"Chemistry in the Universe"

Dmitry Semenov
MPIA Heidelberg

http://www.mpia-hd.mpg.de/~semenov/

Outline

- Molecules in space
- Different ways to detect molecules
- Chemical processes in space
- Chemistry in the early Universe
- Physics and chemistry of the interstellar medium
- Physics and chemistry of protoplanetary disks

Background reading

- S. Kwok, "Physics and Chemistry of the Interstellar Medium" (2006)

- A. G.G.M. Tielens, "The Physics and Chemistry of the ISM" (2007)

- Master course in Astrochemistry, Ewine van Dischoek (2011)
http://www.strw.leidenuniv.nl/~sanjose/astrochem

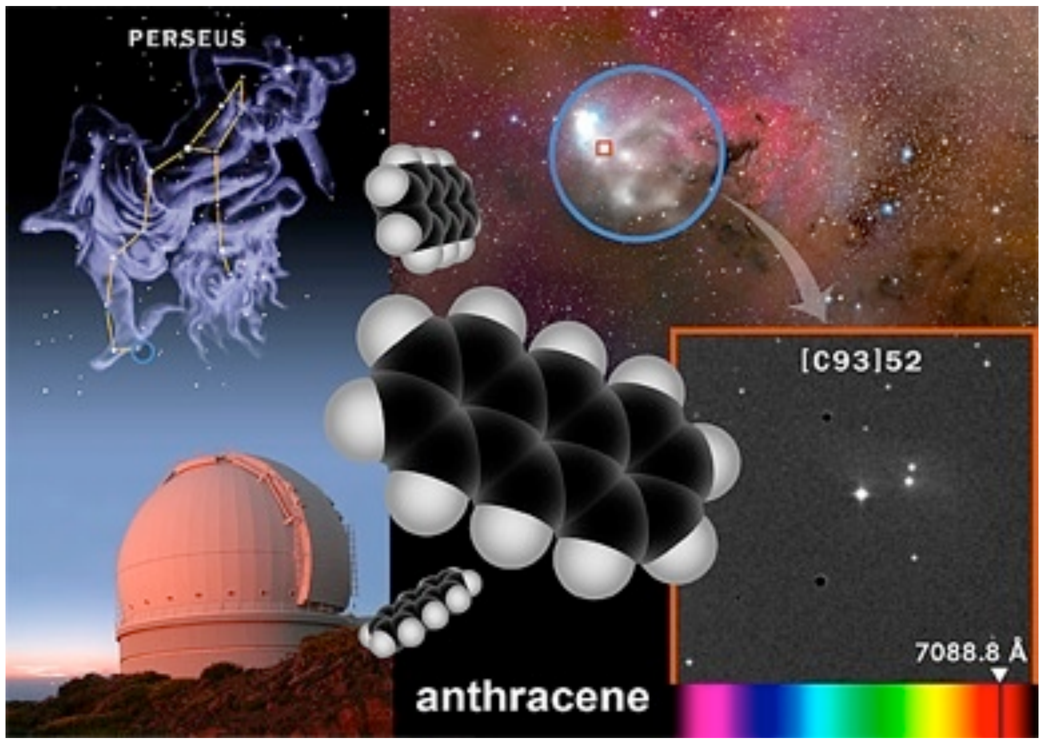
- E. Herbst & E. van Dishoeck, "Complex Organic Interstellar Molecules" (2009), Annual Rev. in Astron. & Astrophys., 47, 427

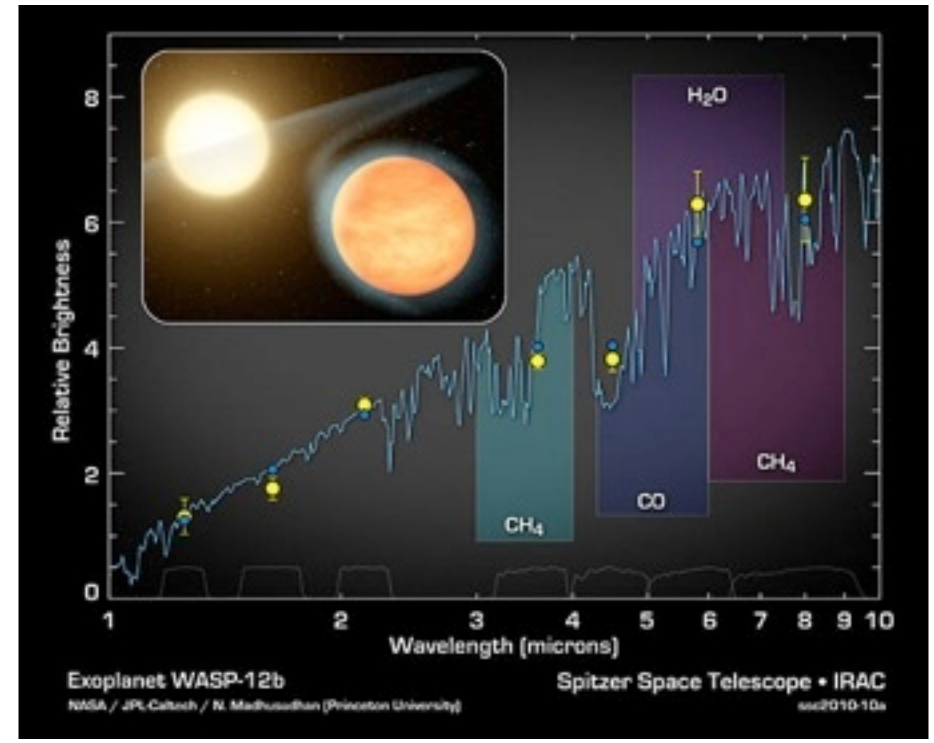
- "Protostars & Planets V" (2007), Part VI, eds. B. Reipurt et al., Univ. Arizona P.

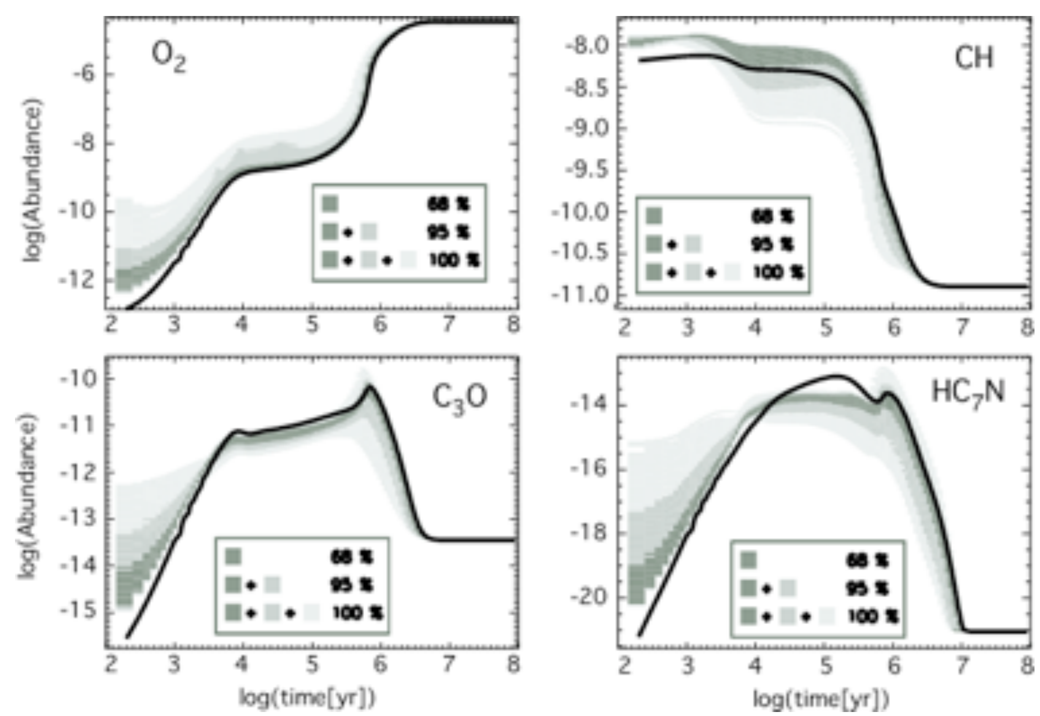
Astronomical units

- 1 pc = parsec = 206,265 AU = 3.086×10^{18} cm
- 1 Å = 10^{-8} cm = 10 nm
- 1 eV = 1.602×10^{-12} erg
- 1 Debye = 10^{-18} esu cm
- 1 year = 3.1536×10^{7} s
- 1 M_{sun} = solar mass = 1.99×10^{33} g
- 1 L_{sun} = solar luminosity = 3.90×10^{33} erg s^{-1}
- 1 Jansky = 10^{-23} erg s^{-1} cm^{-2} Hz^{-1}
- Proton mass = 1.6726×10^{-24} g
- Boltzmann's constant = 1.3807×10^{-16} erg K^{-1}
- Planck's constant = 6.6261×10^{-27} erg s

Lecture 1: Introduction to astrochemistry







What is "astrochemistry"?

- "Study of formation and destruction of molecules in the Universe, their interaction with radiation, and their feedback on physics of the environments"

- Interdisciplinary field: chemistry + physics + astronomy (+biology?)

- Observations + theoretical astrophysics and chemistry + laboratory experiments

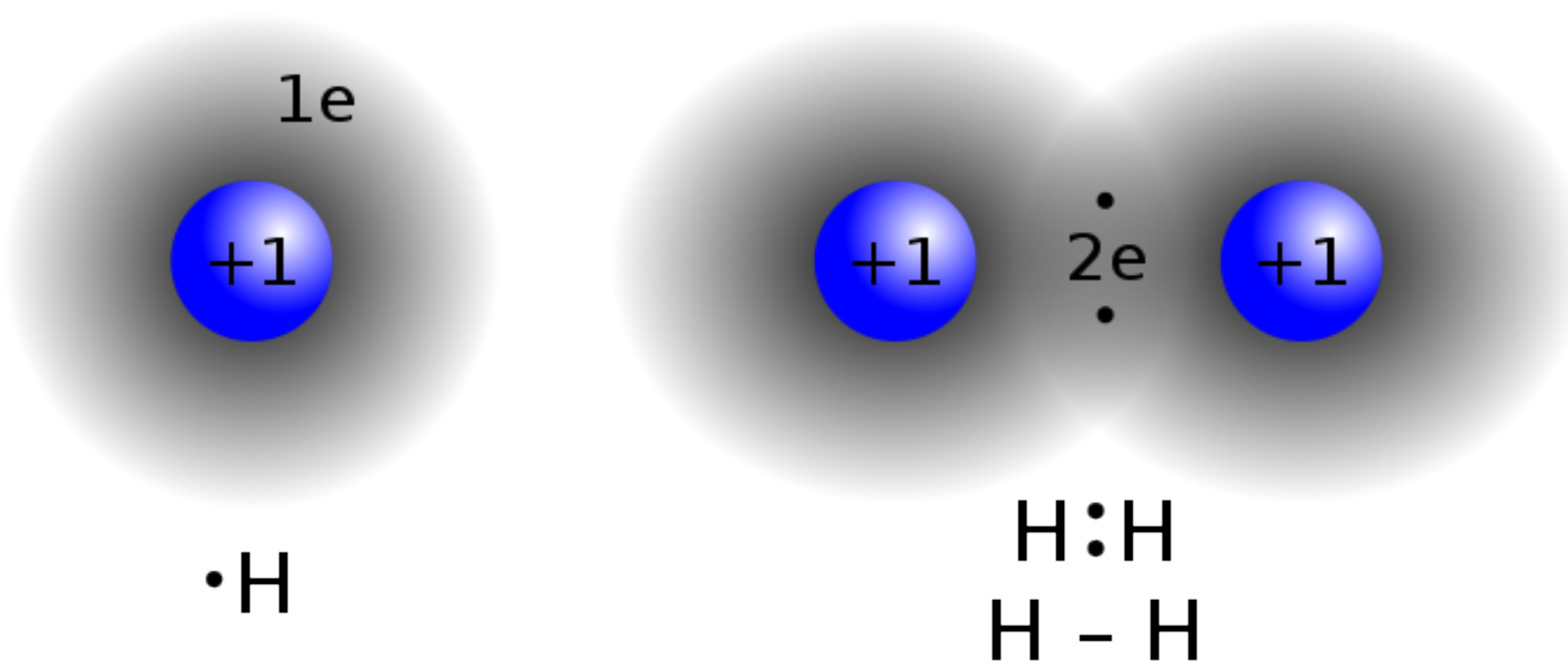
What is a"molecule"?

