Photochemistry: rates, opacity, and heating

processes overview and basics

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KROME

better science through chemistry

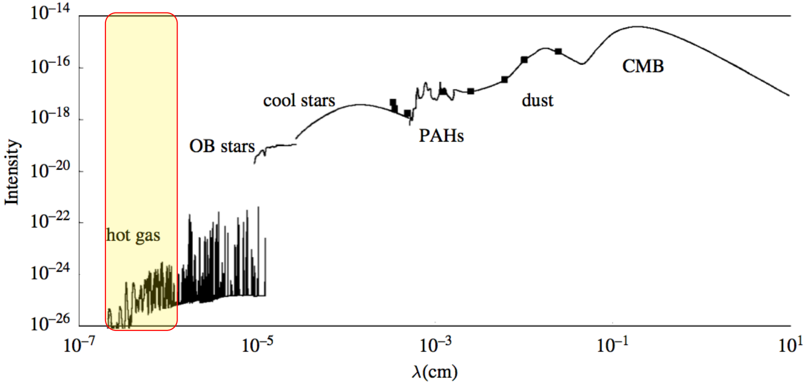
Aims and goals

- have an overview of the radiation sources in the Universe
- how the radiation interact with the gas
- how the photochemistry works
- how much photodissociation is complex
- something about the optical depth

Radiation sources in the Universe

mean intensity in units of erg cm^{-2} s^{-1} Hz^{-1} sr^{-1}

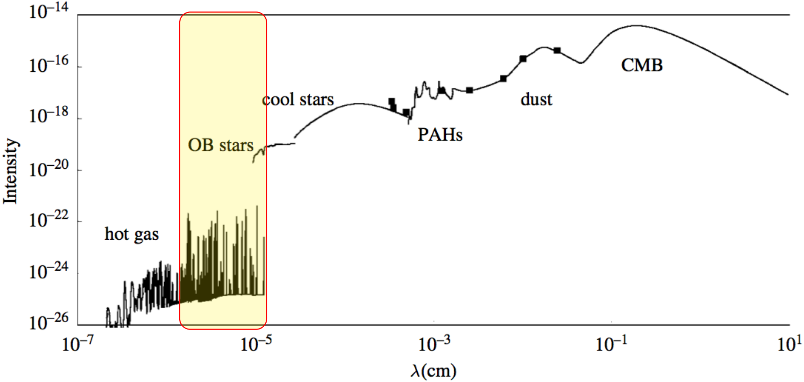
The ISM is permeated by various photon fields,
which influence the physical and chemical state of the gas and dust.



- Diffuse X-rays (> 124 eV)

Radiation sources in the Universe

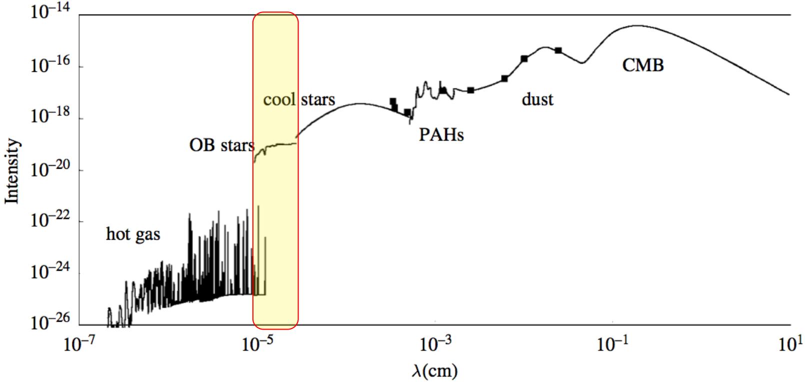
mean intensity in units of erg $\mathrm{cm}^{-2}\ \mathrm{s}^{-1}\ \mathrm{Hz}^{-1}\ \mathrm{sr}^{-1}$



- EUV (10.25 – 124 eV)

