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Radiative transfer: molecular physics

Benjamin Godard

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(diatomic) Molecular physics

International Research Track

2023

Outline

- introduction
- energy structure
- molecular lines
- photo-processes
- conclusion

1. Introduction

2. Energy structure

Born-Oppenheimer

Vibration / rotation

Additional couplings

3. Molecular lines

Dipole transitions

Quadrupole transitions

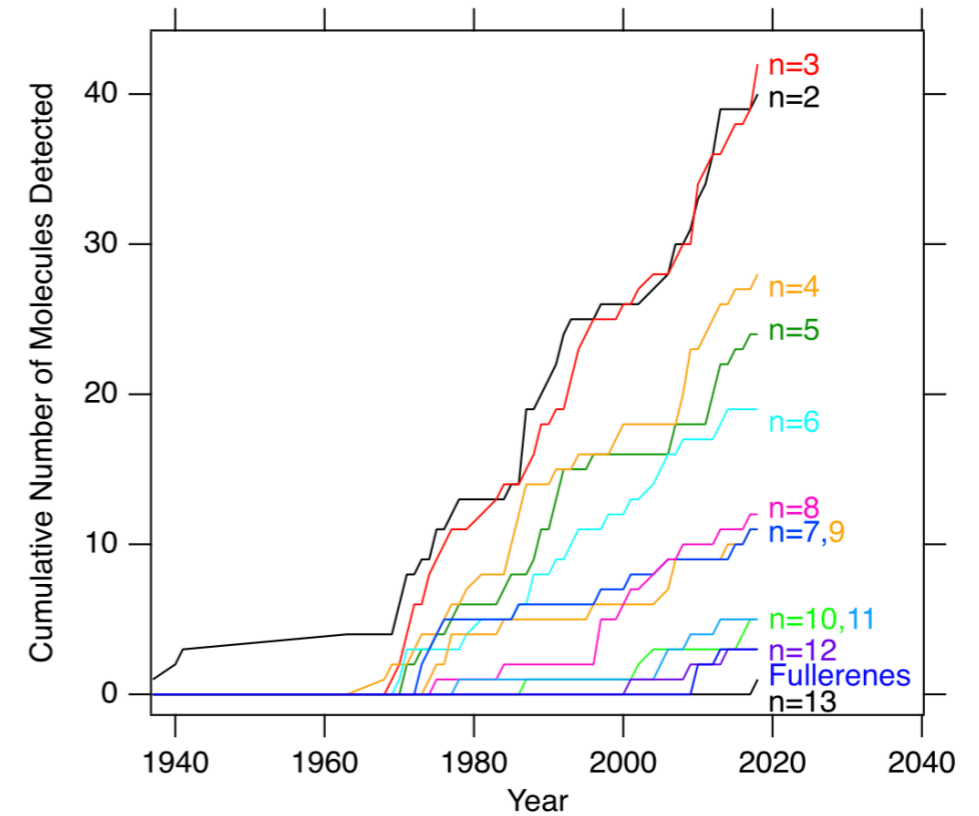
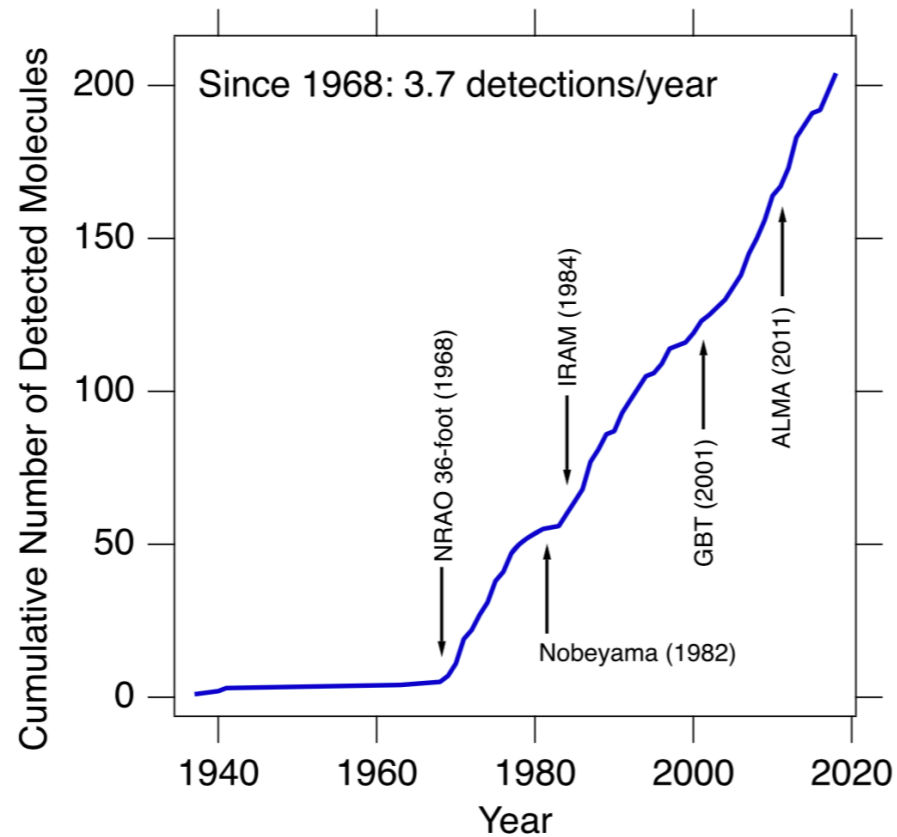
4. Photo-processes

5. Conclusions

Molecules are ubiquitous in astrophysics

Outline

- introduction
- energy structure
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- photo-processes
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B. McGuire (2018)

In summary, in 2018

- 204 individual molecular species
- comprised of 16 different elements
- composed of 2 to 70 atoms
- detected from tens-cm wavelength to ultraviolet

Molecules are ubiquitous in astrophysics

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Table 2
List of Detected Interstellar Molecules with Two to Seven Atoms, Categorized by Number of Atoms, and Vertically Ordered by Detection Year

2 Atoms		3 Atoms		4 Atoms	5 Atoms	6 Atoms	7 Atoms
CH	CP	H ₂ O	N ₂ O	NH ₃	HC ₃ N	CH ₃ OH	CH ₃ CHO
CN	NH	HCO ⁺	MgCN	H ₂ CO	HCOOH	CH ₃ CN	CH ₃ CCH
CH ⁺	SIN	HCN	H ₃ ⁺	HNCO	CH ₂ NH	NH ₂ CHO	CH ₃ NH ₂
OH	SO ⁺	OCS	SiCN	H ₂ CS	NH ₂ CN	CH ₃ SH	CH ₂ CHCN
CO	CO ⁺	HNC	AlNC	C ₂ H ₂	H ₂ CCO	C ₂ H ₄	HC ₅ N
H ₂	HF	H ₂ S	SiNC	C ₃ N	C ₄ H	C ₅ H	C ₆ H
SiO	N ₂	N ₂ H ⁺	HCP	HNCS	SiH ₄	CH ₃ CN	c-C ₂ H ₄ O
CS	CF ⁺	C ₂ H	CCP	HOCO ⁺	c-C ₃ H ₂	HC ₂ CHO	CH ₂ CHOH
SO	PO	SO ₂	AlOH	C ₃ O	CH ₂ CN	H ₂ C ₆	C ₆ H ⁻
SiS	O ₂	HCO	H ₂ O ⁺	l-C ₃ H	C ₅	C ₅ S	CH ₃ NCO
NS	AlO	HNO	H ₂ Cl ⁺	HCNH ⁺	SiC ₄	HC ₃ NH ⁺	HC ₅ O
C ₂	CN ⁻	HCS ⁺	KCN	H ₃ O ⁺	H ₂ CCC	C ₅ N	
NO	OH ⁺	HOC ⁺	FeCN	C ₃ S	CH ₄	HC ₄ H	
HCl	SH ⁺	SiC ₂	HO ₂	c-C ₃ H	HCCNC	HC ₄ N	
NaCl	HCl ⁺	C ₂ S	TiO ₂	HC ₂ N	HNCCC	c-H ₂ C ₃ O	
AlCl	SH	C ₃	CCN	H ₂ CN	H ₂ COH ⁺	CH ₂ CNH	
KCl	TiO	CO ₂	SiCSi	SiC ₃	C ₄ H ⁻	C ₅ N ⁻	
AlF	ArH ⁺	CH ₂	S ₂ H	CH ₃	CNCHO	HNCHCN	
PN	NS ⁺	C ₂ O	HCS	C ₃ N ⁻	HNCNH	SiH ₃ CN	
SiC		MgNC	HSC	PH ₃	CH ₃ O		
		NH ₂	NCO	HCNO	NH ₃ D ⁺		
		NaCN		HOCN	H ₂ NCO ⁺		
				HSCN	NCCNH ⁺		
				HOOH	CH ₃ Cl		
				l-C ₃ H ⁺			
				HMgNC			
				HCCO			
				CNCN			

Table 3
List of Detected Interstellar Molecules with Eight or More Atoms, Categorized by Number of Atoms, and Vertically Ordered by Detection Year

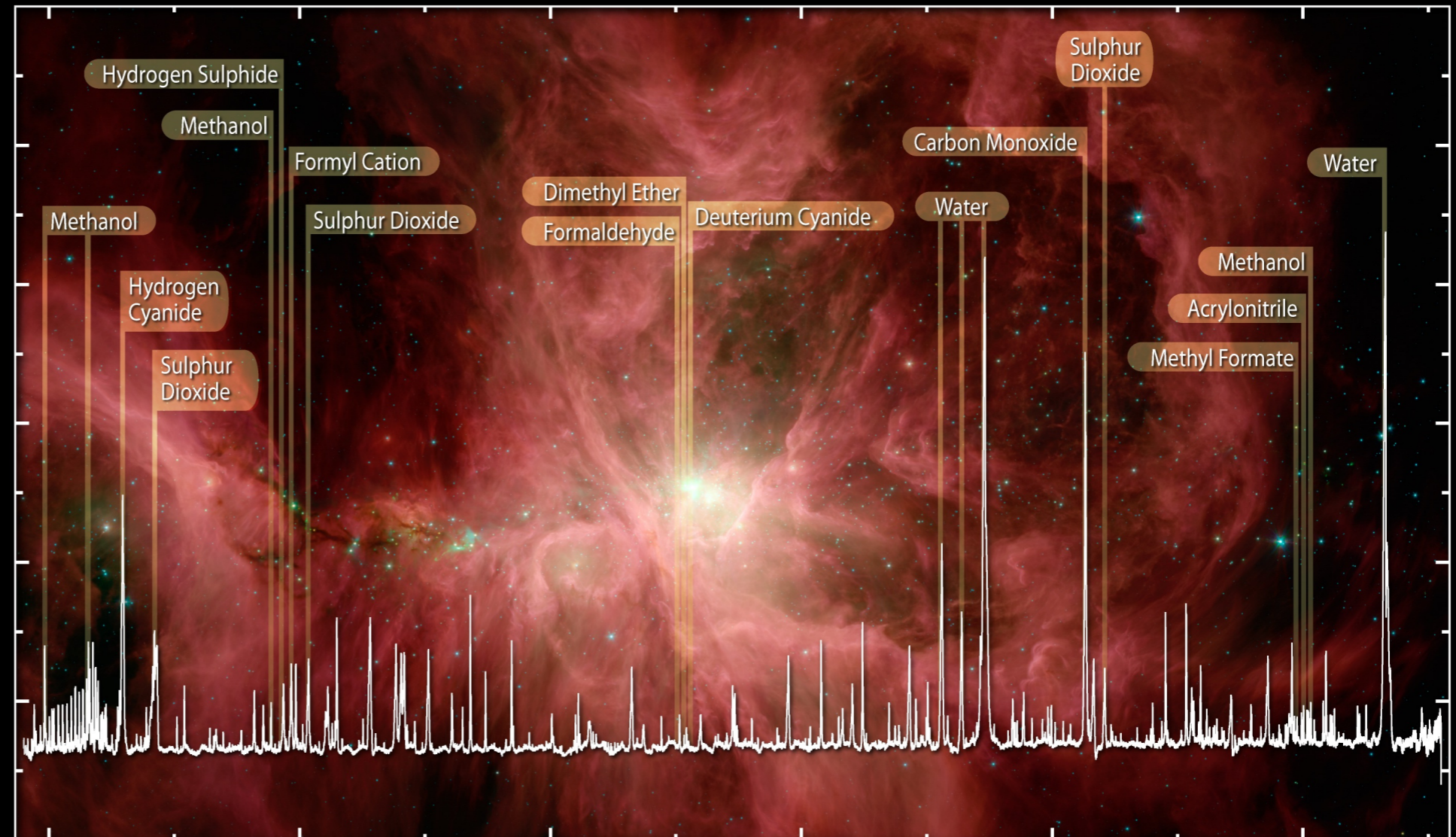
8 Atoms	9 Atoms	10 Atoms	11 Atoms	12 Atoms	13 Atoms	Fullerenes
HCOOCH ₃	CH ₃ OCH ₃	(CH ₃) ₂ CO	HC ₉ N	C ₆ H ₆	c-C ₆ H ₅ CN	C ₆₀
CH ₃ C ₃ N	CH ₃ CH ₂ OH	HO(CH ₂) ₂ OH	CH ₃ C ₆ H	n-C ₃ H ₇ CN		C ₆₀ ⁺
C ₇ H	CH ₃ CH ₂ CN	CH ₂ CH ₂ CHO	CH ₃ CH ₂ OCHO	i-C ₃ H ₇ CN		C ₇₀
CH ₃ COOH	HC ₇ N	CH ₃ C ₅ N	CH ₃ COOCH ₃			
H ₂ C ₆	CH ₃ C ₄ H	CH ₃ CHCH ₂ O				
CH ₂ OHCHO	C ₈ H	CH ₃ OCH ₂ OH				
HC ₆ H	CH ₃ CONH ₂					
CH ₂ CHCHO	C ₈ H ⁻					
CH ₂ CCHCN	CH ₂ CHCH ₃					
NH ₂ CH ₂ CN	CH ₃ CH ₂ SH					
CH ₃ CHNH	HC ₇ O					
CH ₃ SiH ₃						