- From Latin word "moles" (small unit of mass)

- An electrically neutral complex of two or more atoms held together by covalent chemical bonds

- Chemical bond = electrostatic force (e^- and p^+, dipole attraction)

- Smallest molecule is H_2 (0.74 Å)



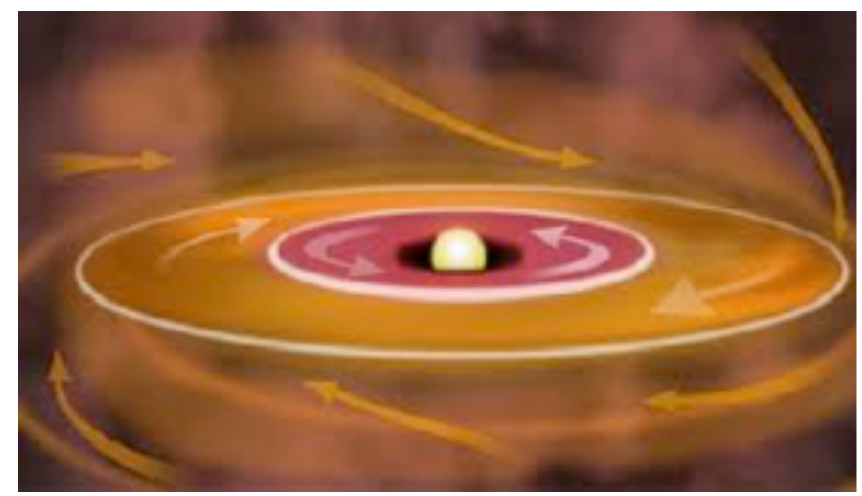
Typical bond energies

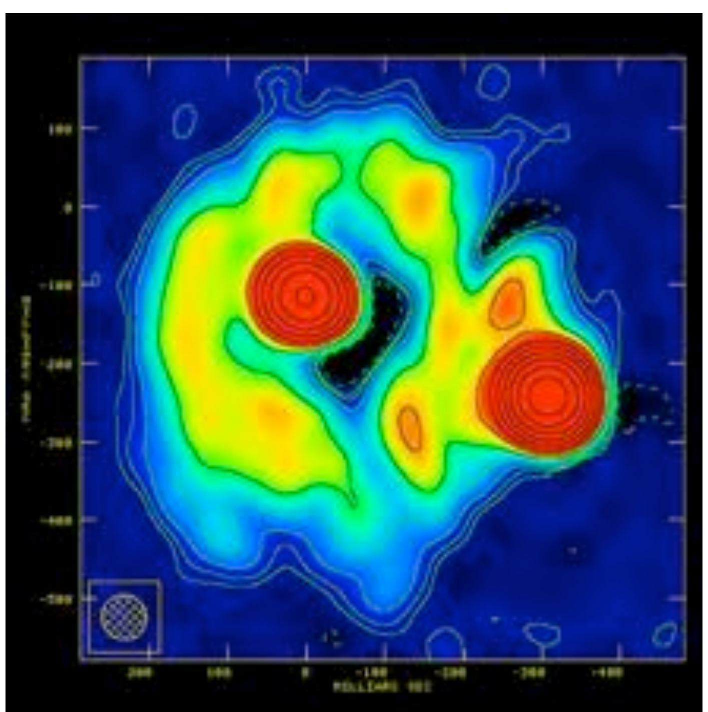
C≡O	**Carbon monoxide**	11.16 eV
H–C≡C–H	Acetylene	10.07 eV
N≡N	Nitrogen	9.71 eV
C≡N	Cyanogen	7.77 eV
O=C=O	Carbon dioxide	5.50 eV
O=O	Oxygen	5.11 eV
H–O–H	**Water**	5.11 eV
NH_3	Ammonia	4.58 eV
CH_4	Methane	4.49 eV
H–H	**Hydrogen**	4.478 eV
O–H	Hydroxyl	4.41 eV

Molecules are everywhere!

- Early Universe
- High-z quasars and galaxies
- Milky Way: interstellar and circumstellar medium
- Solar system: solar photosphere, planetary atmospheres, comets,

meteorites





Physical conditions in various astrophysical objects

- Interstellar medium: T_{kin}~10–100 K, n ~10^2–10^8 cm^{-3}
- Protoplanetary disks: T_{kin}~10–1000 K, n ~10^4–10^{14} cm^{-3}
- Circumstellar shells of evolved stars: T_{kin} ~300–3,000 K, n<10^{14} cm^{-3}

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

Ultra high vacuum conditions, hard to achieve in laboratory

Typical timescales

- Collisional time: ~1 month at 10 K and 10^4 cm^{-3}
- Chemical time: >10^4–10^5 years
- Life-time of a cloud: ~10^6–10^7 years
- Star formation: ~10^5–10^6 years

Chemistry is slow yet there are many molecules

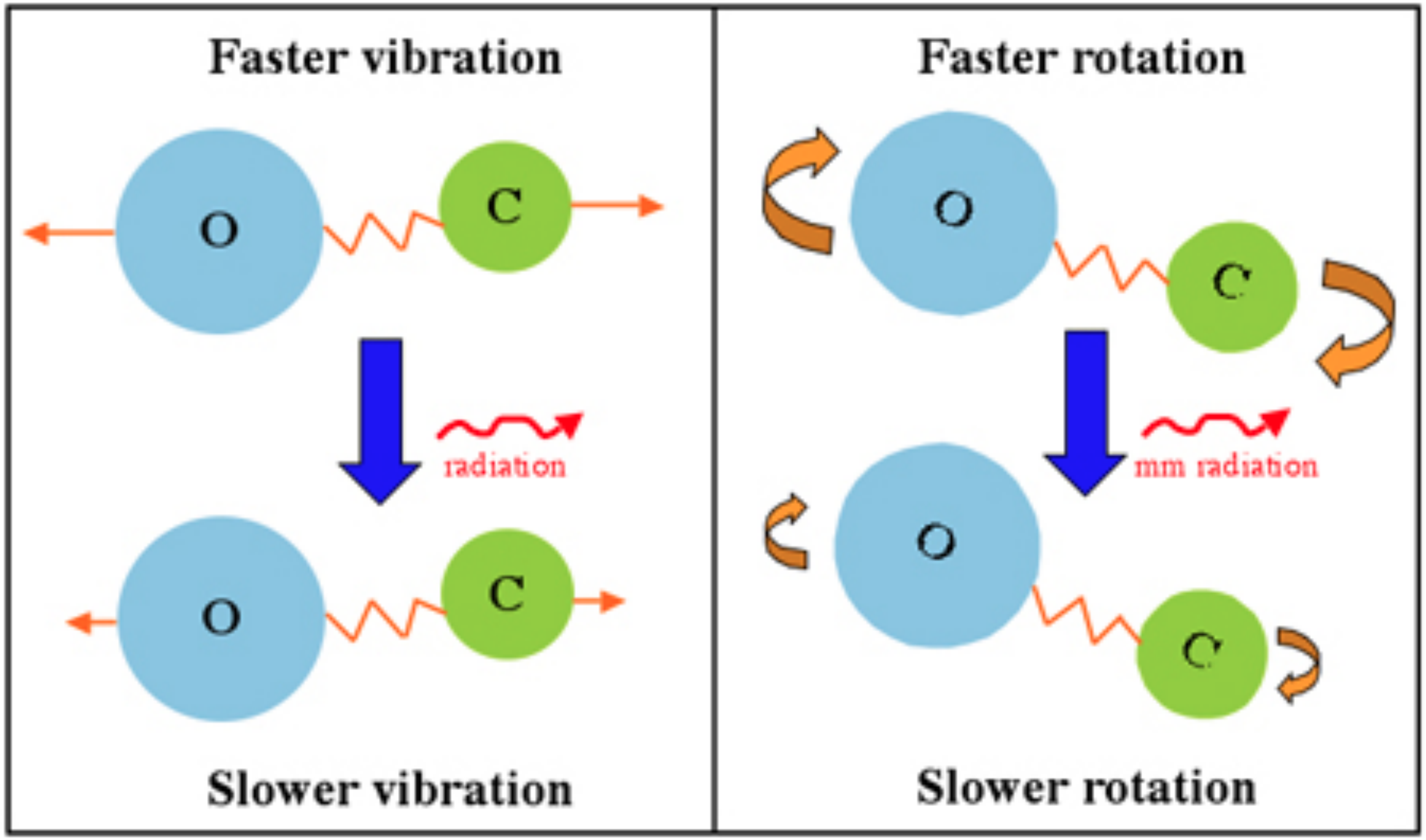
Importance of molecules

- **Physical conditions:**
  - Temperature
  - Density
  - Ionization
  - Magnetic field

- Kinematics

- Chemical composition
- Gas thermal balance

Energy levels of molecules



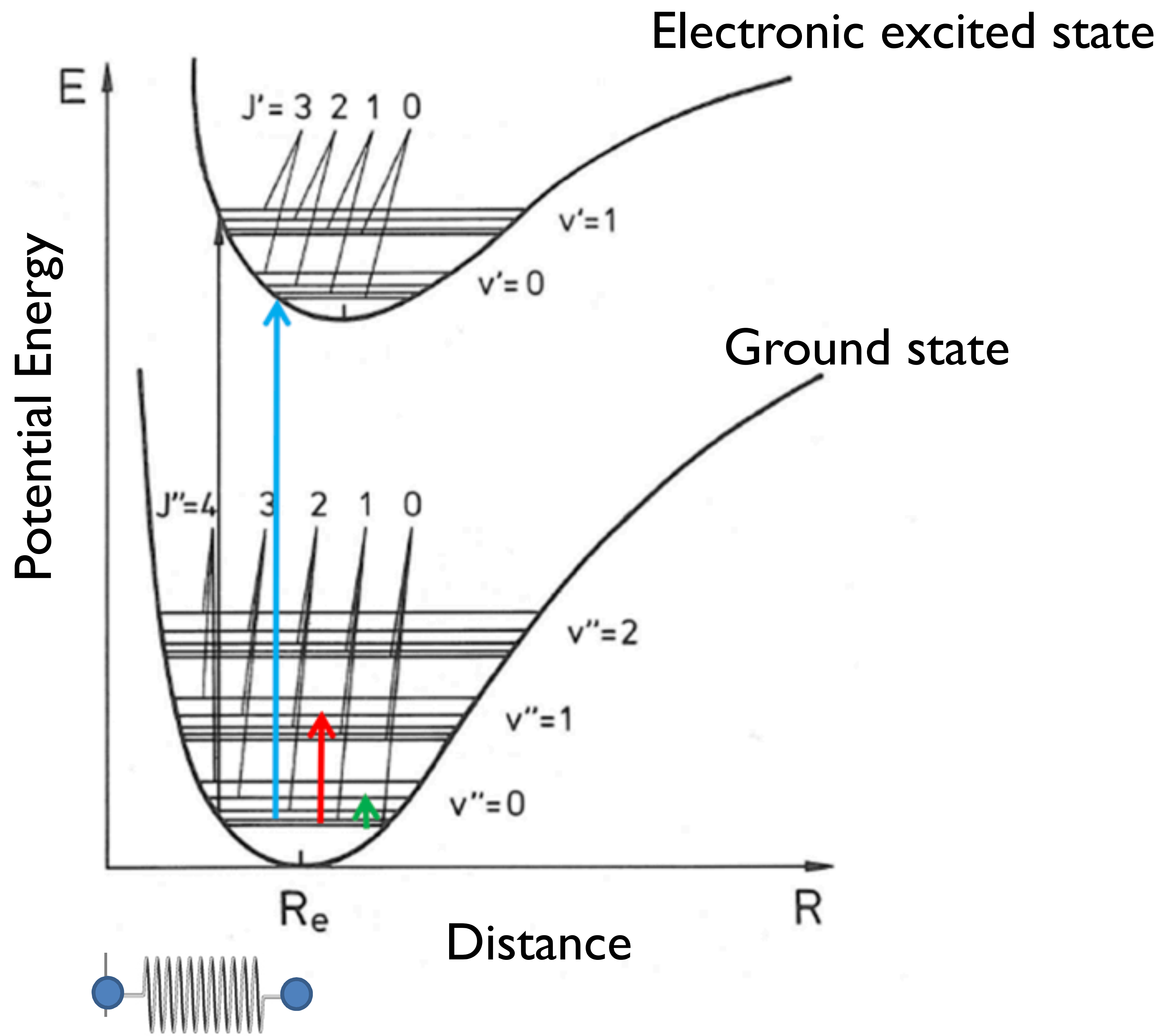
- Rotational, vibrational, electronic transitions
- Collisional or radiative excitation
- Quantum numbers for each level (J, ν,...)
- Selection rules (e.g., $\Delta J = \pm 1$)

