Photodissociation in astrophysics

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

Van Dishoeck & Visser 2015

Thanks to many colleagues

Photodissociation workshop, Leiden, February 3. 2015

Molecules are found in dark clouds exposed to UV radiation

HST Carina nebula

UV is main destruction route if extinction not too high (<5 mag)

The ingredients

Cosmic (solar) abundances elements by number

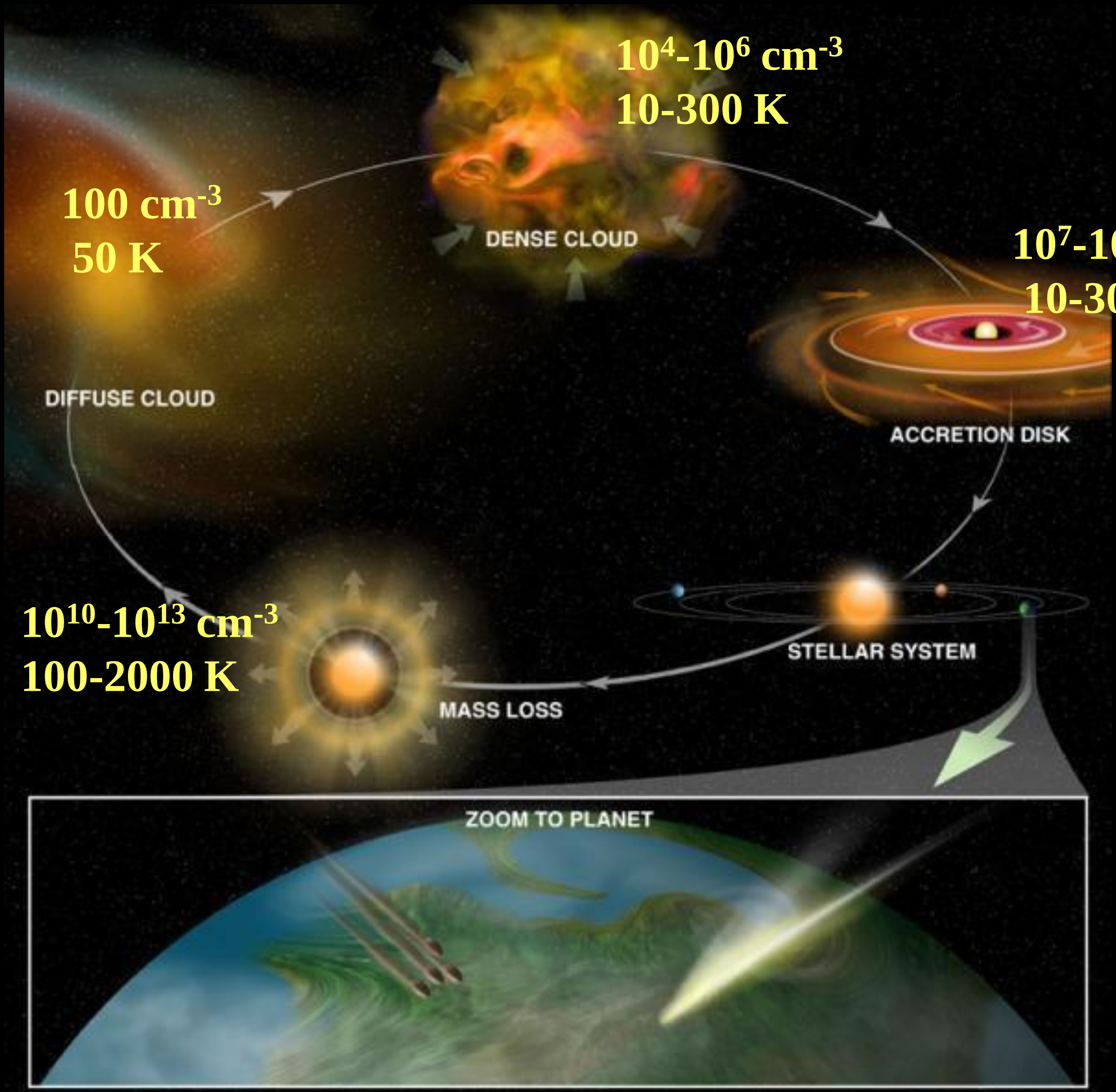
Element	Abundance	Element	Abundance
H	1.00	Mg	4.2×10^{-5}
He	0.075	Al	3.1×10^{-6}
C	3.5×10^{-4}	Si	4.3×10^{-5}
N	8.5×10^{-5}	S	1.7×10^{-5}
O	5.5×10^{-4}	Ca	2.2×10^{-6}
Na	2.1×10^{-6}	Fe	4.3×10^{-5}

Precise numbers under debate

-Not all of these atoms available for gas chemistry, some locked up in grains (‘depletion’)
 i.p.. all of Si, 2/3 of C

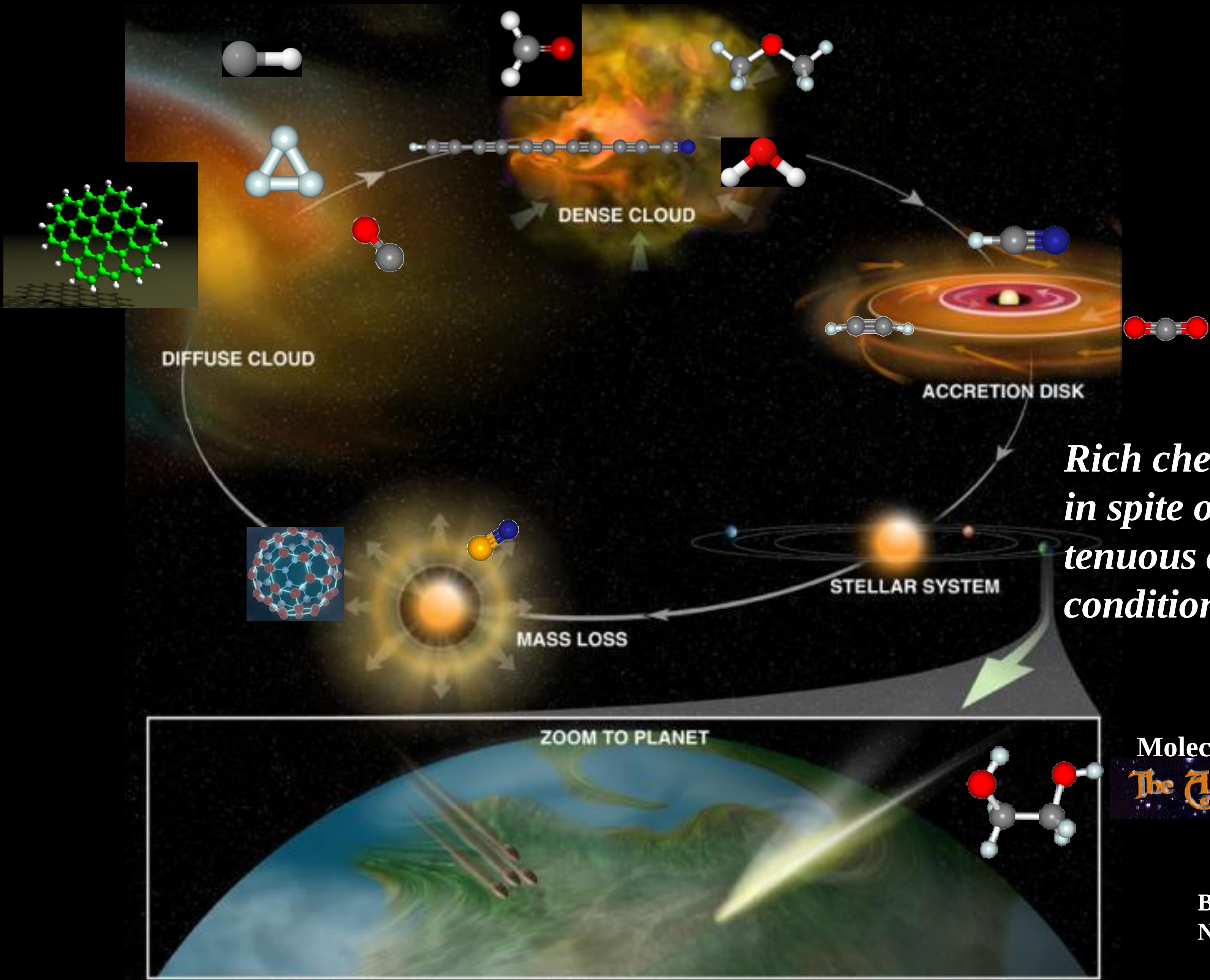
- Dust attenuates UV

From clouds to stars and planets



B. Saxton
NRAO

From clouds to stars and planets

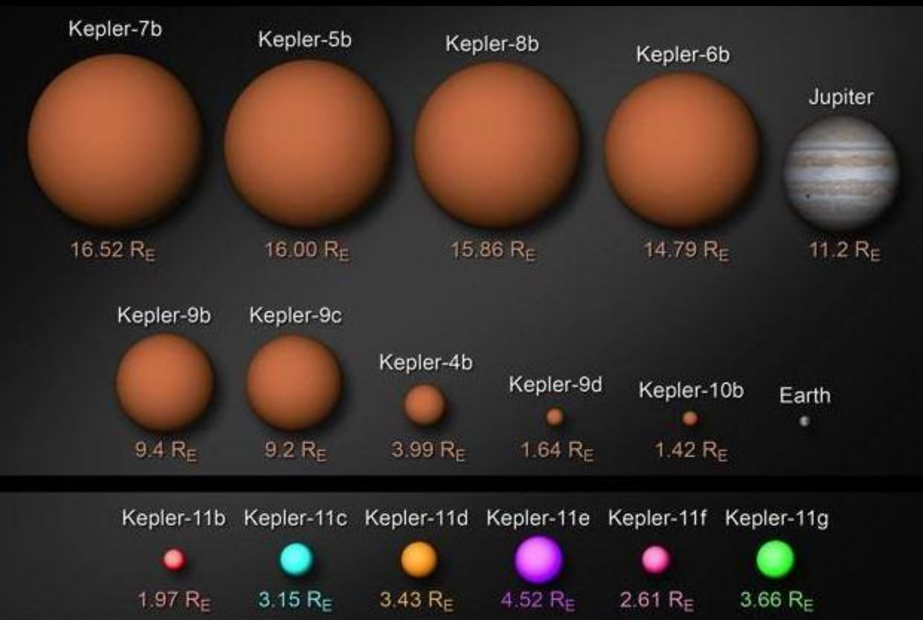


Rich chemistry in spite of tenuous and harsh conditions

Molecule images:

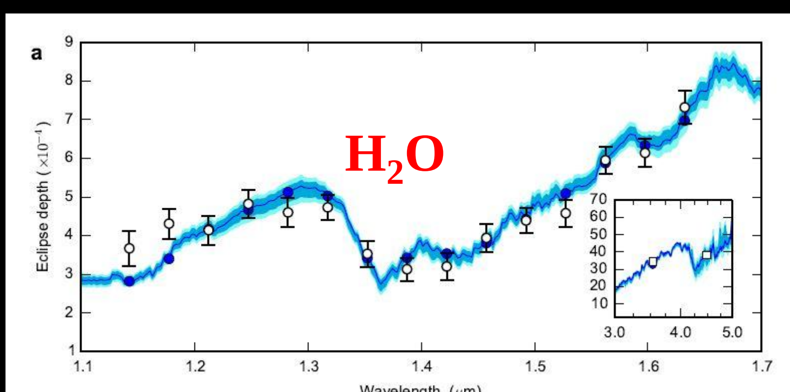
B. Saxton
NRAO

Diversity of exoplanets and their atmospheres

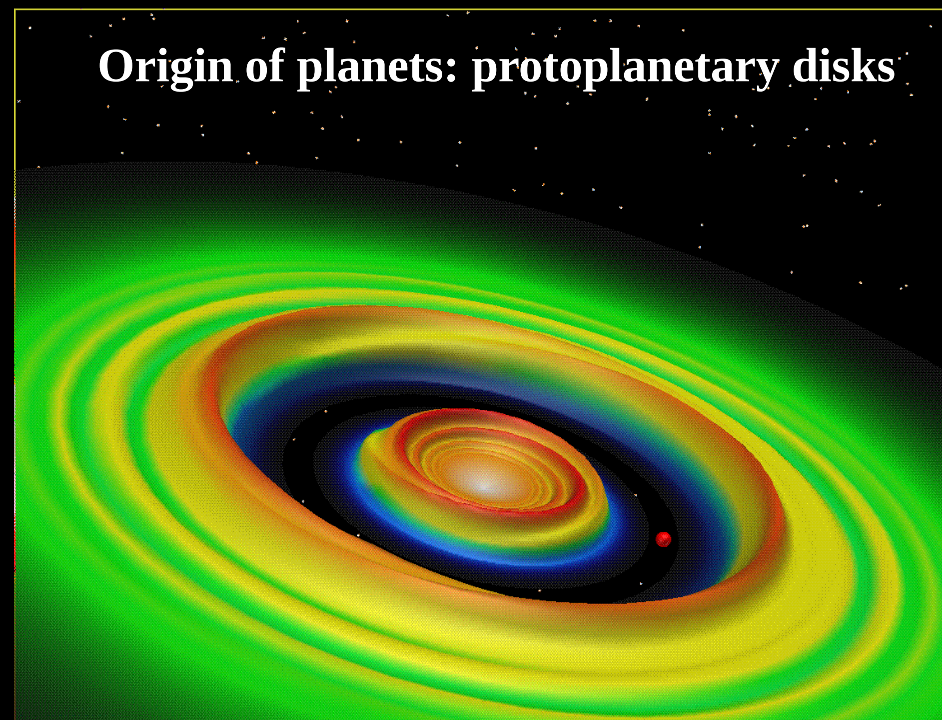


Kepler: Borucki et al. 2011

-Bulk of detected planets orbit close to their parent star → irridiated

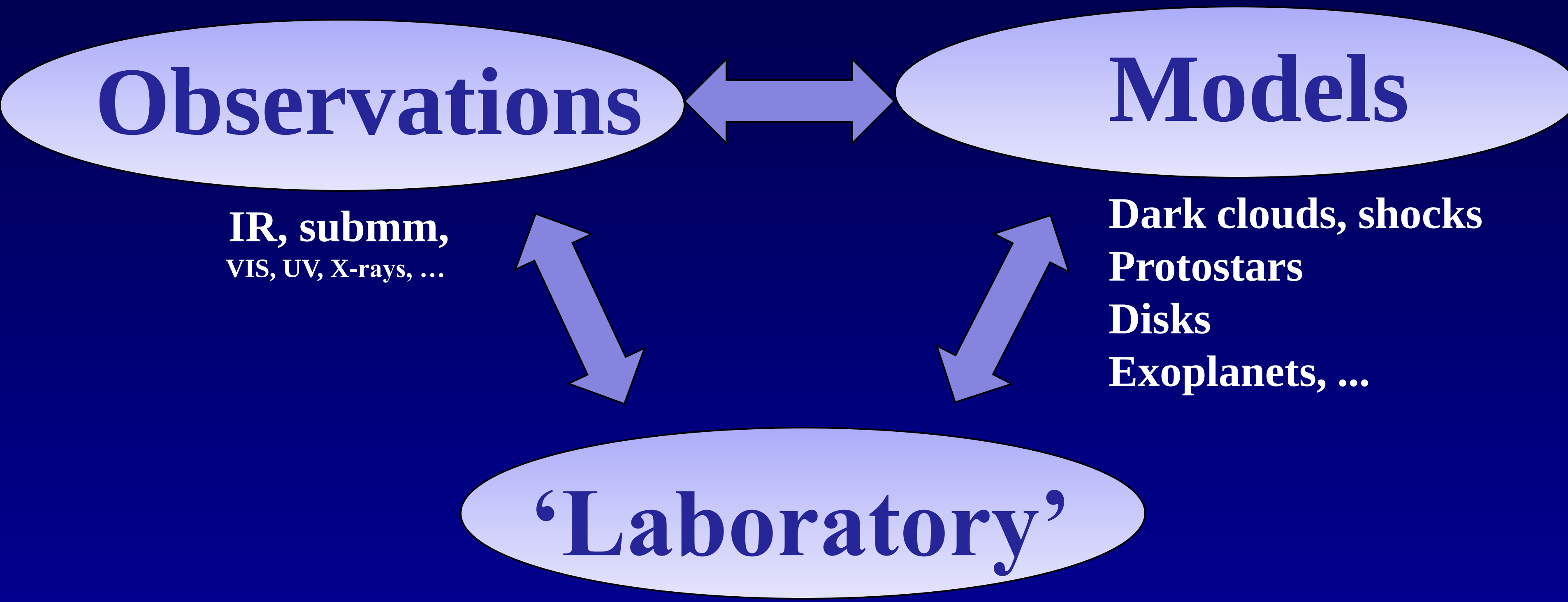


Kreidberg et al. 2014



Simulation G. Bryden

Interdisciplinary approach



IR, submm,
VIS, UV, X-rays, …

Dark clouds, shocks
Protostars
Disks
Exoplanets, ...

Spectroscopy,…
Collision rates, photorates, …
Grain surface processes, …..

Overviews in van Dishoeck 2014, Faraday Discussions
Herbst 2014, PCCP
van Dishoeck et al. 2013, Chem. Rev.
Tielens 2013, Rev. Mod Physics

Types of chemical reactions

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

IR and millimeter telescopes

Herschel

IRAM 30m

- Observe pure rotational and vibration-rotation transitions of molecules

Atacama Large Millimeter Array (ALMA)

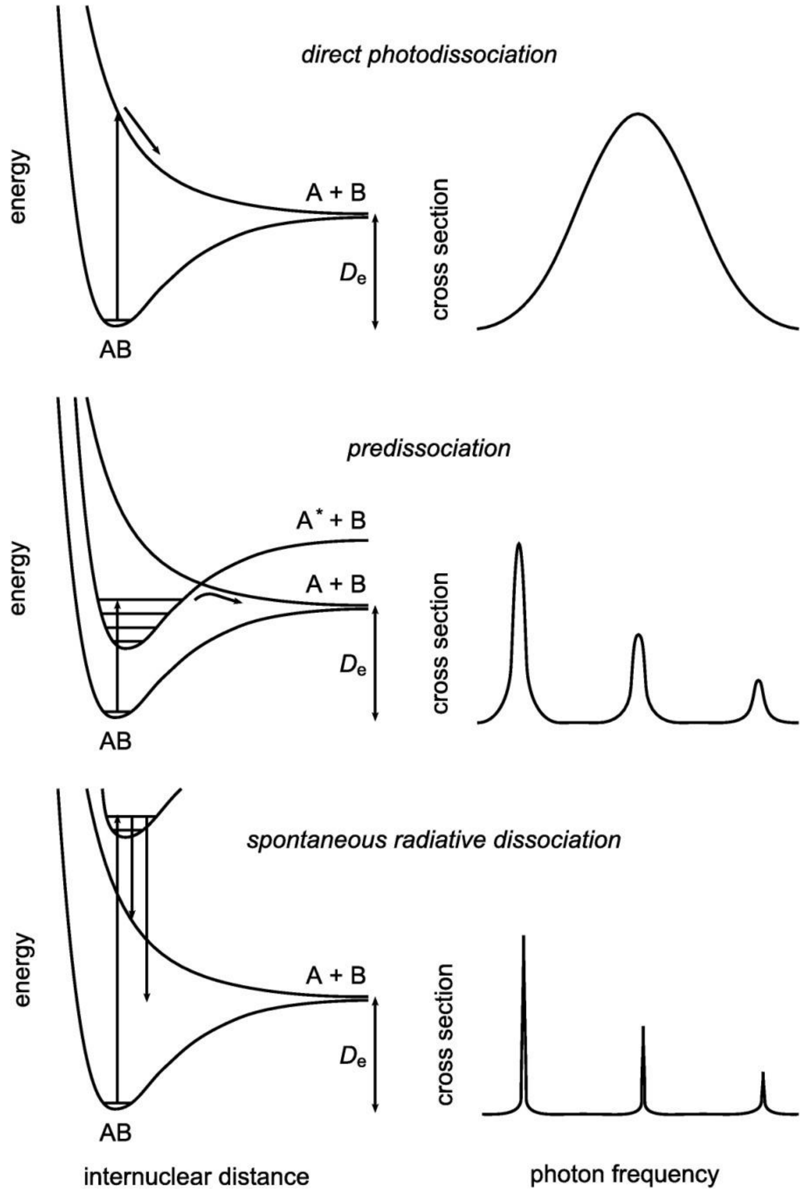
Inauguration March 2013

Overview

- Processes
- Radiation fields of astrophysical interests
- Theory vs. experiments
- Small molecules
- Large molecules: PAHs
- Ices
- Conclusions and questions

Van Dishoeck 1988
Van Dishoeck et al. 2006, Far. Discussions
Van Dishoeck & Visser 2011→2015 astro-ph

Summary processes small molecules



Direct p.d.

