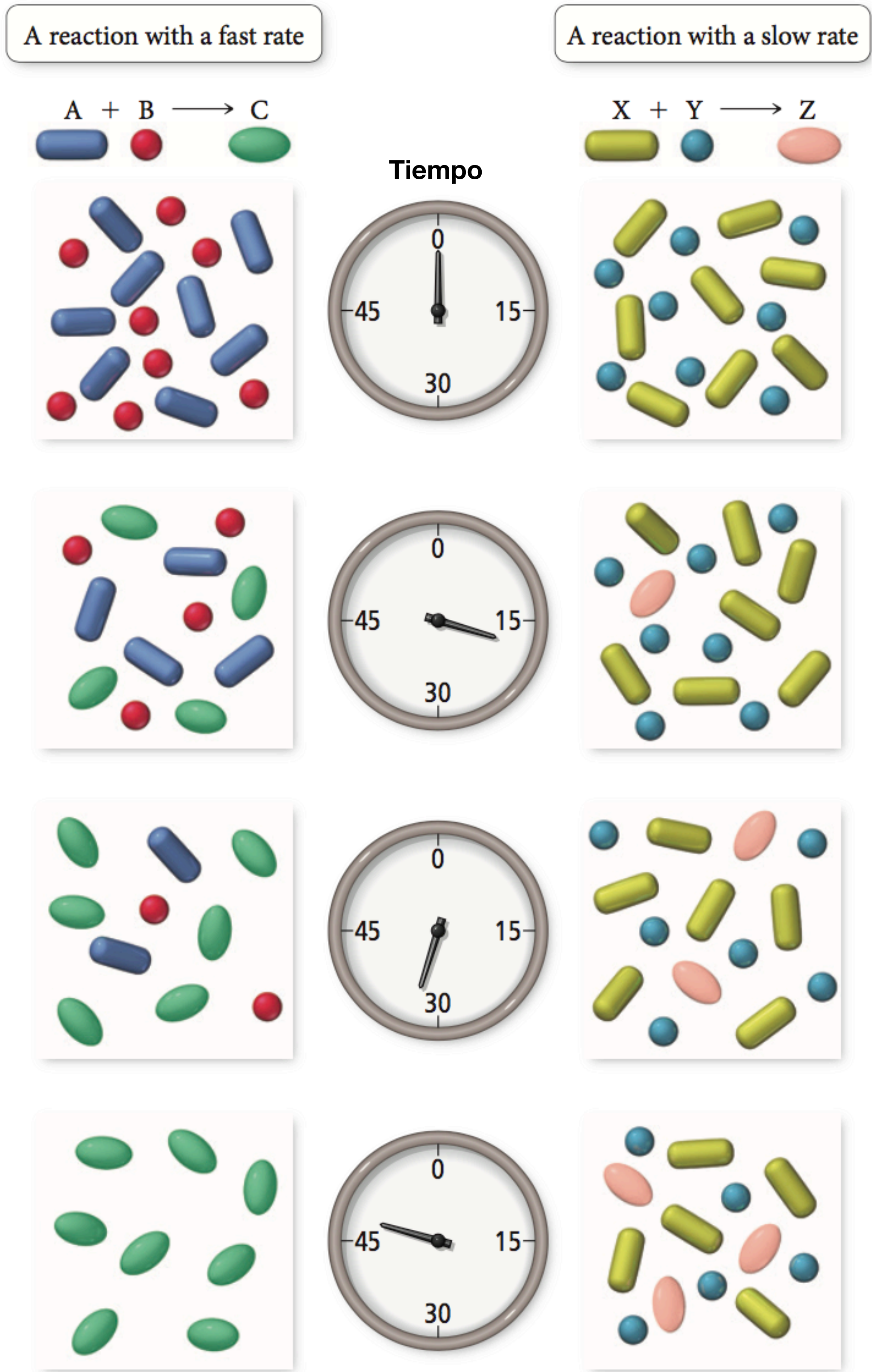


CHEMISTRY IN THE ISM (SUMMARY)

- The ISM is not empty. It is populated by matter in different forms:
    - Atoms, ions, molecules, electrons, dust particles
    - The ISM can be seen as a gas phase volume where gas phase kinetics can be applied
- Temperatures are low: molecules form mainly in cold regions
- Densest circumstellar clouds up to 10^{11} cm^{-3} but at sea level Earth atmosphere 2.5 x 10^{19} cm^{-3}
- Low probability of reactions, mainly two-body reactions (low-densities)

Chemistry under different conditions

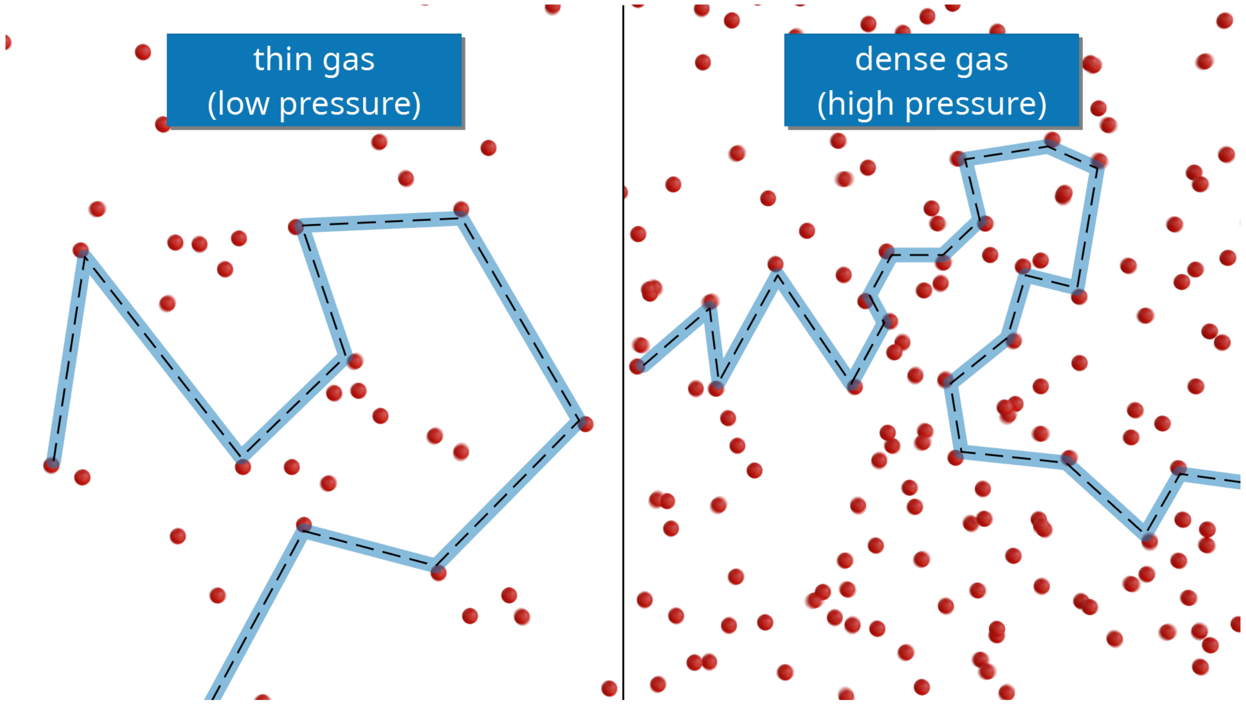
- Chemical and physical conditions have effects on the speed of a reaction



Chemistry under different conditions

Collisional time in years

$$t_{col} \approx \frac{4000}{n\sqrt{T}}$$



$n = 1\ \ \mathrm{cm}^{-3}$ $T = 100\ \ \mathrm{K}$

$n = 10^4\ \ \mathrm{cm}^{-3}$ $T = 10\ \ \mathrm{K}$

$t_{col} = 400$ Years

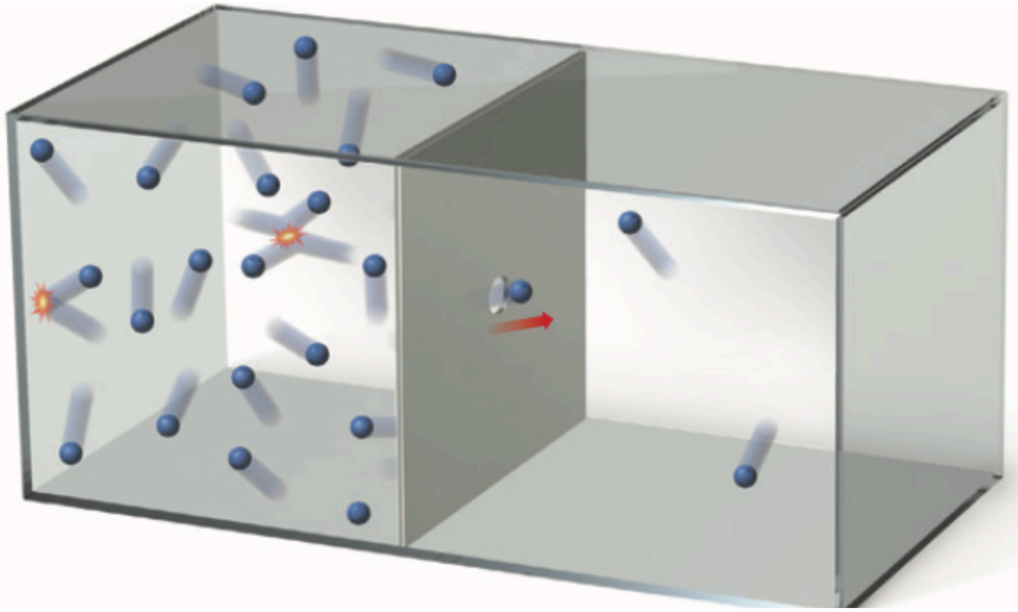
$t_{col} = 0.12$ Years $\longrightarrow$ 1 month

Chemistry under different conditions

The ISM is a very diluted medium

$t_{col} = 400$ Years

$t_{col} = 0.12$ Years ⟶ 1 month



The star formation time is **1 Myr**

The time to form planetesimals is **10 Myr**

Collisions

Govern many key processes in the ISM

- Distribute energy
- Ionize the medium (collisional ionization)
- Recombination (radiative recombination)
- Excitation and loss of energy via de-excitation
- Govern chemistry (reactions)
- Gas-dust interaction and grain-grain

Different kinds of collisions in the ISM

- Elastic collisions → only kinetic energy is exchanged

Determine momentum transfer, hence the *transport coefficients*: viscosity (resistance to flow), electrical conductivity (resistance to electric currents), thermal conductivity (resistance to heat flow).

- Inelastic collisions → kinetic and internal energy is exchanged

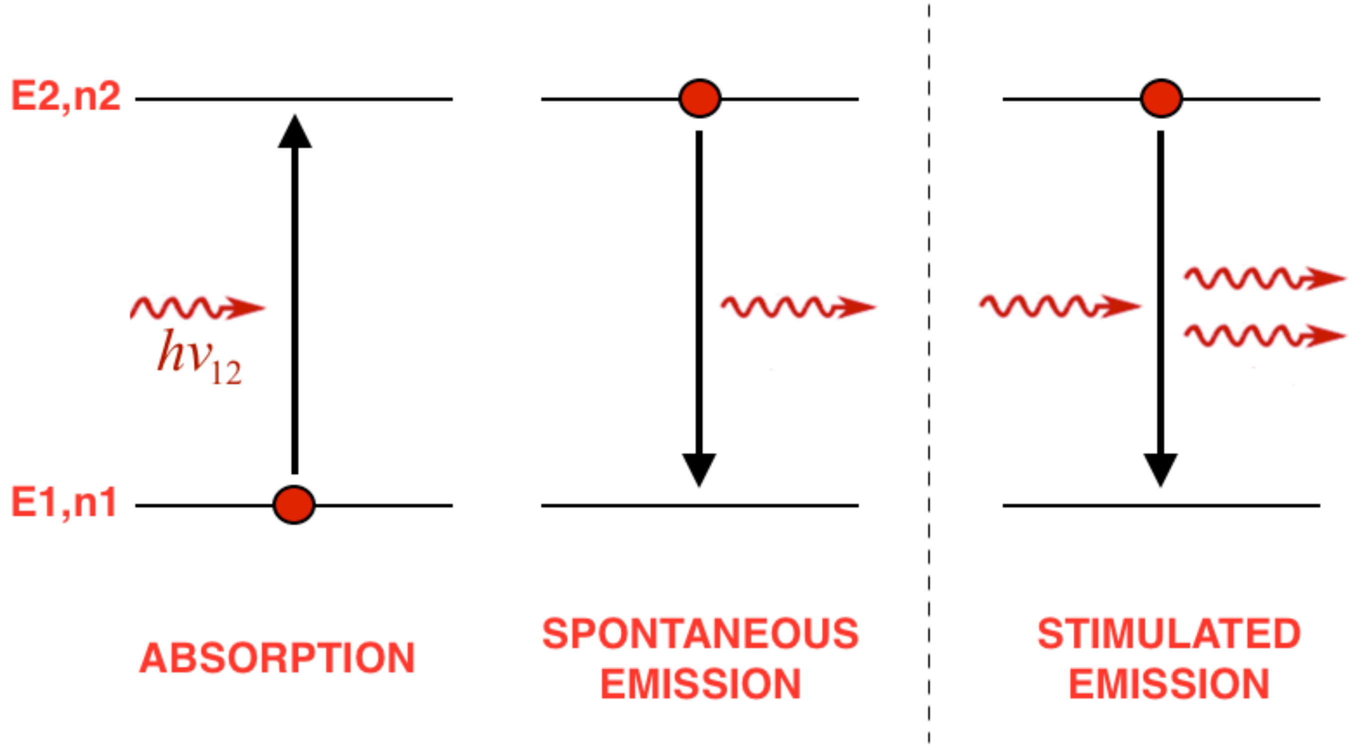
Control the transfer of energy in astrochemical environments (excitation/de-excitation of rovibrational and electronic transitions).