Radiation sources in the Universe

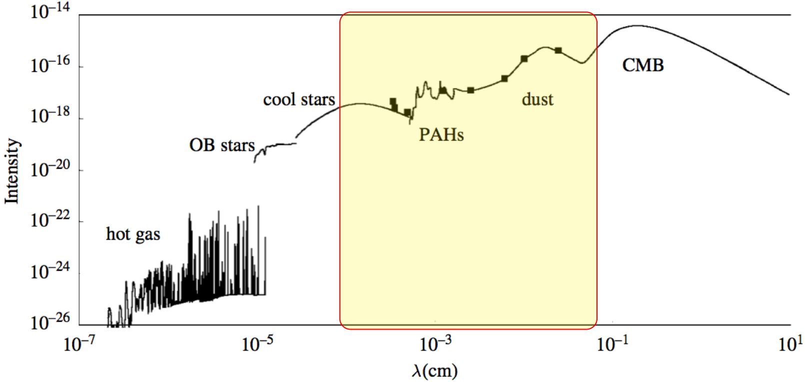
mean intensity in units of erg cm^{-2} s^{-1} Hz^{-1} sr^{-1}



- FUV (6.20 – 13.6 eV, including Ly-α edge)

Radiation sources in the Universe

mean intensity in units of erg cm^{-2} s^{-1} Hz^{-1} sr^{-1}



- IR (0.0012 – 1.2 eV)

Radiation sources in the Universe (cont’d)

- FUV emission mostly from early-type stars
- A-type stars visible region
- late-type stars far-red to near-IR
- hot plasmas (e.g. SNRs) X-rays
- Ly-α edge at 13.6 eV $\rightarrow$ due to HI absorption

Radiation needs to be included

- HI/HII regions, PDR
- shocks
- molecular clouds
- black holes
- ISM
- ...

Reference: Tielens, 2005

Main processes induced by radiation
overview

In any astrophysical region where UV photons can penetrate the following processes can occur:

1. photoionization
2. photodissociation
3. heating of the medium
4. (secondary ionizations)

Photoionization/photodissociation are the main destruction processes for atoms/molecules.

Main processes induced by radiation (1)

photoionization

Photons with energies $h\nu > E_0$ eject electrons from the atoms

Atoms

$$\mathrm{A^{+n} + h\nu \rightarrow A^{+(n+1)} + e^-}$$

Molecules

$$\mathrm{AB + h\nu \rightarrow AB^+ + e^-}$$

- $\mathrm{n = 0} \rightarrow$ ionization of a neutral atom
- $E_0 \rightarrow$ ionization potential of the atom (see table)
- the electrons of energy $(h\nu - E_0)$ produced can
  - elastically collide with ambient atoms/electrons (heating sources)
  - excite other ions/atoms (e.g. secondary ionization processes)

Ionization potential

Atom	E_0 (eV)	Atom	E_0 (eV)
HI	13.6	OI	13.61
HeI	24.6	OII	35.1
HeII	54.4	SiI	8.1
CI	11.2	SiII	16.3
CII	24.4	FeI	7.9

Photoionization

how to evaluate the rates

assume here an optically thin medium (see next slides)

$$k_{ph} = 4\pi \int_{\nu_0}^{\infty} \frac{I(\nu)\sigma(\nu)}{h\nu} d\nu \qquad \Longrightarrow \text{ in terms of frequency}$$

$$k_{ph} = \frac{4\pi}{h} \int_{E_0}^{\infty} \frac{I(E)\sigma(E)}{E} dE \qquad \Longrightarrow \text{ in terms of energy}$$

Note: KROME works in terms of energy

Photoionization

how to evaluate the rates

- radiation flux per energy

$$k_{ph} = \frac{4\pi}{h}\int_{E_0}^{\infty} \frac{I(E)}{E}\,\sigma(E)\,dE$$

$\mathrm{Hz} = \mathrm{s}^{-1}$

Photoionization

how to evaluate the rates

- radiation flux per energy

$$k_{ph} = \frac{4\pi}{h} \int_{E_0}^{\infty} \frac{I(E)}{E} \sigma(E)\, dE$$

- photoionization cross-sections

Hz = s^{-1}

Photoionization

how to evaluate the rates

- radiation flux per energy

$$k_{ph} = \frac{4\pi}{h}\int_{E_0}^{\infty} \frac{I(E)}{E}\,\sigma(E)\,dE$$

- photoionization cross-sections
- units check: $\frac{\mathrm{sr}}{\mathrm{eV\ \ s}}\frac{\mathrm{eVs^{-1}cm^{-2}Hz^{-1}sr^{-1}}}{\mathrm{eV}}\mathrm{cm^{2}eV}$