Ex: H_2^+, OH, H_2O

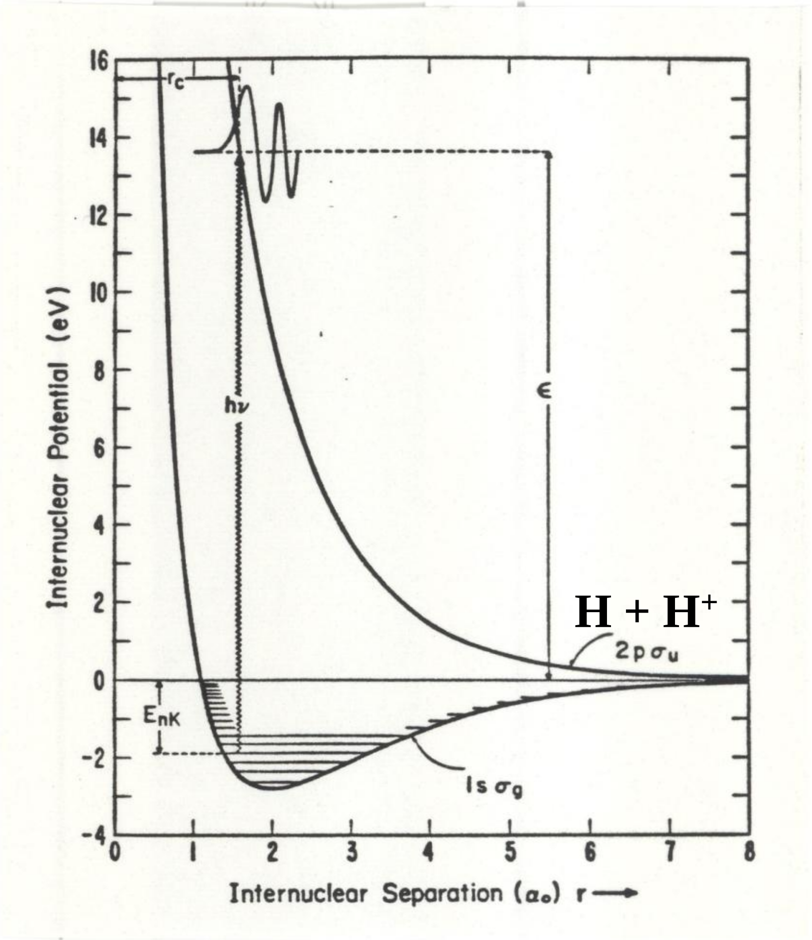
Predissociation

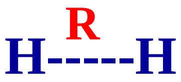
Ex: CO

Spontaneous radiative dissociation

Ex: H_2

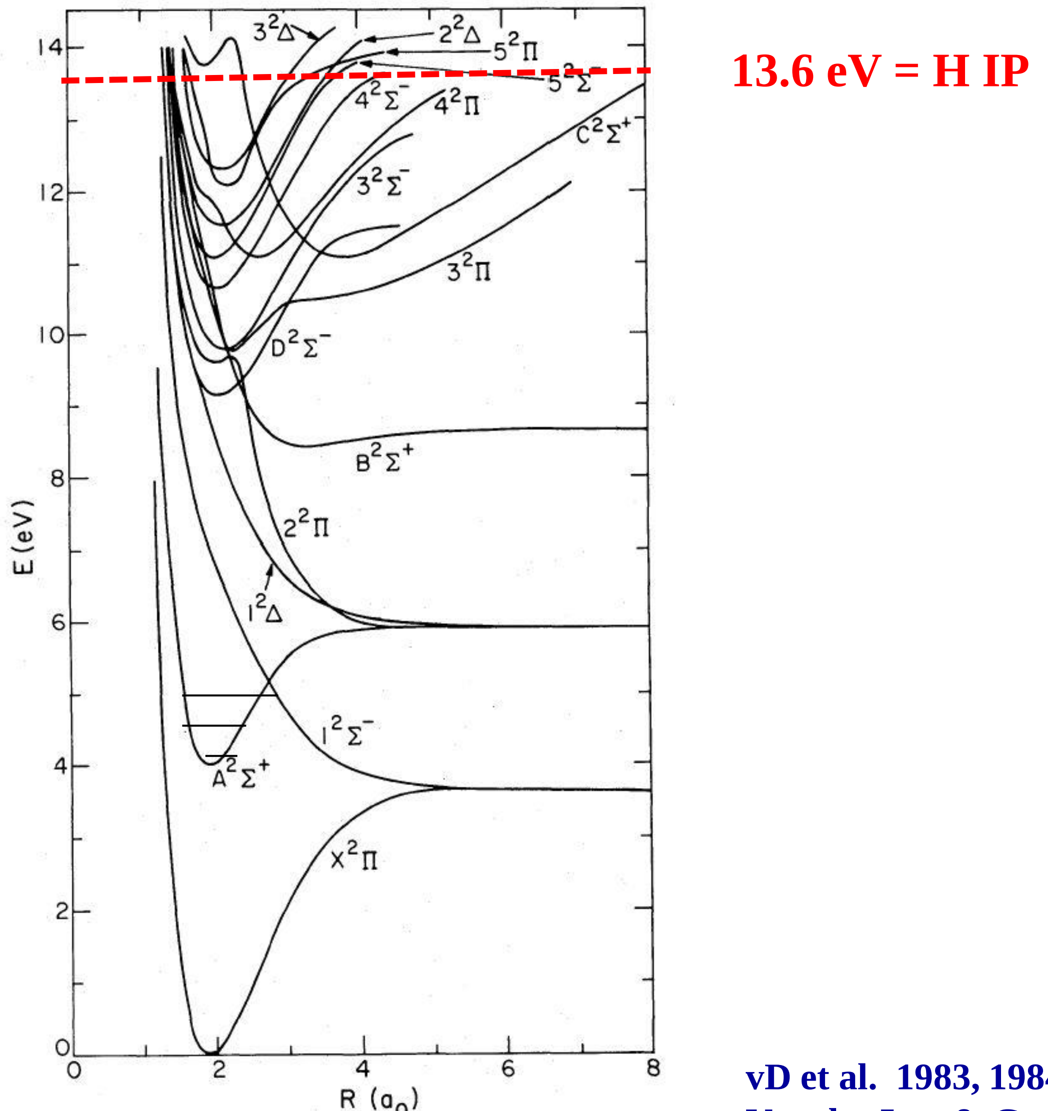
Example: H_2^+ ion





- Important in early universe chemistry
- Vibrationally excited states important

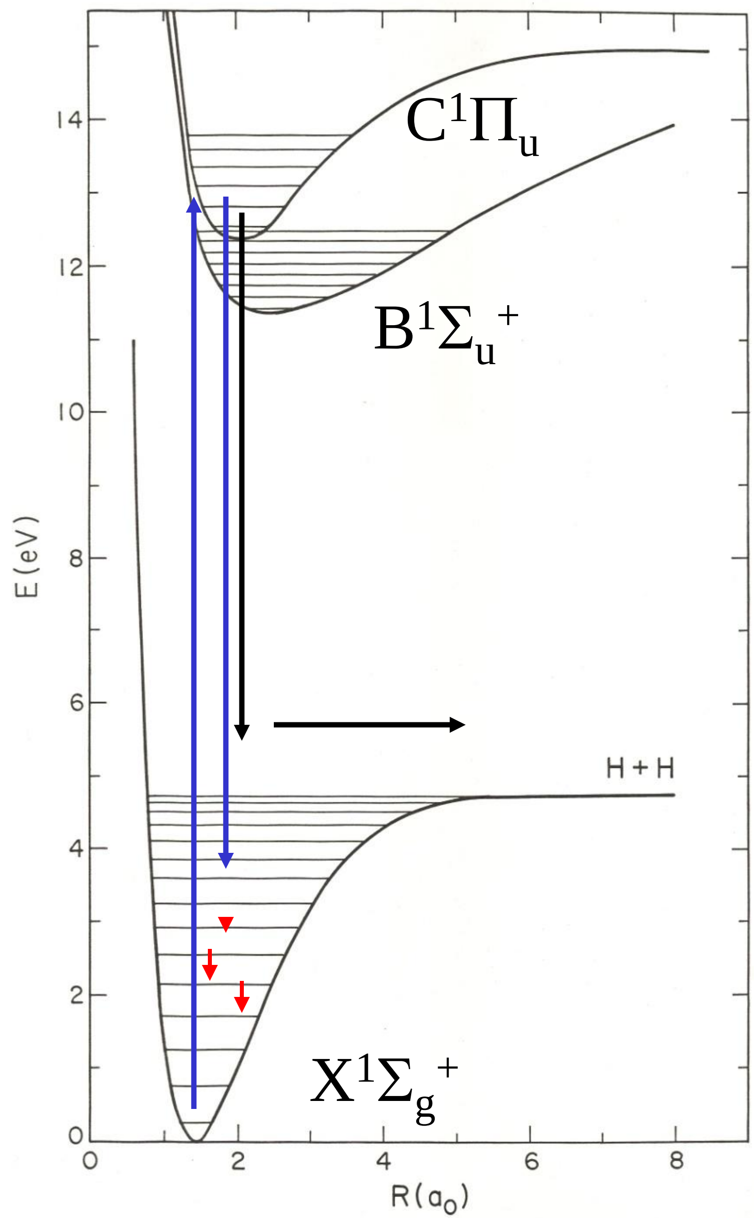
Example: OH



vD et al. 1983, 1984
Van der Loo & Groenenboom

- All processes play a role

H_2 spontaneous radiative dissociation



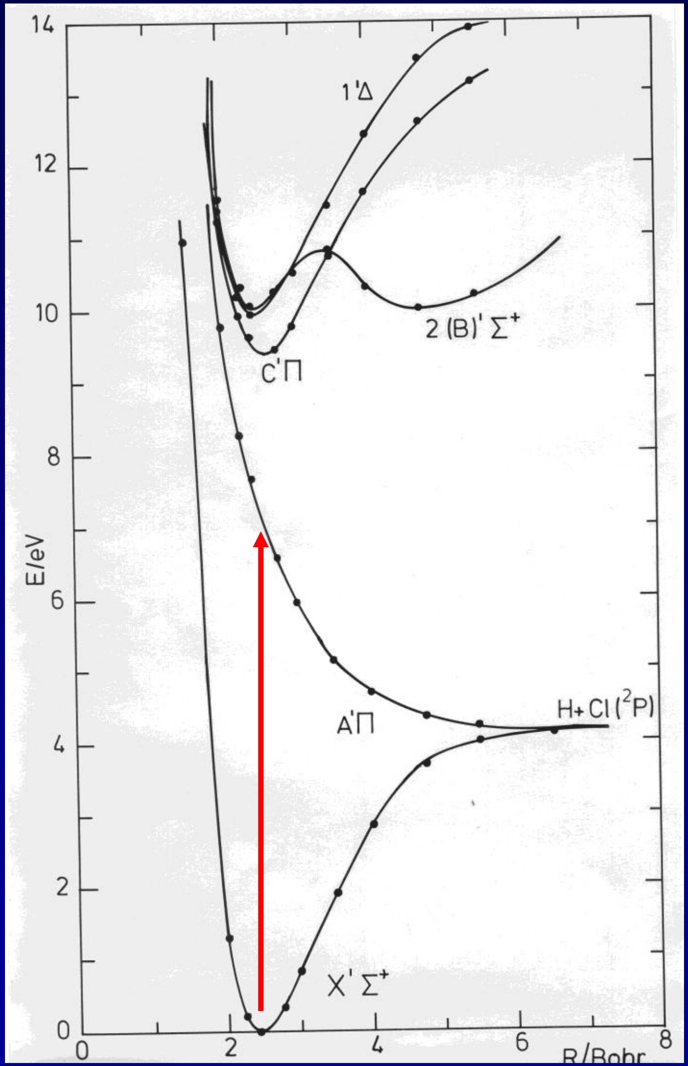
- 90% of absorptions into B and C states are followed by emission back into <u>bound</u> vibrational levels of the X state
- 10% of the absorptions are followed by emission into the <u>unbound</u> vibrational continuum, leading to dissociation

Cross sections: theory

- Ab initio quantum chemical calculation of potential curves and transition dipole moments for lowest ~5-10 roots of each symmetry
- Solve for nuclear motion on surfaces, taking couplings between states into account
- Compute cross sections by integration of product vibrational wave functions of ground and excited states and transition dipole moment.

Works well if number of electrons not too large: ~30
Most hydrides of astrophysical interest calculated, some heavier diatomics

HCl as a test case

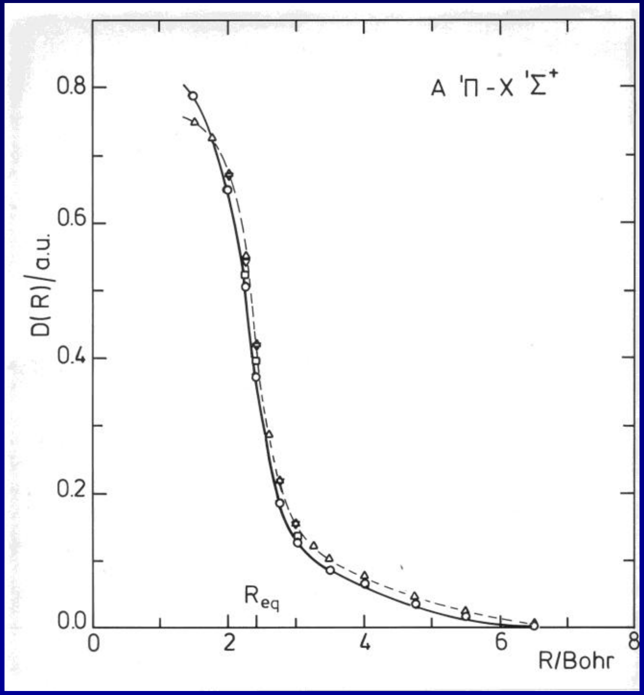


vD, vH & Dalgarno 1982

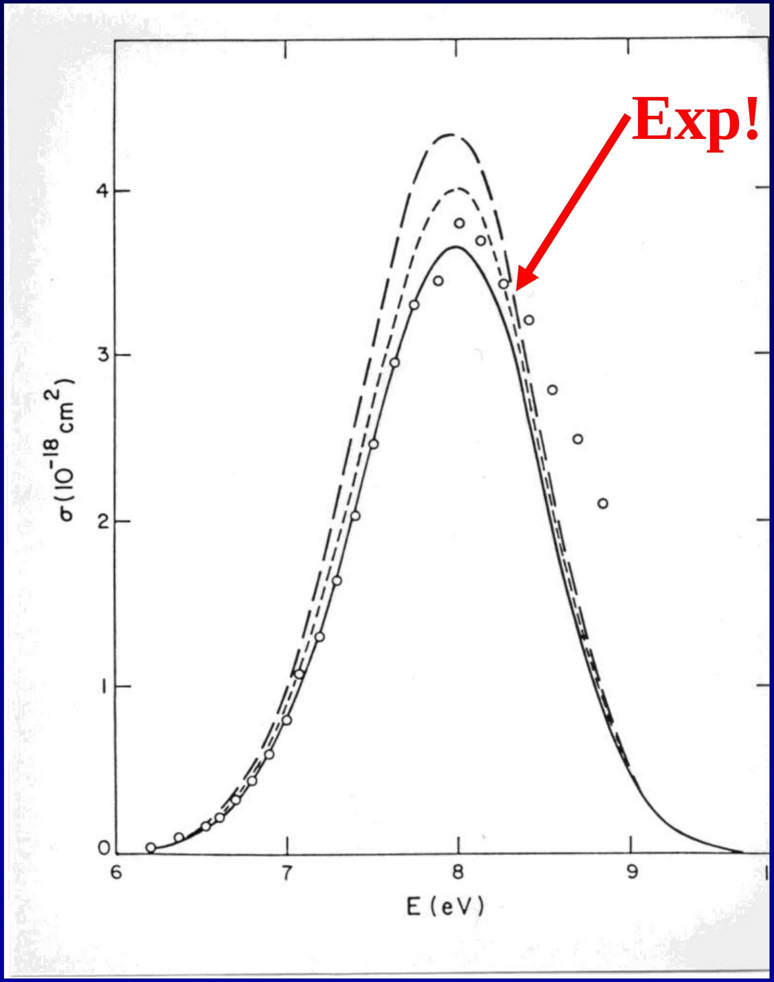
- See also H_2O as a test case

Quantitative comparison with experiment

Transition dipole moment function



HCl cross section A-X



- Excitation energies within 0.2-0.3 eV

- Oscillator strengths and cross sections within 20-30%

Small carbonaceous molecules

- Use increased computing power to determine vertical excitation energies and oscillator strengths of 9 states per symmetry of heavier species
- C_3, C_4, C_2H, *l*- and *c*-C_3H, *l*- and *c*-C_3H_2, HC_3H, *l*-C_4H and *l*-C_5H
- Compute E_{dis} and IP
- Assume all absorptions above E_{dis} and below IP lead to dissociation

Van Hemert & van Dishoeck 2008, Chem. Phys.

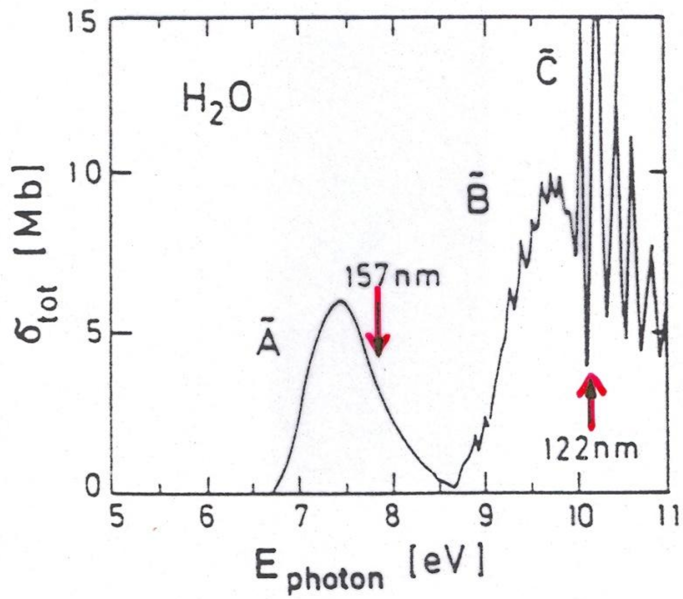
Caveats

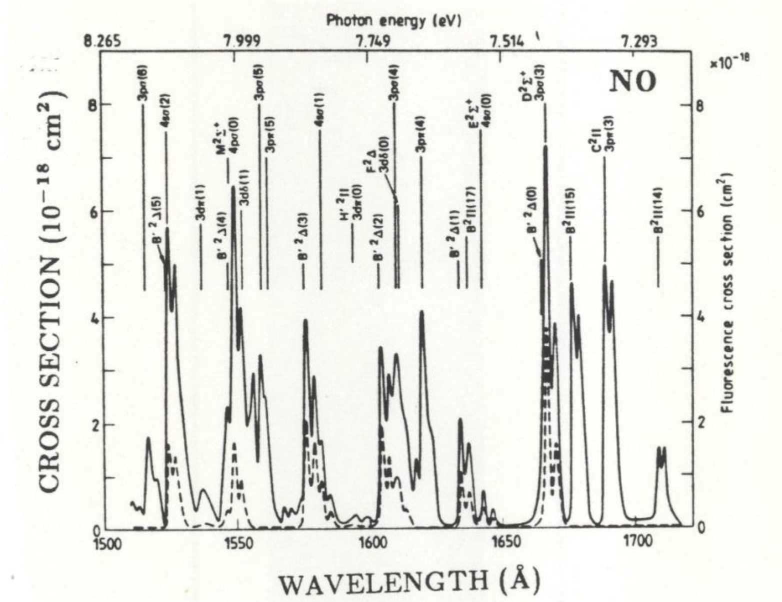
- Comparison with exp and other calculations shows that E_{ex} accurate to 0.2-0.3 eV and *f* to better than 30% for lower states
- Higher states (> 5'th root per symmetry) difficult to calculate because of heavy mixing of states and orbitals
  - E_{ex} O.K. to determine whether below IP or 13.6 eV
  - Magnitude of *f* (strong, weak) O.K.
  - Several new, strong Rydberg states found
- Rates are upper limits (but expected to be close to actual values)