B. McGuire (2018)

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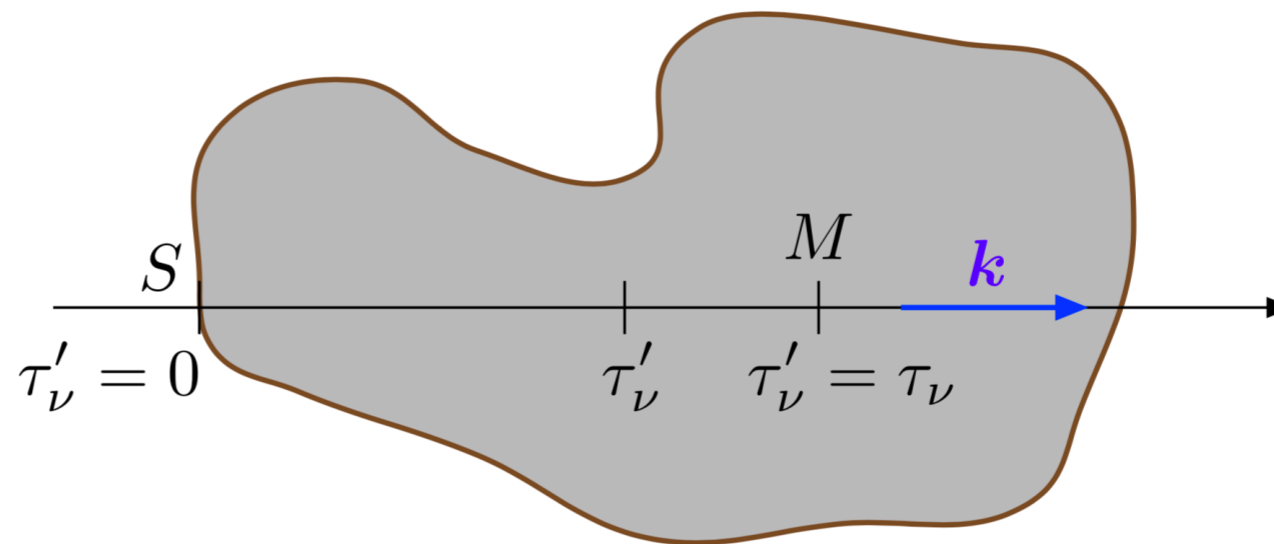
HIFI Spectrum of Water and Organics in the Orion Nebula

© ESA, HEXOS and the HIFI consortium
E. Bergin

Radiative transfer equation

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F. Levrier - radiative transfer lecture

$$\frac{dI_\nu}{dl} = -[\alpha_\nu + \sigma_\nu] I_\nu + j_\nu + \frac{1}{4\pi} \int_{\Omega'} \tilde{\sigma}_\nu(\mathbf{k}' \rightarrow \mathbf{k}) I_\nu(\mathbf{k}') d\Omega'$$

- absorption coefficient $\alpha_\nu = \sum_a n_a s_{\nu,a}$ cm^{-1}
- diffusion coefficient $\sigma_\nu = \sum_d n_d s_{\nu,d}$ cm^{-1}
- emissivity j_ν $\text{erg s}^{-1} \text{cm}^{-3} \text{Hz}^{-1} \text{sr}^{-1}$
- opacity $d\tau_\nu = [\alpha_\nu + \sigma_\nu] dl$
- source function S_ν $\text{erg s}^{-1} \text{cm}^{-2} \text{Hz}^{-1} \text{sr}^{-1}$

Questions related to molecules in radiative transfer

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through which processes do molecules interact with light ?

- absorption / emission
- polarization
- dissociation / ionization / fluorescence

what are the properties of the microphysical processes ?

- transitions (energy structure / selection rules)
- interaction cross sections
- products of ionization and dissociation

how to implement these processes in radiative transfer codes ?

- what data are required ?
- couplings expected ?
- analytical considerations & numerical methods

Outline

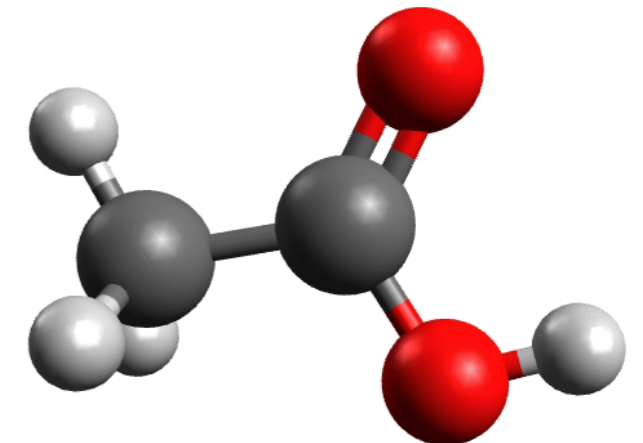
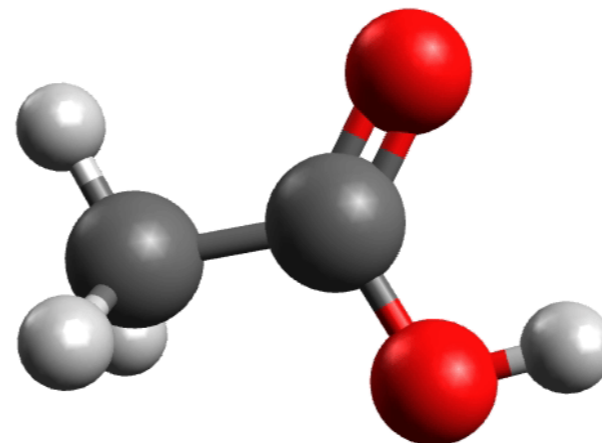
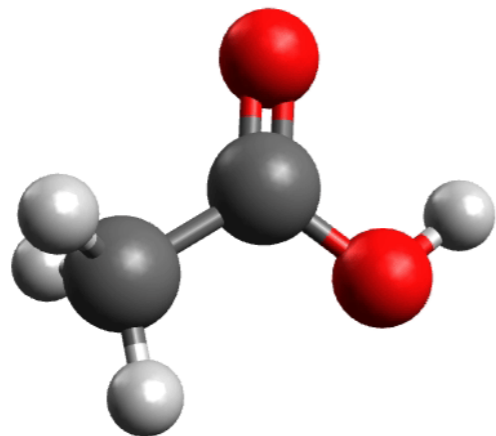
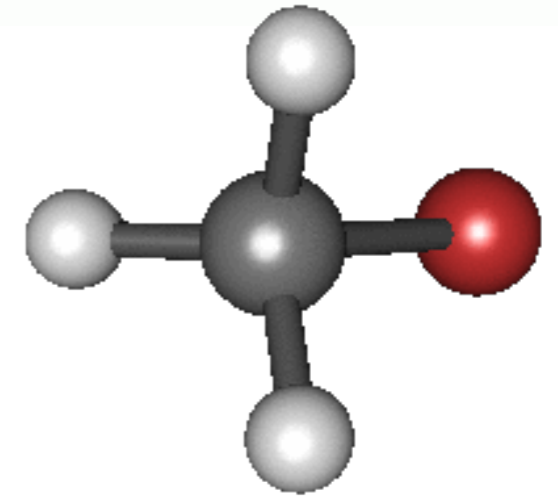
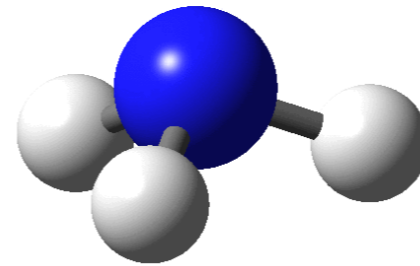
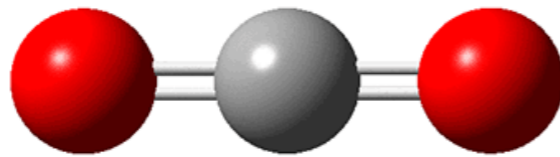
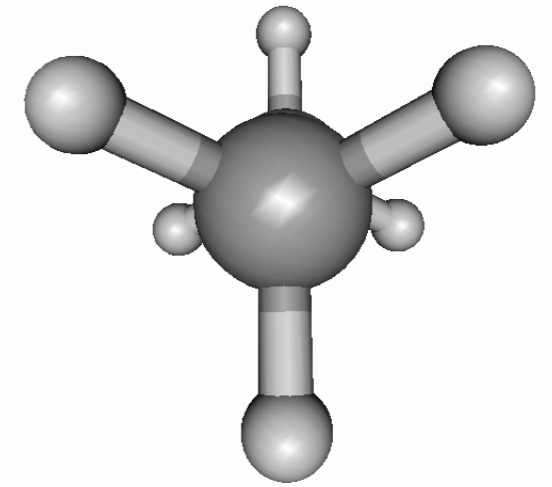
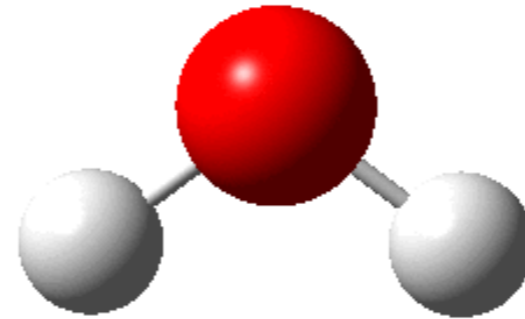
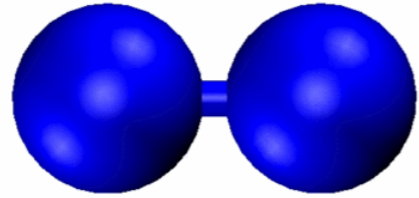
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Energy structure of molecules