Energy levels of molecules

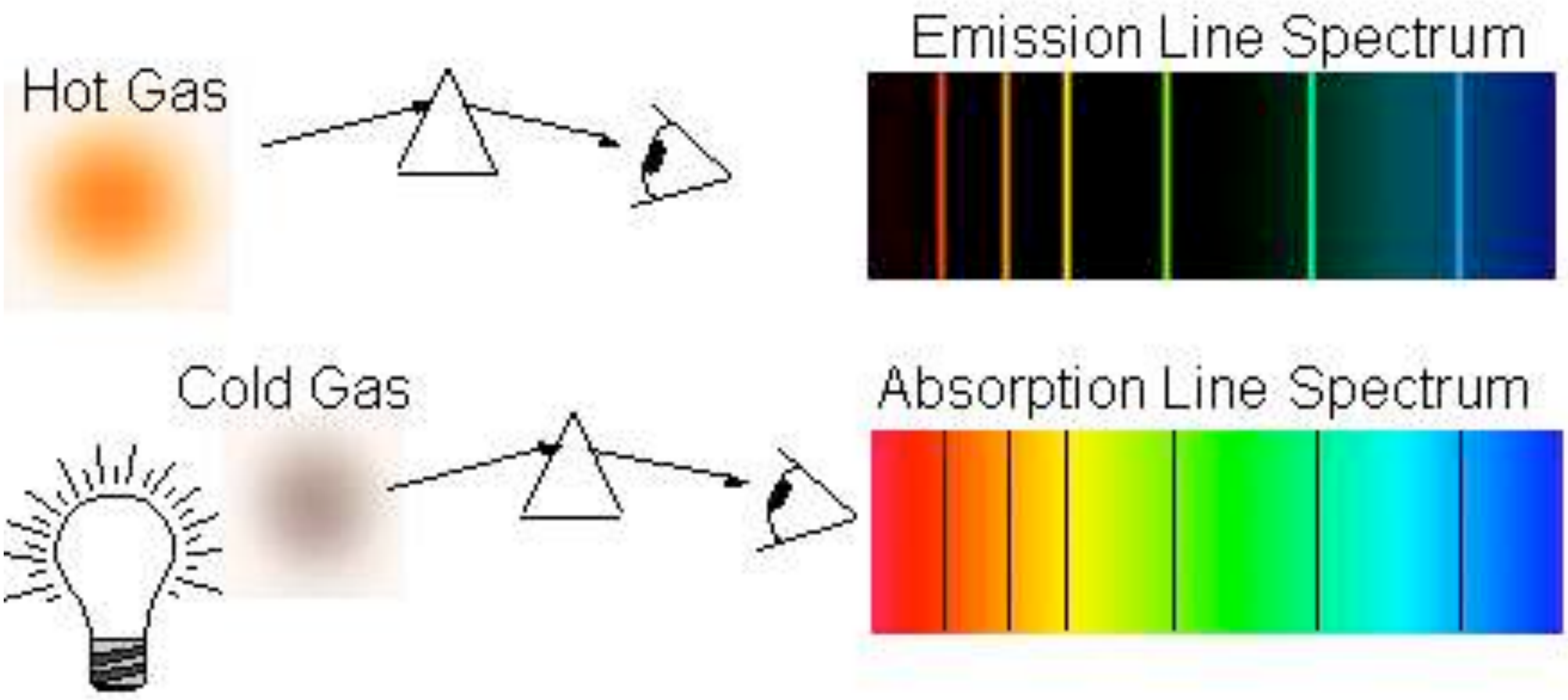
Electronic
Transitions:
ΔE = 1-15 eV
Visible-UV

Vibrational
Transitions:
ΔE = 0.1-1 eV
Infrared

Rotational
Transitions:
ΔE = 0.01-0.1 eV
(sub)-Millimeter

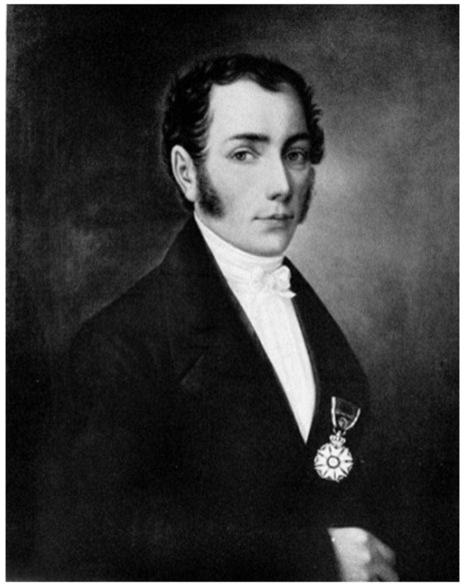


Emission and Absorption Lines

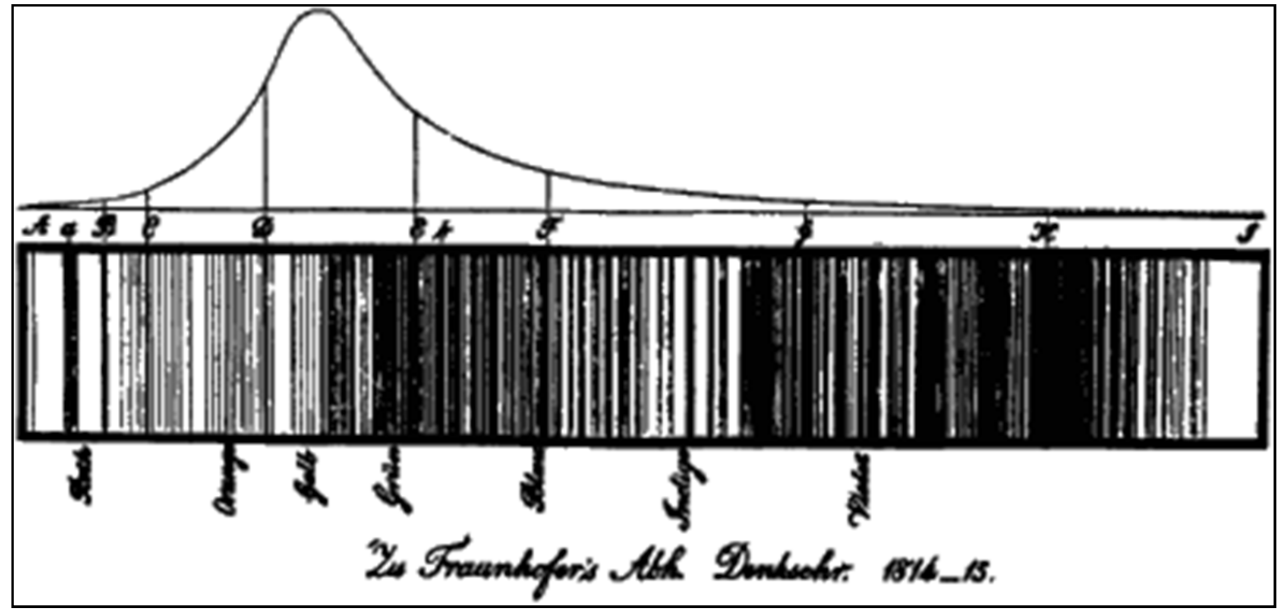


- Absorption: UV, optical, IR
- Emission: IR, (sub-)millimeter
- Gas-phase & ices

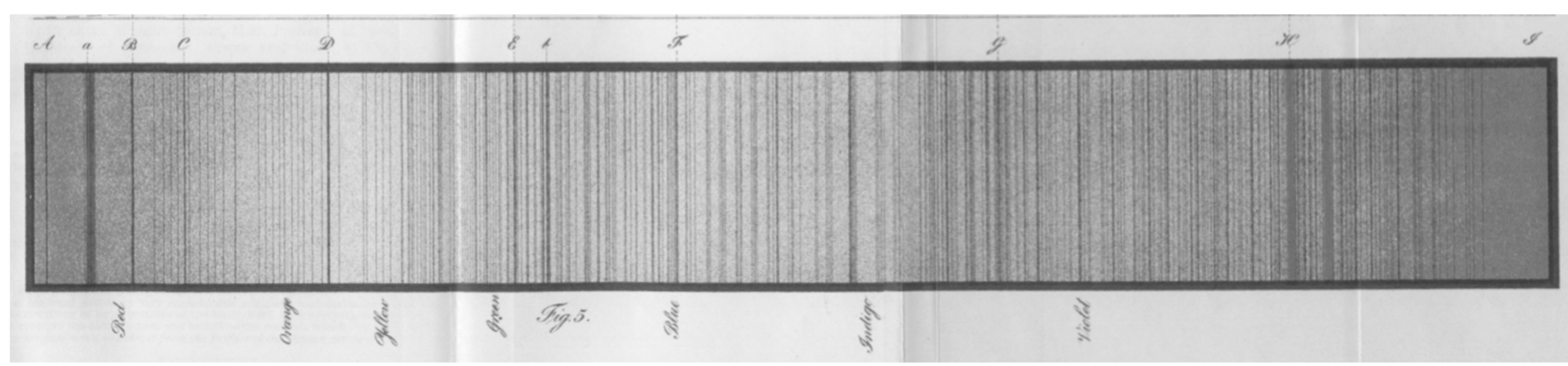
Spectroscopy



Joseph von Fraunhofer



- Fraunhofer lines in solar spectrum (1814)

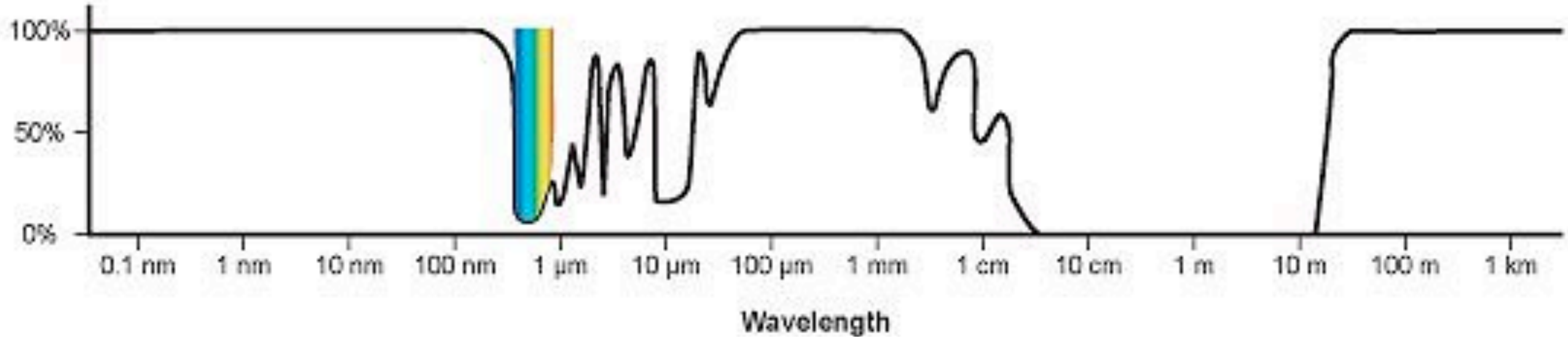


therefore, from the occurrence of the lines D in the solar spectrum, the presence of sodium in the sun's atmosphere may be concluded.

- Birth of spectral analysis: Gustav Kirchoff (1860)