Cross sections: experiments

- Limited (mostly) to stable molecules
  - Limited data on radicals and ions
- Absorption cross sections of many (stable) molecules measured over broad energy
  - High accuracy (~20%) if absorption is continuous
  - Large uncertainties (~order of magnitude) if absorption is discrete and lines unresolved
- Need to measure fluorescence and ionization cross sections to determine dissociation cross sections
  - Usually assume all absorptions above IP lead to ionization

Examples experiments

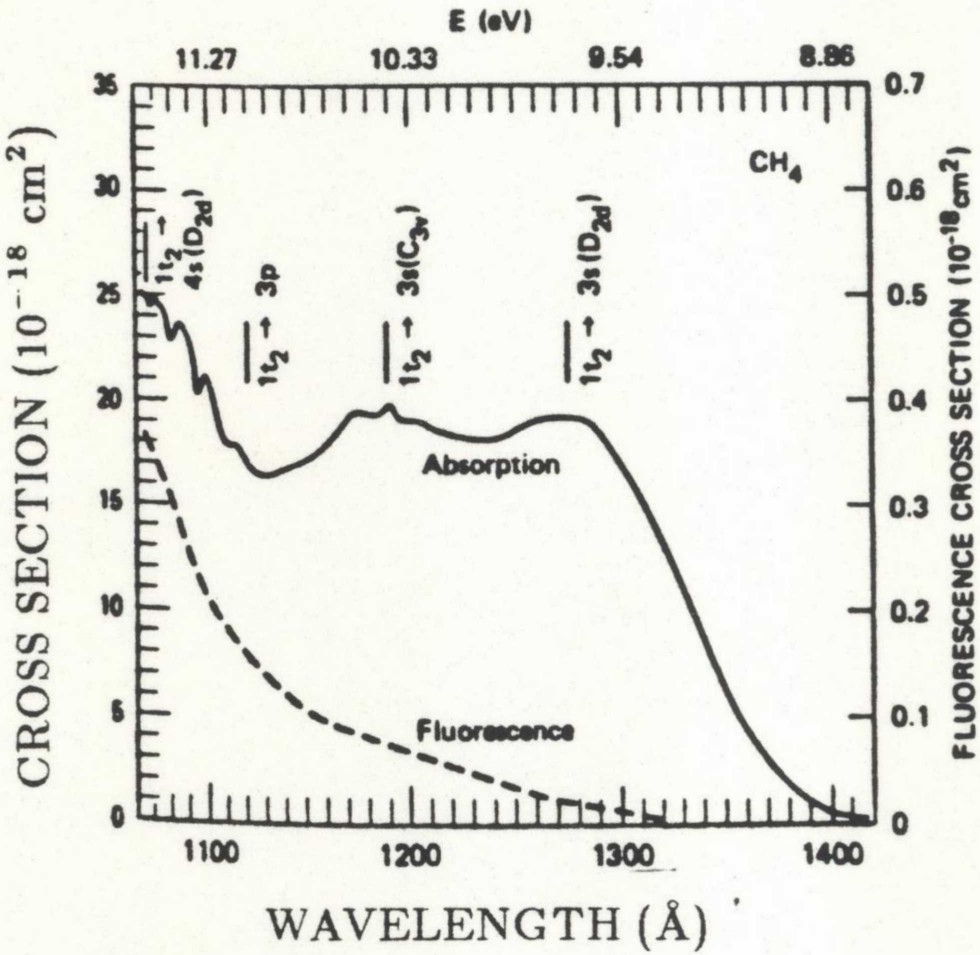




H_2O absorption followed by direct dissociation: accurate cross sections within 20%

NO absorption (full) and fluorescence (dashed); mostly predissociation through discrete transitions; large uncertainties (order of magnitude)

Example: CH_4



High accuracy

Not all absorptions lead to dissociation?

Lee & Chiang 1983

Products

- *Diatomics:* computed from dynamics
  - Outcome of predissociation process not well known if multiple states involved
  - OH => O(^{3}P), O(^{1}D), O(^{1}S)
  - CH^+ => C + H^+
  - Product ratio varies depending on radiation field
- *Triatomics:* computed from dynamics for light hydrides, but only accurate for lowest states
- *Polyatomics:* unknown, both from theory and experiments, except at a few specific wavelengths; no reasonable guesses, except which products are energetically accessible
  - Watch out for experiments at high pressure => subsequent reactions

Lots of work needed!

Photodissociation rate

- Continuum photodissociation

$$k_{\rm pd}=\int \sigma(\lambda) I(\lambda)\, d\lambda$$

where $\sigma_{\rm pd}$ is the cross section in cm^2, I= radiation field

- Discrete photodissociation

$$k_{pd} = \sum_{\rm lines} \frac{\pi e^2}{m_e c^2} \lambda^2_{\rm line} f_{\rm line} \eta_{\rm line} I(\lambda_{\rm line})$$

where f is oscillator strength and η is the dissociation probability

Interstellar radiation field

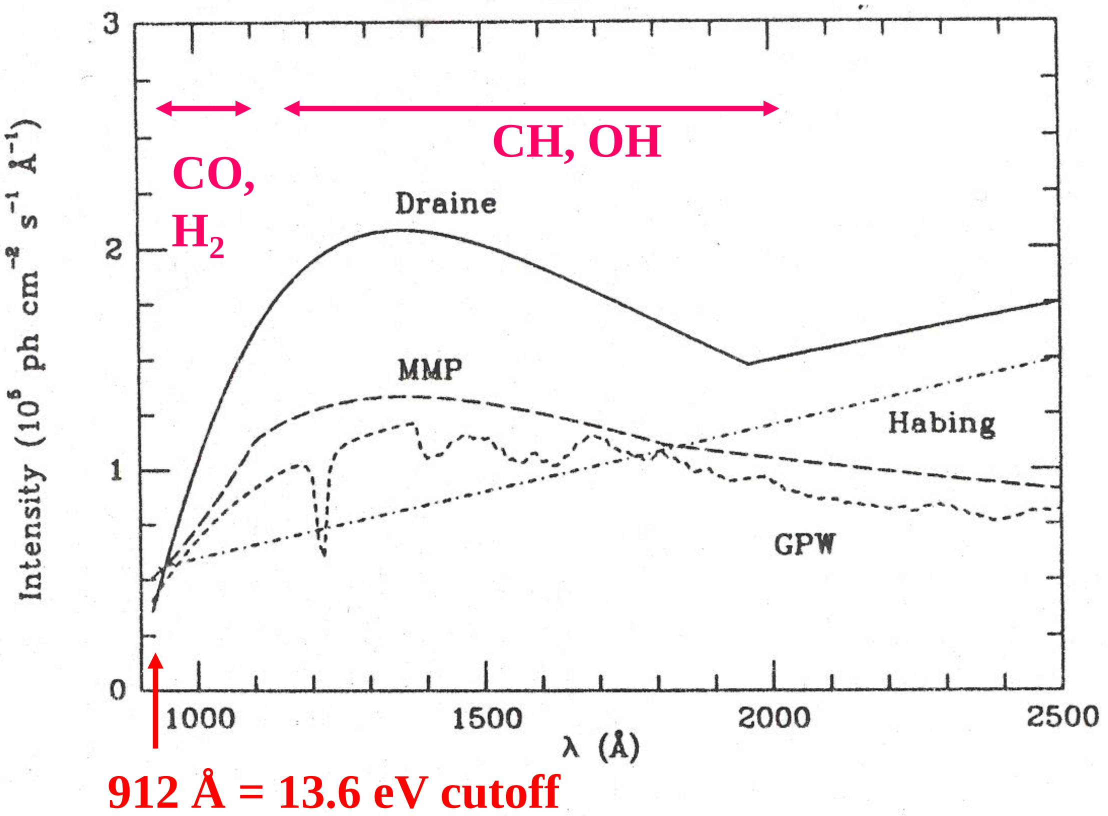
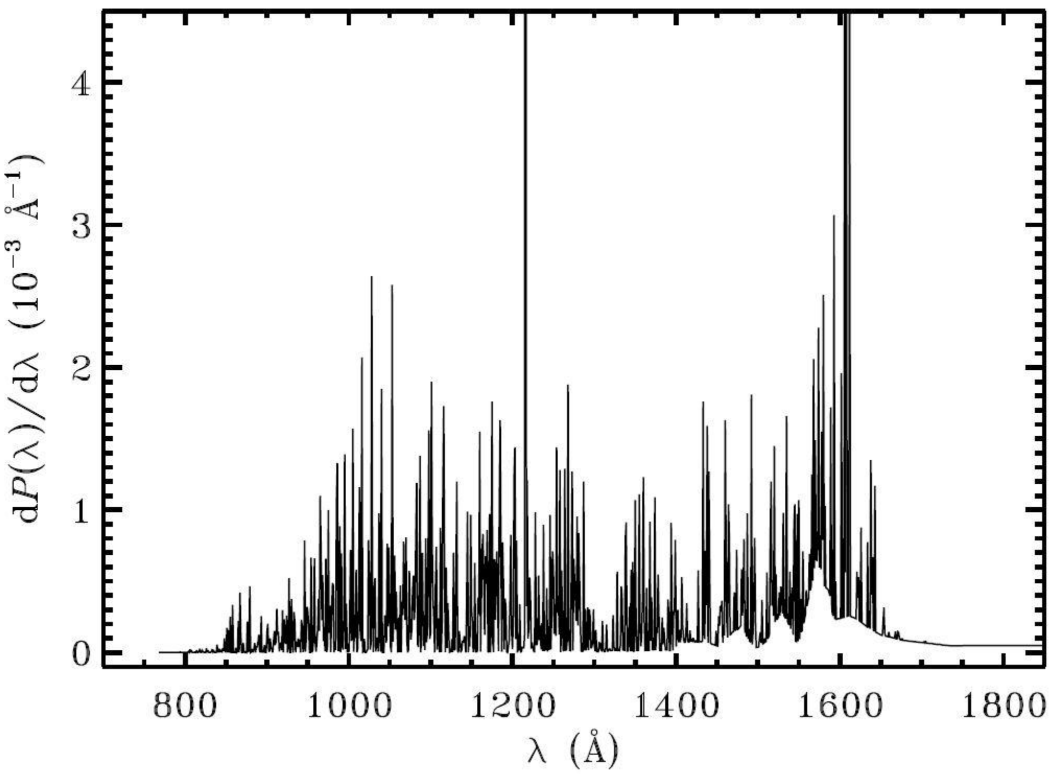


Figure 5. *The intensity of the interstellar radiation field as a function of wavelength cf. Draine (1978) (full line), Mathis et al. (1983) (long–dashed line), Gondhalekar et al. (1980) (short–dashed line) and Habing (1968) (dash–dotted line).*

- Average radiation provided by young O + B stars in solar neighborhood
- Incident on every cloud