Complexity of the task

Outline

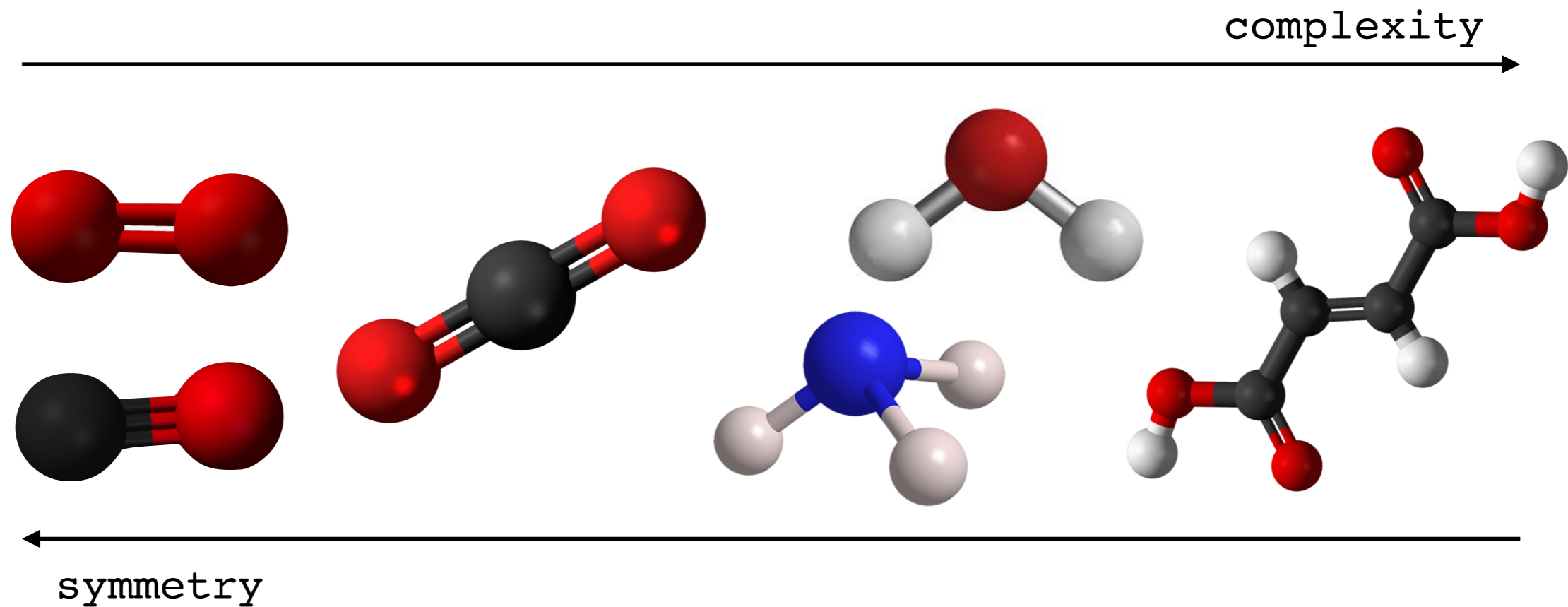
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Complexity of the task

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Compared to atomic energy structure

- less symmetry, complicated electronic wavefunctions
- nuclei move, additional freedom, rotational and vibrational motions

Focus on diatomic (homonuclear or heteronuclear)

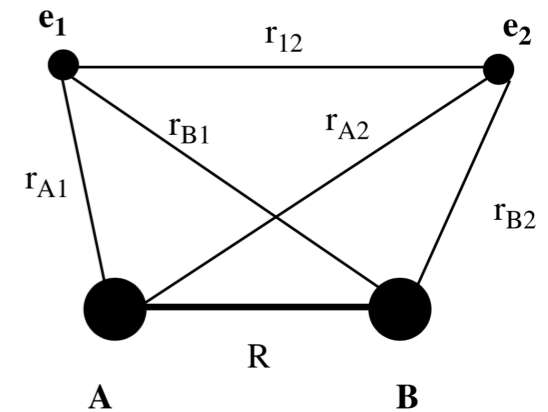
- gives a strong foothold to understand molecular spectra

Stationary states and usual hypothesis

Stationary Schrödinger equation for diatomic molecules

$$\left(-\frac{\hbar^2}{2M_A} \nabla_A^2 - \frac{\hbar^2}{2M_B} \nabla_B^2 - \frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_i^2 + V_e - E \right) \psi(\mathbf{R}_A, \mathbf{R}_B, \mathbf{r}_i) = 0$$

$$V_e = \frac{e^2}{4\pi\epsilon_0} \left(-\sum_{i=1}^N \frac{Z_A}{r_{Ai}} - \sum_{i=1}^N \frac{Z_B}{r_{Bi}} + \sum_{i=2}^N \sum_{j=1}^{i-1} \frac{1}{r_{ij}} + \frac{Z_A Z_B}{R} \right)$$



Usual simplifications & hypothesis

→ Born-Oppenheimer

$$\psi(\mathbf{R}_A, \mathbf{R}_B, \mathbf{r}_i) = \psi_e(\mathbf{r}_i) \psi_n(\mathbf{R}_A, \mathbf{R}_B)$$



→ center of mass frame

$$\psi_n(\mathbf{R}_A, \mathbf{R}_B) \rightarrow \psi_n(\mathbf{R})$$



→ separation vibration - rotation $\psi_n(\mathbf{R}) = \psi_v(R) \psi_r(\theta, \phi)$



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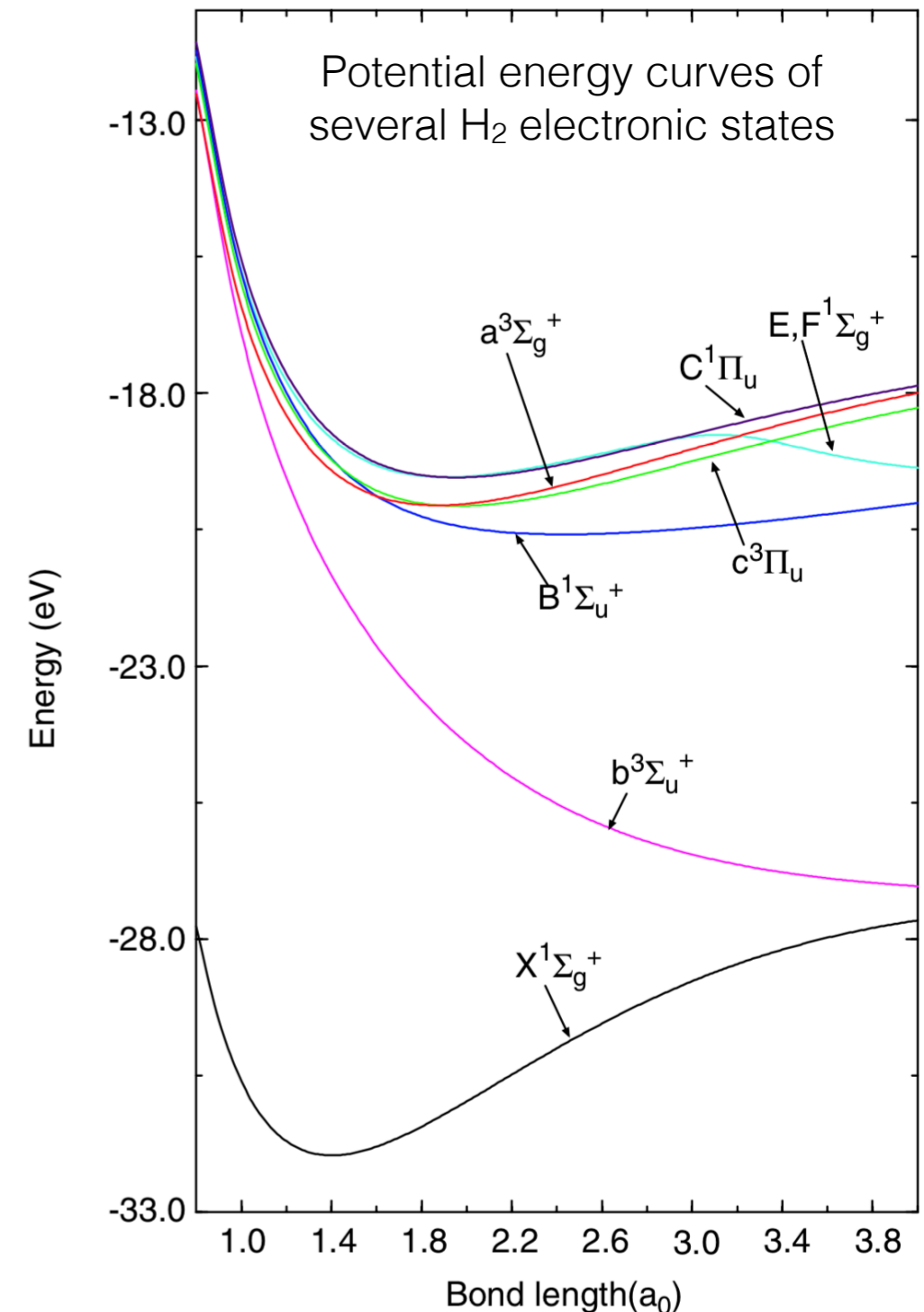
Electronic structure

Stationary Schrödinger equation for electronic wavefunction

$$\left(-\frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_i^2 + V_e - E_e \right) \psi_e(\mathbf{r}_i) = 0$$

- solve at each internuclear separation R
- gives eigenvalue $E_e(R)$
- gives Ψ_e & quantum numbers without couplings
 $S, \Lambda, g/u, +/ -$
- gives potential $V(R)$ seen by nuclei
- gives equilibrium radius & dissociation energy

J. Tennyson (2005)



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Electronic structure

$$\text{letter}^{(2S+1)} \Lambda_{g/u}^{+/-}$$

Labelling of electronic states

$$\longrightarrow S = \sum_i s_i$$

total electronic spin
(careful with paired e⁻ in closed shells)

$$\longrightarrow \Lambda = \left(L = \sum_i l_i \right) |z$$

total angular momentum projected on z

Λ	0	1	2	3	4	...
states	Σ	Π	Δ	Φ	Γ	...

$$\longrightarrow g/u \text{ (gerade/ungerade)}$$

parity upon nuclei swap
(for homonuclear only)

$$\longrightarrow +/ - \text{ (parity)}$$

parity upon reflexion through nuclei plane
(for Σ states only)

$$\longrightarrow \text{letter}$$

label states of same quantum numbers

X = ground electronic state (GES)

A, B, ... = same spin multiplicity as GES

a,b, ... = diff spin multiplicity than GES

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Vibrational structure

Stationary Schrödinger equation for nuclei vibration

$$\left(-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + V(R) - E_v \right) \psi_v(R) = 0$$

→ for $V(R)$ approx by a parabolic potential $V_{\text{HO}}(R) = V_0 + \frac{1}{2}k(R - R_{\text{eq}})^2$

quantum harmonic oscillator

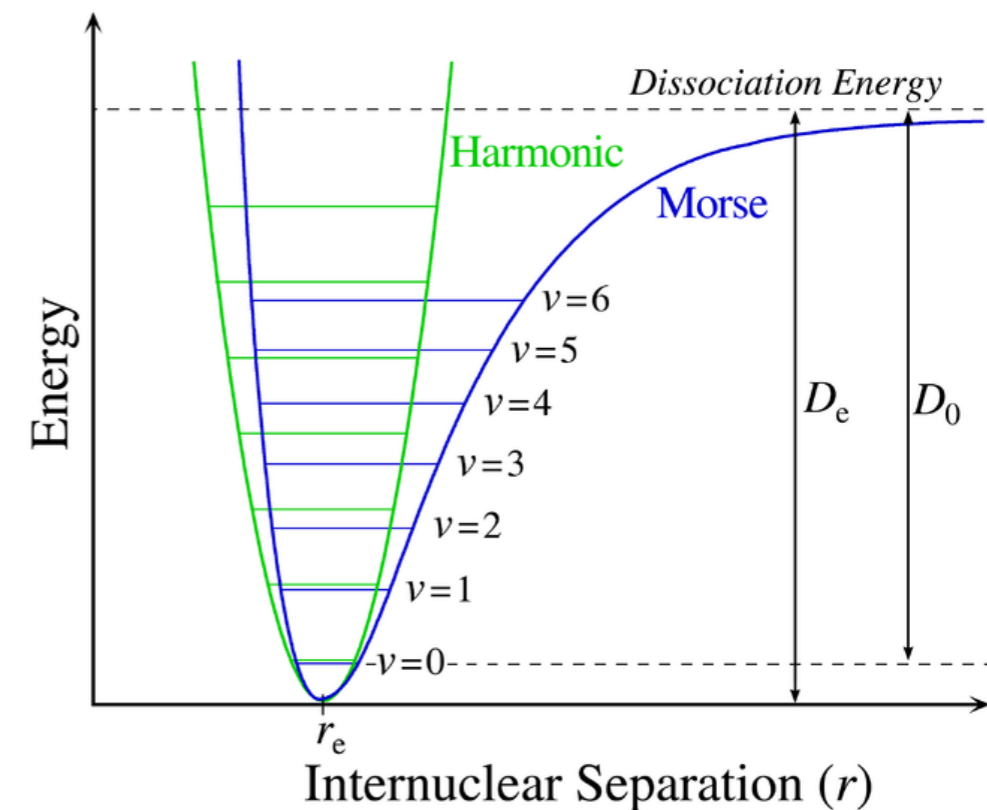
$$E_v = V_0 + \hbar \left(\frac{k}{\mu} \right)^{\frac{1}{2}} \left(v + \frac{1}{2} \right)$$

wavefunction derived from

Hermite polynomials

→ zero point energy

$$\text{zpe} = \frac{1}{2} \hbar \left(\frac{k}{\mu} \right)^{\frac{1}{2}}$$



wikipedia - Morse potential

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Rotational structure

Stationary Schrödinger equation for nuclei rotation

$$\left(-\frac{\hbar^2}{2\mu R^2} \left[\frac{1}{\sin\theta} \frac{d}{d\theta} \left(\sin\theta \frac{d}{d\theta} \right) + \frac{1}{\sin^2\theta} \frac{d}{d\phi} \right] - E_r \right) \psi_r(\theta, \phi) = 0$$