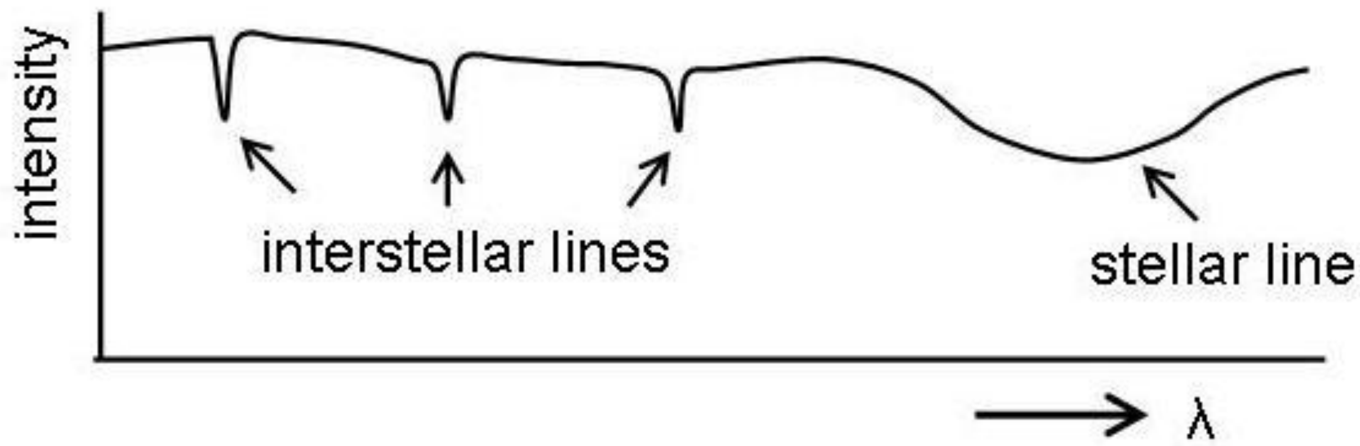
Detecting molecules

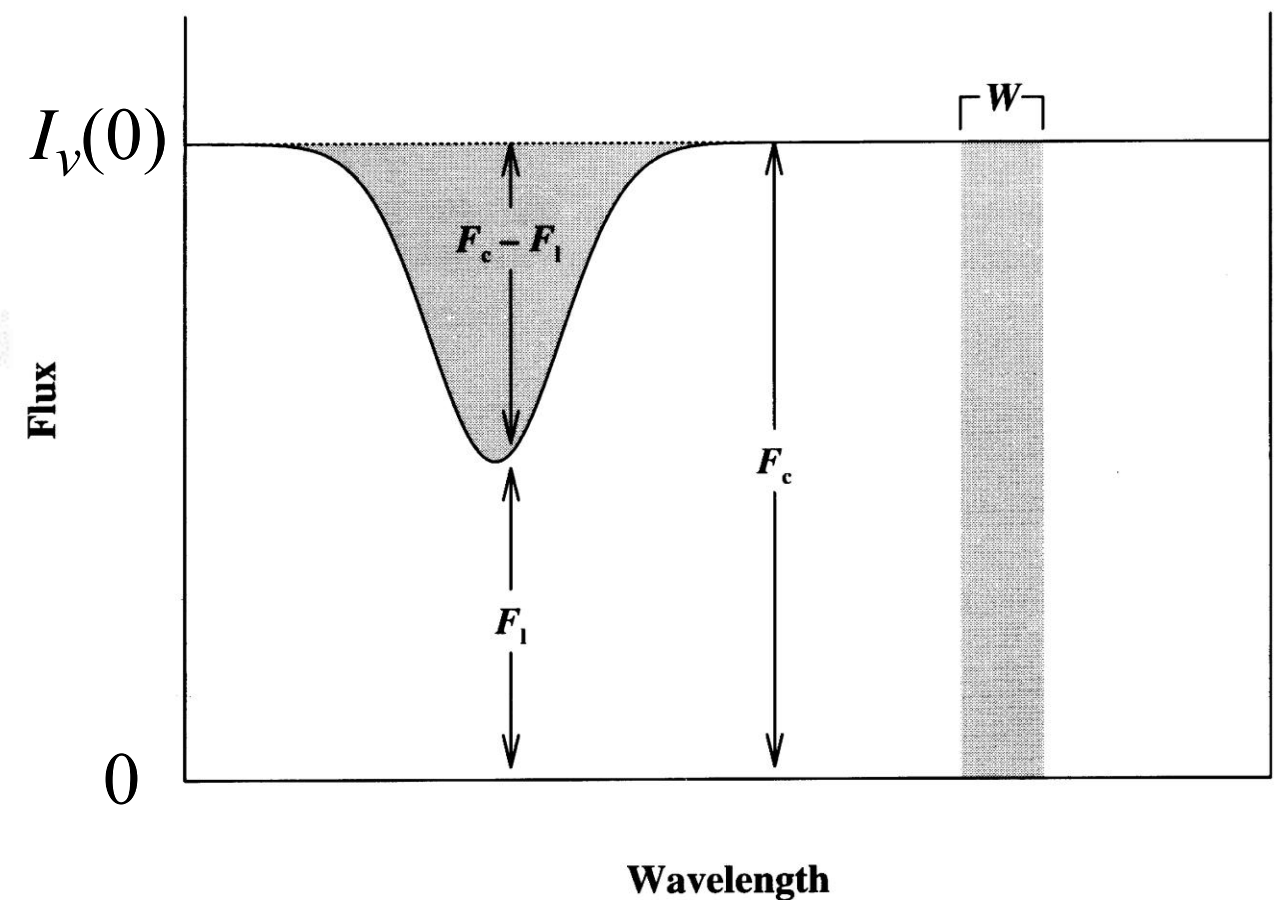
Atmospheric opacity



- Space: FUV, IR (2–10µm, 20–300µm) wavelengths
- Ground: visual, near-IR, (sub-)millimeter wavelengths
- Good spectral resolution ($\Delta\nu/\nu > 10^4$–10^6)
- **Laboratory spectra need to be known**

Absorption lines



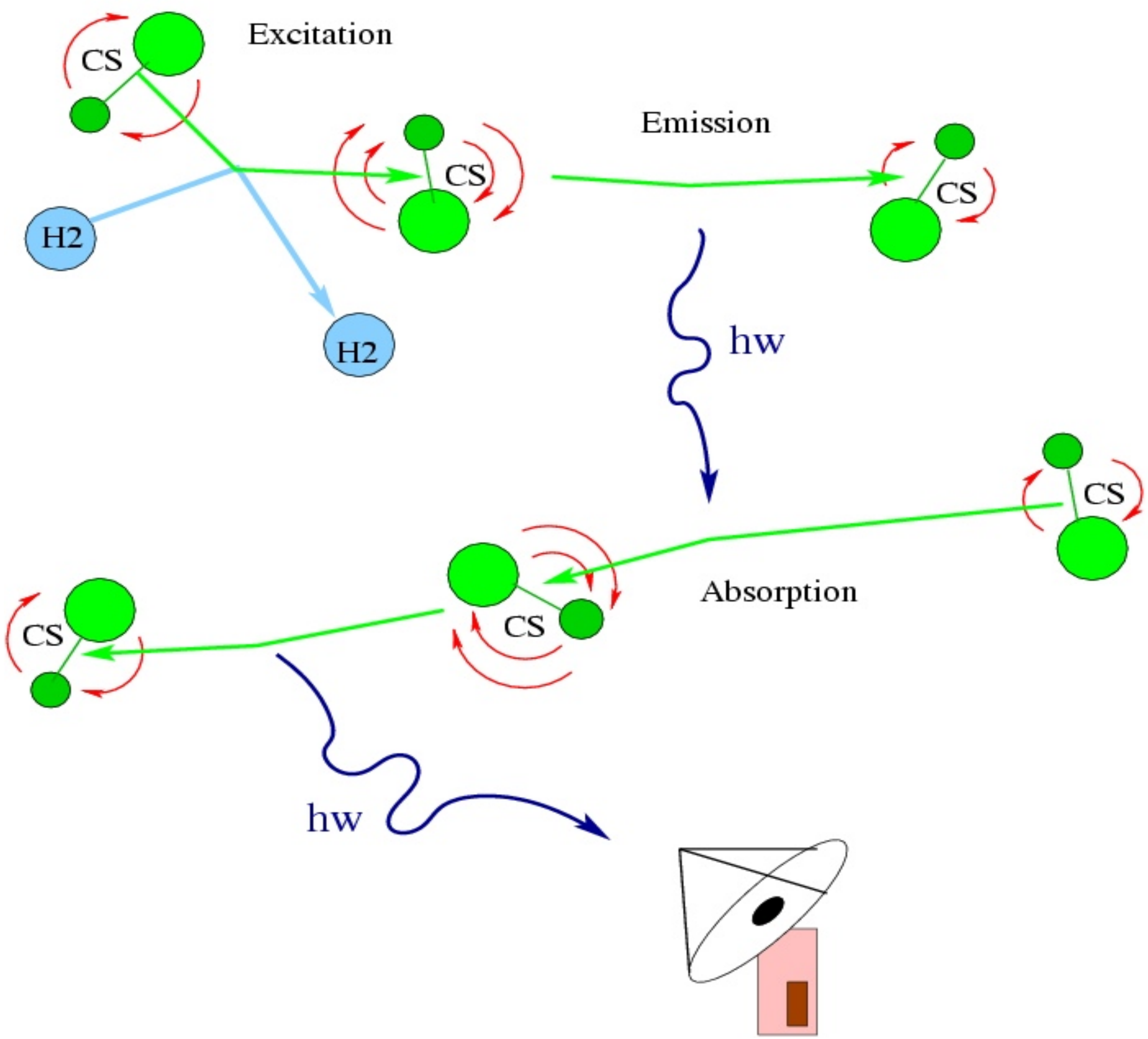


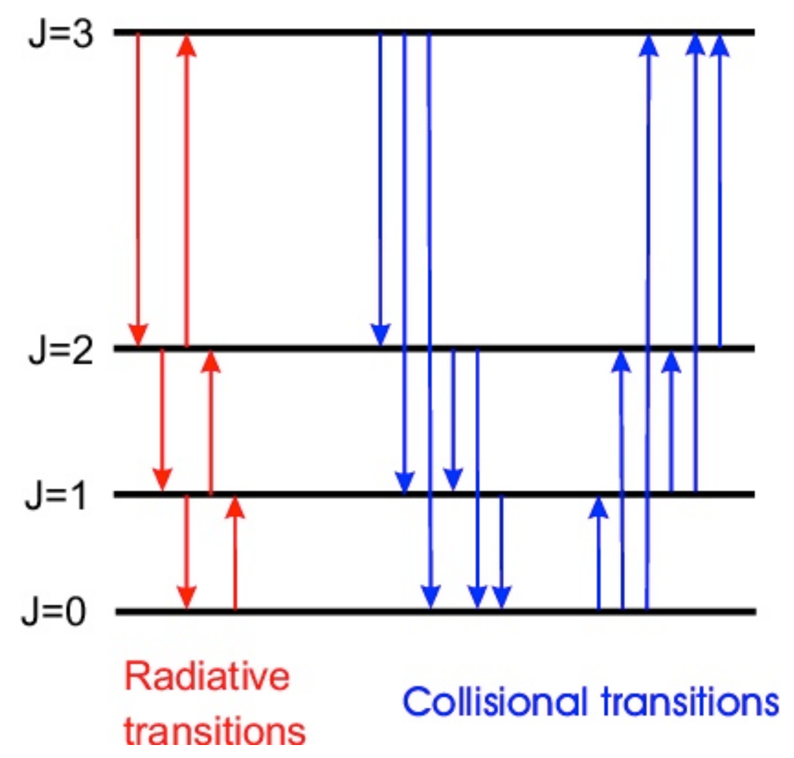
- Optical spectroscopy often lacks resolving power
- Measure "equivalent width of line":

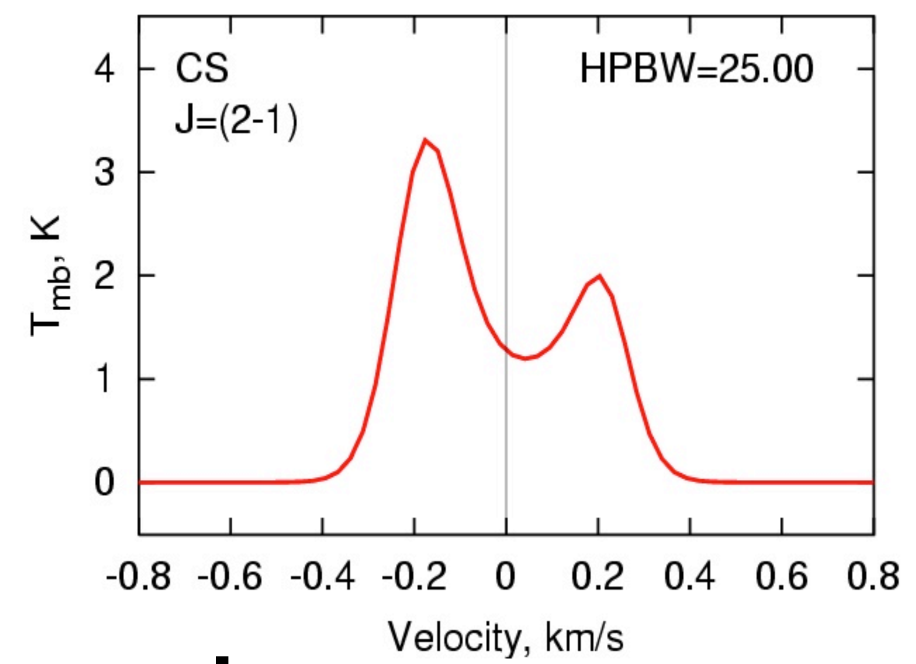
$$W_\nu = \int_{-\infty}^{\infty} \left(1 - e^{-\tau_\nu}\right) \mathrm{d}\nu = \int_{-\infty}^{\infty} \left[\frac{I_\nu(0) - I_\nu}{I_\nu(0)} \right] \mathrm{d}\nu \quad \mathrm{Hz}$$