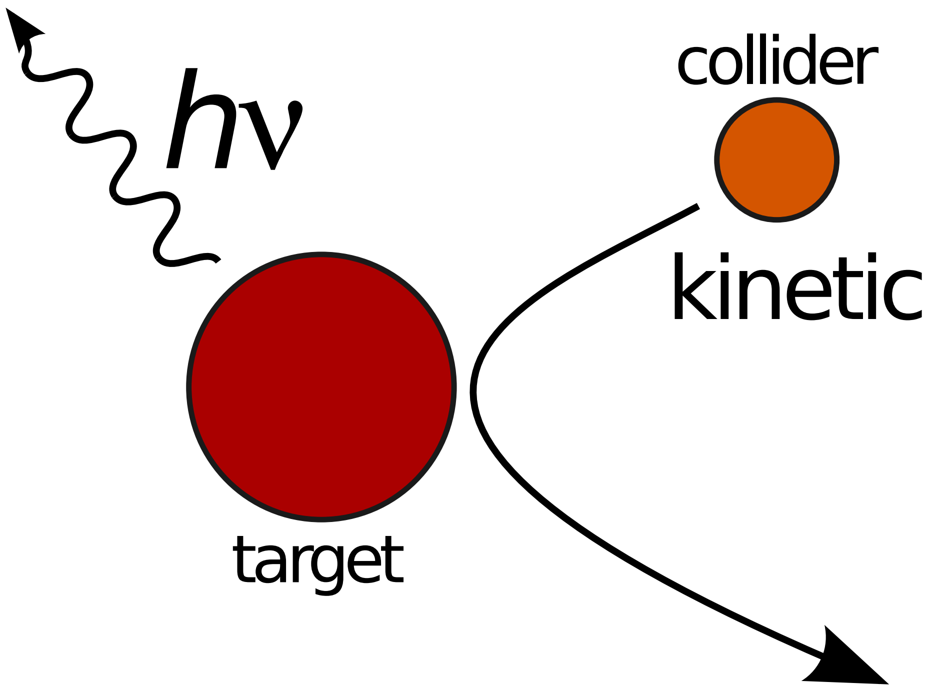
- Reactive collisions → the chemical structure of the collision partners is changed

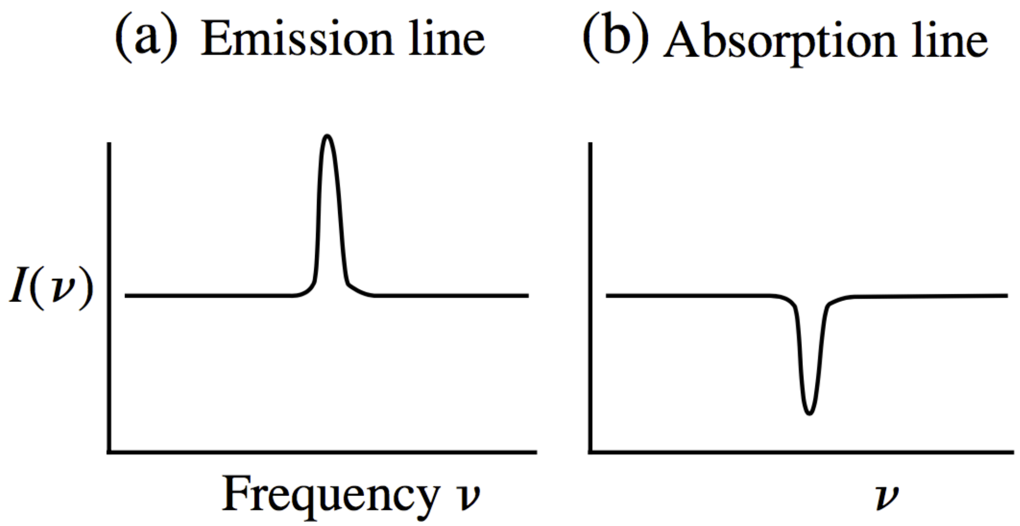
Control the chemistry. Studied in the lab and with quantal methods (NB: the cost of solving the Schrödinger increases dramatically with the number of degrees of freedom!)

DANIELE GALLI'S SLIDE

$$\Delta E = E_{12} = E_2 - E_1 = h\nu_{12}$$

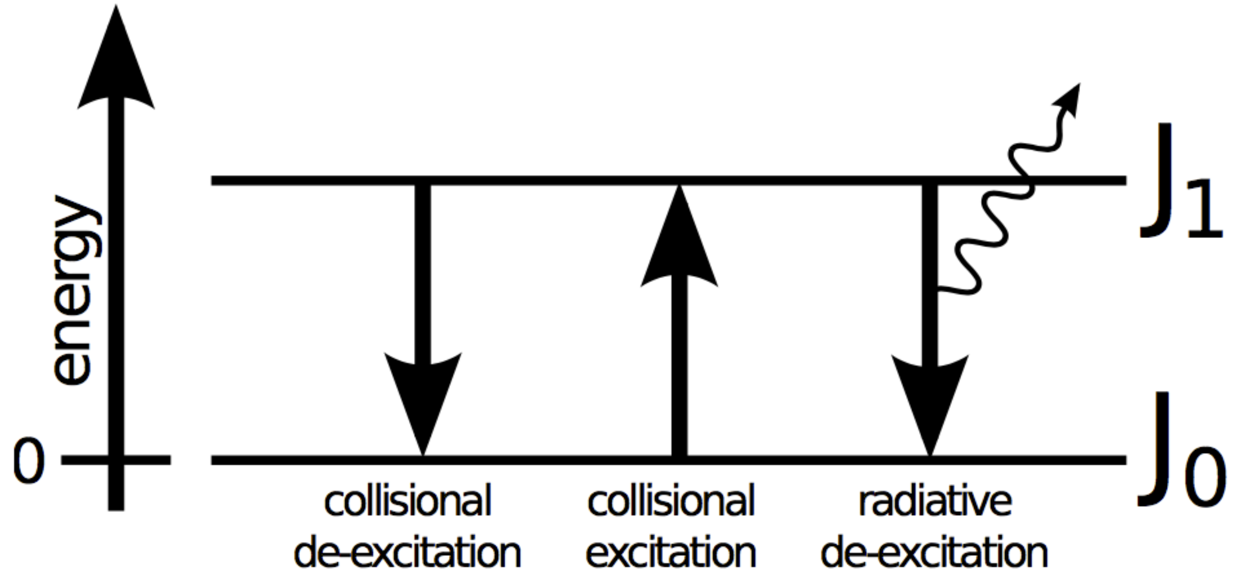






INELASTIC COLLISIONS: CHANGE OF INTERNAL ENERGY

Molecules are excited through collisions and $\Delta J = \pm 1$



Spontaneous emission:

$$A_{ul} \propto \nu^3 |\mu_d|^2 \tag{2}$$

- the molecule must have a permanent dipole moment
- a critical density required for significant excitation

REMINDER QUANTUM MECHANICS BASICS

$$\lambda = \frac{h}{p}$$

Duality

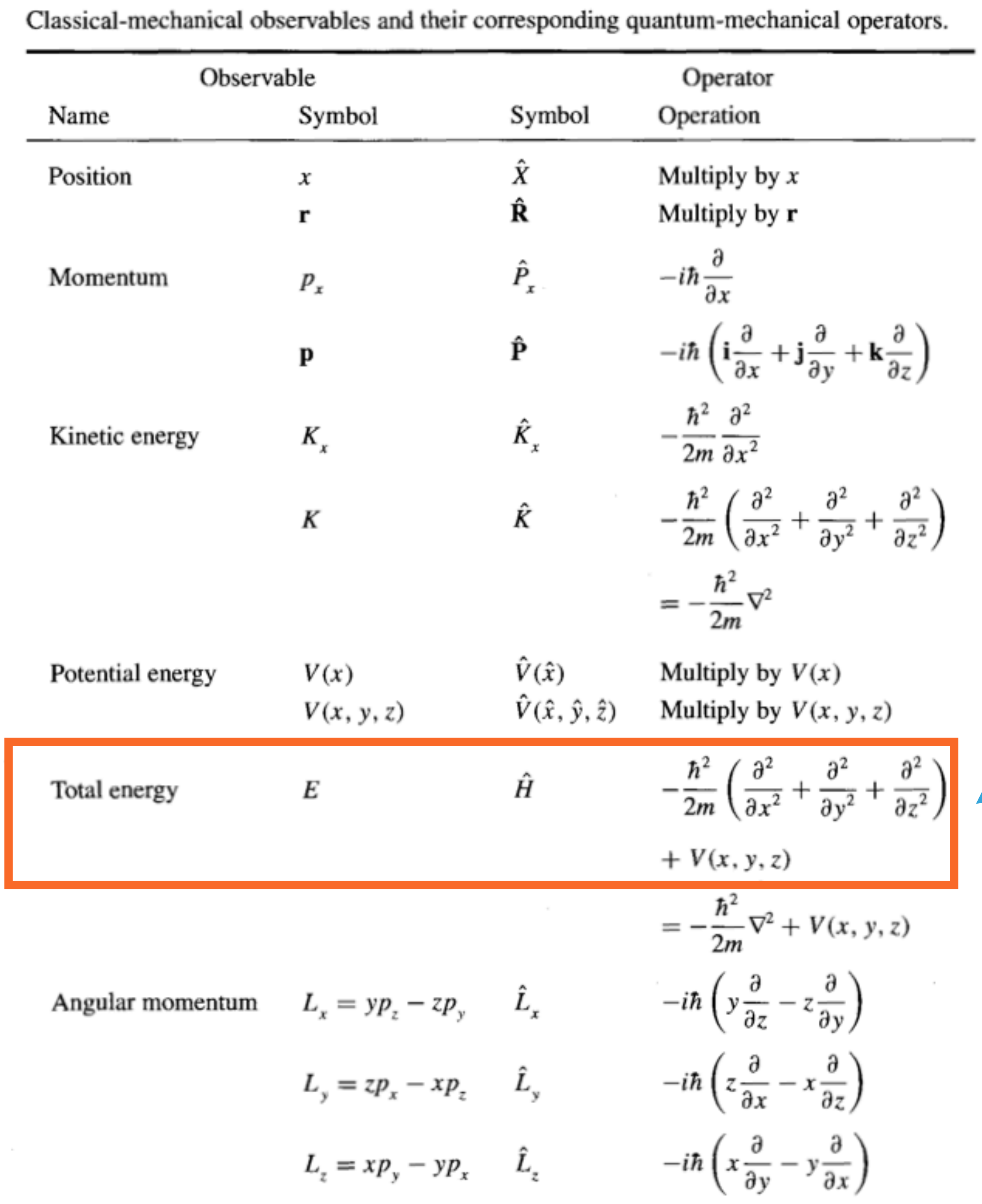
$$\Psi(x) \rightarrow |\Psi(x)|^2$$

Probability

REMINDER QUANTUM MECHANICS BASICS (CONT’D)

- The wave function contains all the information about the state of a quantum mechanical system!
- An operator describes a physical observable and act on the WF
- Eigenvalues are the only possible results of a measurement

OPERATORS EXAMPLE



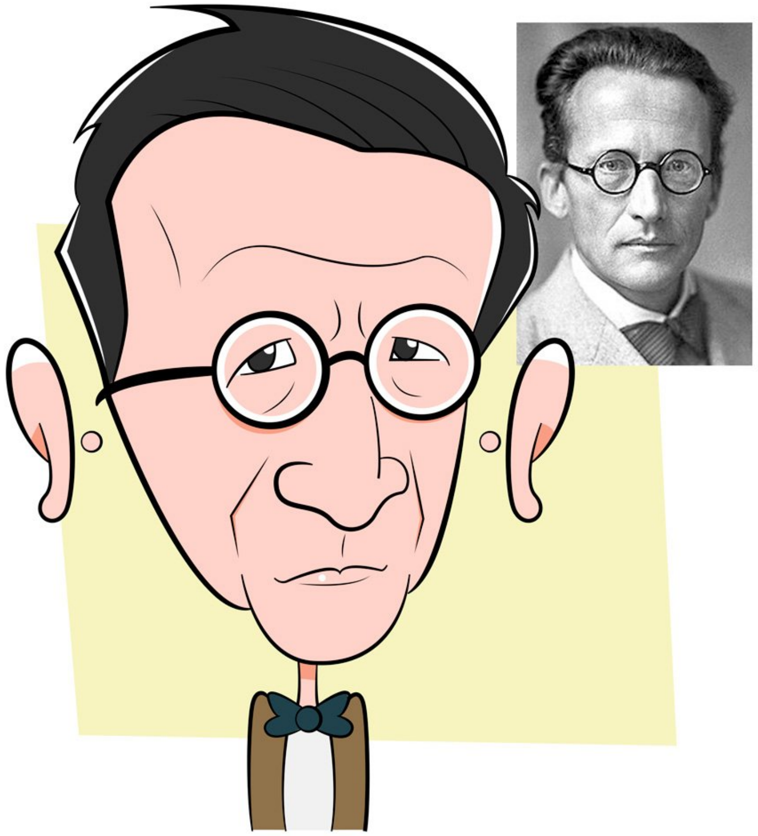
Classical-mechanical observables and their corresponding quantum-mechanical operators.

Observable		Operator	
Name	Symbol	Symbol	Operation
Position	x	$\hat{X}$	Multiply by x
	$\mathbf{r}$	$\hat{\mathbf{R}}$	Multiply by $\mathbf{r}$
Momentum	p_x	$\hat{P}_x$	$-i\hbar\frac{\partial}{\partial x}$
	$\mathbf{p}$	$\hat{\mathbf{P}}$	$-i\hbar\left(\mathbf{i}\frac{\partial}{\partial x}+\mathbf{j}\frac{\partial}{\partial y}+\mathbf{k}\frac{\partial}{\partial z}\right)$
Kinetic energy	K_x	$\hat{K}_x$	$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$
	K	$\hat{K}$	$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)$ $=-\frac{\hbar^2}{2m}\nabla^2$
Potential energy	$V(x)$	$\hat{V}(\hat{x})$	Multiply by $V(x)$
	$V(x, y, z)$	$\hat{V}(\hat{x}, \hat{y}, \hat{z})$	Multiply by $V(x, y, z)$
Total energy	E	$\hat{H}$	$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)$ $+V(x, y, z)$ $=-\frac{\hbar^2}{2m}\nabla^2+V(x, y, z)$
Angular momentum	$L_x = yp_z - zp_y$	$\hat{L}_x$	$-i\hbar\left(y\frac{\partial}{\partial z}-z\frac{\partial}{\partial y}\right)$
	$L_y = zp_x - xp_z$	$\hat{L}_y$	$-i\hbar\left(z\frac{\partial}{\partial x}-x\frac{\partial}{\partial z}\right)$
	$L_z = xp_y - yp_x$	$\hat{L}_z$	$-i\hbar\left(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right)$

Hamiltonian in quantum mechanics

- Time independent (wave equation)

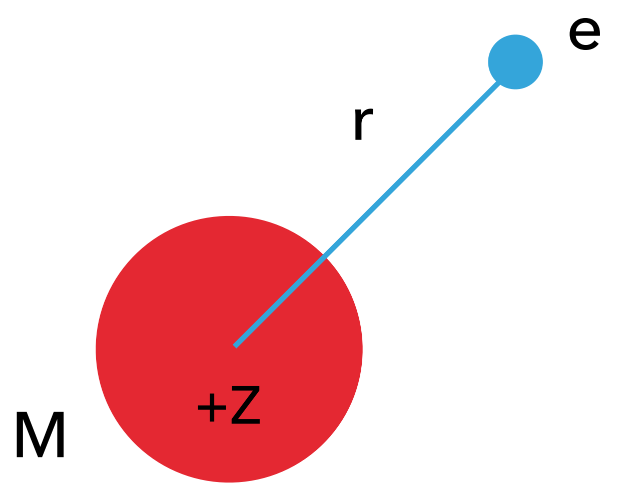
$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)|\Psi\rangle = E|\Psi\rangle$$

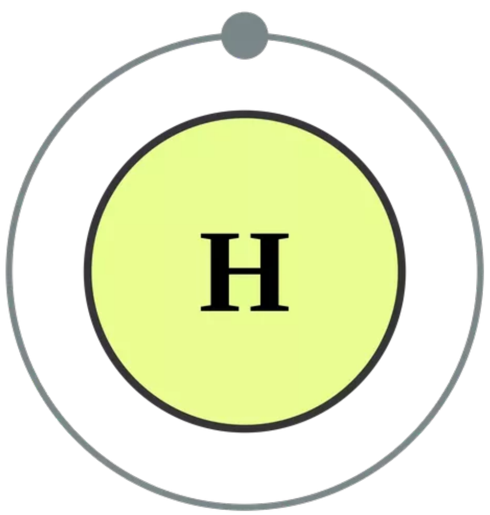


- SE plays the role of Newton's laws and conservation of energy
- Predict the future behavior of a dynamic system in QM