→ spherical harmonics solution $\psi_r(\theta, \phi) = Y_{J, M_J}(\theta, \phi)$

Y_{J, M_J} → already seen for H atom

J → rotational angular momentum

M_J → projection of J onto molecular axis

μ → reduced mass

→ rotational eigenvalues $E_r = \frac{\hbar^2}{2\mu R^2} J(J + 1)$

→ if rotation as rigid body $E_r = B_0 J(J + 1)$

→ degeneracy of rotational levels $g_r = 2J + 1$

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Fine structure / hyperfine structure

Couplings between angular momenta

- electron angular momentum and spin, nuclei rotational motion and spin
- coupling schemes known as Hund's cases - (a) and (b) most common
- R = rotational angular momentum

Hund's case (a)	Hund's case (b)
1 - $\Lambda = L_{ z}, \Sigma = S_{ z}$	1 - $\Lambda = L_{ z}$
2 - $\Lambda + \Sigma \rightarrow \Omega$	2 - $\Lambda + R \rightarrow N$
3 - $\Omega + R \rightarrow J$	3 - $N + S \rightarrow J$

- hyperfine coupling
coupling with nuclear spin I
 $J + I \rightarrow F$

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Detailed electronic / vibrational / rotational structure

In reality, anharmonic & non rigid rotation with rot / vib couplings

- corrections terms (used in a polynomial expansion)
- derived from spectroscopic measurements of molecular lines
- anharmonic correction, centrifugal distortion, correction of rot constant

example for CH⁺

$$\begin{aligned}
 E(\Lambda, v, J) = & T_e(\Lambda) + \omega_e(\Lambda) \left(v + \frac{1}{2} \right) - \omega_e x_e(\Lambda) \left(v + \frac{1}{2} \right)^2 + \omega_e y_e(\Lambda) \left(v + \frac{1}{2} \right)^3 \\
 & + \left[B_e(\Lambda) - \alpha_e(\Lambda) \left(v + \frac{1}{2} \right) + \gamma_e(\Lambda) \left(v + \frac{1}{2} \right)^2 + \varepsilon_e(\Lambda) \left(v + \frac{1}{2} \right)^3 \right] \\
 & \times (J(J+1) - \Lambda^2) - \left[D_e(\Lambda) + \beta_e(\Lambda) \left(v + \frac{1}{2} \right) + \delta_e(\Lambda) \left(v + \frac{1}{2} \right)^2 \right] \\
 & \times (J(J+1) - \Lambda^2)^2 + \left[H_e(\Lambda) - \alpha_{H_e}(\Lambda) \left(v + \frac{1}{2} \right) \right] (J(J+1) - \Lambda^2)^3 \\
 & \pm \frac{1}{2} \left[q_e(\Lambda) + \alpha_{q_e}(\Lambda) \left(v + \frac{1}{2} \right) \right] (J(J+1)) \\
 & \pm \frac{1}{2} q_{D_e}(\Lambda) (J(J+1))^2, \tag{1}
 \end{aligned}$$

constant	$X^1\Sigma^+$		$A^1\Pi$	
T_e			2.41187262	(+4)
ω_e	2.8575609	(+3)	1.864402	(+3)
$\omega_e x_e$	5.93179	(+1)	1.158317	(+2)
$\omega_e y_e$	2.2534	(-1)	2.6301	
B_e	1.41774612	(+1)	1.1886774	(+1)
α_e	4.94739	(-1)	9.1629	(-1)
γ_e	2.4904	(-3)	-2.292	(-2)
ε_e			4.952	(-3)
D_e	1.38914	(-3)	1.929606	(-3)
β_e	-2.66	(-5)	1.07331	(-4)
δ_e			-1.3123	(-5)
H_e	1.2036	(-7)		
α_{H_e}	2.079	(-8)		
q_e			4.1018	(-2)
α_{q_e}			-3.135	(-3)
q_{D_e}			-2.2	(-5)

Hakalla et al. (2006)

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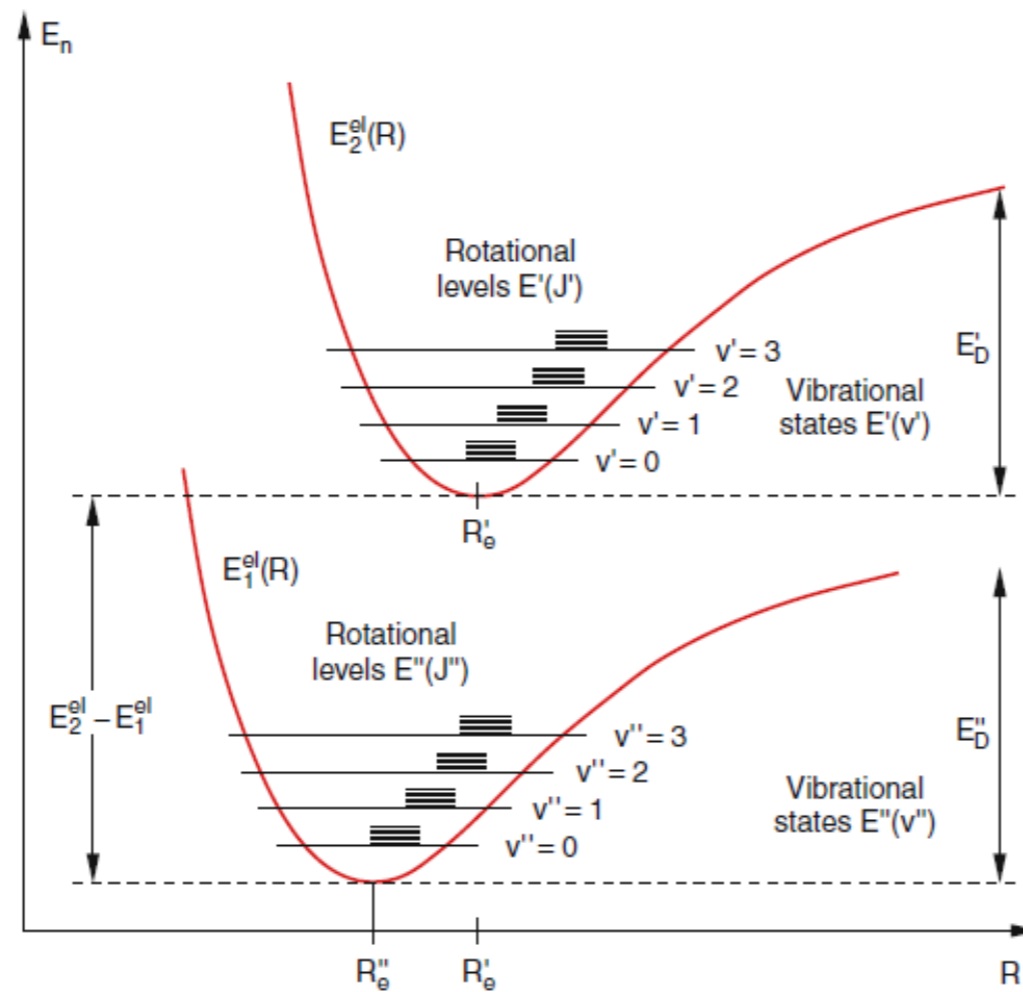
- conclusion

Detailed electronic / vibrational / rotational structure

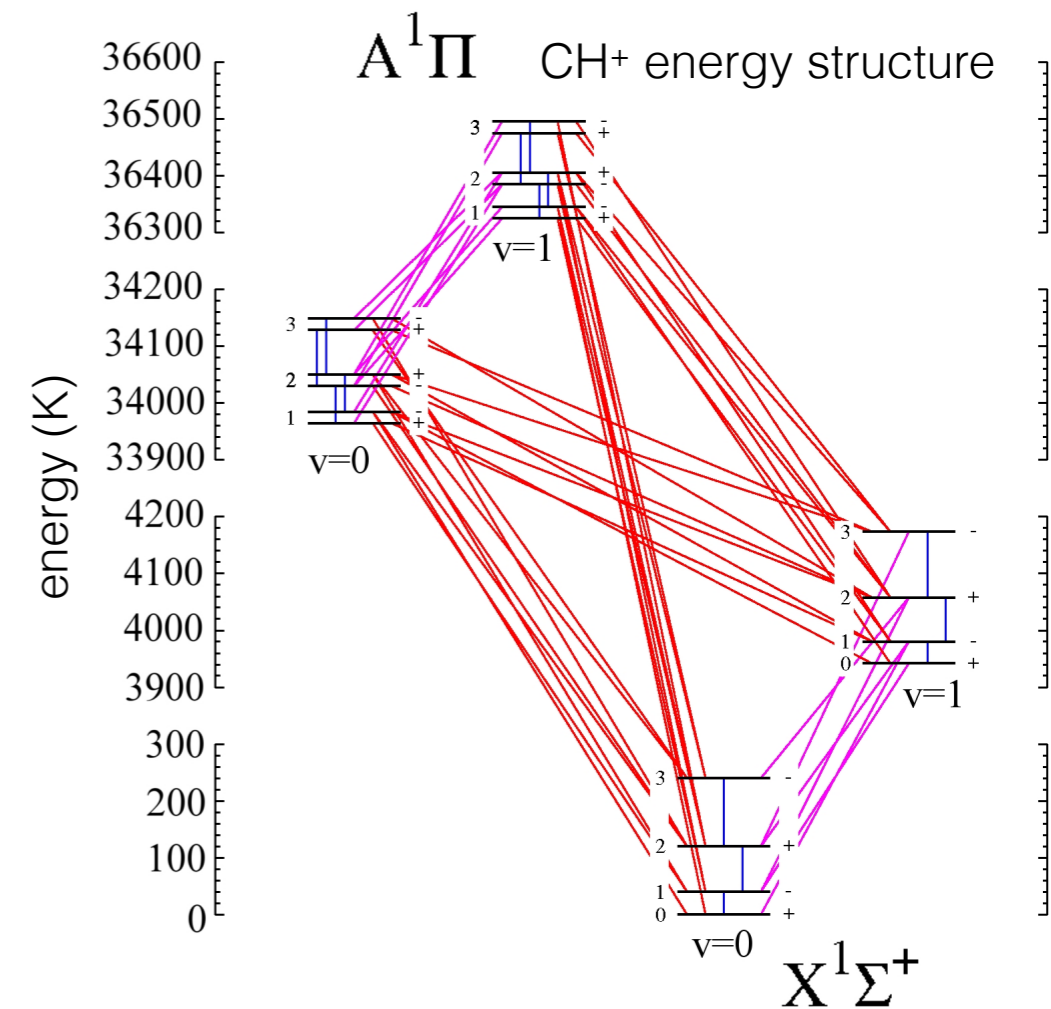
Hierarchical energy structure

→ rule of thumb $E_e > E_v > E_r$

→ ladders are not separated but superimposed



Mihály Benedict



Godard et al. (2013)