Direct measurement of column density of absorbing molecules

Emission lines

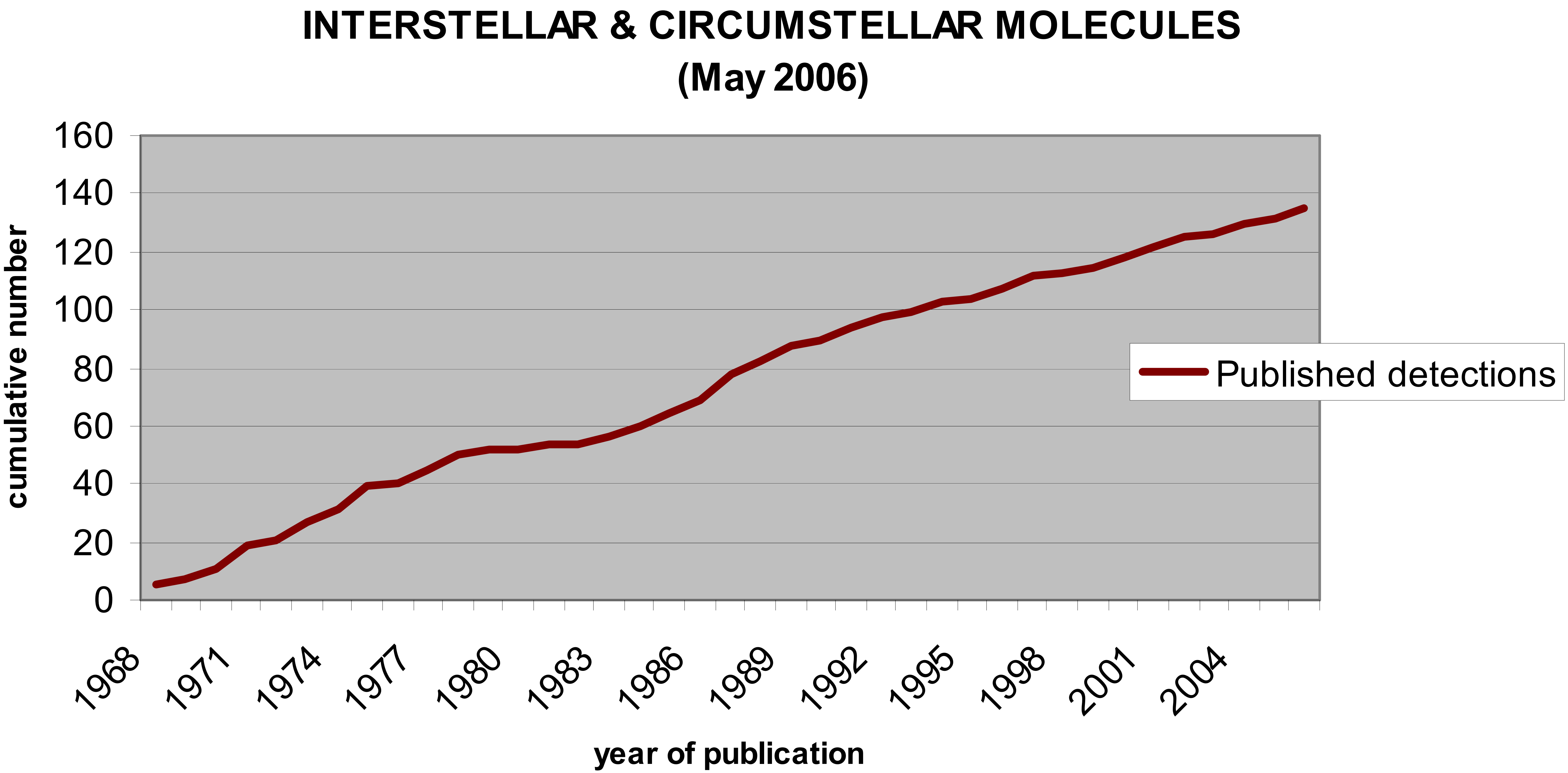






Spectrum depends on physical conditions and distribution of molecules

History of molecules in space

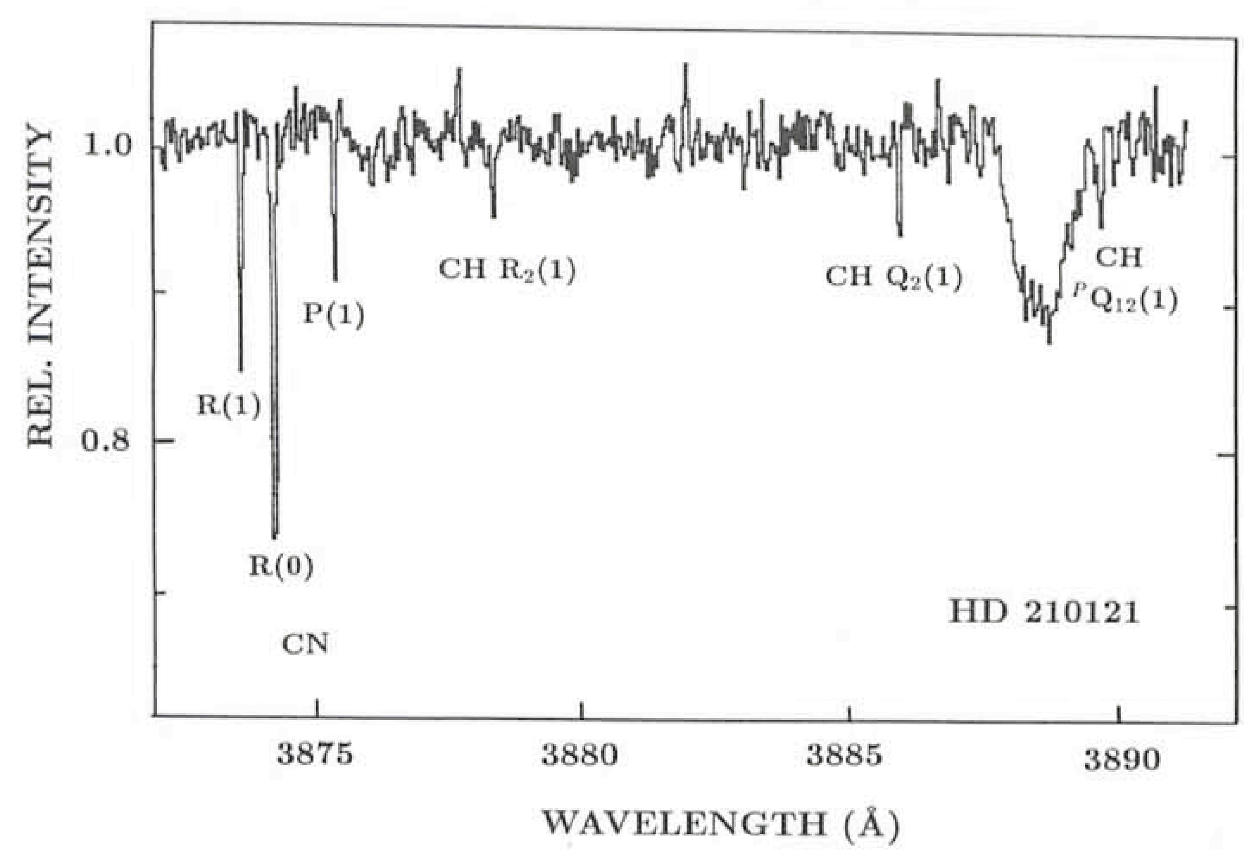


M. Guelin, Nobel Symposium, June 2006

History of molecules in space

- Diffuse Interstellar Bands (DIBs), optical:
  - Discovered by Heger (1922) and Merill (1934):
  - Remains unidentified (polyaromatic hydrocarbons?)

- Absorption bands (optical):
  - CH: Swings & Rosenfeld (1937)
  - CN: McKellar (1940)
  - CH^+: Douglas & Herzberg (1941)



- First theory by Bates and Spitzer (1951), Herbst & Klemperer (1973)

History of molecules in space

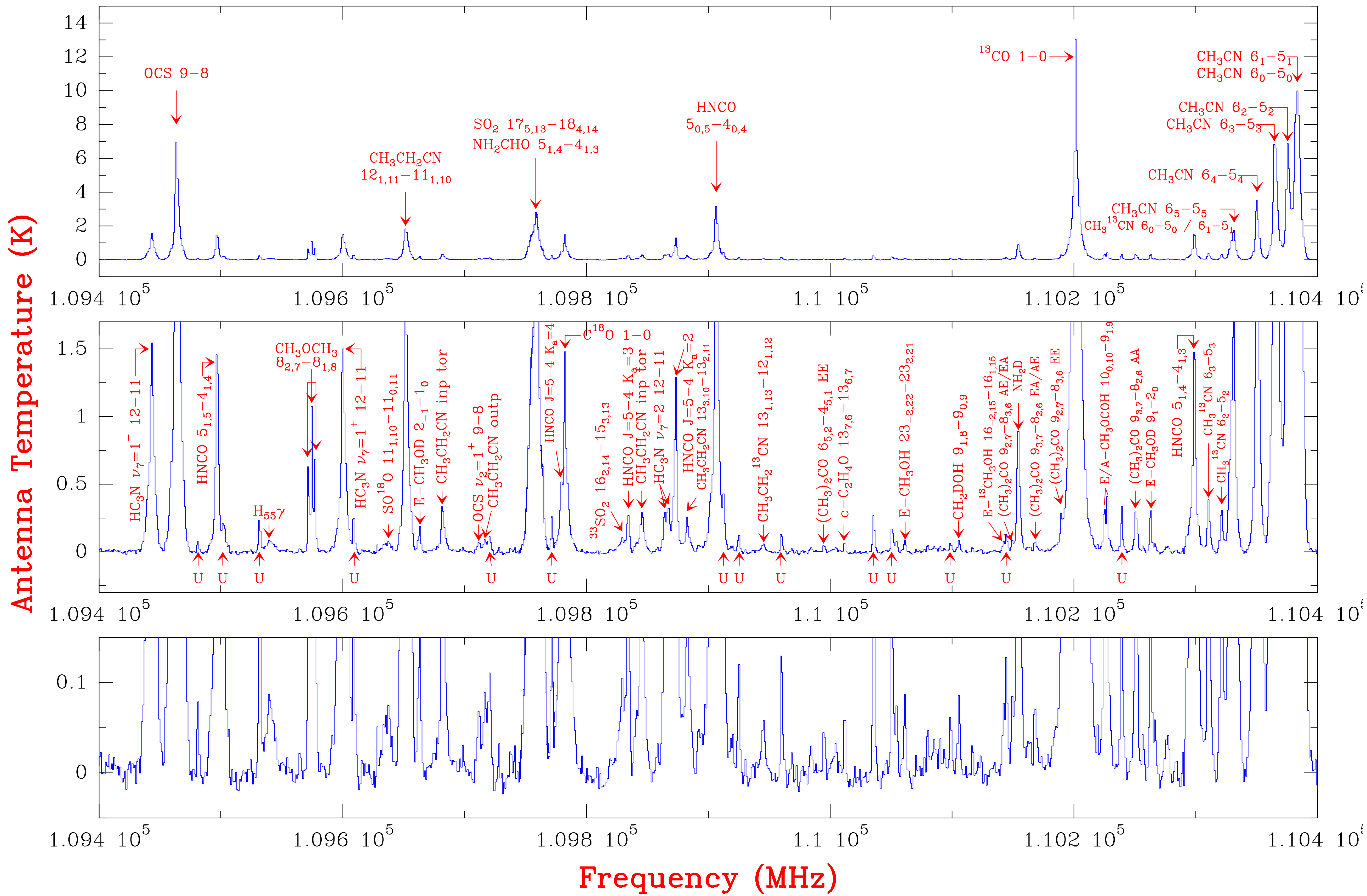
- Radio telescopes:
  - H 21 cm: Ewen & Purcell (1951)
  - OH 18 cm: Weinreb et al. (1963)
  - NH_3 1 cm: Cheung, Townes et al. (1968)
  - H_2O 1 cm: Cheung et al. (1969)

- UV telescopes: Copernicus (1970): H_2 at ~125nm (1970), later N_2

- (Sub-)millimeter telescopes: CO at 115 GHz (1970), H_2CO (1970), and many others

Pause

Orion KL Survey, 3 mm, IRAM 30-m



Tercero et al. (2010)

History of molecules in space

- IR telescopes:
  - **IRAS** (1983): 0.6 m, 12–100 μm, first sky survey, warm dust

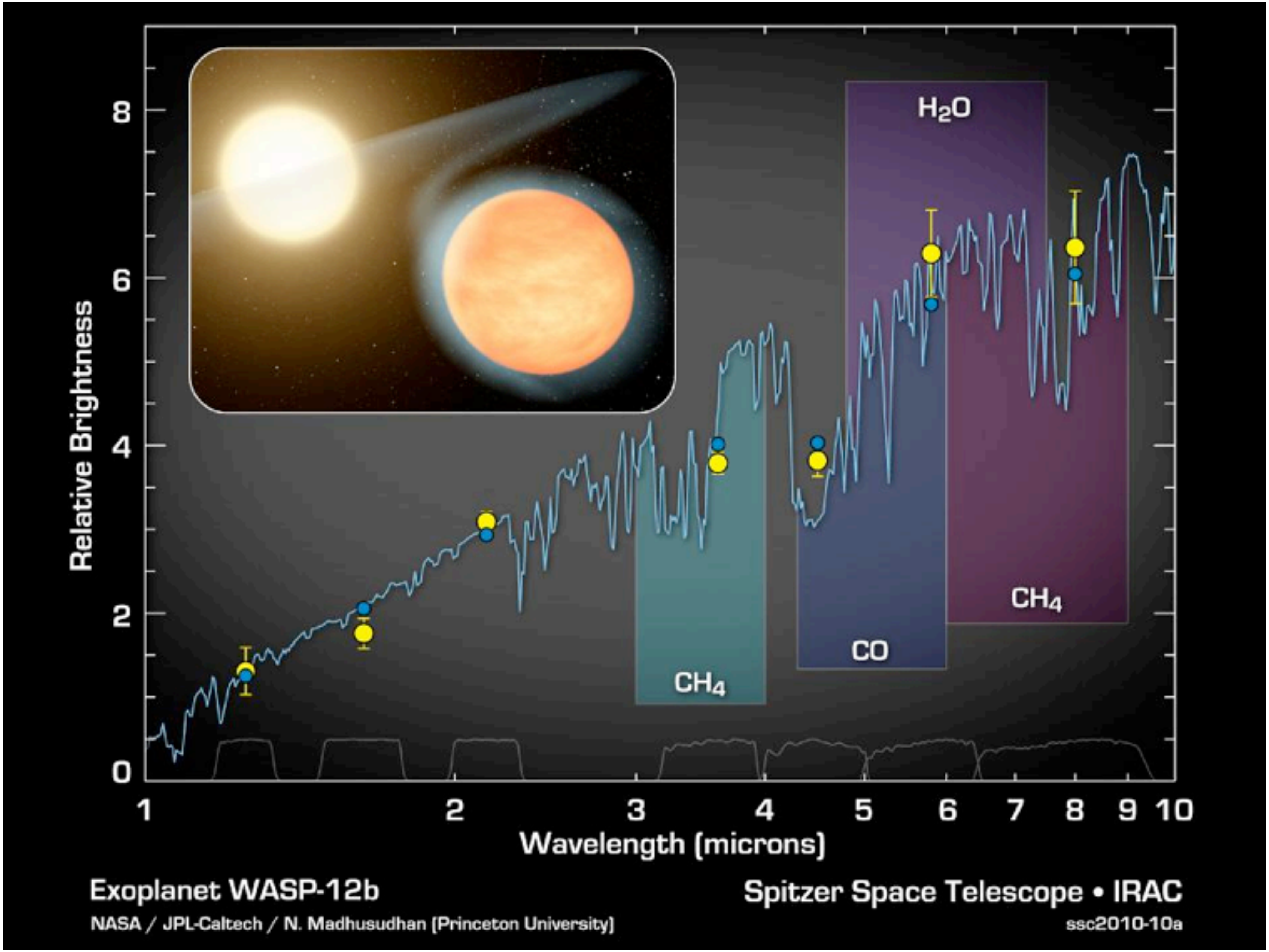
  - **Infrared Space Observatory** (1995–1998): 0.6 m, 2.5–240 μm, molecules and ices