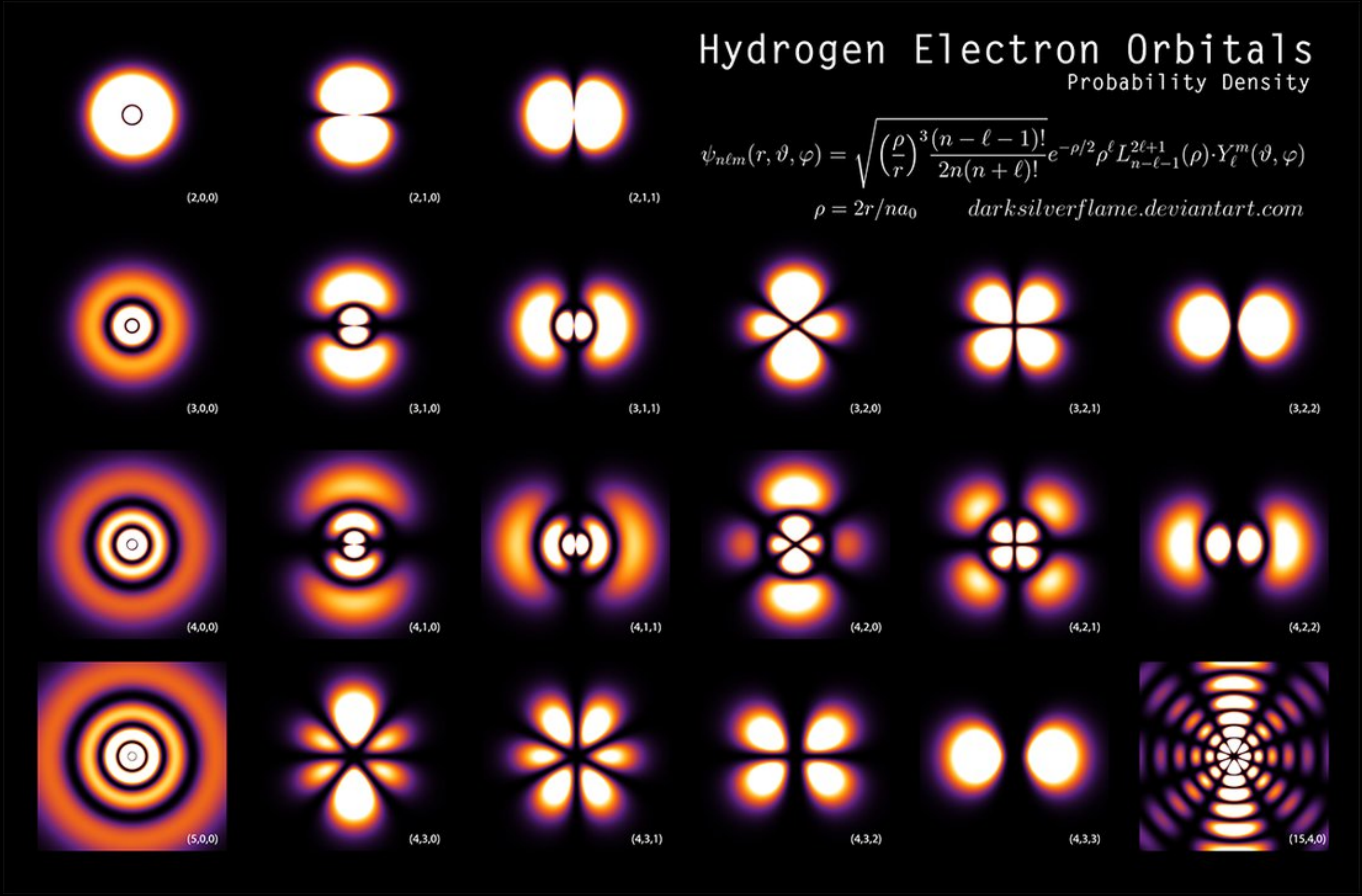
HYDROGEN ATOM: THE UNIQUE SYSTEM

- Provided energy levels for Hydrogen atom fully in agreement with Rydberg's law
- The atomic SE can be solved analytically for H in spherical coordinates





SOLUTION OF SCHRÖDINGER EQUATIONS FOR HYDROGEN



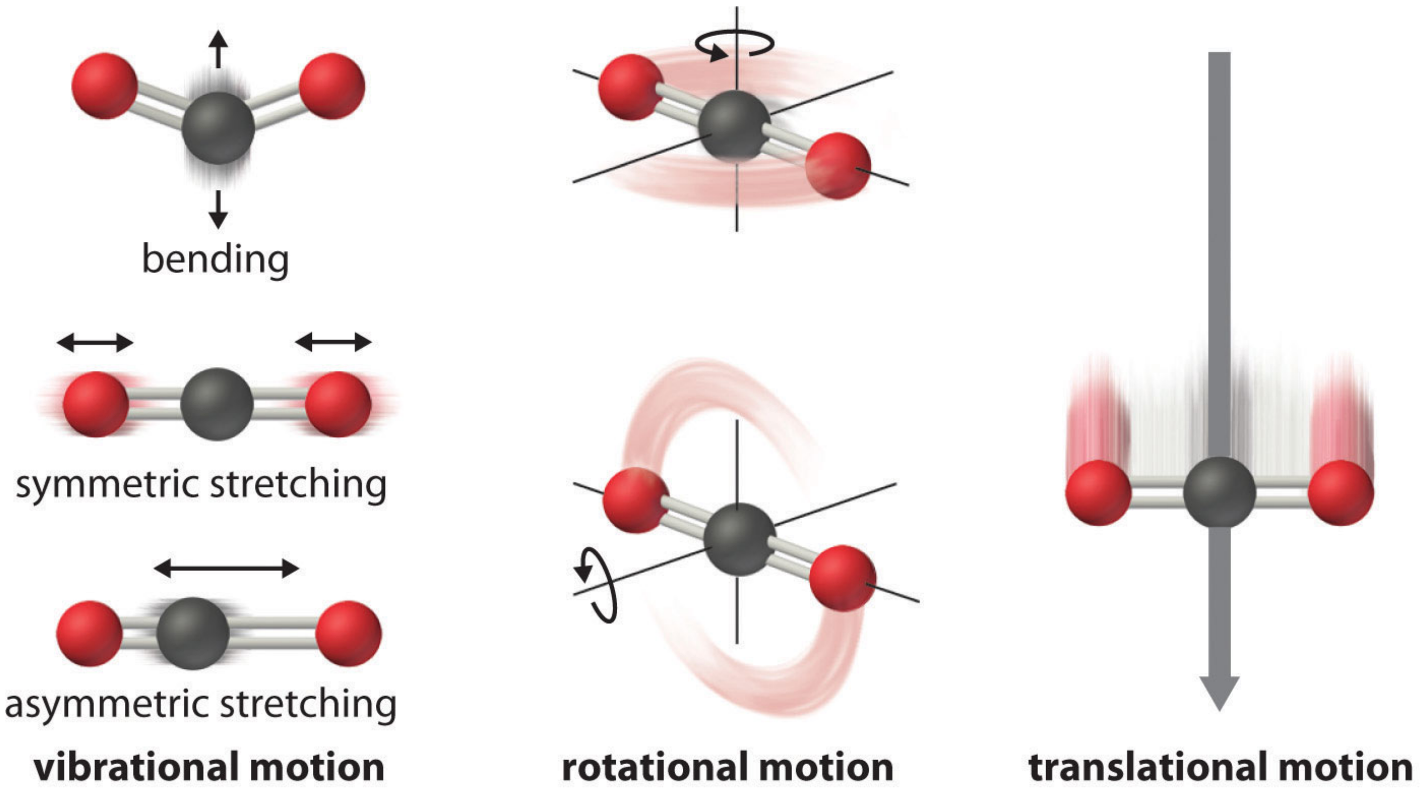
Hydrogen Electron Orbitals

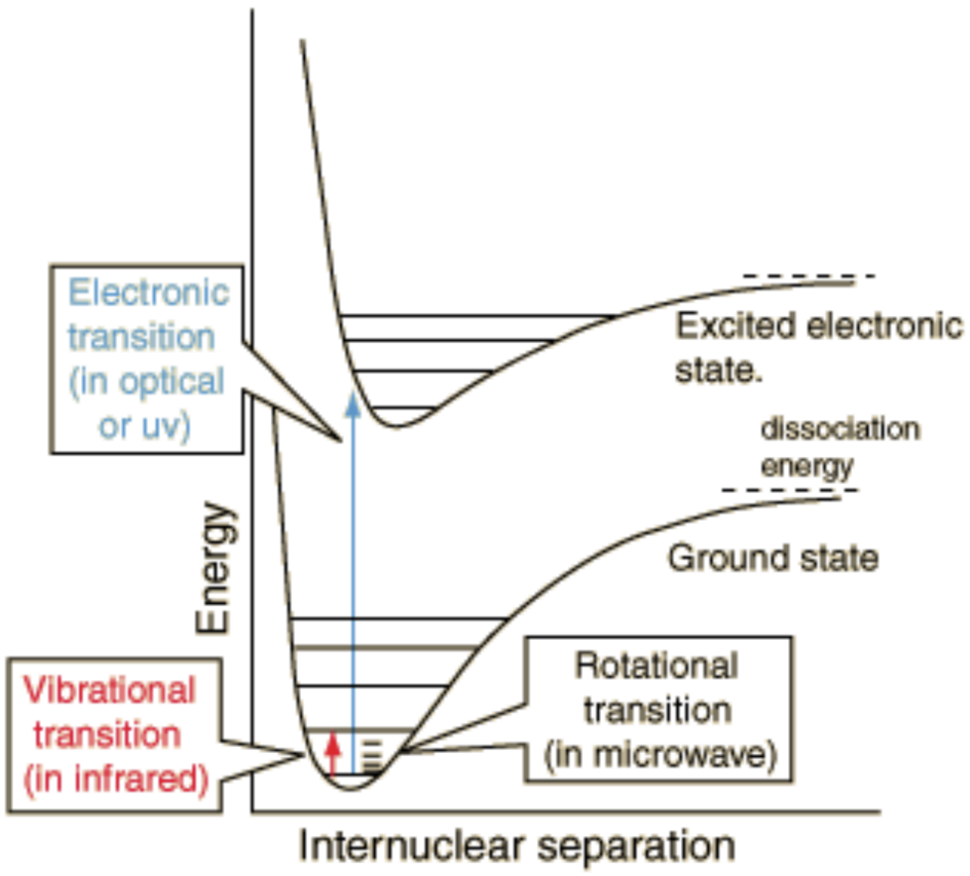
Probability Density

$$\psi_{n\ell m}(r,\vartheta,\varphi)=\sqrt{\left(\frac{\rho}{r}\right)^3\frac{(n-\ell-1)!}{2n(n+\ell)!}}e^{-\rho/2}\rho^\ell L_{n-\ell-1}^{2\ell+1}(\rho)\cdot Y_\ell^m(\vartheta,\varphi)$$

$\rho = 2r/na_0$ *darksilverflame.deviantart.com*

MOLECULAR STRUCTURE



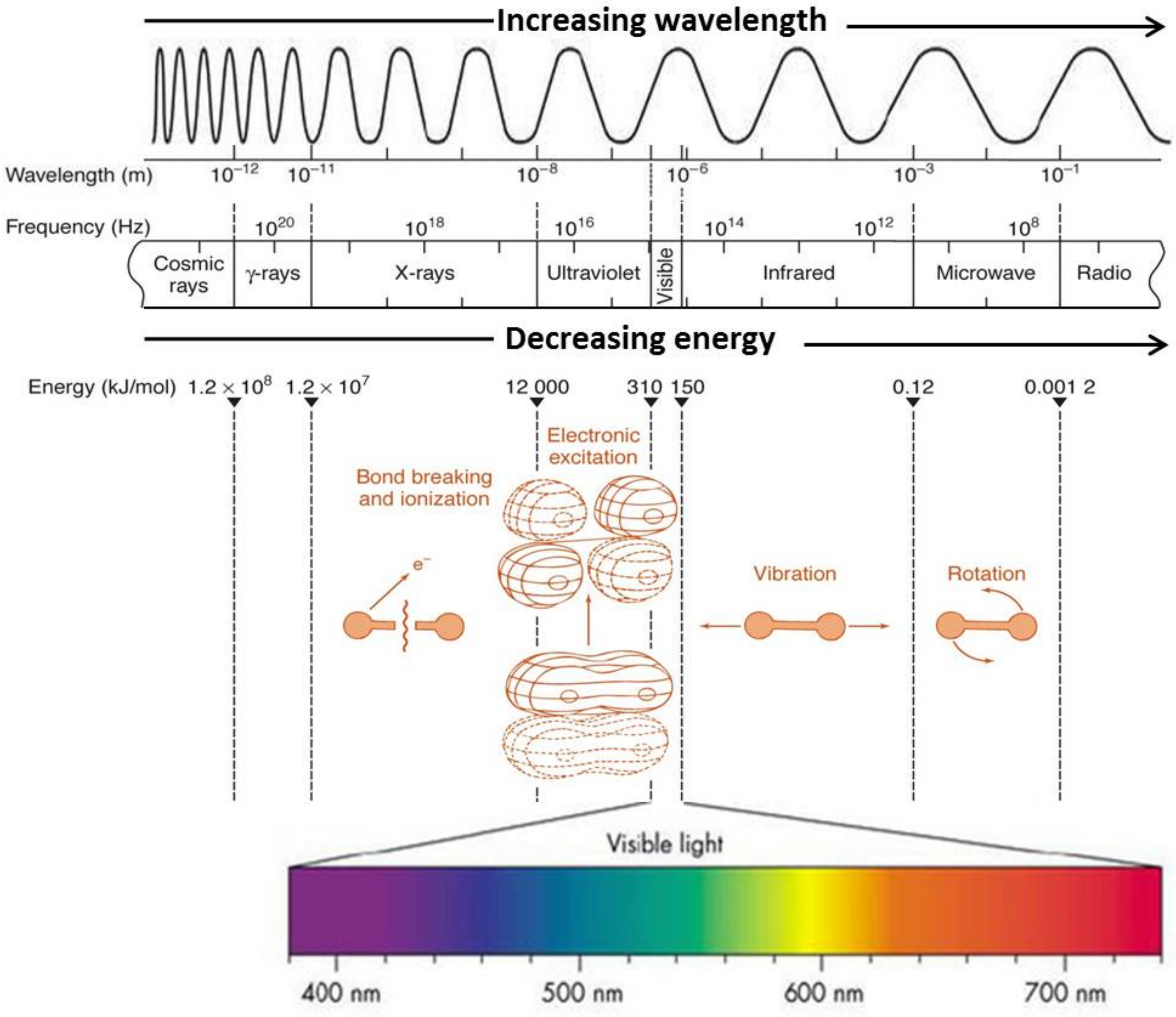


fact to know:

- the internal energy is *quantized*

  $$E_t = E_{el} + E_{vib} + E_{rot}$$

MOLECULAR STRUCTURE



Order of magnitudes

$E_{el} \sim 1\text{-}10$ eV

$E_{vib} \sim 10^{-2}–10^{-1}$ eV

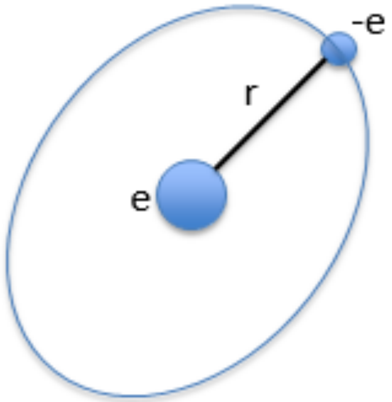
$E_{rot} \sim 10^{-3}–10^{-2}$ eV

1 eV = 11604.52 K

INCREASING COMPLEXITY

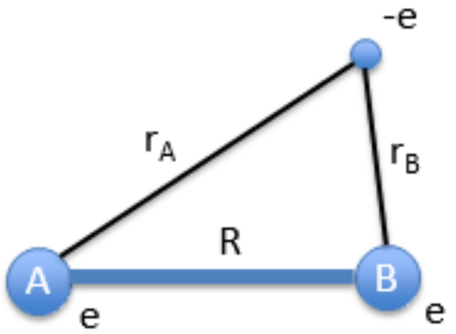
- H_2^+ simplest molecular system (2 nuclei + 1 electron)

H



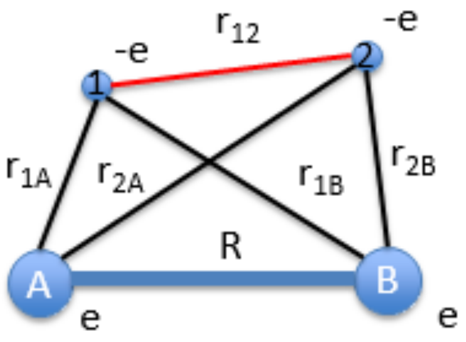
$$\widehat{H} = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}$$

H_2^+



$$\widehat{H} = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{\hbar^2}{2m_p}(\nabla_A^2 + \nabla_B^2) - \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r_A} + \frac{1}{r_B}\right) + \frac{e^2}{4\pi\epsilon_0 R}$$

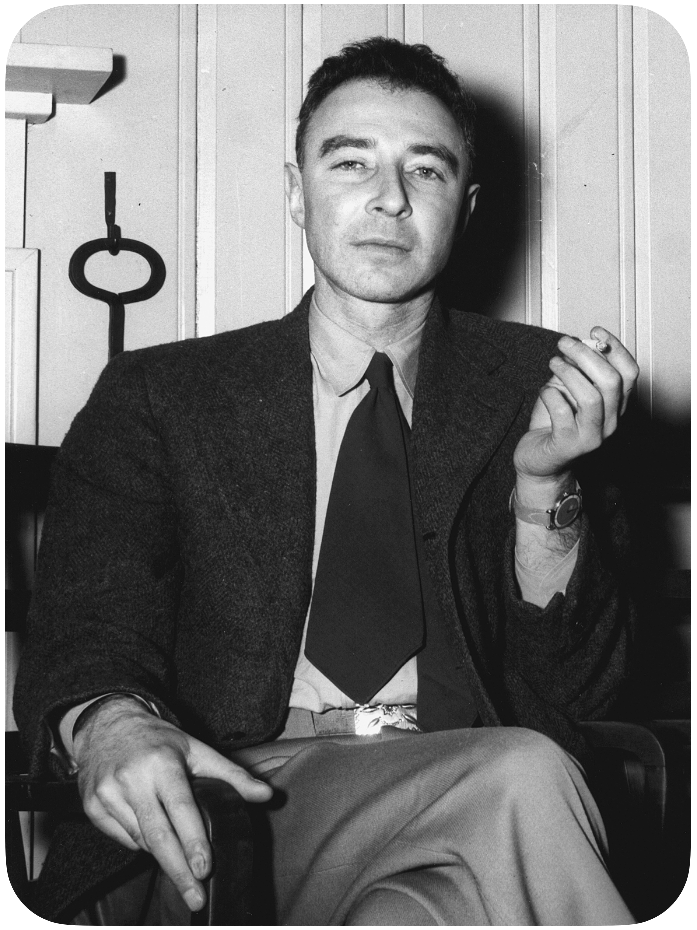
H_2



$$\widehat{H} = -\frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) - \frac{\hbar^2}{2m_p}(\nabla_A^2 + \nabla_B^2) - \frac{2e^2}{4\pi\epsilon_0}\left(\frac{1}{r_{1A}} + \frac{1}{r_{1B}} + \frac{1}{r_{2A}} + \frac{1}{r_{2B}}\right) + \frac{e^2}{4\pi\epsilon_0 R} + \frac{e^2}{4\pi\epsilon_0 r_{12}}$$

HOW DO WE SOLVE THE SE FOR MOLECULES?

ROBERT OPPENHEIMER



MAX BORN

Born-Oppenheimer approximation (2)

$$M_{nuclei} >> m_e$$
$$v_{nuclei} << v_e$$

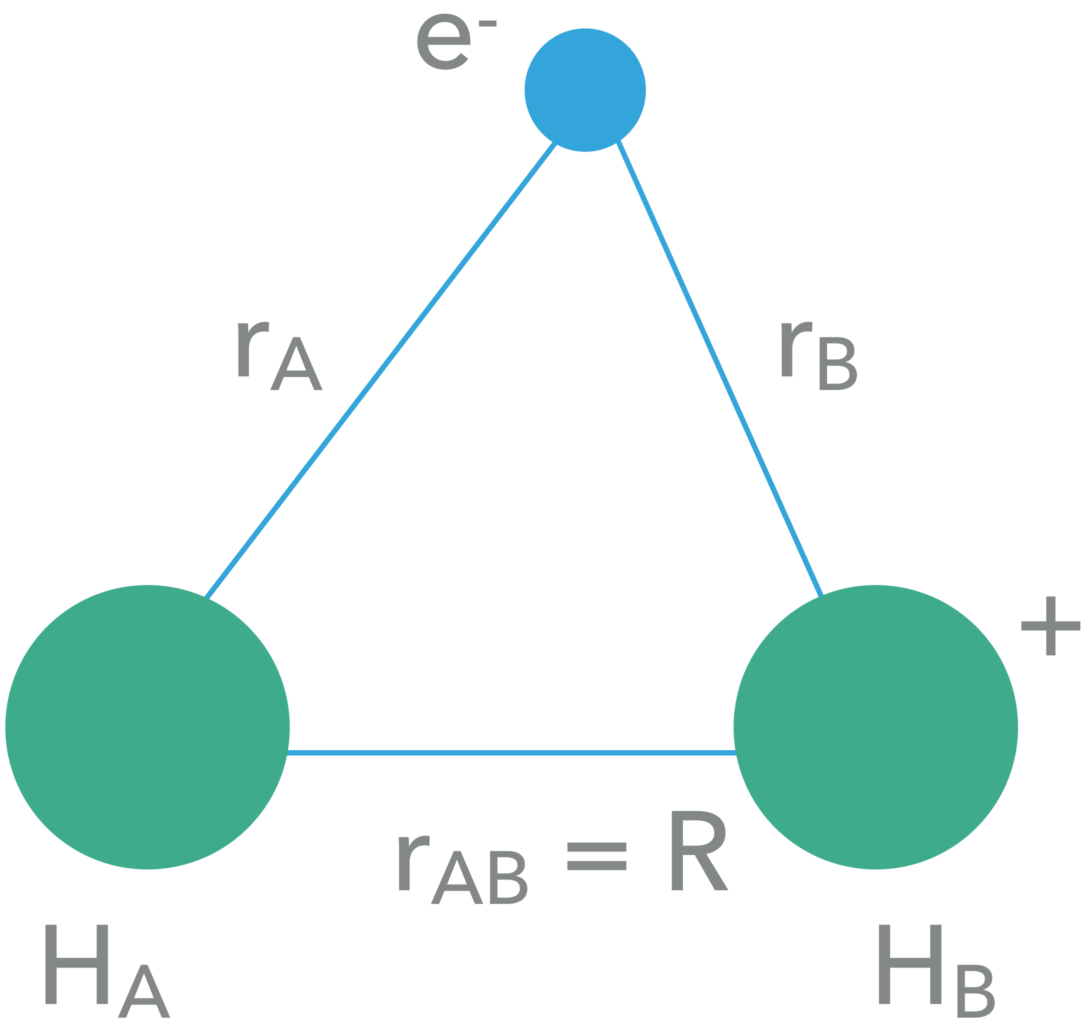
- Electrons can respond almost instantaneously to displacement of nuclei (like flies)

Born-Oppenheimer approximation (3)

We can treat them as stationary while the electrons move

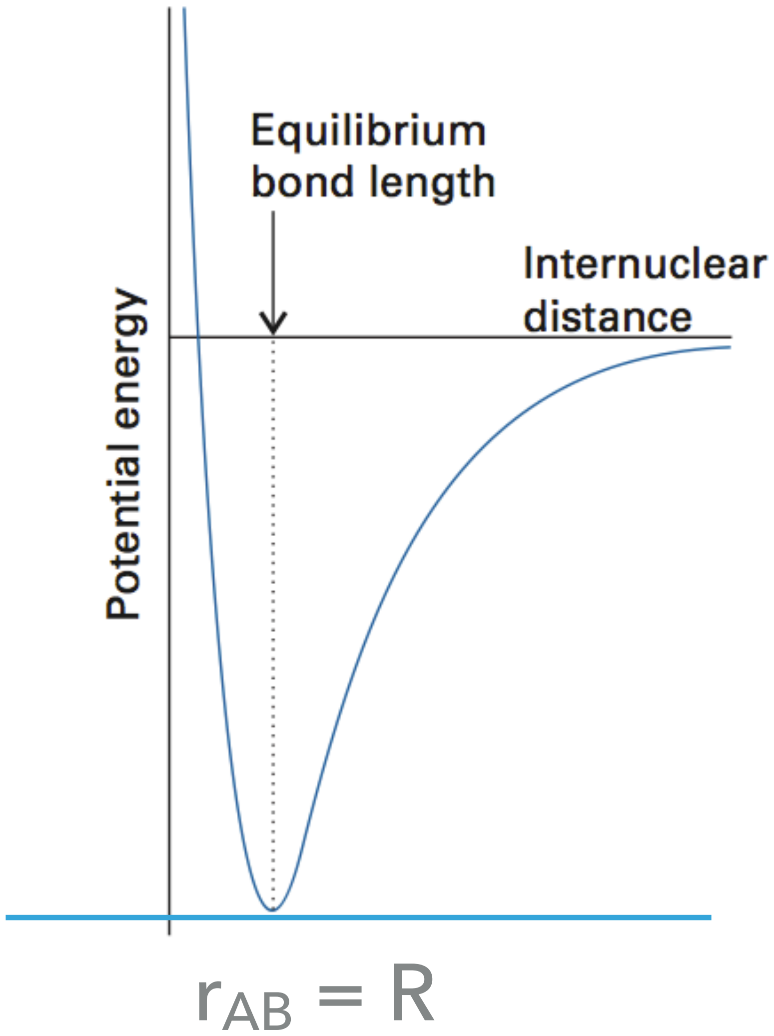
- Solve the SE considering the nuclei as being fixed (R parameter)
- Nuclei provide a static potential at fixed geometry
- Different nuclei arrangements may then be adopted and the calculations repeated
- The set of solutions provide the molecular potential energy curve (diatomic molecule) or a surface in general

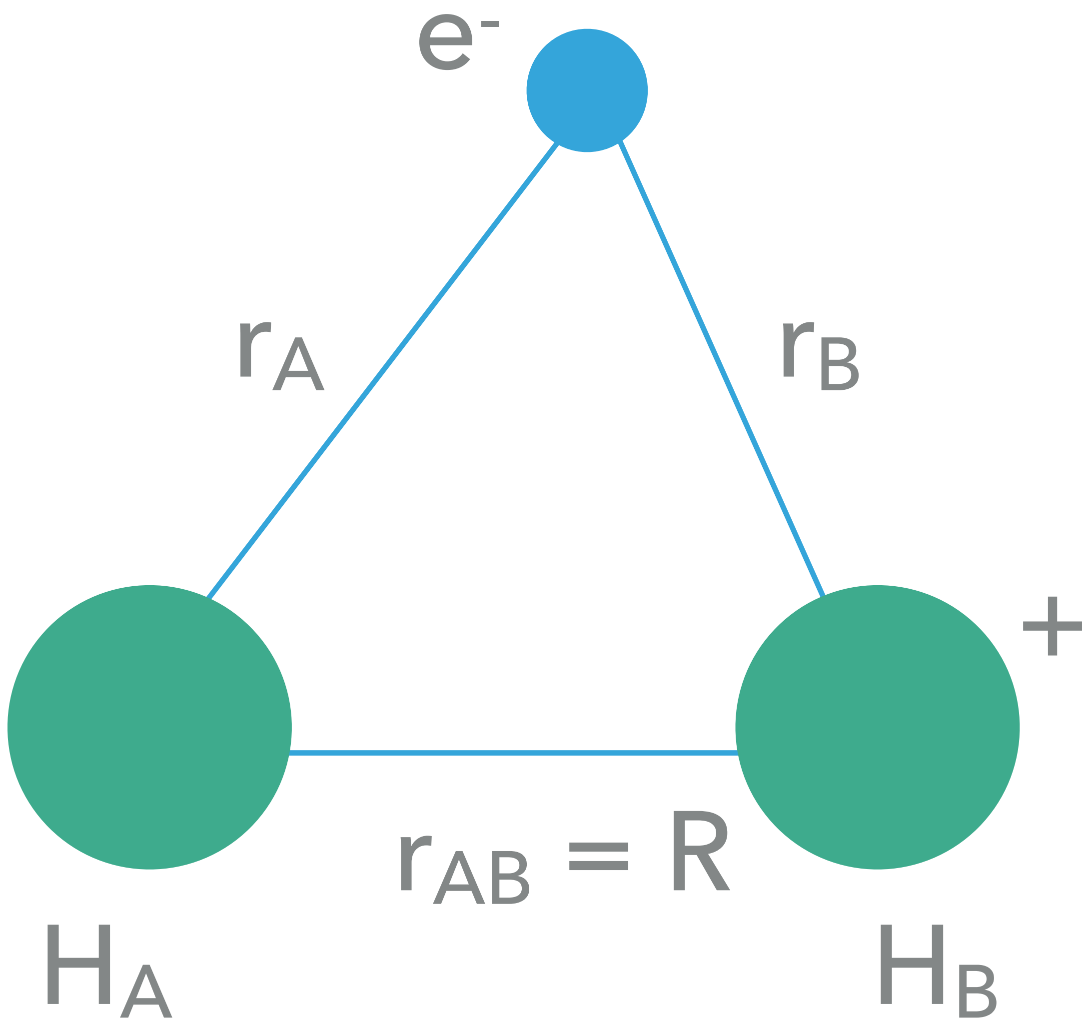
Separation of variables



SOLUTION

- (a) electrons: nuclei fixed in space (R)
- In this way we can build the so called PEC or PES (for polyatomic molecules)