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Molecular spectra

Electric dipole transitions

Interaction of a molecule with EM field

- electric dipole, magnetic dipole, electric quadrupole, ...
- electric dipole terms $\sim 10^5 - 10^6$ times larger than the others
- electric dipole transition probability from Ψ'' to Ψ'

$$P \propto |\mathbf{M}|^2 \quad \text{with} \quad \mathbf{M} = \int \psi'^* \boldsymbol{\mu} \psi'' d\mathbf{r}$$

\mathbf{M} electric dipole moment integral

$\boldsymbol{\mu}$ dipole moment operator

- symmetry properties of Ψ', Ψ'' and $\boldsymbol{\mu}$ give the selection rules

$$\Delta S, \Delta \Lambda, \Delta v, \Delta J, \dots$$

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Selection rules on electronic quantum numbers

for allowed electric dipole transitions

→ $\Delta S = 0$ spin conserving selection rule

→ $\Delta \Lambda = 0, \pm 1$ projection of orbital momentum

→ $\Sigma^+ \leftrightarrow \Sigma^+$ for Σ states only

$\Sigma^- \leftrightarrow \Sigma^-$

→ $g \leftrightarrow u$ for homonuclear diatomic molecules

⇒ no *dipole allowed* vibration-rotation transition

within an electronic state for homonuclear species

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Selection rules on vibrational quantum number

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transitions from two different electronic states

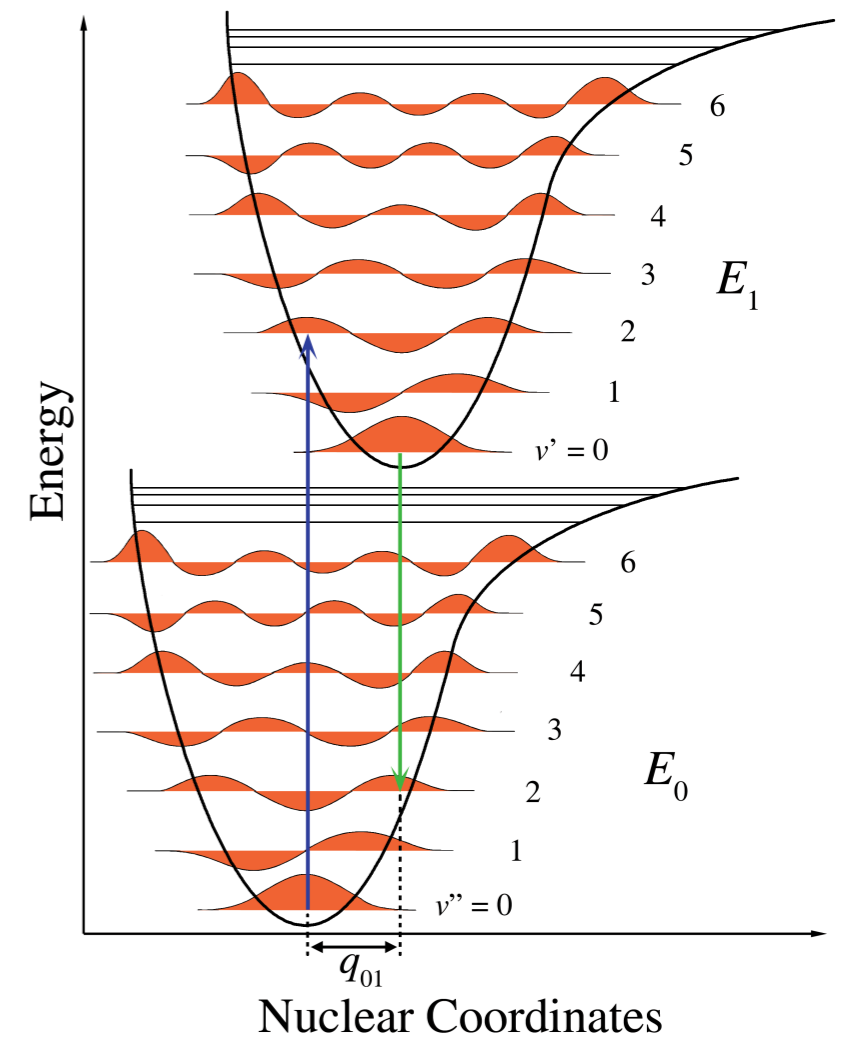
- Franck-Condon principle
nuclei static during elec transition
transition probability proportional to
wavefunctions overlap

$$\left| \int \psi'_v(v')^* \psi''_v(v'') d\mathbf{r} \right|^2$$

- $\Delta v = \text{any}$ no selection rule

transition within the same electronic state

- $\Delta v = \text{any}$ for anharmonic oscillators
stronger transitions for $\Delta v = \pm 1$ (HO)



Selection rules on rotational quantum number

for allowed electric dipole transitions

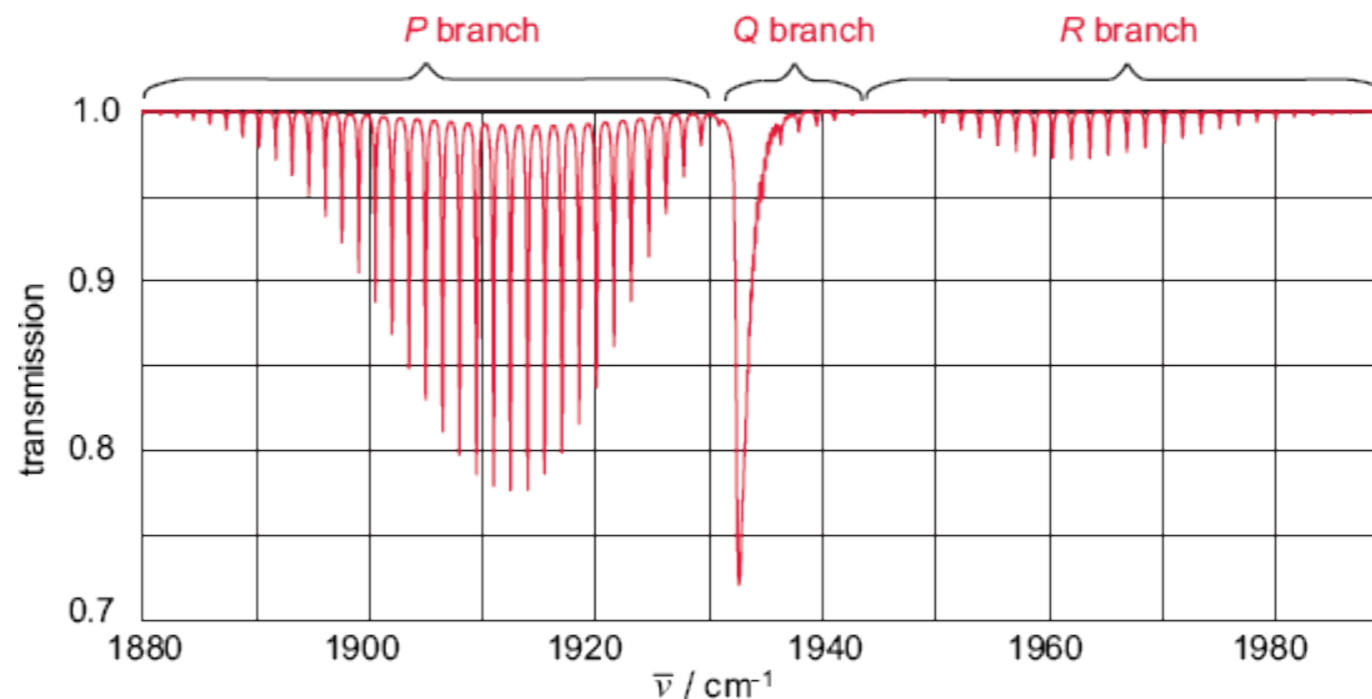
→ $\Delta J = \pm 1$ for $\Lambda = 0 - 0$ transitions

$\Delta J = 0, \pm 1$ ($0 \leftrightarrow 0$) for other $\Delta\Lambda$

→ labelling: J' (J'') associated with the upper (lower) energy level

name	$R(J'')$	$Q(J'')$	$P(J'')$
$\Delta J = J' - J''$	+1	0	-1

→ for transition within the same electronic state → regular structure



CO₂ simulated spectrum Hertel & Schultz

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Oscillator strength and Einstein coefficients

for allowed electric dipole transitions

→ the Einstein coefficient

$$A_{\Lambda'v'J'\Lambda''v''J''} = \frac{8\pi^2\nu^2e^2}{m_e c^3} \frac{2J'' + 1}{2J' + 1} f_{\Lambda'v'J'\Lambda''v''J''}$$

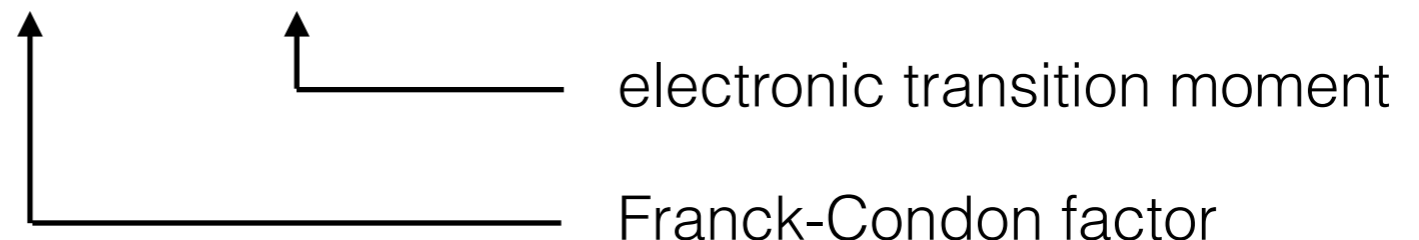
→ with the oscillator strength

$$f_{\Lambda'v'J'\Lambda''v''J''} = \frac{8\pi^2m_e\nu}{3he^2} M_{\Lambda'v'\Lambda''v''}^2 \frac{S_{\Lambda''J''}^{\Lambda'J'}}{2J'' + 1}$$

$S_{\Lambda''J''}^{\Lambda'J'}$ Hönl-London factor, dependence on nuclear angular momentum

→ under the Born-Oppenheimer and the r-centroid approximations

$$M_{\Lambda'v'\Lambda''v''}^2 = q_{\Lambda'v'\Lambda''v''} R_e^2(\bar{r}_{v'v''})$$



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Pure vibration-rotation of homonuclear diatomic molecules

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electric dipole transitions forbidden within an electronic state of homonuclear diatomic molecules (e.g. H₂, C₂, N₂, ...)