Cosmic-ray induced radiation



H_2 + CR → H_2^+ + e*

H_2 + e* → H_2^* + e

H_2^* → H_2 + hν

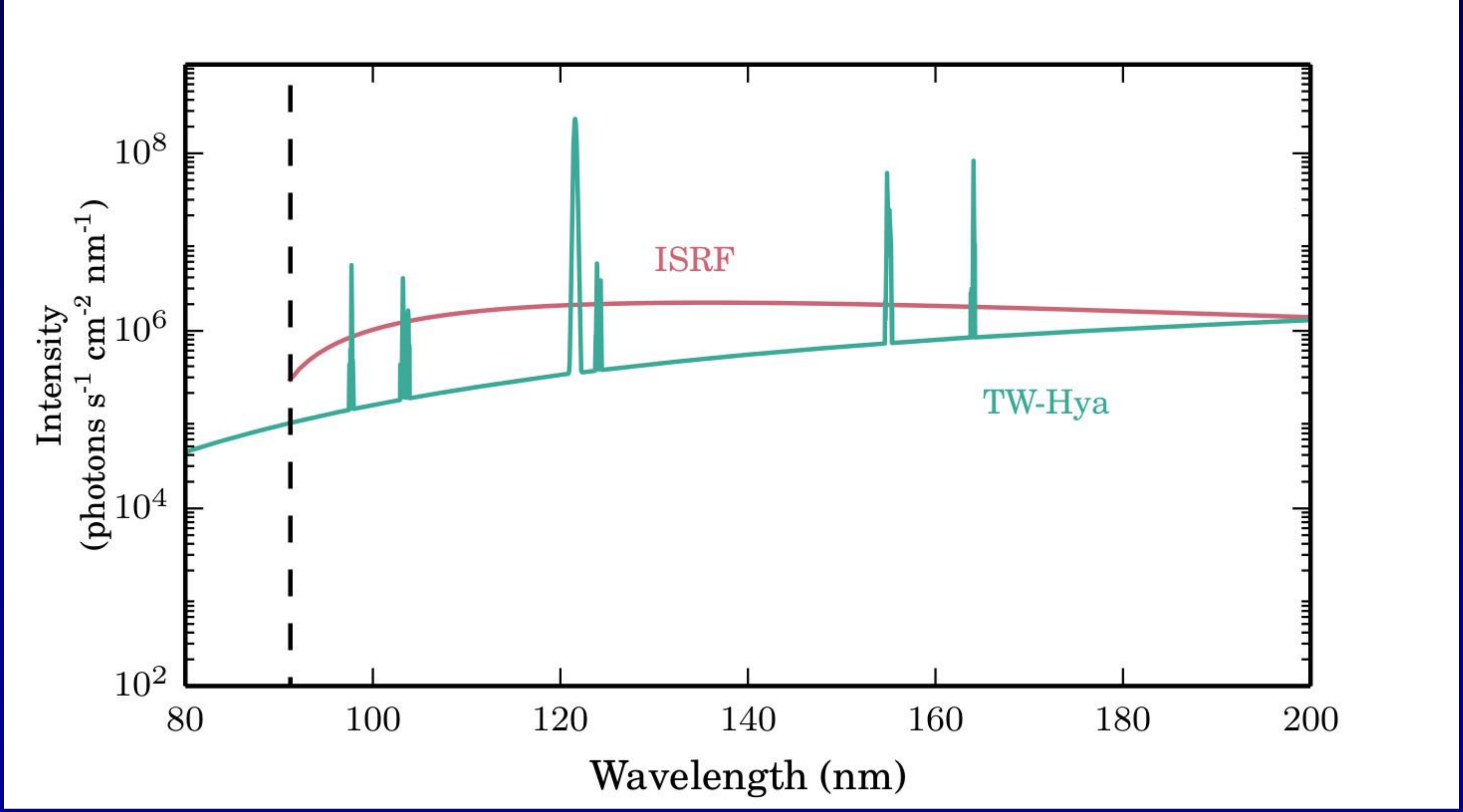
Prasad & Tarafdar 1983
Gredel et al. 1987

- Detailed line + continuum spectrum peaking around 1600 Å and continuing below 912 Å
- Provides low-level radiation field ***deep inside*** cloud

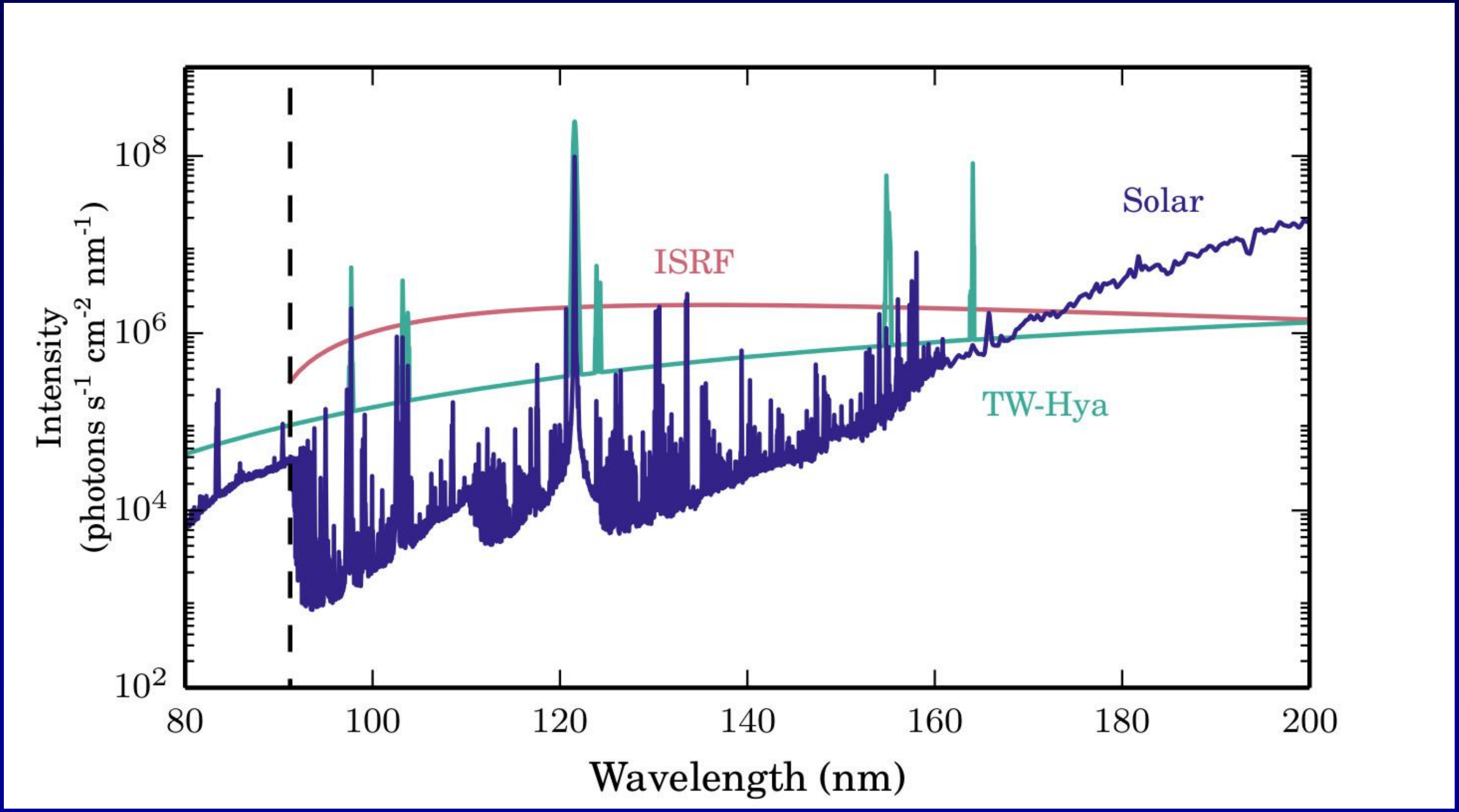
Other radiation fields

- Ly-α dominated
  - Shocks, young stars…..
- Stellar blackbodies $T_{\rm eff}$=4000-10000 K
  - Disks, cool PDRs, …
- Solar radiation $T_{\rm eff}$=5500 K + Ly α
  - Comets

Radiation fields



Radiation fields



Heays et al. in prep.

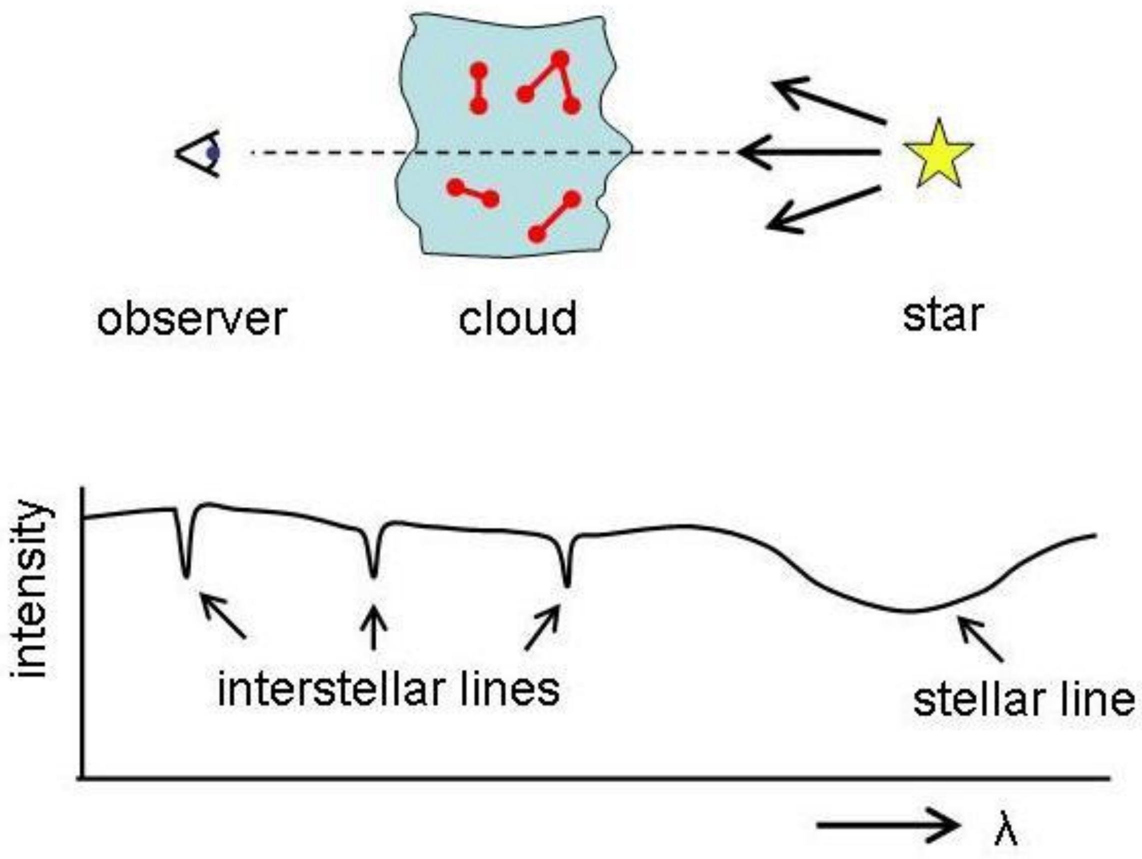
Also cosmic ray induced radiation field

Rosetta: landing on a comet

Photodissociation of molecules in coma by Sun

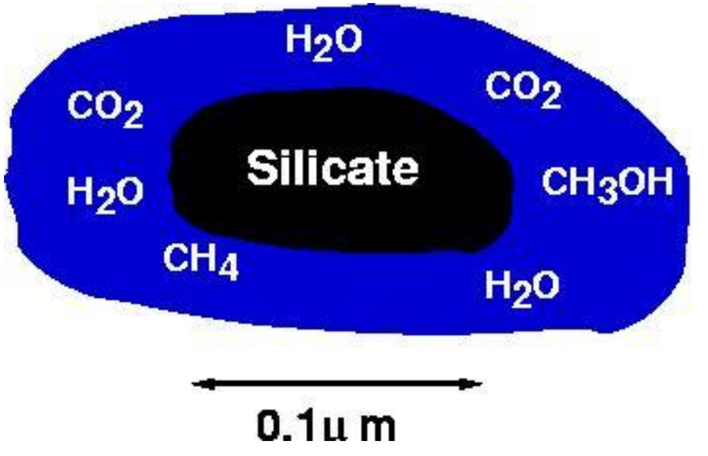
November 12 2014

Attenuation of radiation in clouds



- Radiation decreased due to absorption from atoms, molecules and dust

Interstellar grains



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

Attenuation of radiation in clouds

- **<u>Continuum</u> attenuation by dust grains: calculation depends on scattering properties of grains such as albedo and scattering phase function**

$$I(A_V) \approx I_0(A_V = 0)\exp(-\gamma A_V)$$

↑ Intensity inside cloud

↑ Intensity at edge

↑ **Depends on grain properties (λ):**
Typically 2-3 for 0.1 μm size grains
0.6 for μm size grains

Definitions

- $$\tau_\lambda^{ext} \equiv -\ln(I_\lambda / I_{o\lambda})$$
  $$A_\lambda / \mathrm{mag} \equiv -2.5\log_{10}(I_\lambda / I_{o\lambda})$$
  $$= -2.5\frac{\ln(I_\lambda / I_{o\lambda})}{\ln 10} = 1.086\tau_\lambda$$
- $$Q_{sca} \equiv \frac{\text{scattering cross section}}{\text{geometric cross section} = \pi a^2} \quad \text{for a sphere}$$
- $$Q_{abs} \equiv \frac{\text{absorption cross section}}{\pi a^2}$$
- $$Q_{ext} \equiv \frac{\text{extinction cross section}}{\pi a^2} = Q_{abs} + Q_{sca}$$