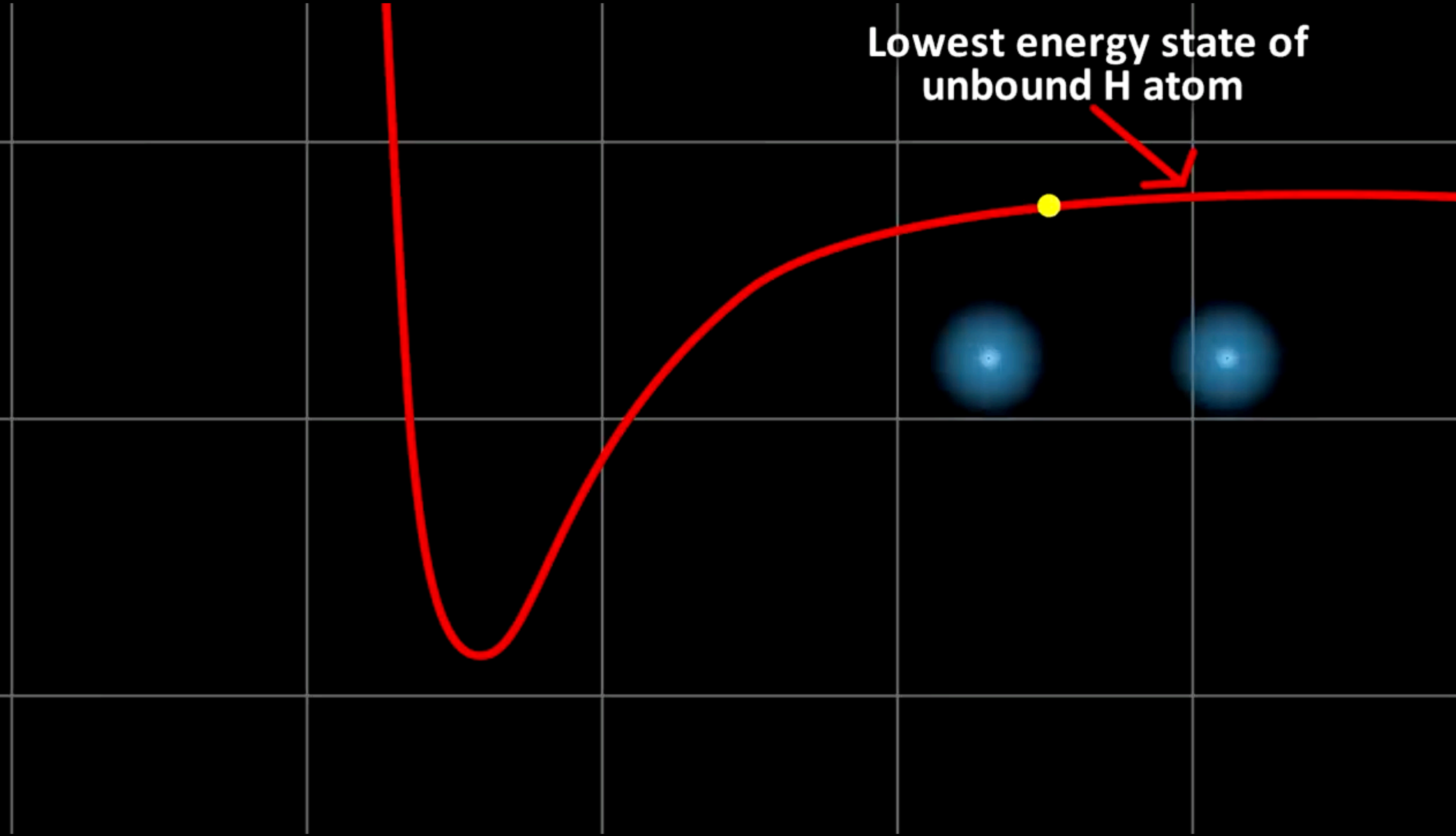




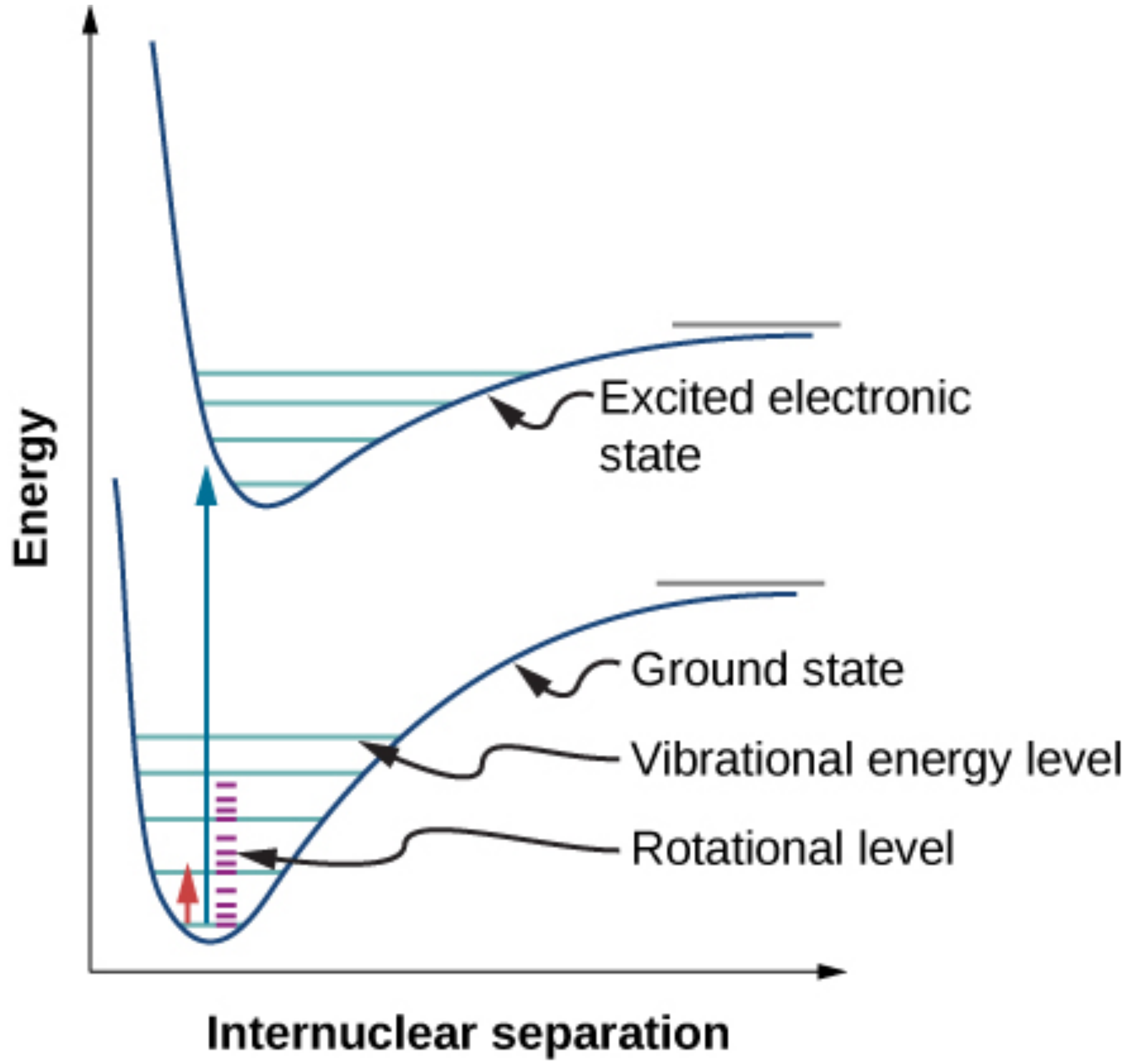
- Electron motion is much faster than nuclear (vibrations and rotations)
- Born-Oppenheimer: we can neglect the coupling terms and solve the SE in two steps

  Motion of nuclei (translation+rotation+vibration)

  Motion of electrons around the nuclei at fixed positions (electronic energy in which the nuclei are moved)