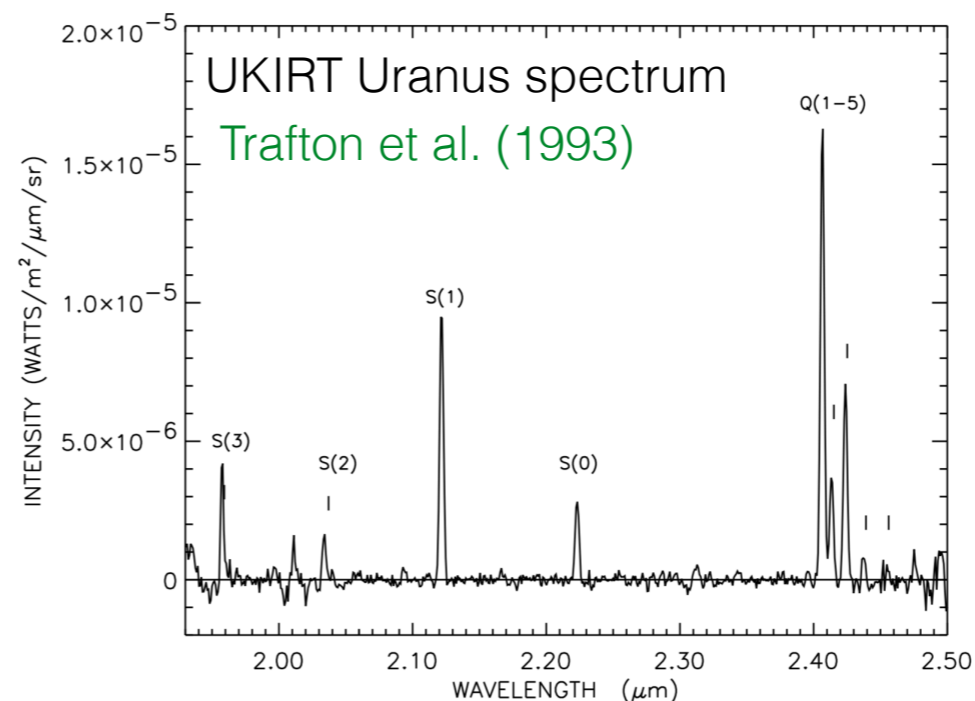
→ dipole magnetic and quadrupole electric transitions

→ example : H₂ - quadrupole electric transitions

selection rule for pure vibration-rotation $\Delta J = 0, \pm 2$ ($0 \leftrightarrow 0$)

labelling: J' (J'') associated with the upper (lower) energy level

name	$S(J'')$	$Q(J'')$	$O(J'')$
$\Delta J = J' - J''$	+2	0	-2



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Ionization / dissociation / fluorescence

Principles of photo-processes

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photoionization and photodissociation processes are fundamental

- to compute radiative transfer in molecular environments
- to compute chemical composition of diffuse & dense ISM, PDRs, protoplanetary disks, cometary & exoplanetary atmosphere, ...

microphysical process

- 1 - excitation of any (bound or not) electronic state



$$k = \int_{\lambda} \sigma(\lambda) N_{\lambda} d\lambda$$

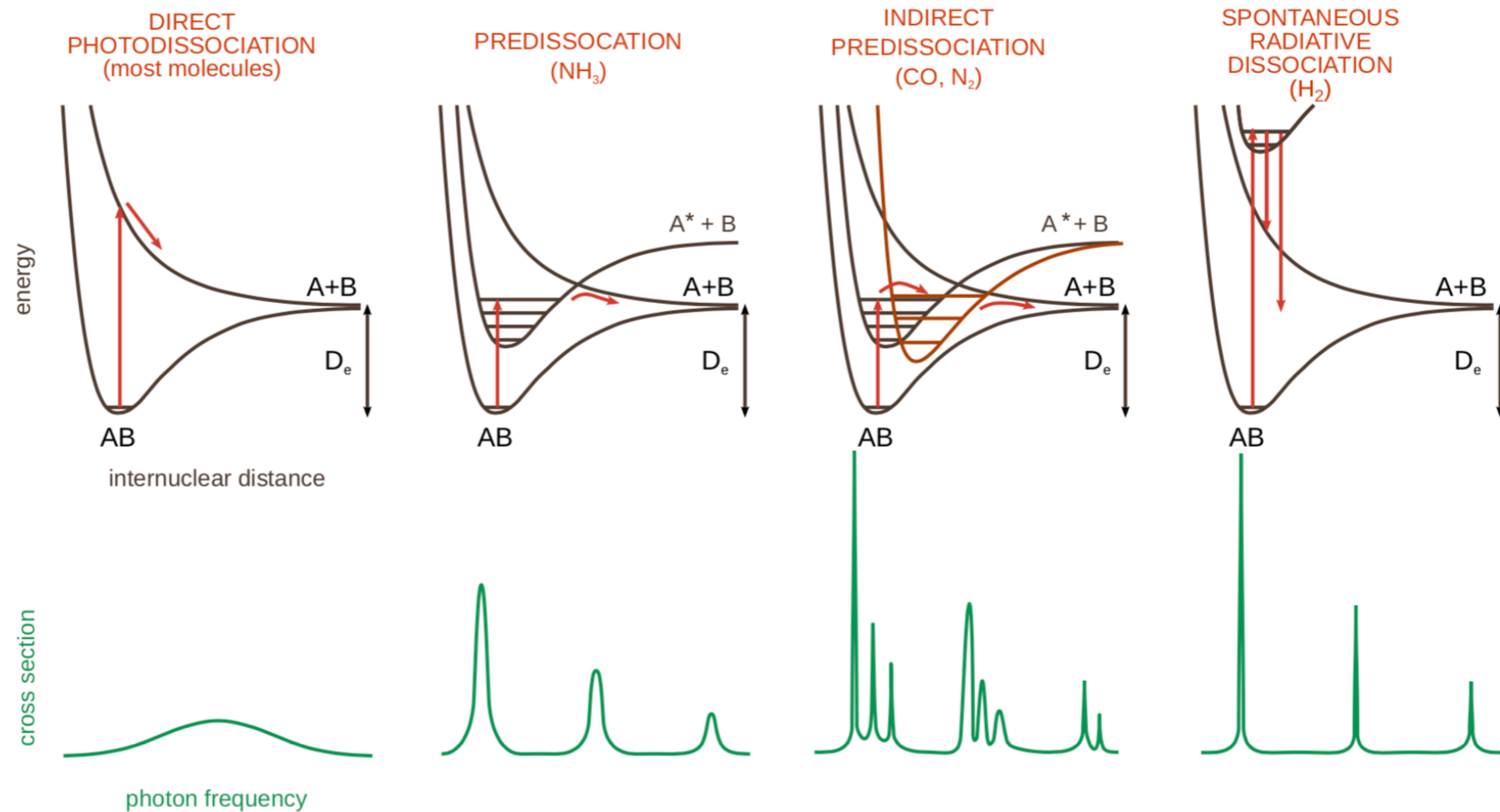
- 2 - relaxation towards a lower state branching ratios



Continuous or discret absorption

Several pathways to photodissociation

Heays et al. (2017)



- photodissociation may be a line or a continuum mechanism
- cross sections must account for all possible process
- line processes favor self-shielding

Outline

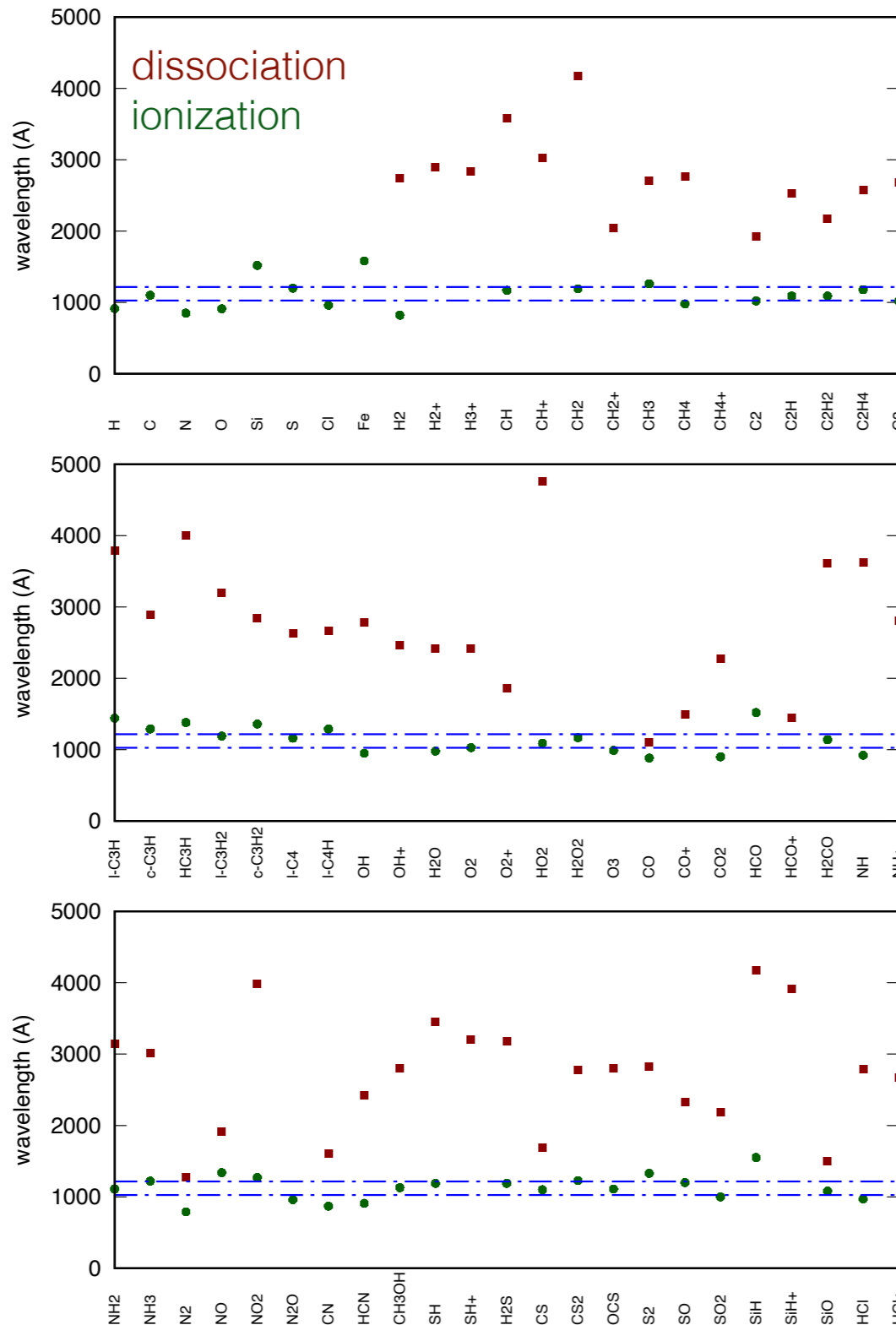
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Threshold and cross sections

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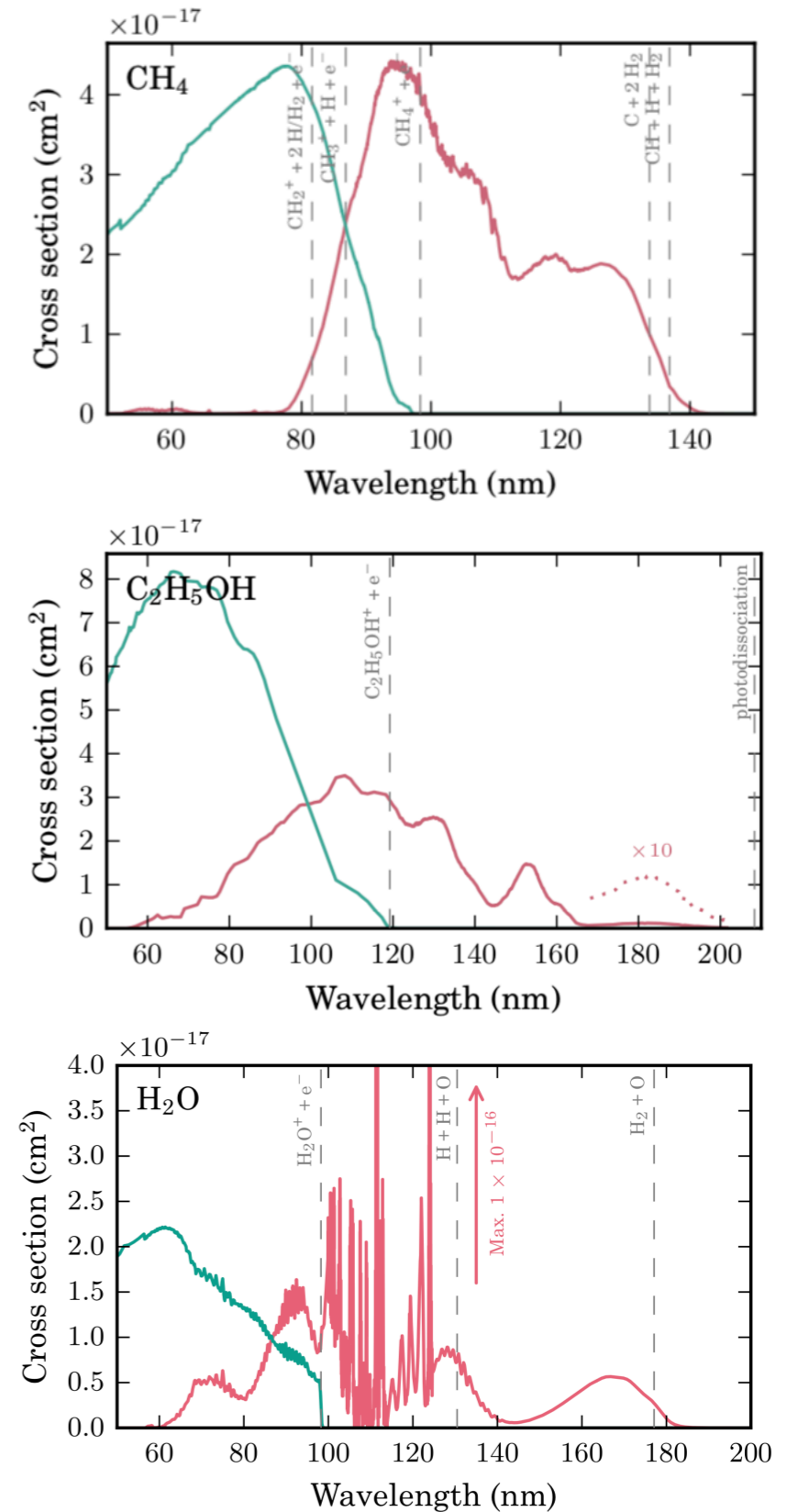
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photo-processes threshold