  - **Spitzer Space Telescope** (2003–2009): 0.8 m, 3–180 μm, high-sensitivity imaging, molecules and ices

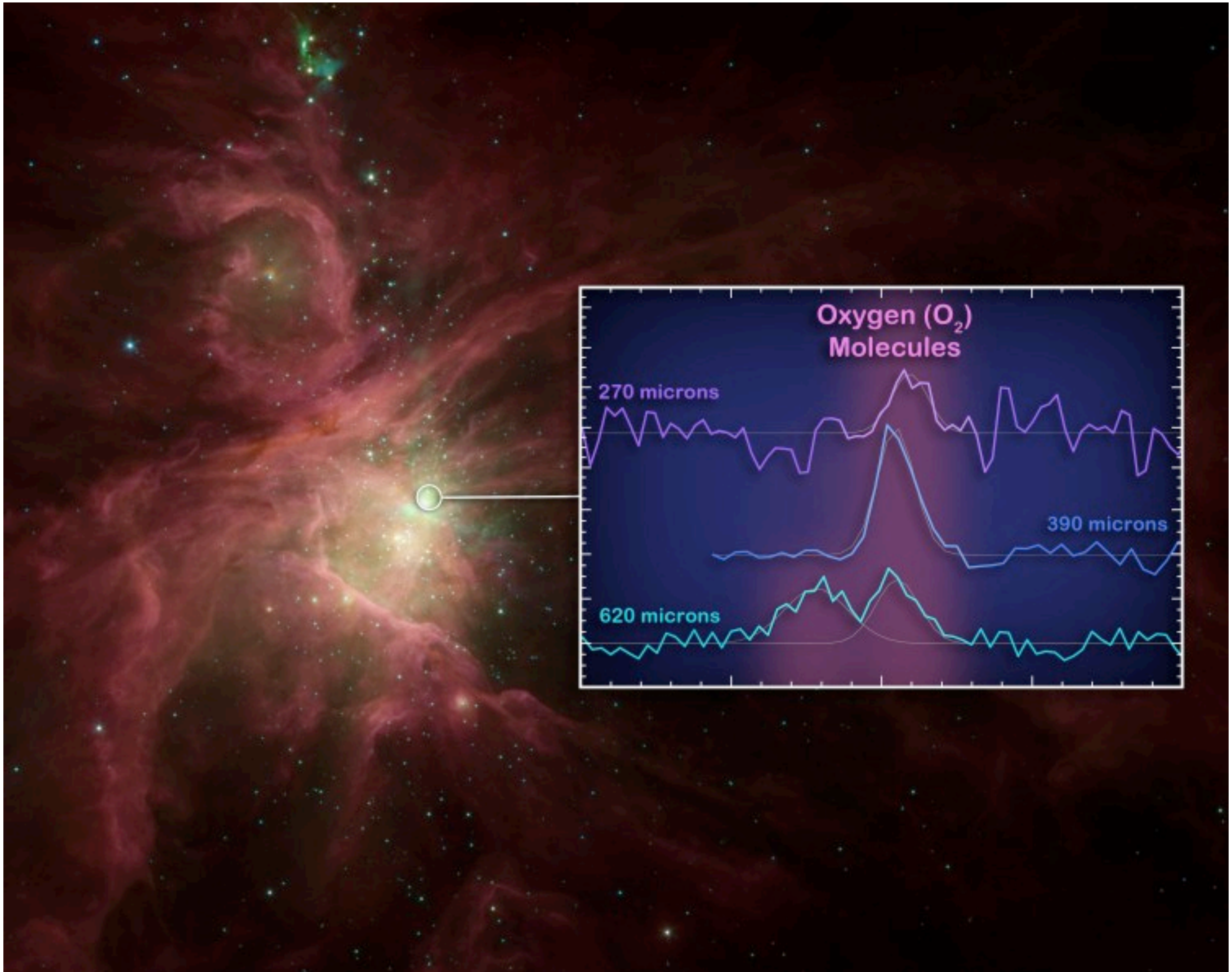
  - **Herschel Space Observatory** (2009–201X): 2.4 m, 60–670 μm, high-sensitivity imaging, molecules and ices

  - Ground-based telescopes: Keck, Very Large Telescope, ...

Molecules, exoplanet WASP-12b, Spitzer



O_2 in Orion, 487–1121 GHz, Herschel



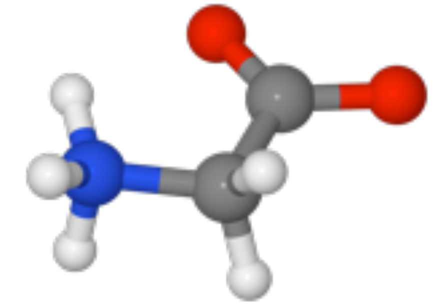
Goldsmith et al. (2011)

Detected molecules (~170)

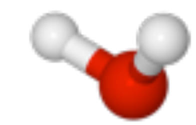
H2	**H3+**	CH3	CH4	CH3OH	CH3NH2	HCOOCH3	(CH3)2O	(CH3)2CO
CO	CH2	NH3	CH2NH	CH3SH	CH3CCH	CH3C3N	C2H5OH	CH3C5N
CS	NH2	**H3O+**	**H2CCC**	C2H4	CH3CHO	HC6H	C2H5CN	CH3CH2CHO
CN	H2O	H2CO	c-C3H2	CH3CN	c-CH2OCH2	**C7H**	CH3C4H	(CH2OH)2
C2	H2S	H2CS	CH2CN	CH3NC	CH2CHCN	HOCH2CHO	**C8H**	HCOOC2H5
CH	**CCH**	c-C3H	NH2CN	CH2CHO	**HC5N**	CH3COOH	**HC7N**	**HC9N**
CH+	**HCN**	**l-C3H**	CH2CO	NH2CHO	**C6H**	H2CCCHCN	CH3CONH2	CH3C6H
HF	HNC	C2H2	HCOOH	HC3NH+	CH2CHOH	**H2C6**	CH3CHCH2	C6H6
CF+	HCO	**HCNH+**	**C4H**	**H2CCCC**	**C6H-**	CH2CHCHO	**C8H-**	C3H7CN
SiO	**HCO+**	H2CN	**HC3N**	**C5H**		NH2CH2CN		**HC11N**
SiS	**HOC+**	HCCN	HCCNC	HC4H				C2H5OCH3
SiC	**N2H+**	HNCO	HNCCC	HC4N				
SiN	HNO	HOCN	**H2COH+**	c-C3H2O				
NH	**HCS+**	HCNO	**C4H-**	CH2CNH				
NO	**C3**	HNCS	SiH4	**C5N-**				
SO	**C2O**	HSCN	**C5**	**C5N**				
SO+	**C2S**	**C3N**	**SiC4**					
CP	SO2	**C3O**	CNCHO					
PO	N2O	**C3S**						
PN	CO2	**C3N-**						
HCl	**H2O+**	**HCO2+**						
KCl	**H2Cl+**	CNCHO						
AlCl	OCS	C-SiC2						
OH	MgNC				AlF	AlNC	AlOH	NaCl
OH+	MgCN				SiNC	CCP	HCP	FeO
SH	NaCN				CO+	O2	N2	
CN-	SiCN							

http://www.astro.uni-koeln.de/cdms/molecules

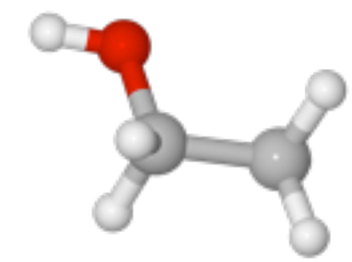
Detected molecules



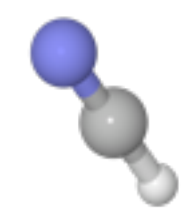
- 41 extragalactic molecules
- 20 positive ions (cations)

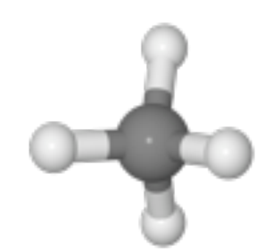


- 6 negative ions (anions)
- ~20 isomers

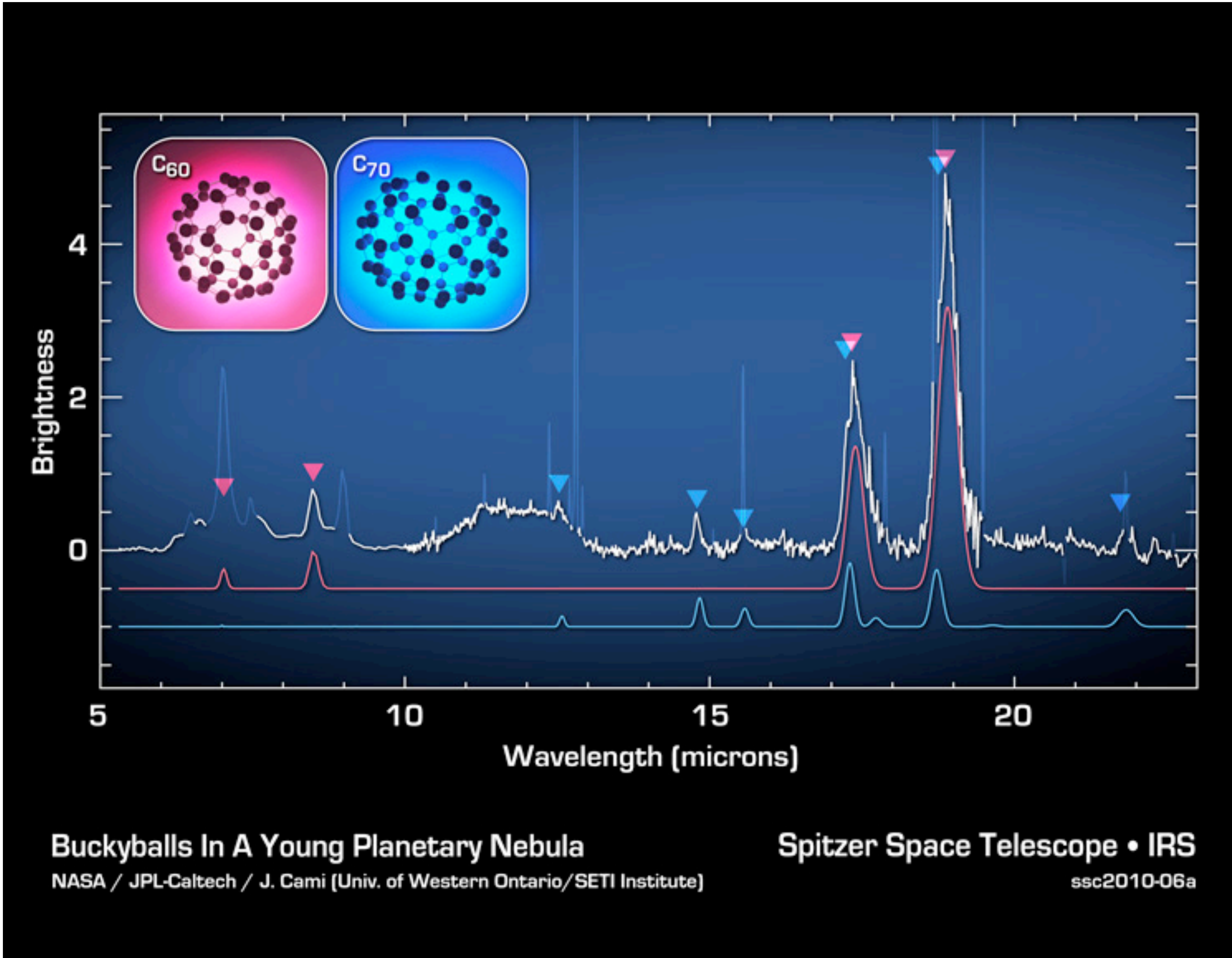


- 6 cyclic species (including benzene, C_6H_6)





Detection of fullerenes (C_{60} & C_{70})



Radiative Association: bond formation

$H + C \Rightarrow CH^*$

$CH^* \Rightarrow CH + h\nu$

or (more likely)