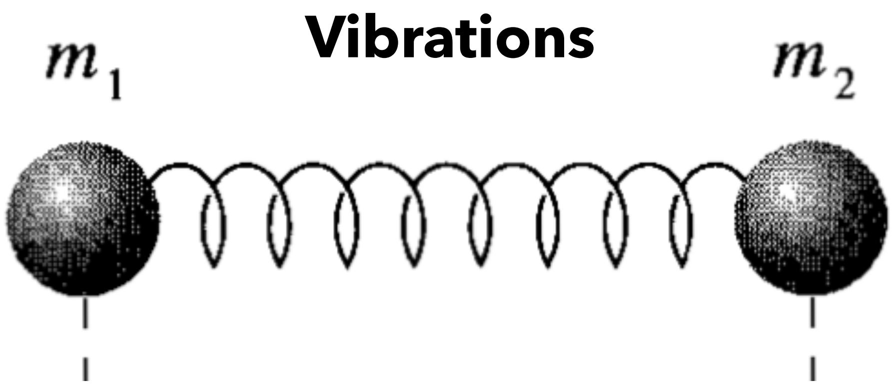

Lowest energy state of unbound H atom

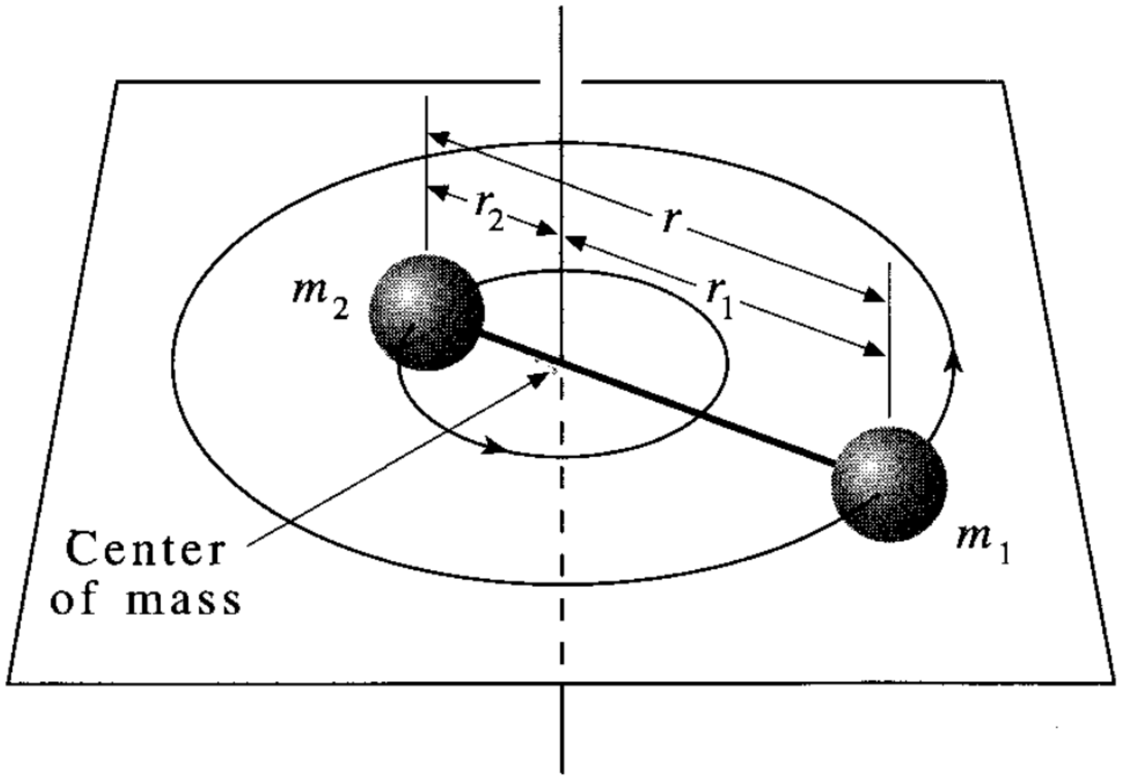
TOTAL ENERGY OF A MOLECULE



$$\Psi_{tot} = \Psi_{el}\Psi_{vib}\Psi_{rot}$$

$$E_{tot} = E_{el} + E_{vib} + E_{rot}$$

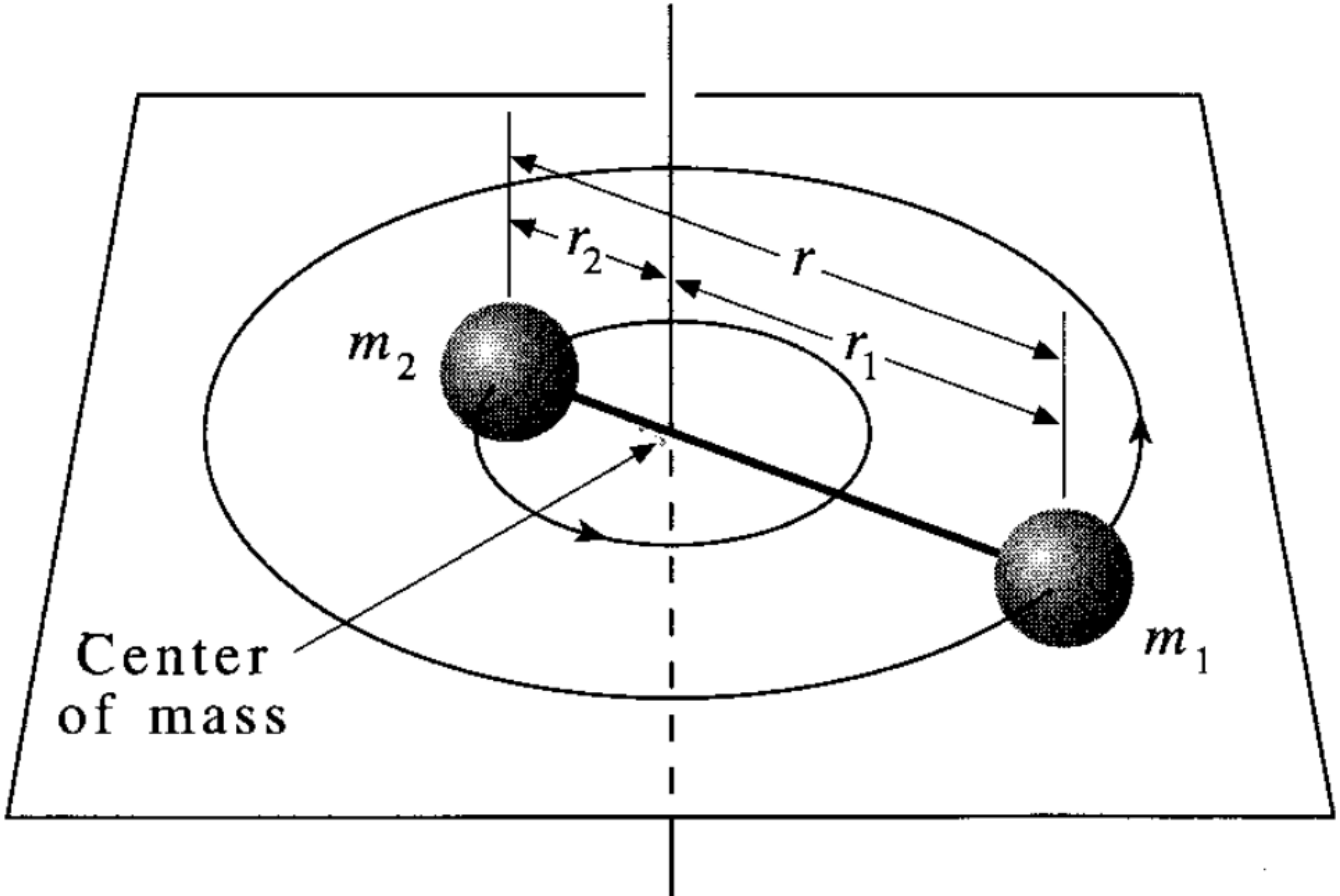




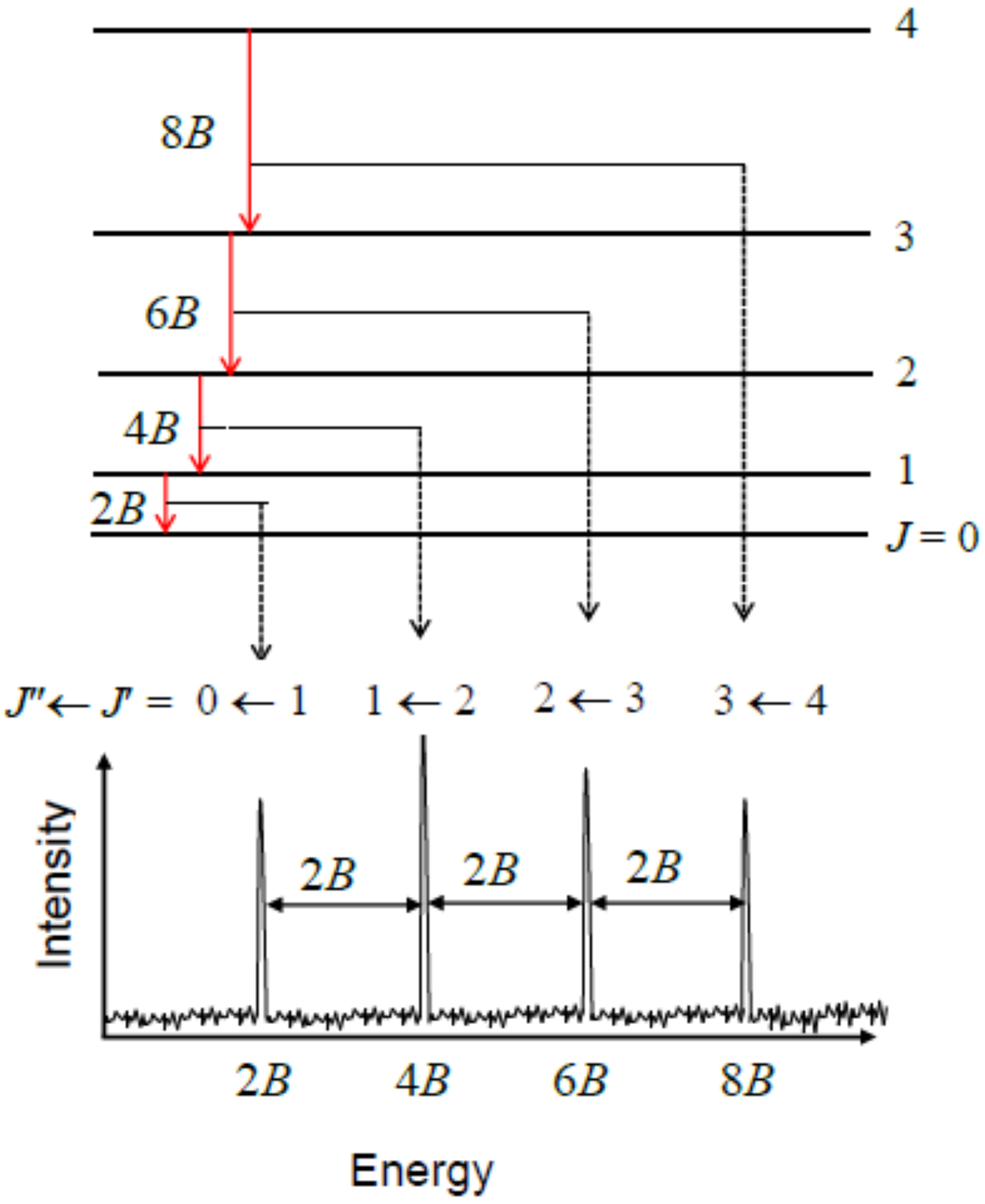
Rotations

ROTATIONS: RIGID ROTOR APPROXIMATION

$$E_{rot} = BJ(J+1) \qquad B = \frac{\hbar^2}{2I}$$

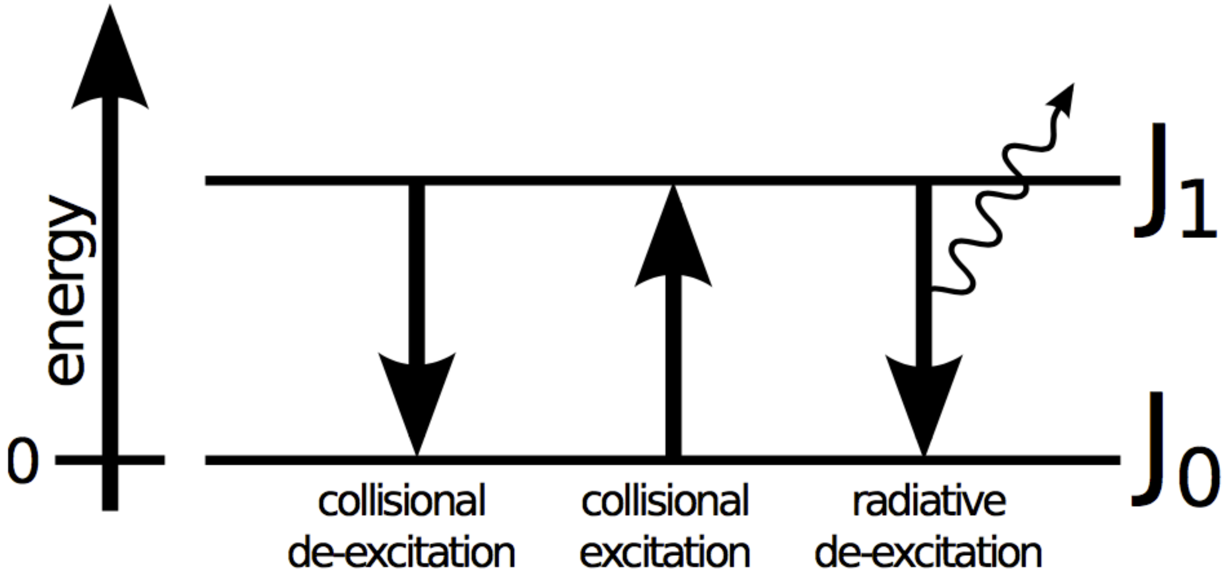


ENERGY SPACING (FOR A RIGID ROTOR)



INELASTIC COLLISIONS: CHANGE OF INTERNAL ENERGY

Molecules are excited through collisions and $\Delta J = \pm 1$



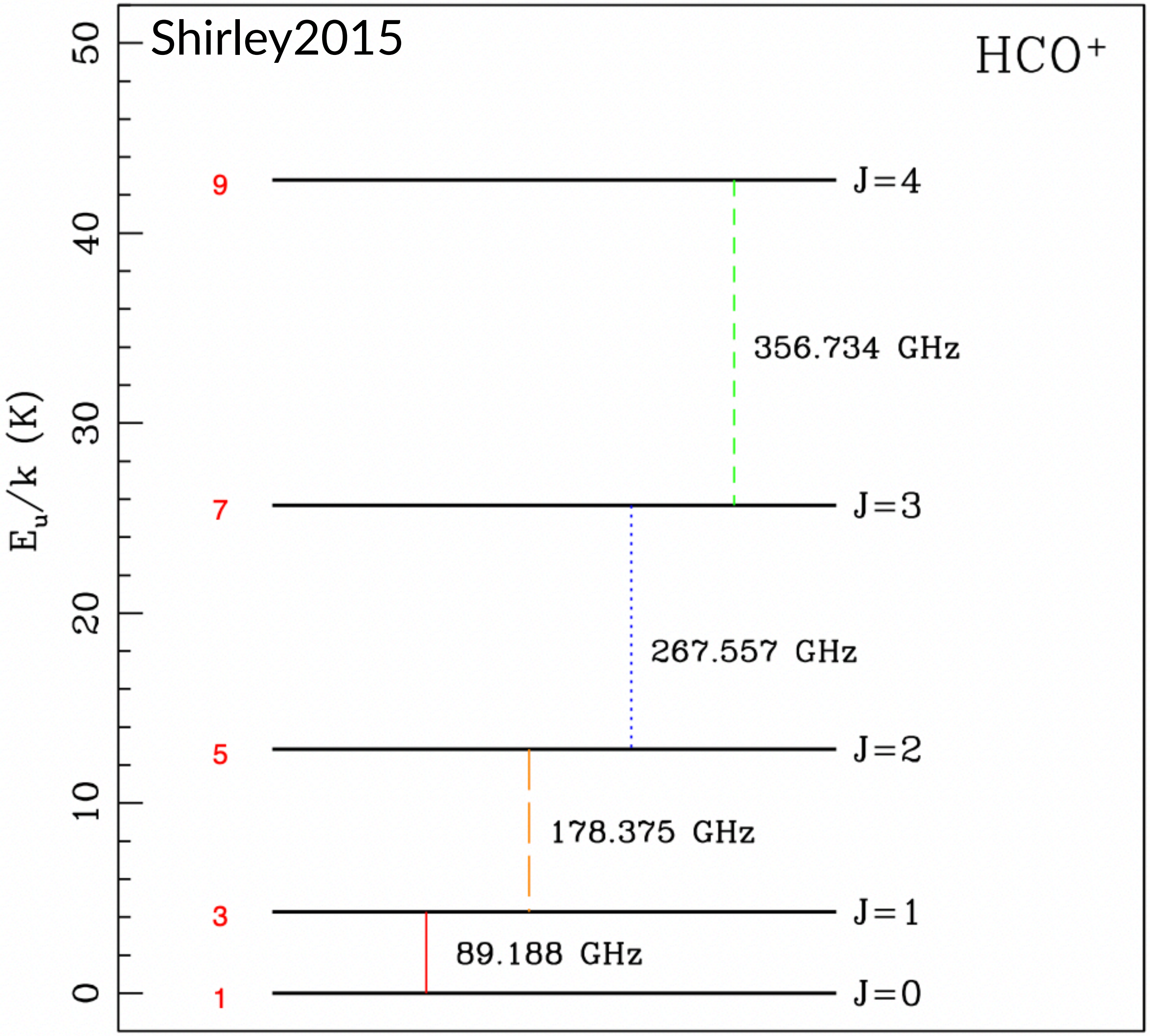
Spontaneous emission:

$$A_{ul} \propto \nu^3 |\mu_d|^2 \tag{2}$$

- the molecule must have a permanent dipole moment
- a critical density required for significant excitation

ROTATIONS: BULK OF MOLECULES TRANSITIONS

- HCN → $\mu_d = 2.98$ D
- H_2O → $\mu_d = 1.85$ D
- CO → $\mu_d = 0.11$ D



DIPOLE MOMENT INTEGRAL: ALLOWED TRANSITIONS

- the interaction of the electric component of the electromagnetic field with the electric dipole associated with the transition

- Selection rules

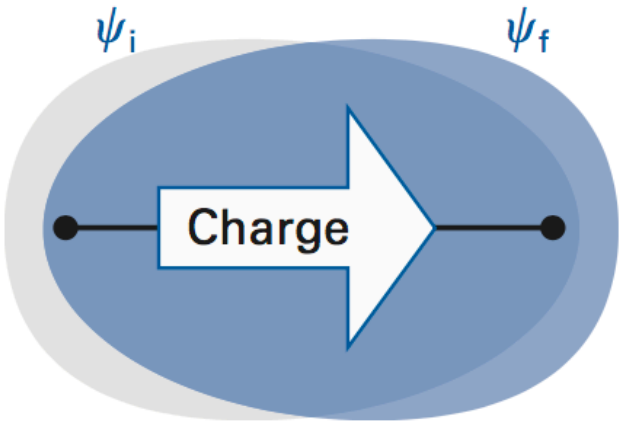
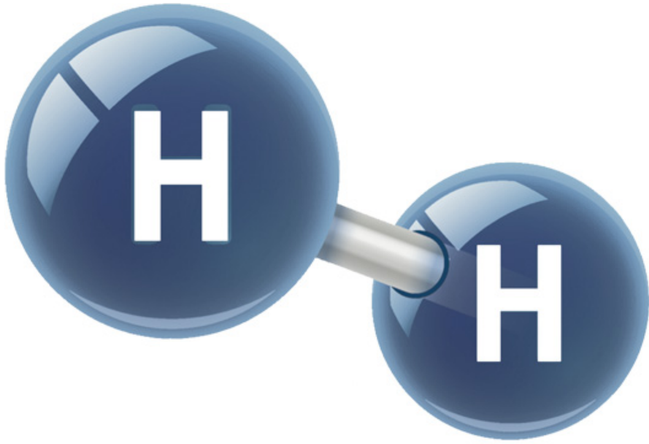


Fig. 10.1 In order for a transition to be electric-dipole allowed, it must possess a degree of dipolar character. A purely spherically symmetrical (or some other non-dipolar) redistribution of charge cannot interact with the electric field vector of the electromagnetic field.

Image from Atkins book

ROTATIONS: BULK OF MOLECULE TRANSITIONS



H_2 symmetric homonuclear molecule:

- no dipole moment
- H_2 possesses a quadrupole (asymmetric distr. of charges)
- strict selection rules for transitions $\Delta J = \pm 2$

A SIMPLE EXERCISE: H_2 EXCITATION TEMPERATURE

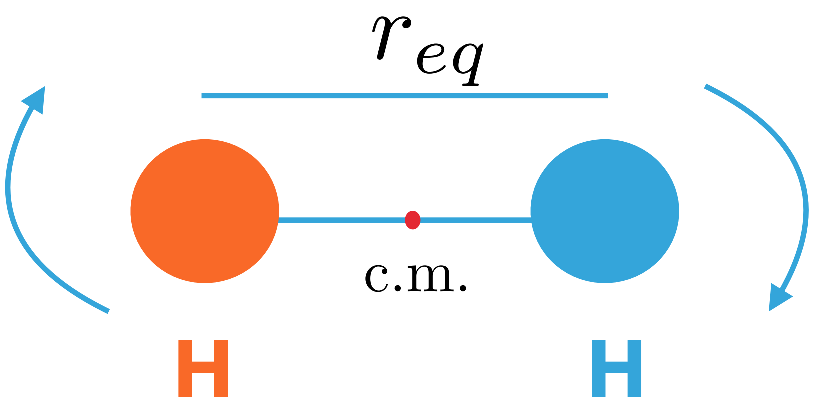
- The excitation rotational temperature for J = 2

$$\hbar = 1.054 \times 10^{-27} \mathrm{erg\,s}$$

$$k_B = 1.38 \times 10^{-16} \mathrm{erg\,K^{-1}}$$

$$r_{eq}(\mathrm{H_2}) = 0.75\text{Å}$$

$$m_\mathrm{H} = 1.67 \times 10^{-24} \mathrm{g}$$



$$E_{rot} = BJ(J+1)$$

Question: Can we observe H_2 in dense regions (T ~ 10 K)?

1 Angstrom = 10^{-8} cm

MOST ABUNDANT MOLECULE IS INVISIBLE !!

514 K!!! (28 μm)

- difficult to observe in dense regions (even if most abundant molecule)
- in shocked regions, where T becomes high enough
- or in the vicinity of hot stars

EXERCISE

Write a simple python code (generalized) to calculate rotational constants of any diatomic molecule given the mass, equilibrium distance, and transition (J'-> J). Units of B must be in Kelvin.