derived from Heays et al. (2017)

examples of cross sections

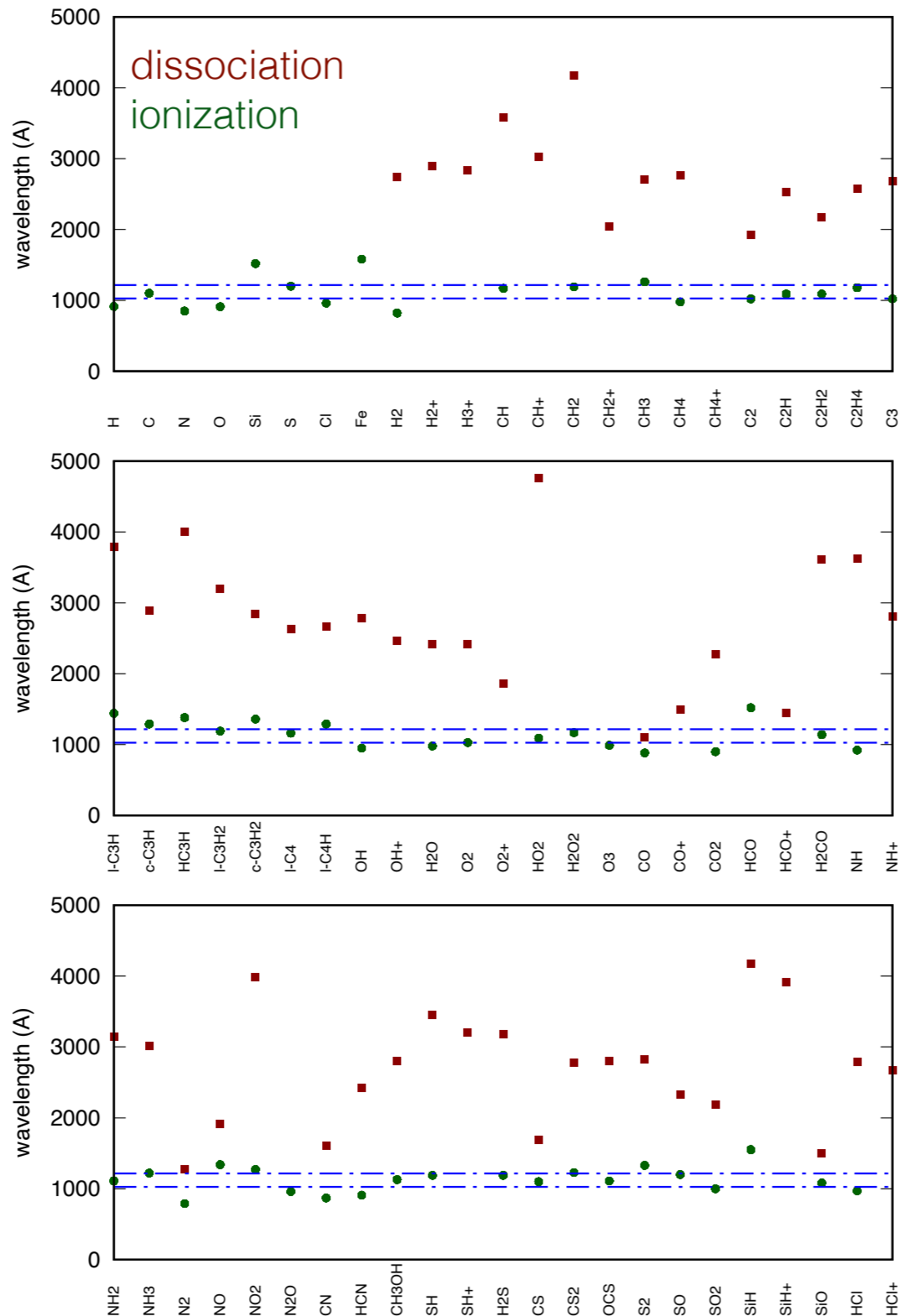


Threshold and cross sections

Outline

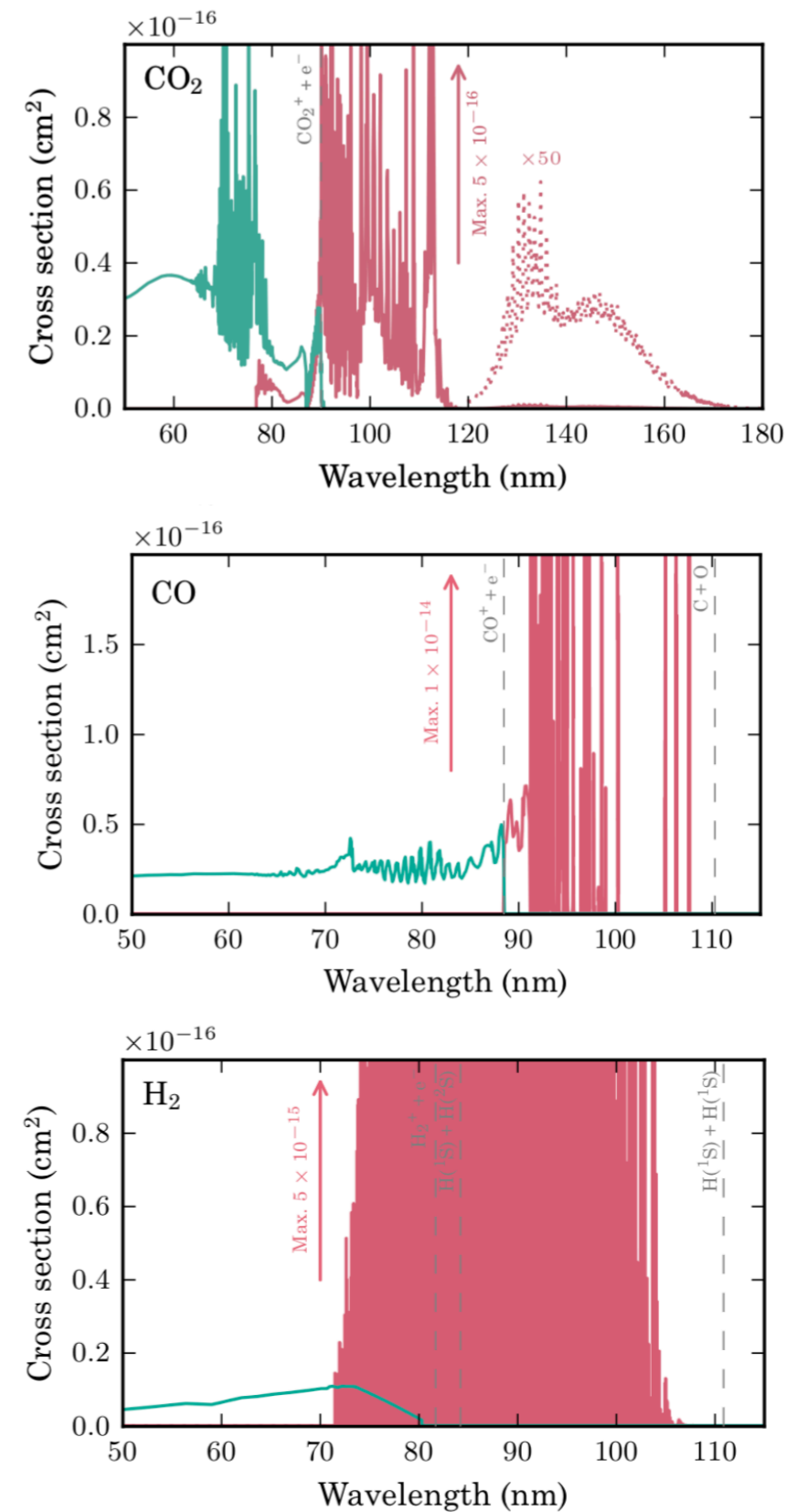
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photo processes threshold



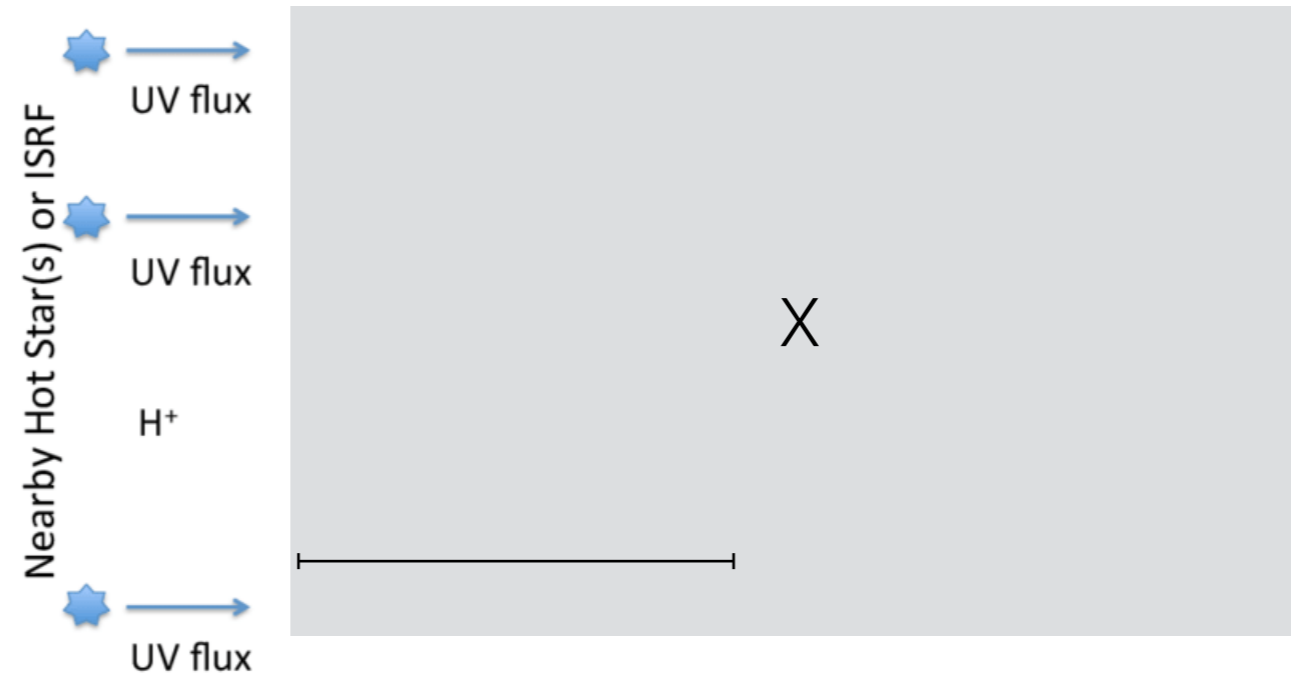
derived from Heays et al. (2017)