Definitions (cont'd)

$$\text{albedo} \equiv \frac{\sigma_{sca}}{\sigma_{ext}} = \frac{Q_{sca}}{Q_{ext}} \leq 1$$

$$g \equiv \langle \cos\alpha \rangle = \text{phase function}$$

g describes the angular redistribution of light

$$A_V \approx \frac{N_{\mathrm{H}}}{1.8 \times 10^{21}\,\mathrm{cm}^{-2}}$$

$N_H = N(H) + 2N(H_2)$

Observed relation between A_V and depth or hydrogen column into cloud

Other types of attenuation

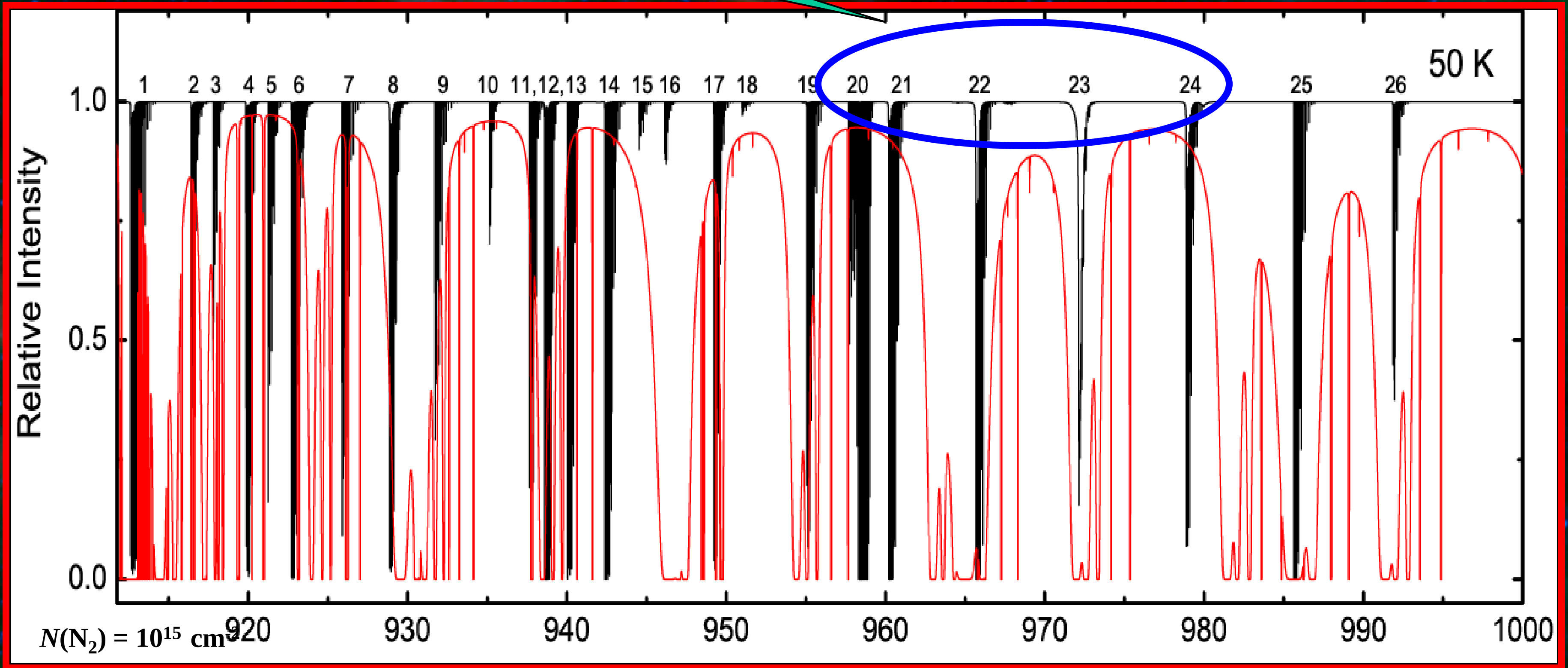
- **Self-shielding: H_2, CO, N_2**
  - **Molecules lying at edge of cloud absorb all available photons at discrete transitions so that molecules deep inside cloud see no photons**
- **Mutual shielding: H_2 shielding CO and N_2**

Need to know discrete spectra very well!

N_2 self-shielding and shielding by H_2 and H

Key range: 958-980 Å, contributes 58% at edge.

N_2 vs H_2+H

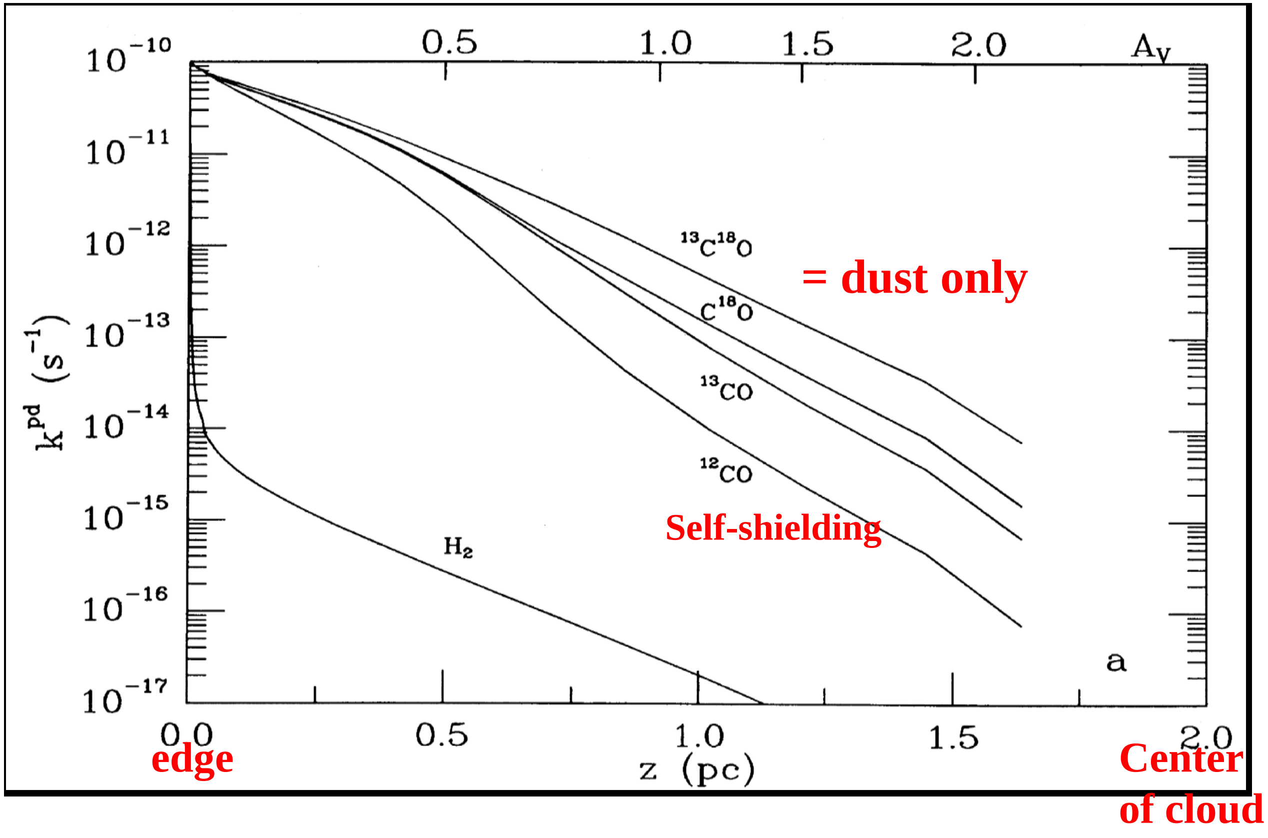


Wave length (Å)

Li, Heays et al. 2013

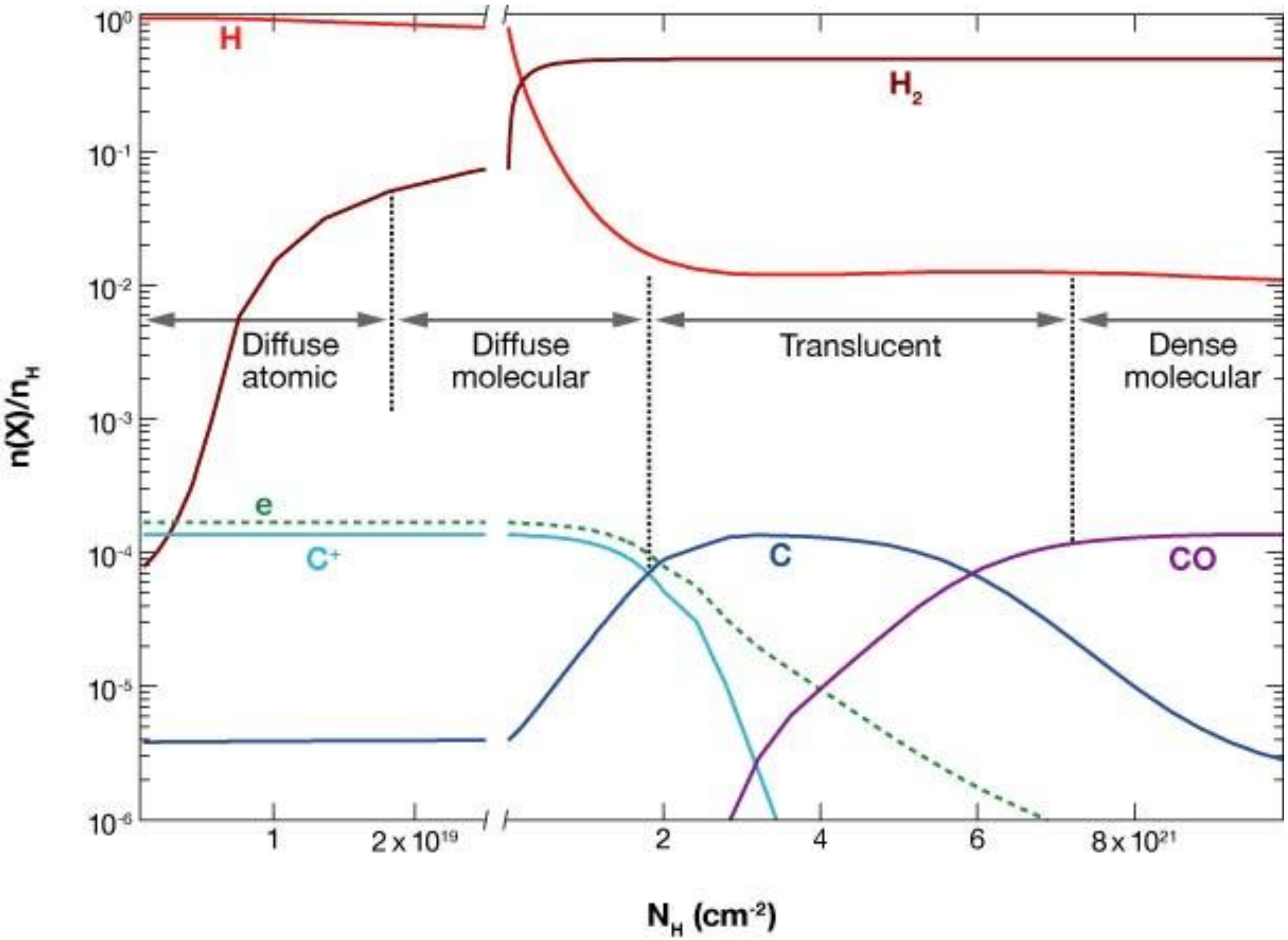
- Absolute rates, self-shielding and mutual shielding quantified