$CH^* \Rightarrow C + H$

- Formation of a excited collisional complex

- Energy conservation => emission of photon

A key process to form first molecules & chemical bonds (early Universe)

$k \approx 10^{-17}\text{-}10^{-12}\ cm^3 s^{-1}$

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

Radiative Association: bond formation

Timescales:

10^{-2} s - vibrational transition,

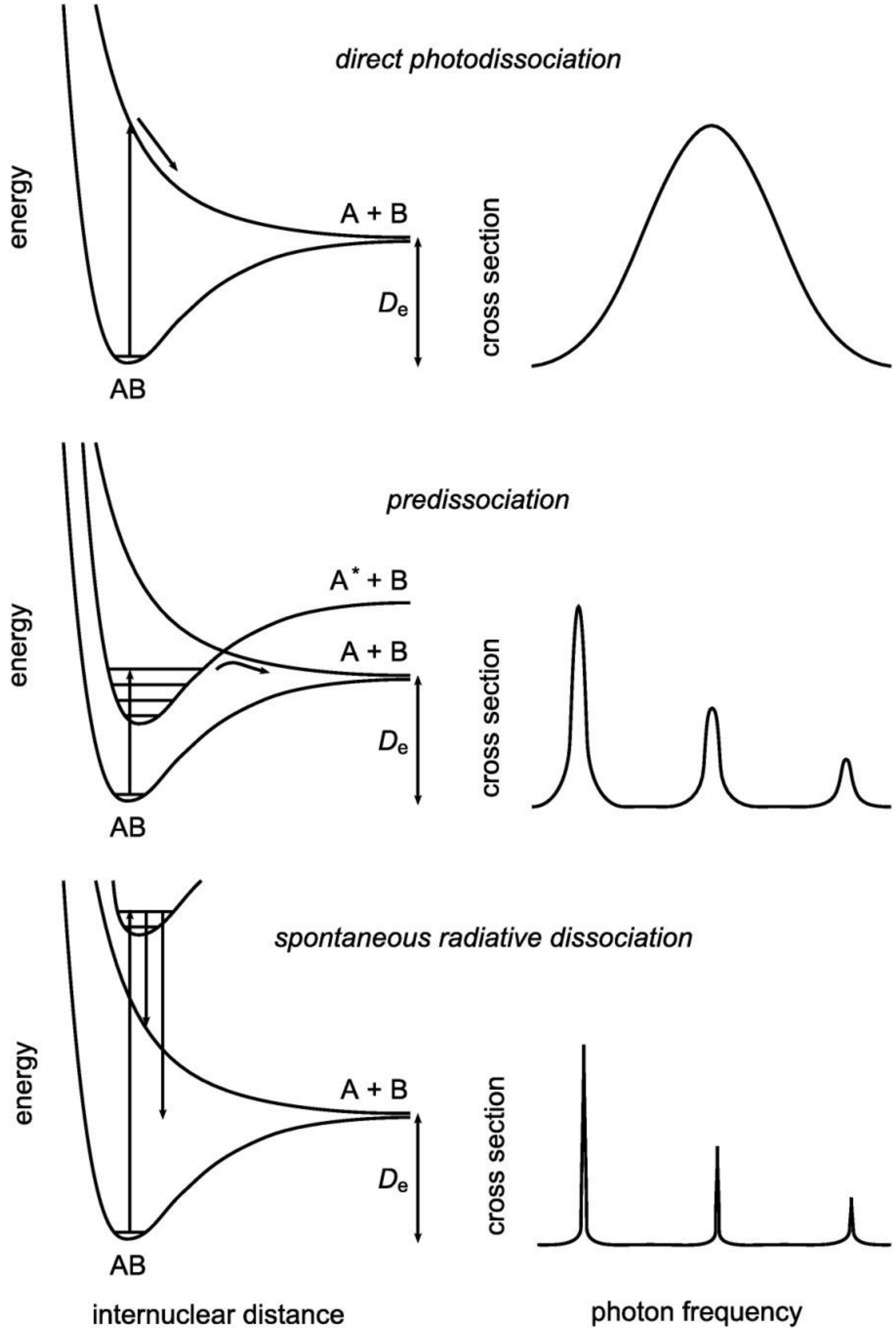
10^{-8} s - electronic transition,

10^{-13} s - collision timescale

=> molecule forms after ~10^{11} collisions (10^{5} if electronic transitions are available)!

- Slow for small reactants, but can be rapid for complex radicals
- Hard to measure in laboratory (3-body processes dominate)
- Hard to calculate for complex species

Photodissociation: bond destruction



Examples:

H_2O, OH, CH_4...

CO

Only H_2

Cosmic Ray, X-ray, UV Ionization

$H_2 + CRP/h\nu \Rightarrow H_2^+ + e^-$

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

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

From observations:

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

- Relativistic energy particles (89% protons, 10% ^4He, 1% heavy elements)
- Can penetrate in heavily obscured regions
- **Produce H_3^+**
- **Produce He^+**: I.P. of He is 24.6 eV $\Rightarrow$

He^+ breaks chemical bonds (also CO)

Ion-Molecule Reactions: bond rearrangement

$H_3^+ + CO \Rightarrow$

$H_2 + HCO^+$

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

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

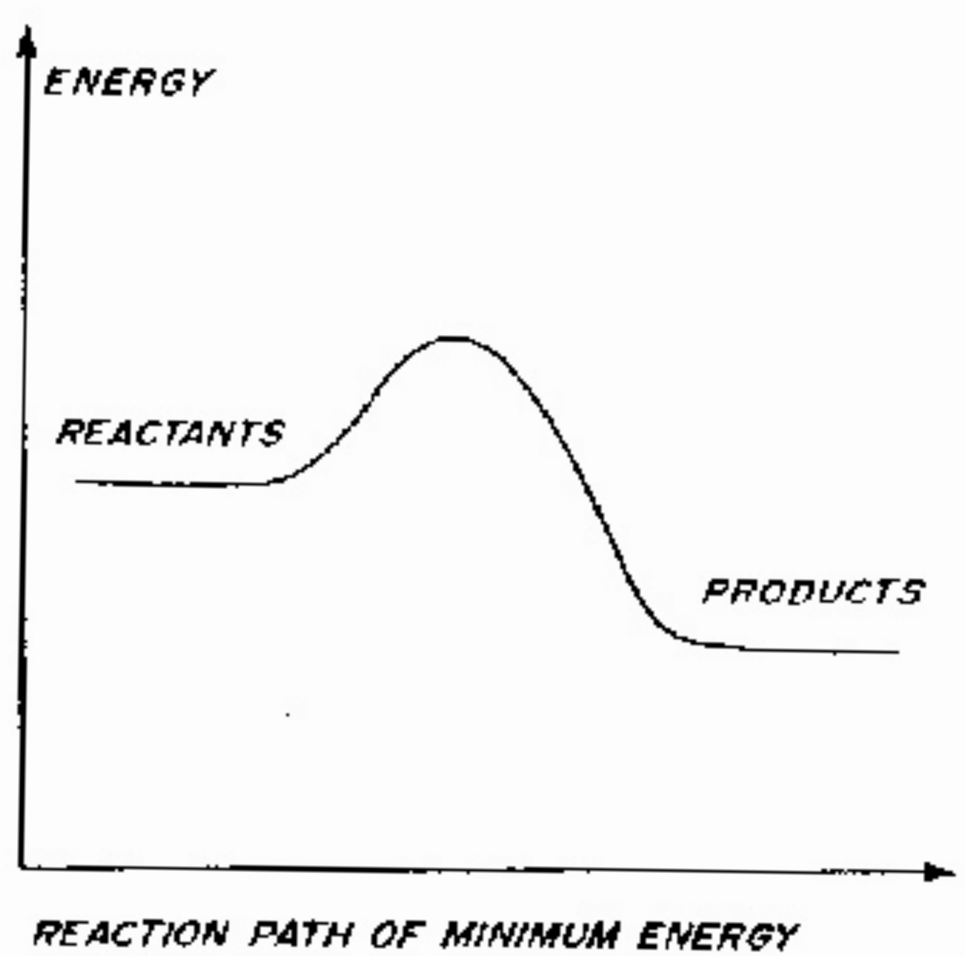
Ion induces dipole moment => long-range Coloumb attraction

- **Key reactions to form molecules**
- **~50% of all processes in astrochemical models**

Neutral-Neutral Reactions: bond rearragement

$N + CH \Rightarrow CN + H$

$N + CH_3 \Rightarrow HCN + H_2$



- Long-range attraction is weak
- Usually have barriers due to bond breaking for molecular rearrangement
- Many barriers are 'guessed' values, ~100-1000 K
- Some are rapid even at ~ 10 K
- **Particularly competitive at high temperatures, >100 K**

$k \approx <10^{-11}–10^{-9}\ cm^3 s^{-1}$

Dissociative Recombination: bond destruction

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

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

$OH + 2H$

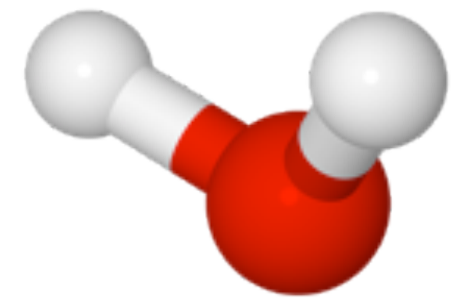
$k \approx 10^{-7}\ cm^3 s^{-1}$

- Capture of e^- by an ion => formation of neutral in excited electronic state => dissociation
- Rapid processes, increased rates at low temperatures
- If radiative (no break-up), then usually slow
- Branching ratios and products are not well known

A final step in formation of neutral species

Formation of water

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



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

$H_3^+ \;+ O \Rightarrow OH^+ \;+\; H_2$

$OH^+ \;+\; H_2 \Rightarrow H_2O^+ \;+\; H$

$H_2O^+ \;+\; H_2 \Rightarrow H_3O^+ \;+\; H$

$H_3O^+ \;+\; e^- \Rightarrow H_2O + H$ or $OH + 2H$ or $OH + H_2$

Formation of complex molecules

$C^+ + H_2 \Rightarrow CH_2^+$

$CH_2^+ + H_2 \Rightarrow CH_3^+ + H$

$CH_3^+ + H_2/O \Rightarrow CH_5^+/HCO^+ + H_2$

$CH_5^+ + e- \Rightarrow CH_3 + H_2$

$CH_3 + O \Rightarrow H_2CO$

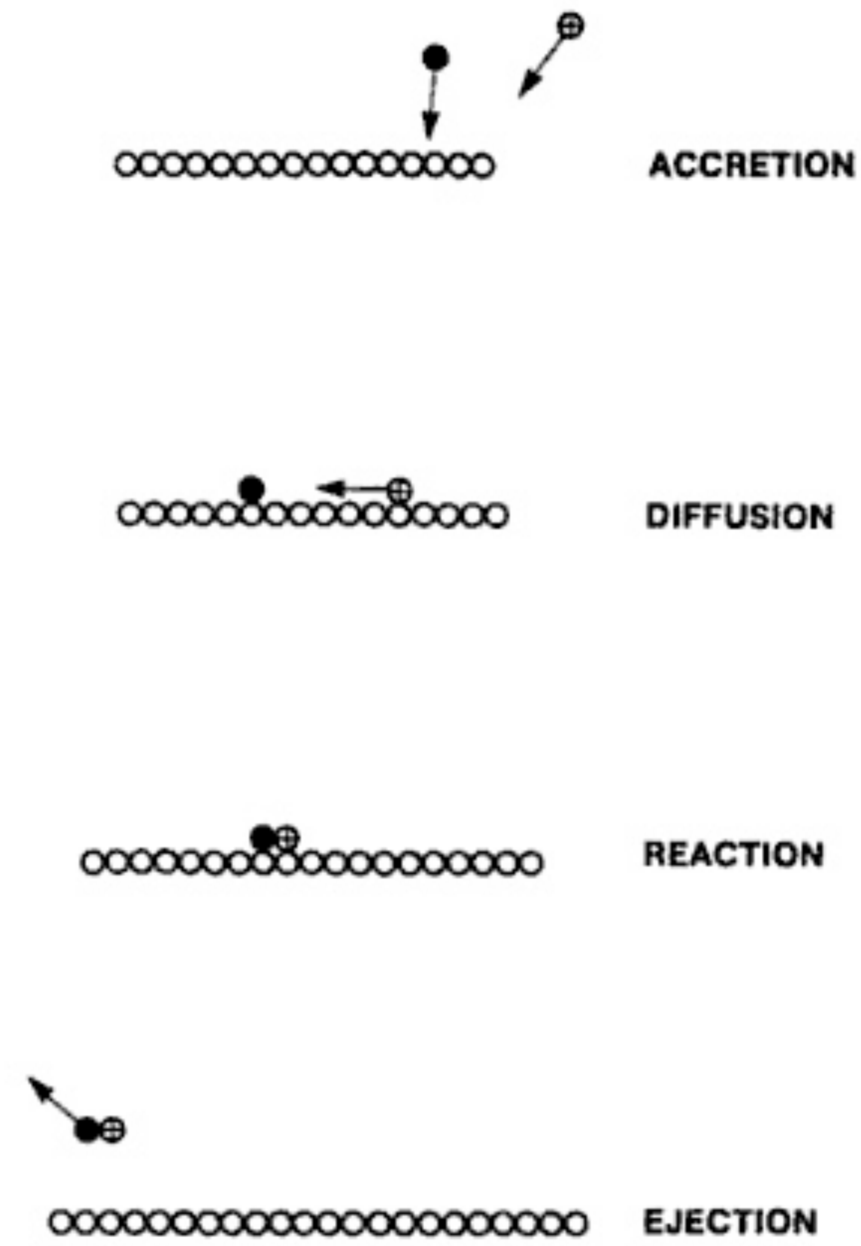
$CH_3^+ + H_2O \not\Rightarrow CH_3OH_2^+$ (too low rate, Luca et al. 2002)