$\mathrm{Hz} = \mathrm{s}^{-1}$

Photoionization

how to evaluate the rates

- radiation flux per energy

$$k_{ph} = \frac{4\pi}{h} \int_{E_0}^{\infty} \frac{I(E)}{E} \sigma(E) \, dE$$

- photoionization cross-sections
- units check: $\frac{\mathrm{sr}}{\mathrm{eV\ \ s}} \frac{\mathrm{eVs^{-1}cm^{-2}Hz^{-1}sr^{-1}}}{\mathrm{eV}} \mathrm{cm^2eV}$
- $\frac{\cancel{\mathrm{sr}}}{\mathrm{eV\ \ s}} \frac{\mathrm{eVs^{-1}cm^{-2}Hz^{-1}}\cancel{\mathrm{sr^{-1}}}}{\mathrm{eV}} \mathrm{cm^2eV}$

Hz = s^{-1}

Photoionization

how to evaluate the rates

- radiation flux per energy

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- photoionization cross-sections
- units check: $\frac{\text{sr}}{\text{eV}\ \ \text{s}} \frac{\text{eVs}^{-1}\text{cm}^{-2}\text{Hz}^{-1}\text{sr}^{-1}}{\text{eV}} \text{cm}^2\text{eV}$
- $\frac{\cancel{\text{sr}}}{\text{eV}\ \ \text{s}} \frac{\text{eVs}^{-1}\text{cm}^{-2}\text{Hz}^{-1}\cancel{\text{sr}^{-1}}}{\text{eV}} \text{cm}^2\text{eV}$
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Hz = s^{-1}

Photoionization

how to evaluate the rates

- radiation flux per energy

$$k_{ph} = \frac{4\pi}{h}\int_{E_0}^{\infty} \frac{I(E)}{E}\,\sigma(E)\,dE$$

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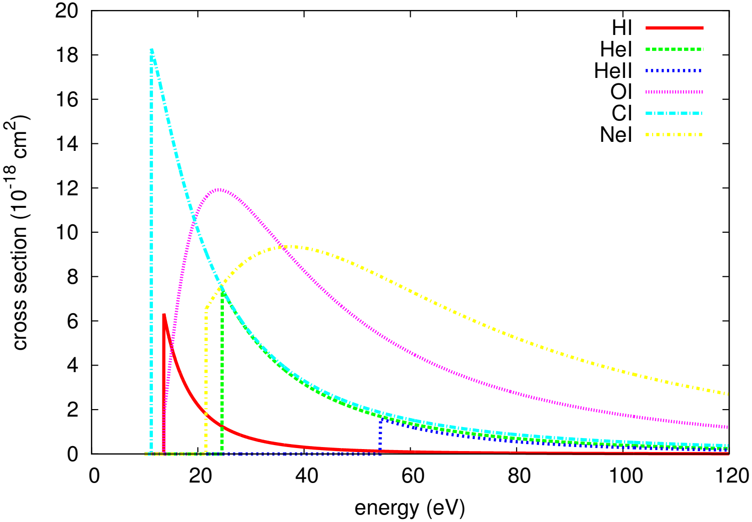
- $\frac{\cancel{\mathrm{sr}}}{\mathrm{eV\ \ s}}\frac{\mathrm{eV s^{-1} cm^{-2} Hz^{-1}}\cancel{\mathrm{sr^{-1}}}}{\mathrm{eV}}\mathrm{cm^2 eV}$
- $\frac{\cancel{\mathrm{sr}}}{\cancel{\mathrm{eV}}\ \ \mathrm{s}}\frac{\cancel{\mathrm{eV}}\mathrm{s^{-1} cm^{-2} Hz^{-1}}\cancel{\mathrm{sr^{-1}}}}{\cancel{\mathrm{eV}}}\mathrm{cm^2}\cancel{\mathrm{eV}}$
- $\frac{\cancel{\mathrm{sr}}}{\cancel{\mathrm{eV}}\ \ \mathrm{s}}\frac{\cancel{\mathrm{eV}}\cancel{\mathrm{s^{-1}}}\cancel{\mathrm{cm^{-2}}}\cancel{\mathrm{Hz^{-1}}}\cancel{\mathrm{sr^{-1}}}}{\cancel{\mathrm{eV}}}\cancel{\mathrm{cm^2}}\cancel{\mathrm{eV}} \Longrightarrow$ [1/s]