Self-shielding of CO and H_2
Photodissociation rates



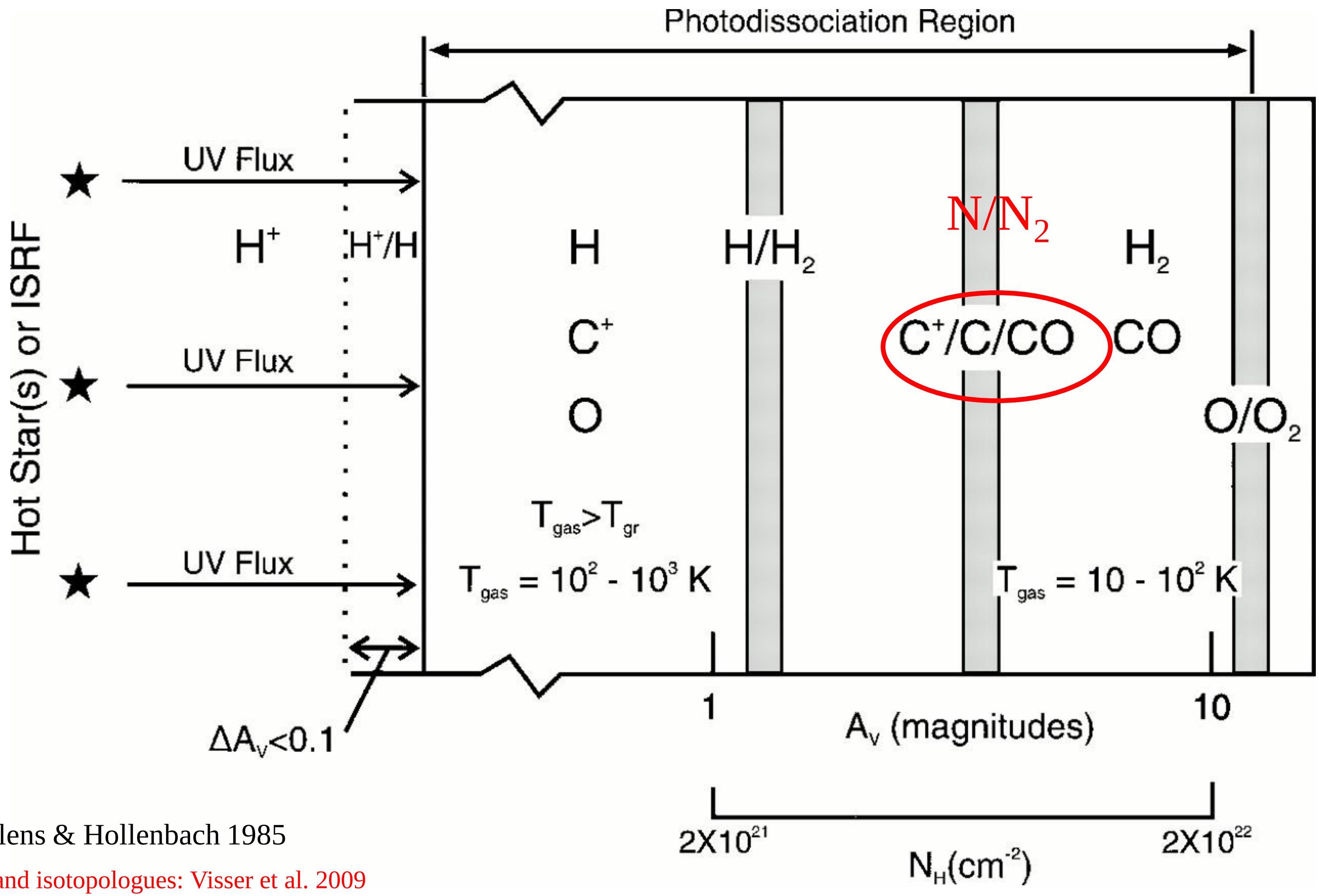
vD&B 1988

Types of molecular clouds defined by photodissociation



Snow TP, McCall BJ. 2006.
Annu. Rev. Astron. Astrophys. 44:367–414

Photon Dominated Regions



Tielens & Hollenbach 1985

CO and isotopologues: Visser et al. 2009

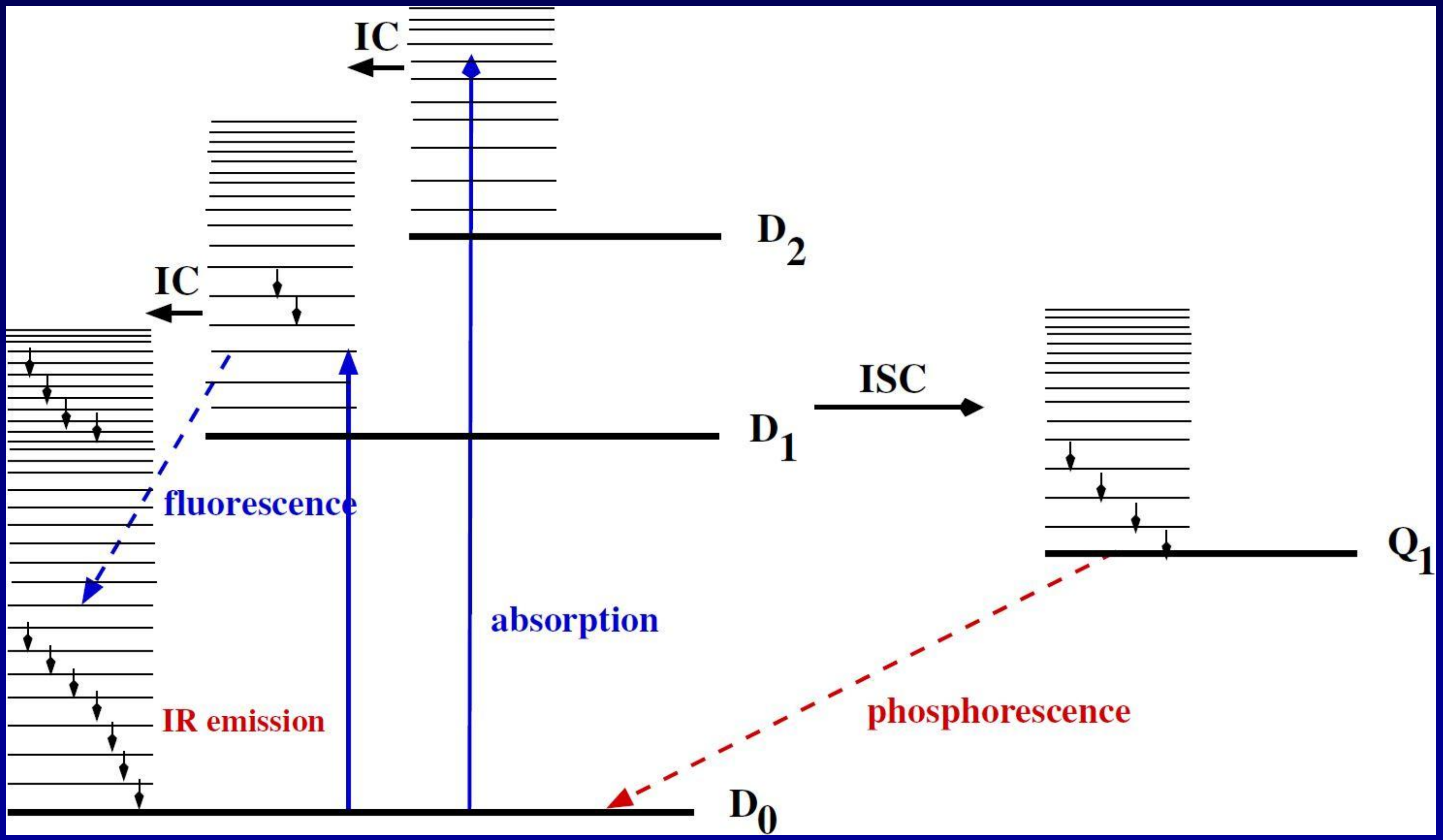
N_2, $^{14}N^{15}N$: Li, Heays et al. 2013, 2014

Hollenbach & Tielens 1997

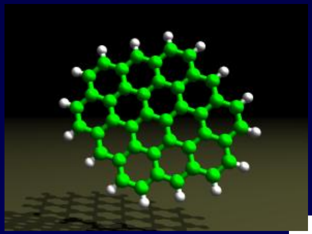
Large molecules

- **Density of vibrational levels of ground state becomes so high that excited states can couple with them non-radiatively: *internal conversion***
  - **Alternatives: fluorescence or intersystem crossing followed by phosphorescence**
- **Some fraction of energy will end up in vibrational mode leading to dissociation; rest will cascade by infrared photons**
- **Main question: when does molecule become stable against photodissociation? When N>25?**
- **Large molecules have first IP around 7 eV => (dissociative) photoionization?**

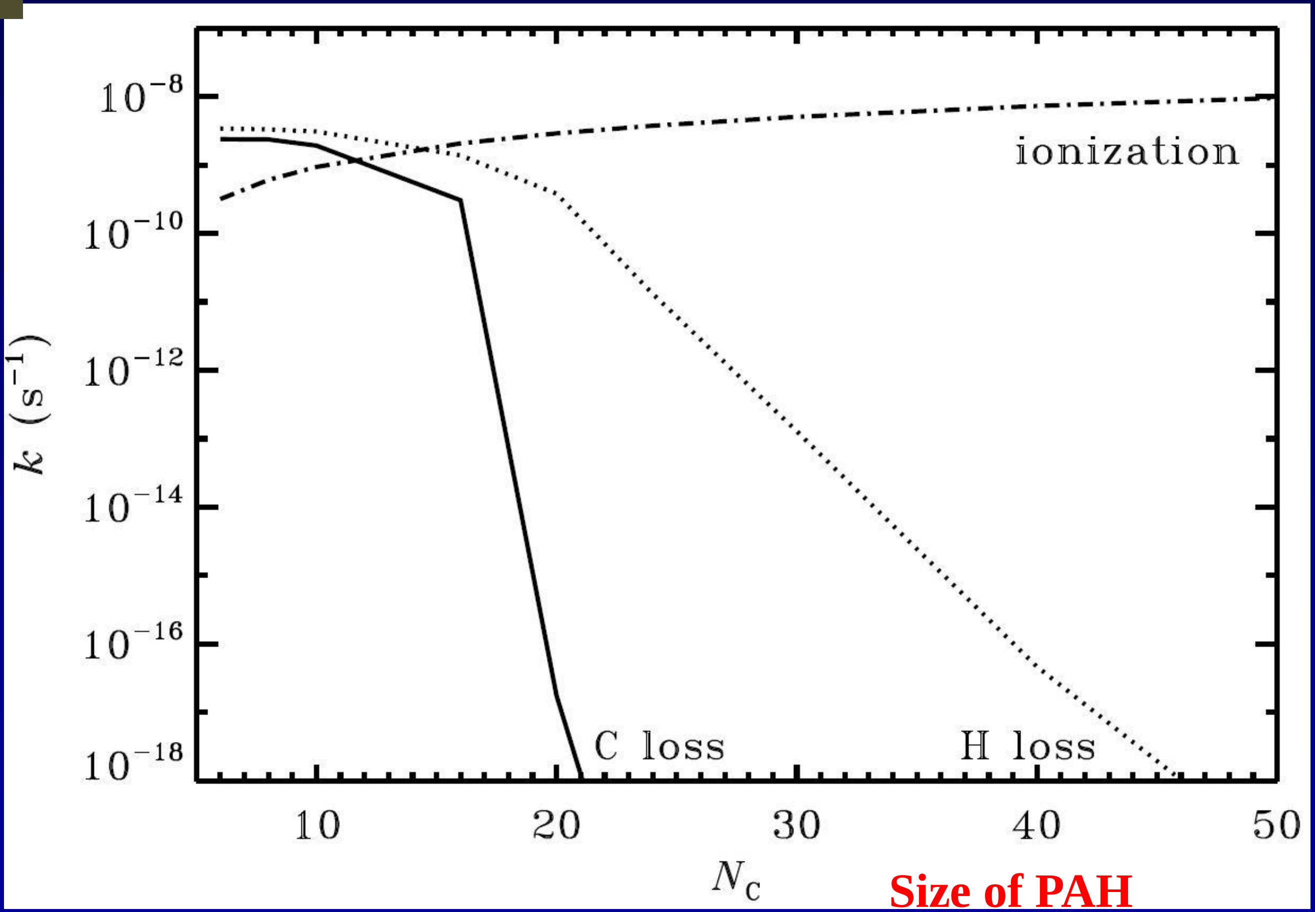
Large molecules
internal conversion vs dissociation



Allamandola et al. 1987
Leger et al. 1988
Joblin et al.
vD & Visser 2011



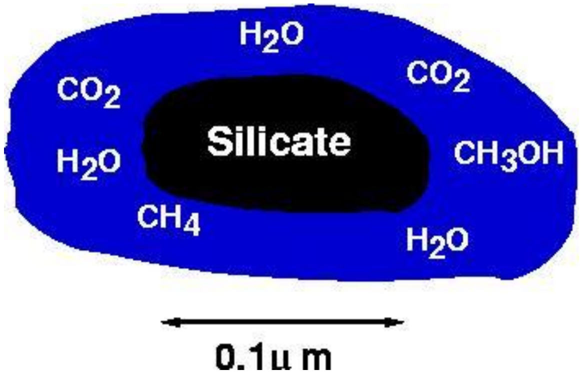
PAHs: H vs C loss

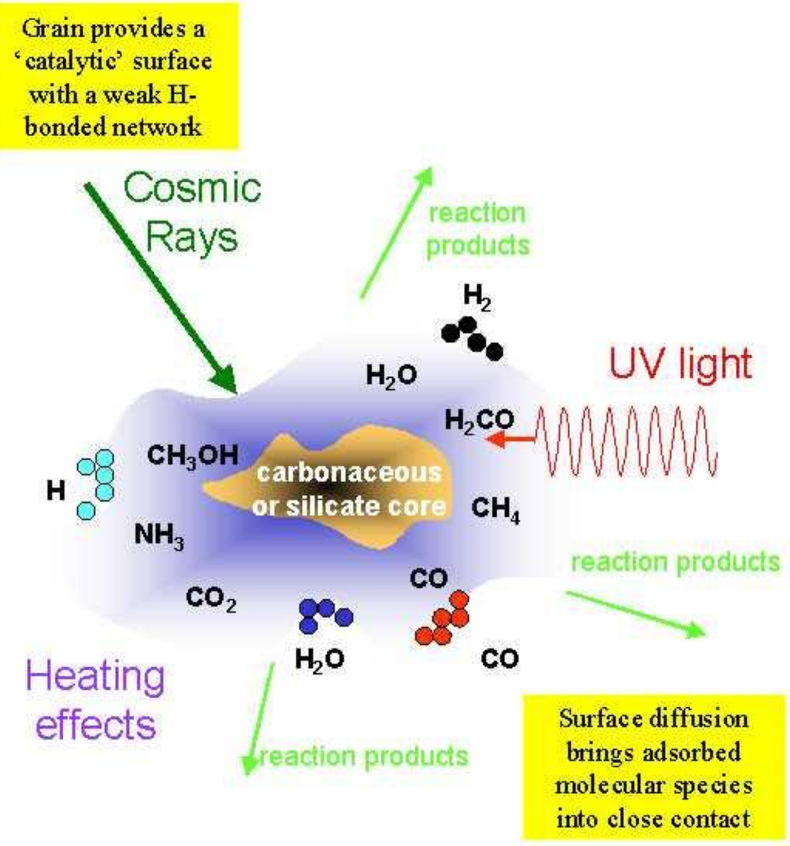


Visser et al. 2007

- Also multiphoton dissociation when exposed to intense UV (disks)