$CH_3OH_2^+ + e- \Rightarrow CH_3OH + H$ (3 ± 2%, Geppert et al. 2006)

Chemistry on surfaces of dust grains

Surface formation of complex molecules

- Accretion
- Diffusion over the surface
- Recombination
- Desorption back to gas



$\mathbf{H + H \Rightarrow H_2}$

$O + H \Rightarrow OH + H \Rightarrow H_2O$

$N + H \Rightarrow NH + H \Rightarrow NH_2 + H \Rightarrow NH_3$

$C + H \Rightarrow CH + H \Rightarrow CH_2 + H \Rightarrow CH_3 + H \Rightarrow CH_4$

$CO + H \Rightarrow HCO + H \Rightarrow H_2CO + H \Rightarrow H_3CO + H \Rightarrow CH_3OH$

Chemical Reaction Databases

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

- **Manchester University (UMIST):**
  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, 5000 reactions, 450 species, 12 elements

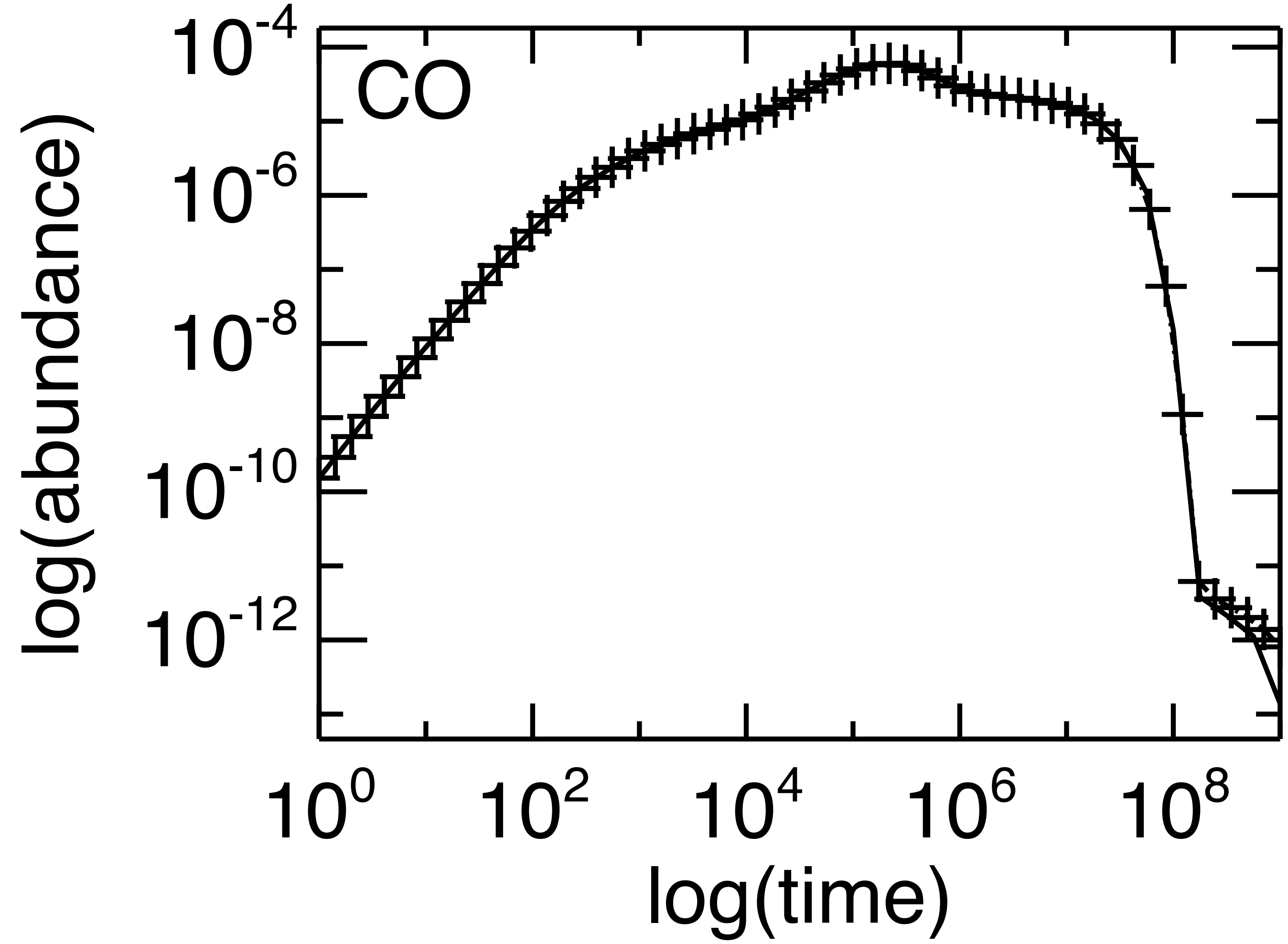
Only ~10-20% of accurate rates!

Courtesy of Eric Herbst

Computational Chemistry

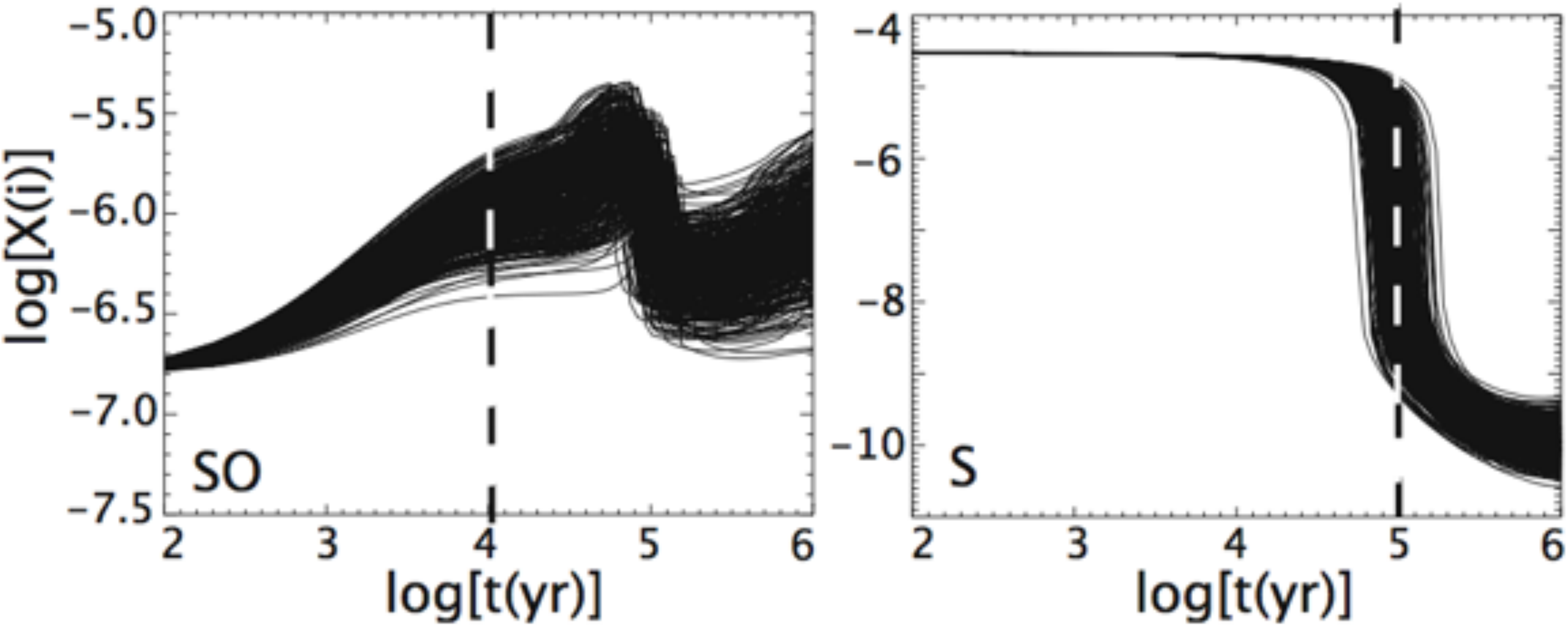
$$\frac{\partial n_i}{\partial t} = \sum_{j,k \neq i} k_{jk} n_j n_k - n_i \sum_l k_l n_l$$

- Physical conditions
- Initial abundances
- Chemical network
- ODE solver



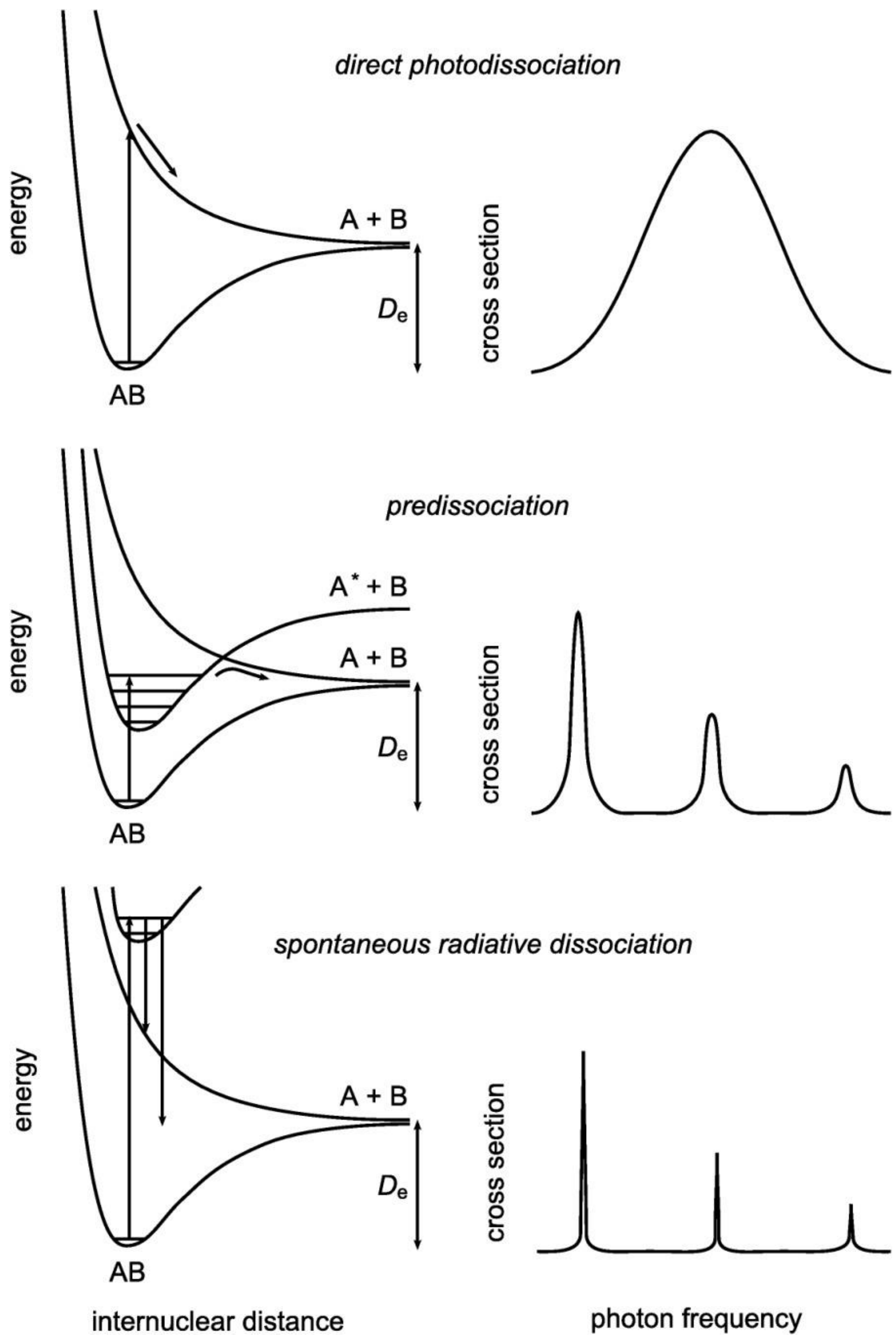
1 run takes ~1 s on a modern CPU

Abundances are uncertainties



Modeled abundances are uncertain by factors of 2–10

Photodissociation: bond destruction



- Direct dissociation: transition to a continuum of excited electronic state
- Predissociation: excited electronic state is mixed with dissociative state
- Spontaneous radiative dissociation: sometimes electronic excited states decay into continuum of the ground-state