Hz = s^{-1}

Photoionization (cont'd)

the cross-sections

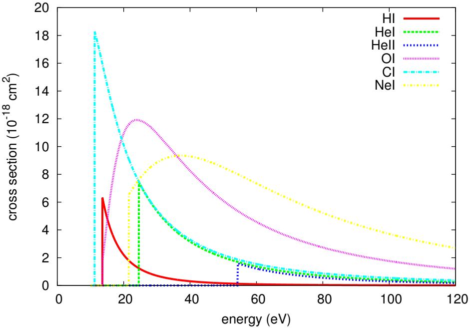


Photoionization (cont'd)

the cross-sections

some considerations:

- $\sigma_H \propto \nu^{-3}$
- $\sigma_{He} \propto \nu^{-2}$
- for $h\nu > 24.6 eV \rightarrow \sigma_{He} > \sigma_H$
- HI and OI same threshold
- KROME database (based on Verner+96)
- see Tommaso's talk



Photoionization

typical spectra

$$k_{ph} = \frac{4\pi}{h}\int_{E_0}^{\infty} I(E)\,\frac{\sigma(E)}{E}\,dE$$

- What kind of spectra should we expect/use?

Photoionization

typical spectra

$$k_{ph} = \frac{4\pi}{h}\int_{E_0}^{\infty} I(E) \, \frac{\sigma(E)}{E} \, dE$$

- What kind of spectra should we expect/use?
- It depends on the environment!

Photoionization (cont'd)

typical spectra

Blackbody radiation pervades much of astrophysics

- The surfaces of "normal" stars emit a spectrum that approximates blackbody radiation
- the 3-K cosmic microwave background radiation (CMB) exhibits a nearly perfect blackbody spectrum
- radio spectra from emission nebulae manifest the rising power-law character of blackbody radiation at low frequencies

Typical spectra

black-body

- proper BB emission only in optically thick media → photons in perfect thermal equilibrium with particles
- a unique temperature T can be defined

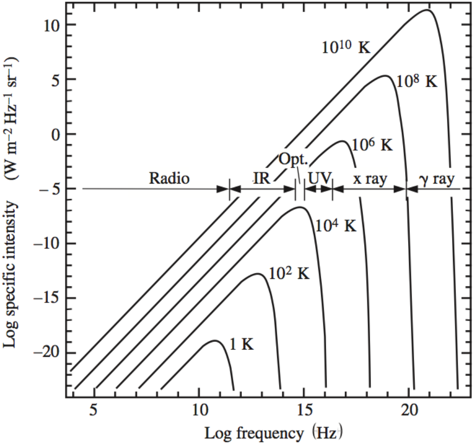
In contrast

- star's atmosphere temperature $\propto$ height
- gas-photons in equilibrium only in local regions
  → *Local thermodynamic equilibrium (LTE)*
- emission: BB spectrum of temperature T only in small region.
- the spectrum in another nearby region will approximate the blackbody form at the somewhat different temperature of that region.