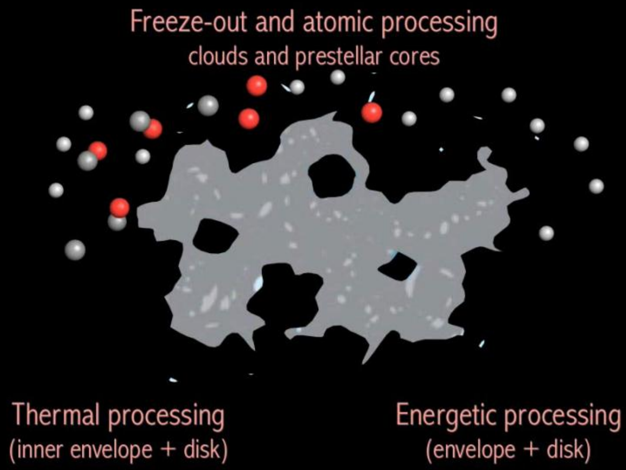
Ices





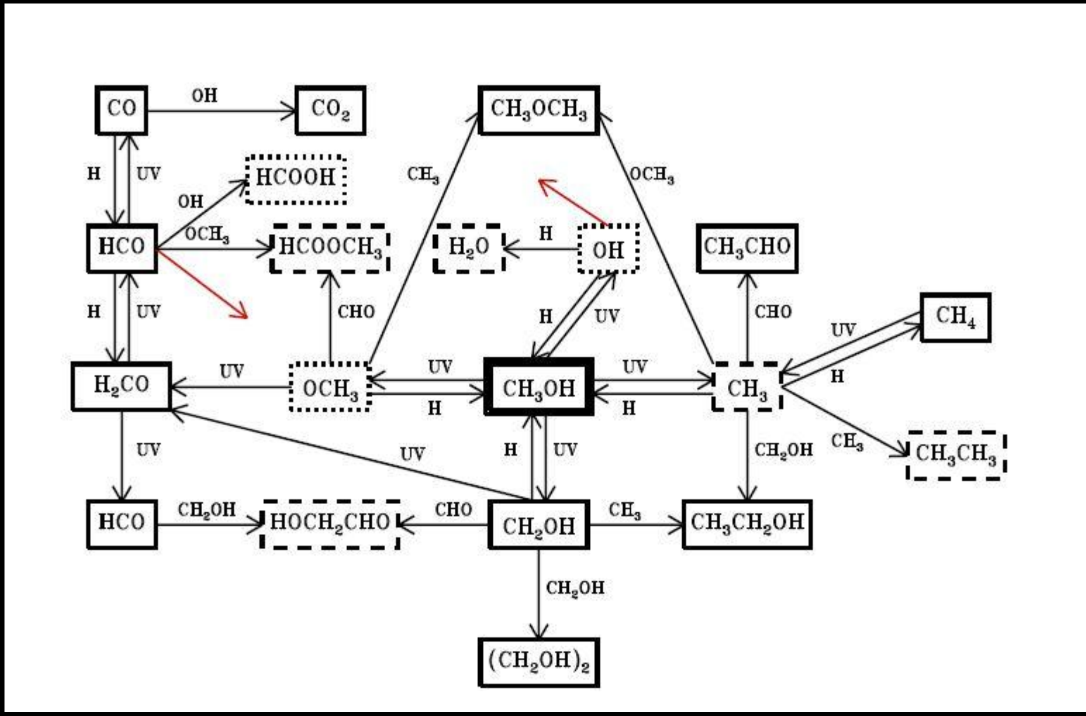
- Cold dense clouds (T_{dust}~10 K): gas-phase species condense on grains forming an icy mantle
- UV radiation dissociates molecules in ices, drives new chemistry

Making complex molecules in ices induced by UV



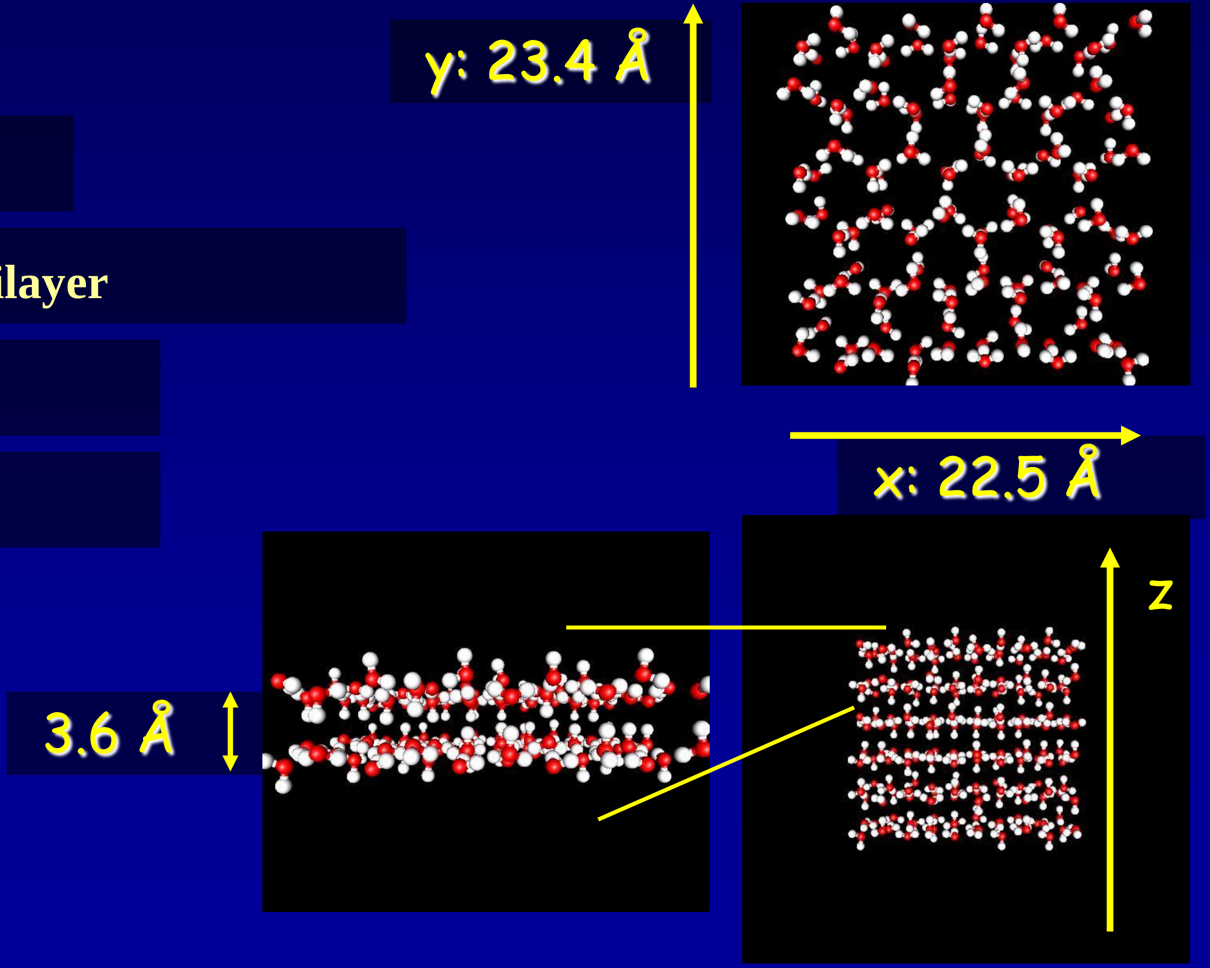
K. Öberg

Following
Garrod & Herbst 2006
Öberg et al. 2009



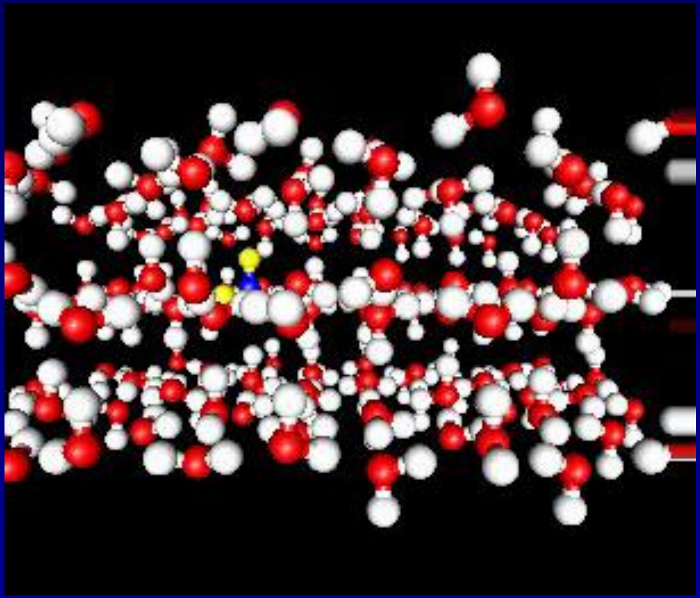
Interaction photons with ices: molecular dynamics study of H_2O

- **Periodic slab of crystalline ice (Ih)**
- **8 bilayers**
- **6 moving bilayers**
- **60 H_2O molecules per bilayer**
- **Rigid H_2O molecules**
- **Classical dynamics**



Andersson et al. 2005

Photodissociation and photodesorption of water ice

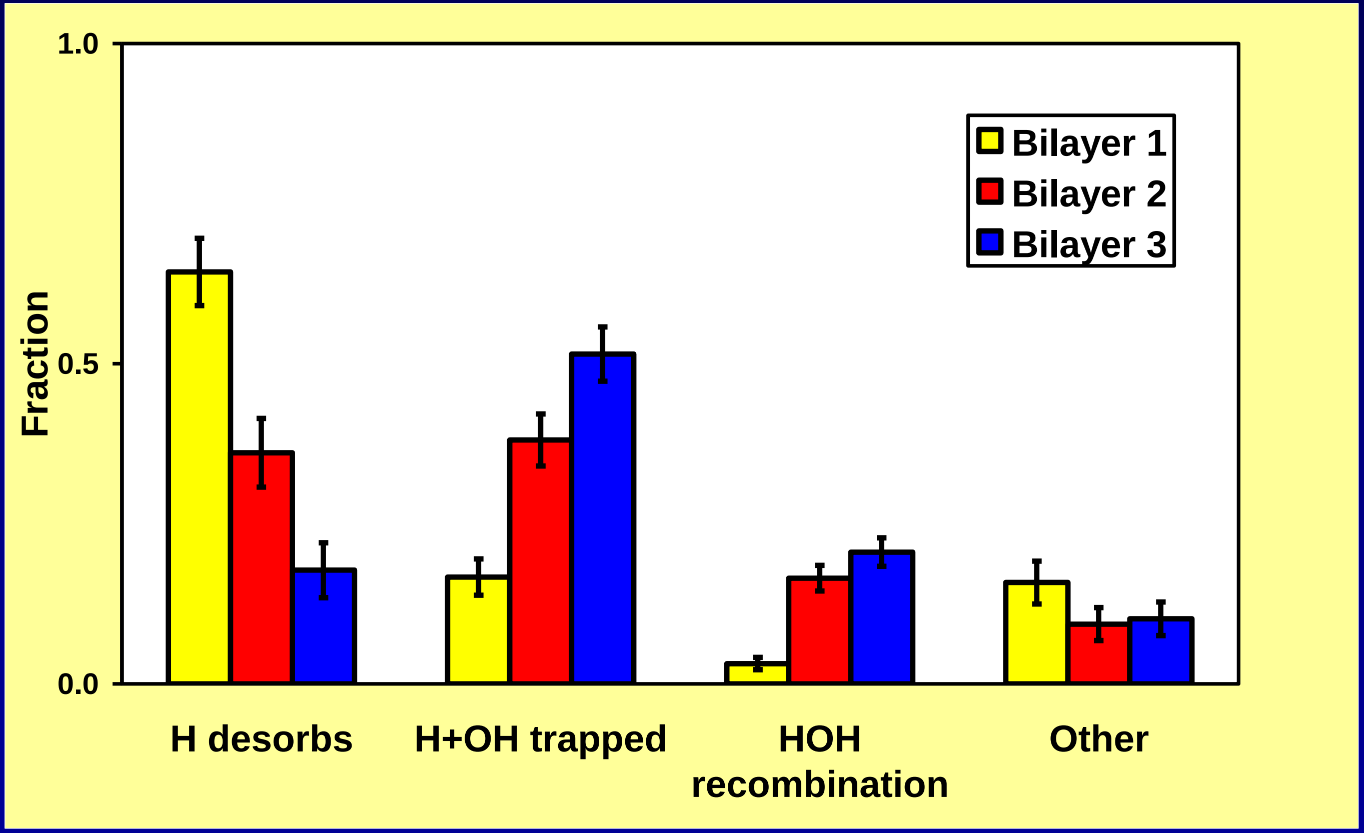


Side view

Two top bilayers
Duration: 0.6 ps

Andersson, Kroes & vD 2005, 2006
Andersson & vD 2008
Arasa et al. 2010, 2011, 2015

Outcome depends on layer



Also kick-out mechanism

What astronomers need

- PD and PI cross section as function of wavelength
  - Stable molecules, radicals, ions, ...
- Photodissociation products
- Radiation fields
- Grain properties

Issues

- Absorption vs dissociation cross section
  - Which fraction of absorptions leads to dissociation?
    - Issue for experiments and theory
    - Importance of dissociative photoionization?
  - At what size do molecules become stable?
- Radicals, carbon chains, ions
  - How far can we push theory?
- Products very poorly determined
- PD in ice vs gas
  - Similar or not (fundamental question!)

Photodissociation databases

- Summarized in reviews and made available on WWW at www.strw.leidenuniv.nl/~ewine/photo
  - 71 molecules photodissociation
  - 21 atoms photoionization
  - 17 molecules photoionization
- Includes cross section files and rates for different radiation fields
- Also: Mainz, Huebner et al., AtmoCIAD databases ; see talk Alan Heays

Uncertainties

- Rates: uncertainties estimated by EvD based on above considerations and critical evaluation of literature; categories A (<50%), B (factor 2) or C (factor of 10) ; will be revisited in new release
  - Includes estimates of higher-lying channels below IP or below 13.6 eV (represented by single line at 1000 Å)
  - Note: these uncertainties only hold for standard ISRF! Could be different for solar radiation field
- Products: no quantification of uncertainties possible, except for simplest diatomics

Enjoy the meeting!

Cat’s Eye
HST

Data needs astronomers (as collected during meeting, incomplete)

PD Cross sections vs λ

- Stable large organics: done?
- C_3H_2, carbon chains: sanity check
- CO isotopologs: minor ^{18}O, ^{17}O isotopes
- HD details
- NO
- P-bearing molecules
- Ions
- Major species at high temperatures

Branching ratios vs λ

- CH_3OH
- CH_4
- Any complex organic
  - CH_3CHO, $HCOOCH_3$, CH_3OCH_3, CH_3CN, ...
- ......