examples of cross sections



Self-shielding process

Consider a cloud illuminated by energetic photons



the abundance of X at any point depends on photo-processes

→ intensity of the radiation field at specific wavelength

→ absorption processes from the border of the cloud

by dust grains - - - - - → dust shielding

by atoms and molecules Y - - - → cross shielding

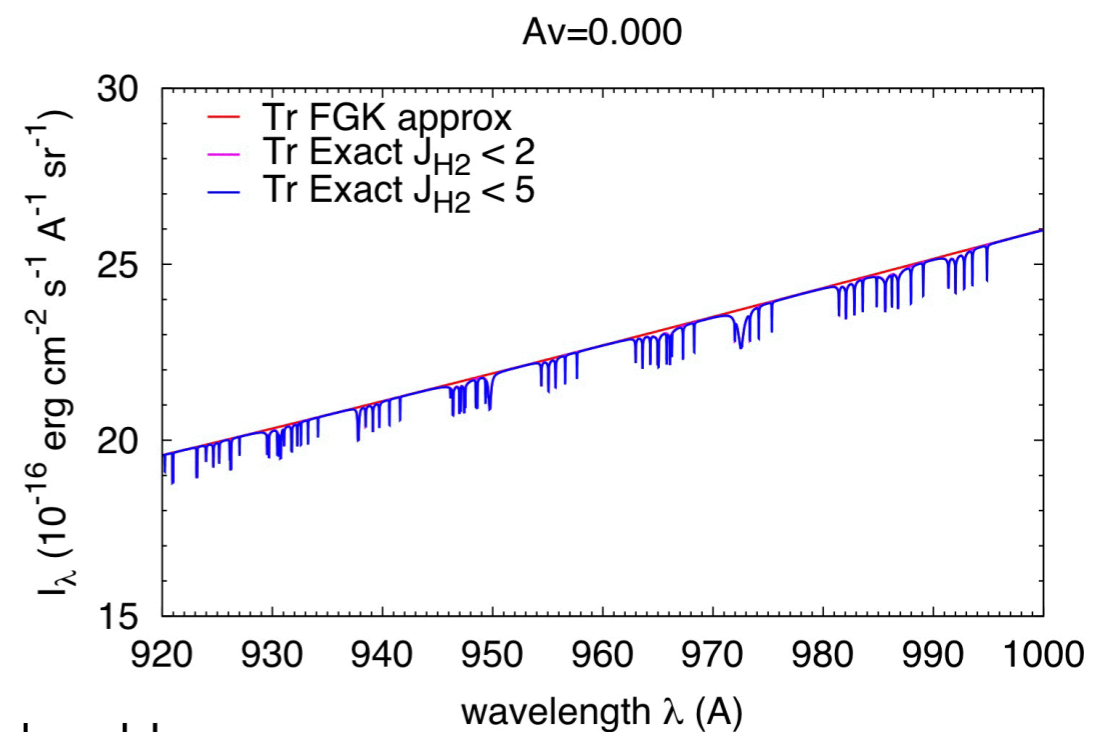
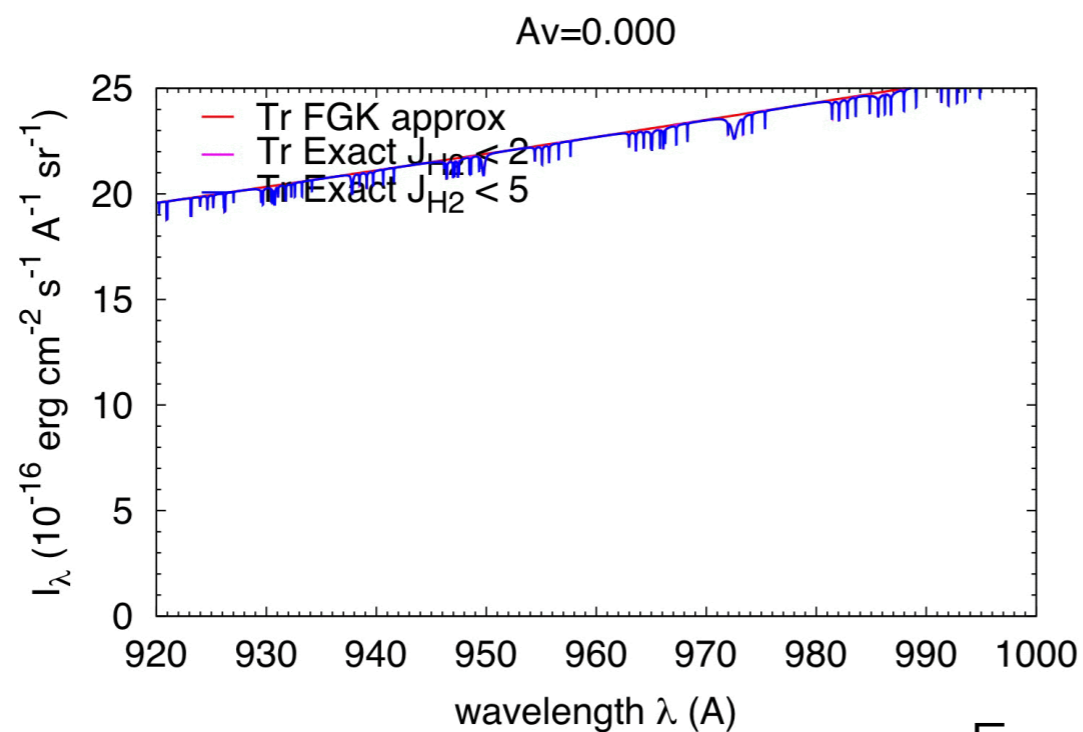
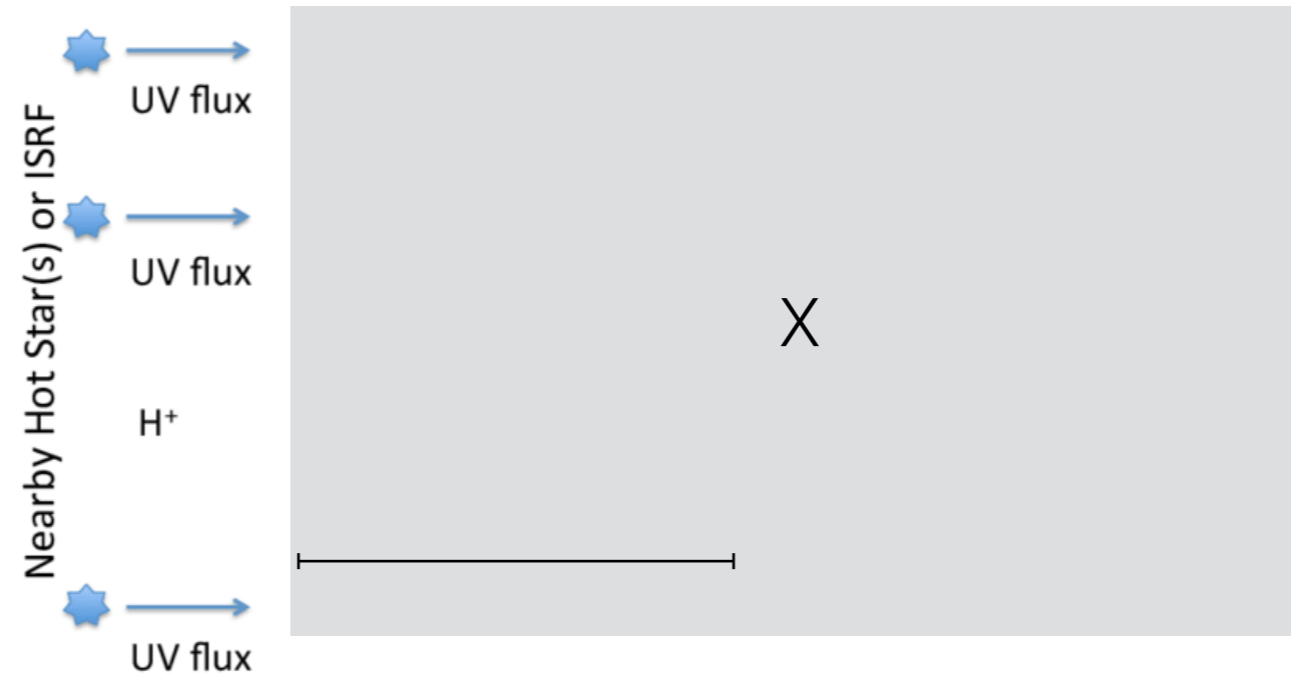
by atoms and molecules X - - - → self-shielding

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Self-shielding process

Consider a cloud illuminated by energetic photons



Example : H₂

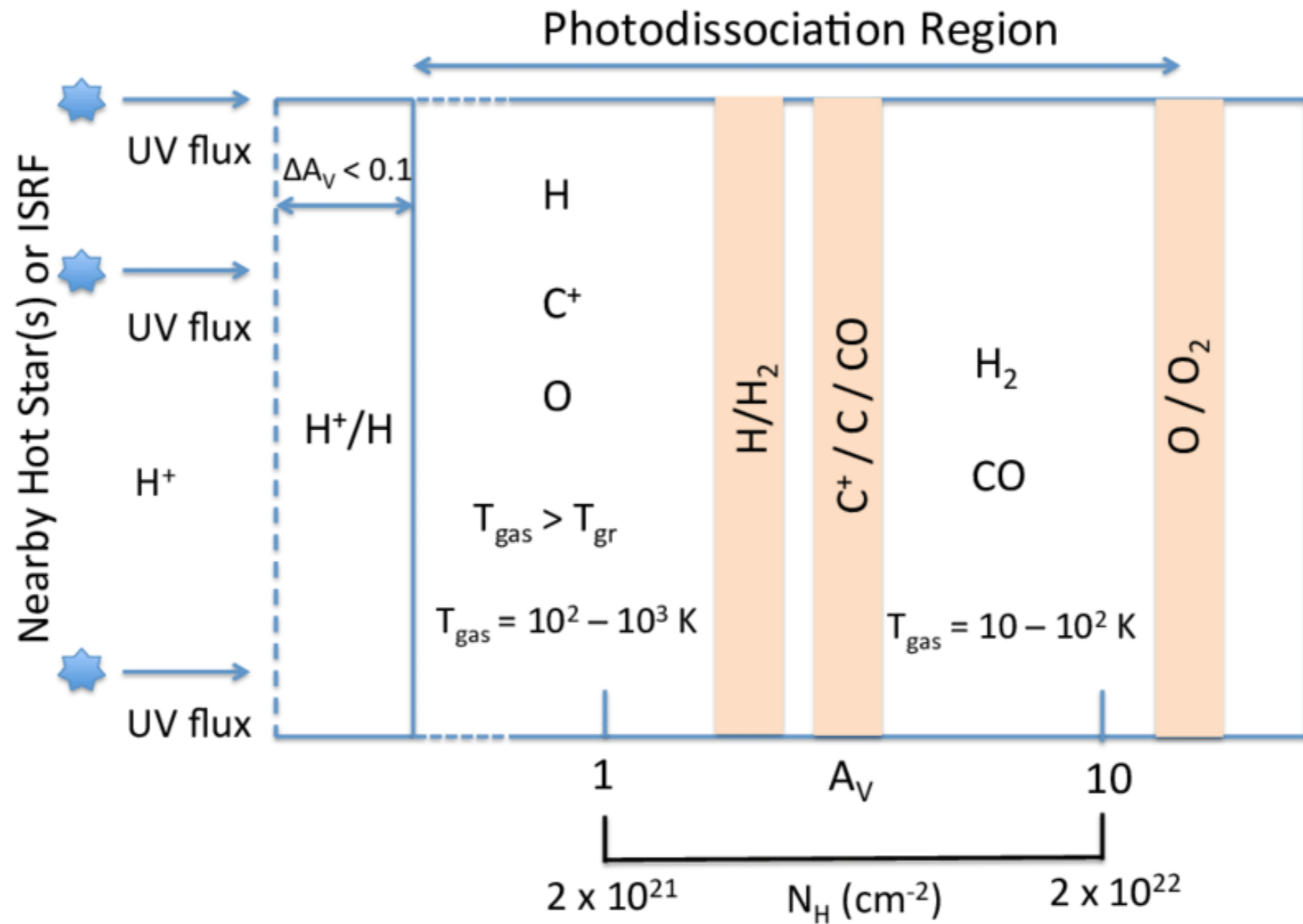
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Self-shielding process

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Hollenbach & Tielens (1999)

Molecular structure and spectroscopy

- simplifications gives strong insight on molecular structure
Born-Oppenheimer → elec orbitals & quantum numbers
separation vibration / rotation → vib oscillator & rotational orbitals
additional couplings → fine & hyperfine structure
- electric dipole transitions obey to stringent transition rules
molecular spectra highly structured (band, branches, fine / hyperfine)
- homonuclear diatomic molecules radiate through quadrupole transitions

Interactions with radiation field

- ionization / dissociation / fluorescence originate from mol transitions
- non linear coupling between transfer and composition (e.g. self-shielding)

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