To calculate the moment of inertia use the following formula

$$I = \mu r_{\mathrm{bond}}^2$$

$$m_{\mathrm{H}} = 1.67 \times 10^{-24}\mathrm{g}$$

$$\hbar = 1.054 \times 10^{-27}\mathrm{erg\,s}$$

$$k_B = 1.38 \times 10^{-16}\mathrm{erg\,K}^{-1}$$

1 Angstrom = 10^{-8} cm

PROBE FOR MOLECULAR HYDROGEN IS CO

- $x_{\mathrm{CO}}/x_{\mathrm{H_2}} \sim 10^{-4}$
- higher Einstein A-values

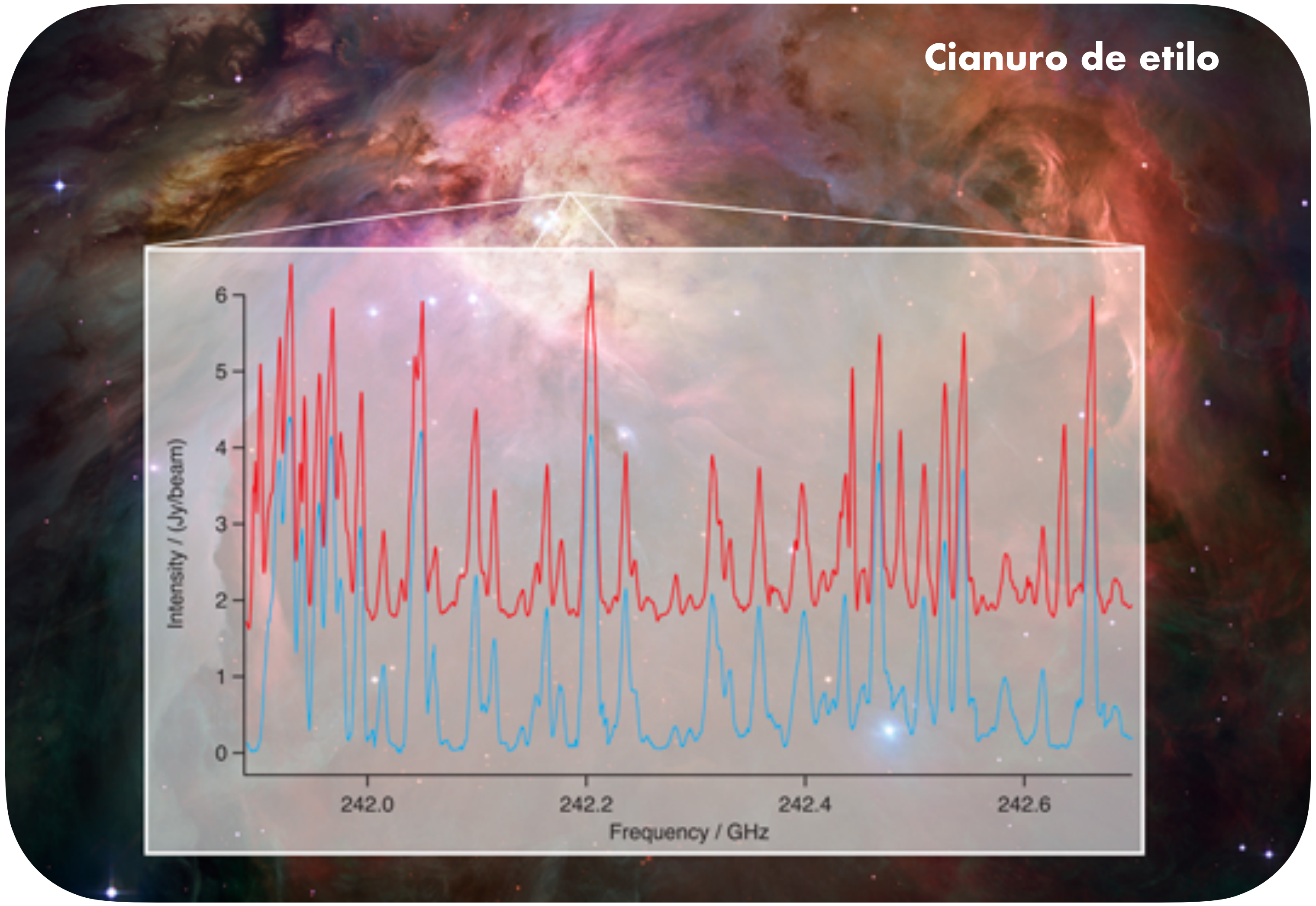
	CO	H_2
Symmetry	asymmetric	symmetric
Dipole moment	0.112 Debye	none
Binding energy	11.09 eV	4.48 eV
Isotope variants	^{13}CO, $C^{17}O$, $C^{18}O$	none
Rotational constant	2.77 K	87.5 K
First transition	2.6 mm (5.5 K)	28.2 μm (514 K)

How do we identify species?

- Every emission spectrum is unique for a given atom/molecule
- Every chemical element (atom/molecule) absorbs, emits and reflects light (photons) in a unique way!

Red: Observed spectrum (ALMA)

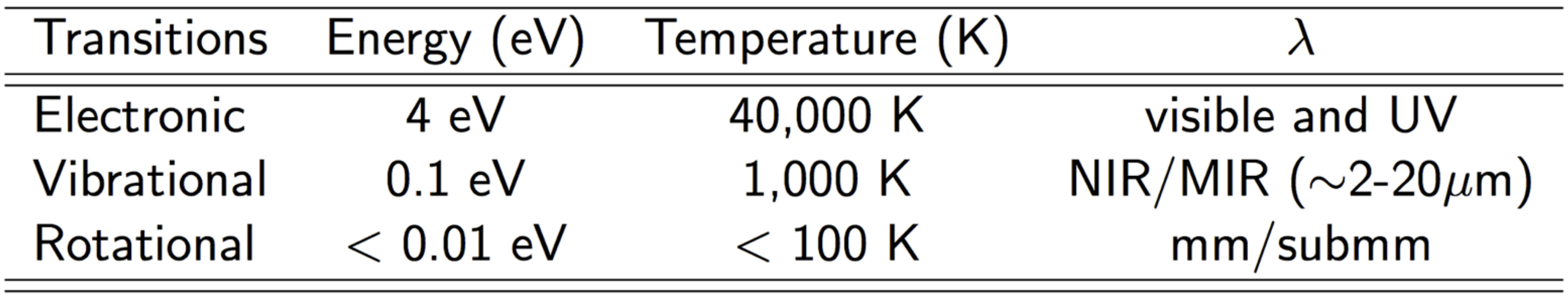
Blue: Measured spectrum (Lab)



Crédito: Fortman, et al., NRAO/AUI/NSF, NASA

OBSERVATIONS

- Molecules introduce complexity compared to atoms
- Molecular energy is quantized
- Born-Oppenheimer approx. allows us to solve for the internal structure of the molecules
- Electronic + Rotational + Vibrational Energies
- Remind: Transitions between different states allow us to observe atoms and molecules in the ISM



Transitions	Energy (eV)	Temperature (K)	λ
Electronic	4 eV	40,000 K	visible and UV
Vibrational	0.1 eV	1,000 K	NIR/MIR ($\sim$2-20μm)
Rotational	$<$ 0.01 eV	$<$ 100 K	mm/submm

WHAT DO WE OBSERVE AND AT WHICH WAVELENGTHS?

- electronic transitions → Vis/UV (Hubble Space Telescope)
  - H_2 + atoms observed directly
  - large oscillator strengths[1], minor species can be detected
- vibrational transitions → IR (Spitzer, Herschel)
  - both gas and solids observed
  - ices, silicates, oxides, PAH mid-far IR
  - molecules without permanent dipole moment (e.g. H_3^+, CH_4, CO_2)
  - moderate oscillator strengths
- rotational transitions → sub-mm (Herschel, ALMA)
  - bulk of interstellar molecules
  - high sensitivity to low abundances (down to $10^{-11}\ x_{\mathrm{H}}$)

DARK CLOUDS

T~10-300 K

n~10^4-10^7 cm^{-3}

Optical/
Infrared

Horsehead nebula

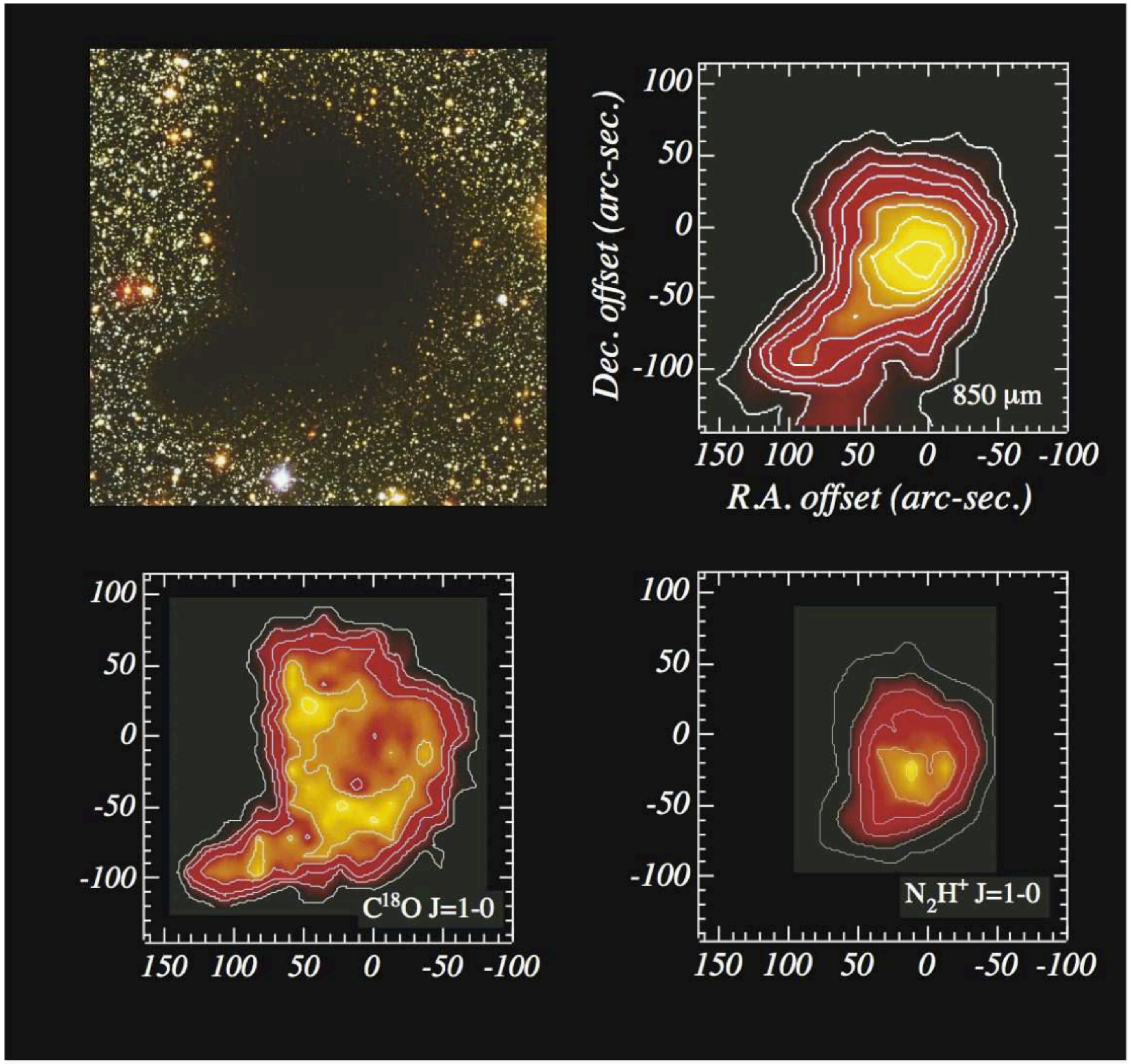


Figure 7: A deep optical image of the dark globule Barnard 68 (*top left*; Alves, Lada & Lada 2001) along with contour maps of integrated intensity from molecular emission lines of N_2H^+ (contour levels: 0.3–1.8 by 0.3 K km s^{-1}), $C^{18}O$ (0.2–0.7 by 0.1 K km s^{-1}), and 850μm dust continuum emission (10–70 by 10 mJy $beam^{-1}$). Molecular data, with an angular resolution of $\sim 25''$, are from Bergin et al. (2002) and dust emission (angular resolution of $14.5''$) from Bianchi et al. (2003).

N_2H^+

CO

H_2D^+

HCO^+

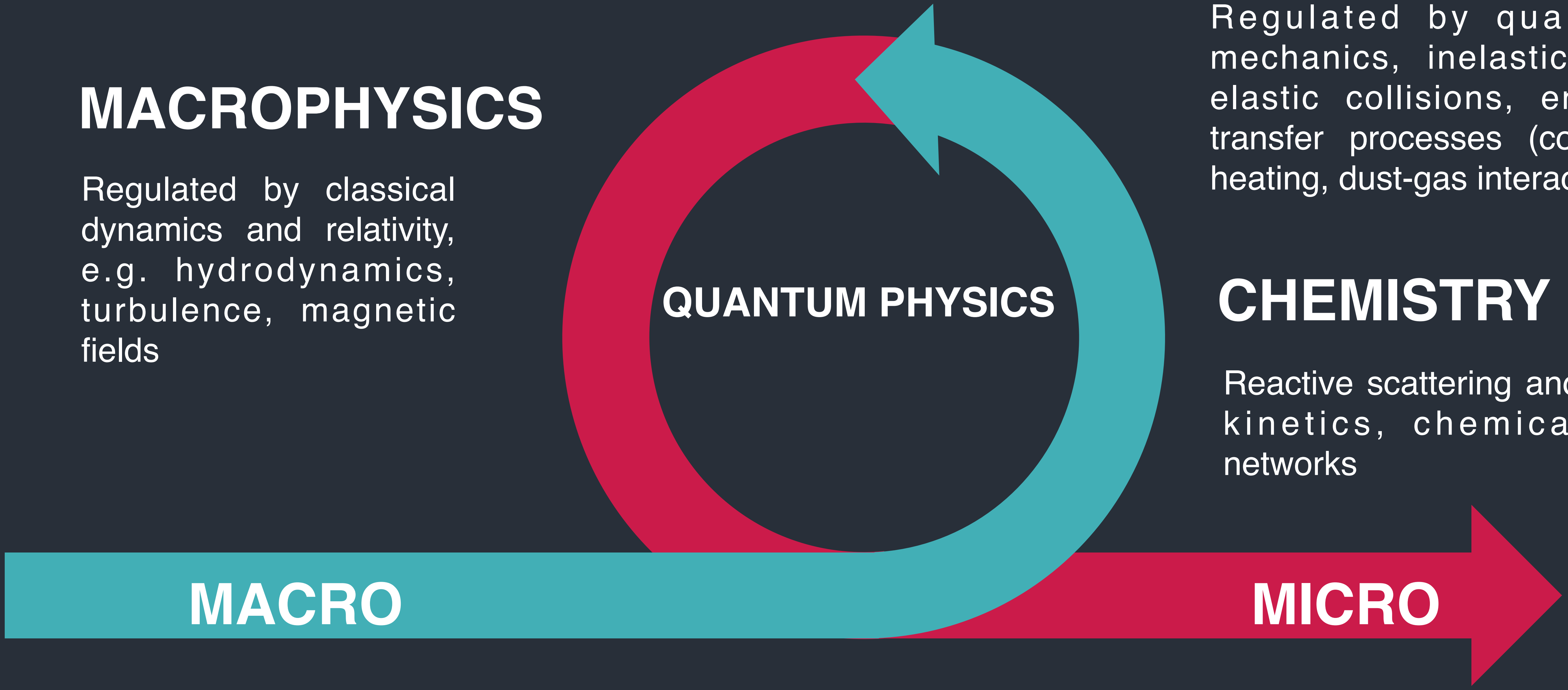
Freeze-out

Gas-grain chemistry

Interconnection

MACROPHYSICS

Regulated by classical dynamics and relativity, e.g. hydrodynamics, turbulence, magnetic fields



QUANTUM PHYSICS

MACRO

MICRO

MICROPHYSICS

Regulated by quantum mechanics, inelastic and elastic collisions, energy transfer processes (cooling, heating, dust-gas interaction)

CHEMISTRY

Reactive scattering and kinetics, chemical networks

Chemical kinetics

The study of the rates of chemical reactions is called **chemical kinetics.**

The changes that take place in the course of reactions and the speed of each step.

Reaction rates

- Fast: the products are formed rapidly

- Slow: products formed over a long period of time

Notation/definitions

Rate: better called rate equation, it represents the evolution of a species in time

Rate coefficient: it represents the speed of a reaction

Concentrations: species volumetric amount

Abundances: concentration of the species divide by another quantity, normally total density

1. $A + B \rightarrow P$ (two-body reactions)
2. $A +$ photon $\rightarrow P$ (photo-reactions)
3. $A + B + C \rightarrow P$ (three-body reactions)

Unimolecular

Bimolecular

Termolecular

$$\boxed{\frac{dn_{\mathrm{P}}}{dt}} = k(T) n_{\mathrm{A}} n_{\mathrm{B}} \qquad (1)$$

units of $k(T)$: $\mathrm{cm}^3\ \mathrm{s}^{-1}$

Rate laws

- The **integrated rate law** for a chemical reaction is a relationship between the concentrations of the reactants and time.

$\text{Rate} = k[\text{A}]^0 = k$	0th-order
$\text{Rate} = k[\text{A}]$	1st-order
$\text{Rate} = k[\text{A}]^2$	2nd-order

Rate laws

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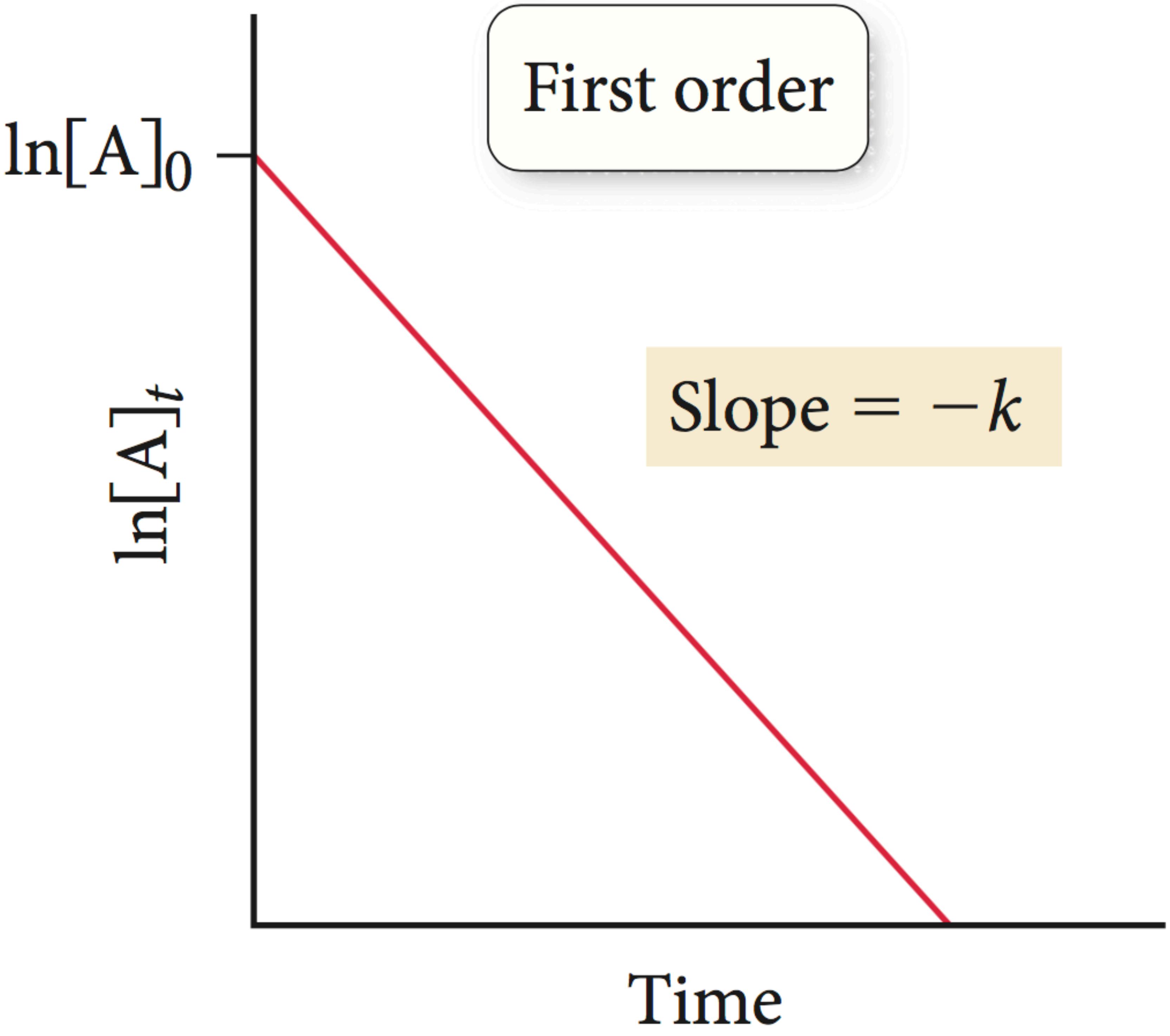
$\text{Rate} = k[\text{A}]^0 = k$ 0th-order

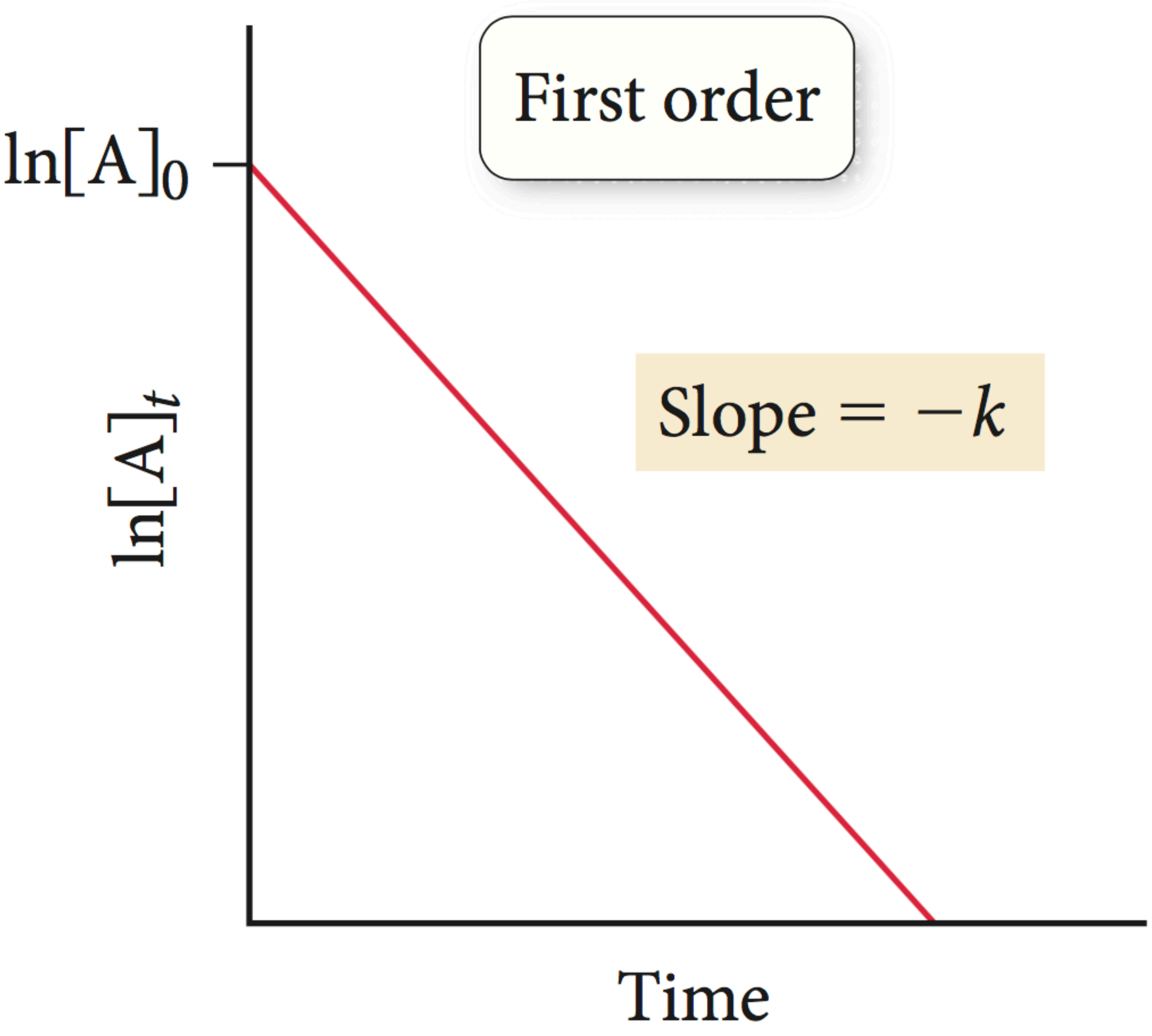
$\boxed{\text{Rate} = k[\text{A}] \qquad \text{1st-order}}$

$\text{Rate} = k[\text{A}]^2$ 2nd-order

Rate law: first order example



Rate law: first order example



$$-\frac{d[A]}{dt} = k[A]$$

$$\frac{d[A]}{[A]} = -kdt$$

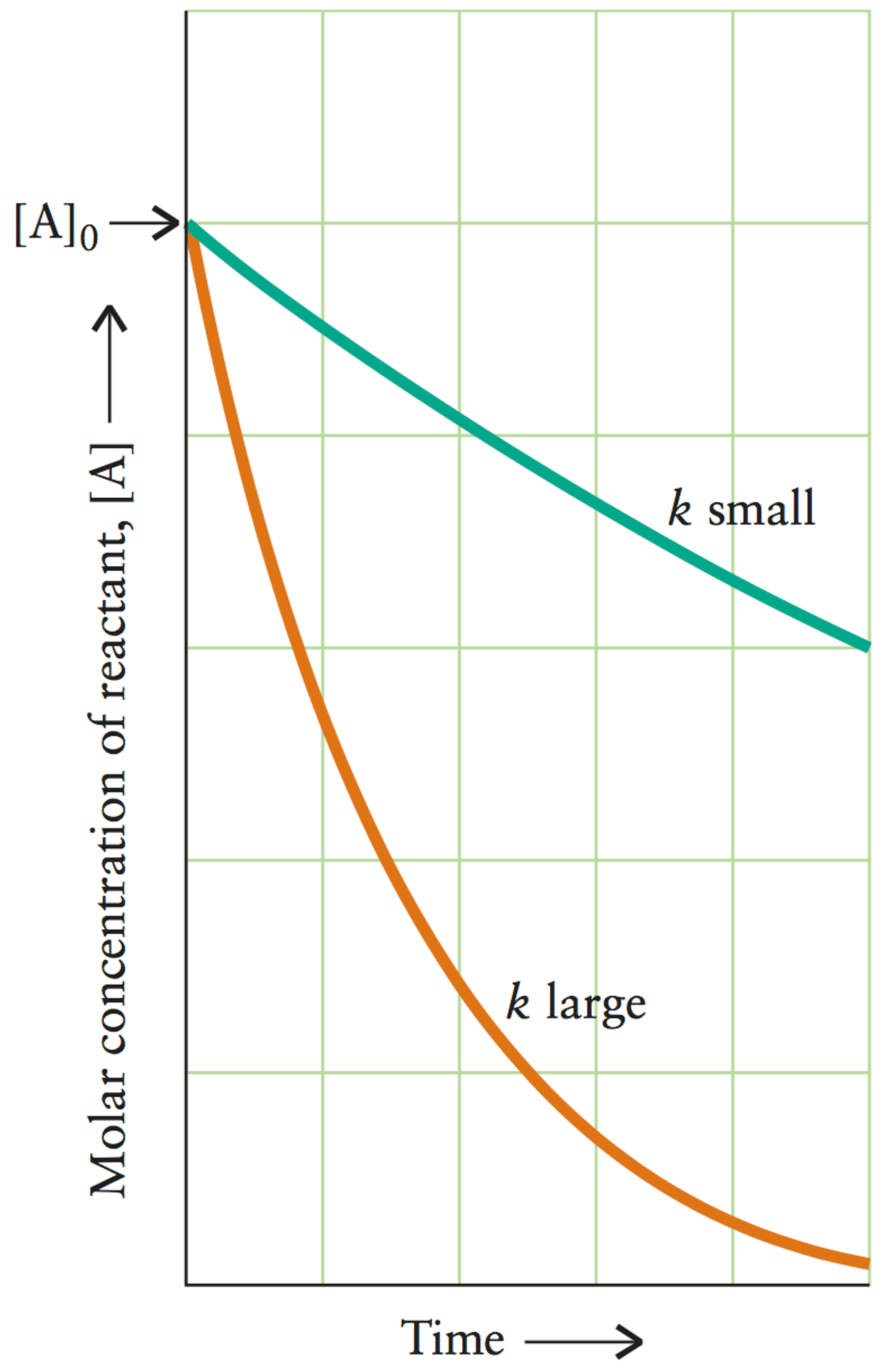
$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = -\int_0^t kdt$$

$$[\ln[A]]_{[A]_0}^{[A]} = -k[t]_0^t$$

$$\ln[A] - \ln[A]_0 = -kt$$

$$\ln[A] = -kt + \ln[A]_0$$

Rate law: first order example



- The larger the rate constant, the faster the decay from the same initial concentration.

Rate equations

- Elementary reactions: sum formation/destruction
- Example H_3^+

Rate equations

- Elementary reactions: sum formation/destruction
- Example H_3^+

$$\zeta L = N(\mathrm{H}_3^+)_{\mathrm{dense}} k_{\mathrm{CO}}[n(\mathrm{CO})/n(\mathrm{H}_2)]$$

$$\approx 6.4 \times 10^{-13}\ \mathrm{cm}^3 \cdot \mathrm{s}^{-1} N(\mathrm{H}_3^+)_{\mathrm{dense}} \quad \textbf{[5]}$$

and

$$\zeta L = N(\mathrm{H}_3^+)_{\mathrm{diffuse}} k_{\mathrm{e}}[n(\mathrm{e}^-)/n(\mathrm{H}_2)]$$

$$\approx 8.3 \times 10^{-11}\ \mathrm{cm}^3 \cdot s^{-1} N(\mathrm{H}_3^+)_{\mathrm{diffuse}}/f, \quad \textbf{[6]}$$

Oka+2006