Typical spectra

black-body intensity (eV/s/cm^2/Hz/sr)

$$B(\nu, T) = \frac{2h\nu^3}{c^2}\frac{1}{(e^{\frac{h\nu}{kT}} - 1)} \Longrightarrow \qquad B(E, T) = \frac{2E^3}{h^2c^2}\frac{1}{(e^{\frac{E}{kT}} - 1)}$$



Useful quantities

flux and number of photons per seconds

The energy flux density (considering a hemisphere)

$$\mathscr{F}_\nu = \pi B(\nu, T) \rightarrow \mathscr{F} = \pi \int_0^\infty B(\nu, T) d\nu = \sigma_{SB} T^4 \quad [\mathrm{eV\ s^{-1} cm^{-2}}]$$

Under the assumption that a star emits a BB radiation, the luminosity

of a star can be expressed as

$$L_\nu = 4\pi R_\star^2 \mathscr{F}_\nu \rightarrow L_\star = 4\pi R_\star^2 \mathscr{F} = 4\pi R_\star^2 \sigma_{SB} T^4$$

Number of photons emitted

$$N_{ph}[1/s] = \int_0^\infty \frac{L_\nu}{h\nu} d\nu$$

$$N_{ph}[1/s] = 4\pi R_\star^2 \int_0^\infty \frac{\pi B(\nu, T)}{h\nu} d\nu$$

Useful quantities

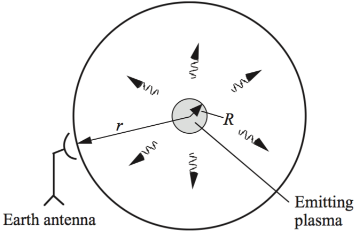
spectral flux density [eV s^{-1} cm^{-2}]

$$S(\nu, T) = \frac{1}{4\pi r^2} \int_0^\infty L_\nu(\nu) d\nu$$

$\Longrightarrow$ in terms of luminosity

$$S(\nu, T) = \pi \frac{R_\star^2}{r^2} \int_0^\infty B(\nu, T) d\nu$$

$\Longrightarrow$ in terms of BB radiation



If you know at which T emits your star, the radius $R_\star$, and the distance from the observer (or a decay region r) you can evaluate the emissivity in units of eV s^{-1} cm^{-2}.
(see the afternoon exercise)

Typical spectra
summary

Typical spectra adopted in modelling:

- stellar sources → black-body at T_{eff}
- quasars sources $\propto (\nu/\nu_{\mathrm{H}})^{-\alpha}$ with different power-law exponent
  - α = 1.0 for FUV sources
  - α = 1.5 for X-rays sources
- interstellar radiation field → Draine flux
  - $N_{ISRF} = 8.530 \times 10^{-5}\lambda^{-1} - 1.376 \times 10^{-1}\lambda^{-2} + 5.495 \times 10^{1}\lambda^{-3}$

Often the flux is normalized to the value at the Lyman limit

$$10^{-21} J_{21} \frac{B(\nu, T_{\mathrm{eff}})}{B(\nu_{\mathrm{H}}, T_{\mathrm{eff}})} \text{ erg cm}^{-2}\text{ Hz}^{-1}\text{ s}^{-1}\text{ sr}^{-1}$$

It is also quite common to find photodissociation rates alrady integrated over the Draine flux and depending on the extinction coefficient A_ν.

- integrated from the threshold ν_i to the Lyman-limit (ν_H = 13.6 eV)
- mostly for diffuse interstellar medium applications
- $k_{pd} = a\exp[-bA_\nu]$ (see photodissociation slides)

Main processes induced by radiation (2)

photodissociation

Molecules can both photoionize or/and photodissociate in the presence of radiation

$$AB + h\nu \to AB^+ + e^-$$

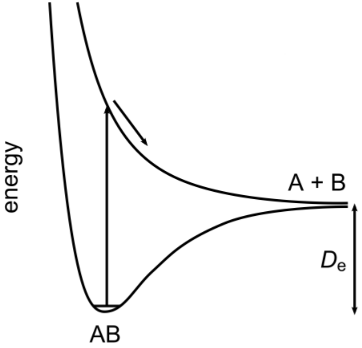
- H_2 photoinization potential is 15.42 eV
- mostly in HII regions

$$AB + h\nu \to A + B$$

- photodissociation is a complex process
- it can proceed through three different paths

Main processes induced by radiation (2)

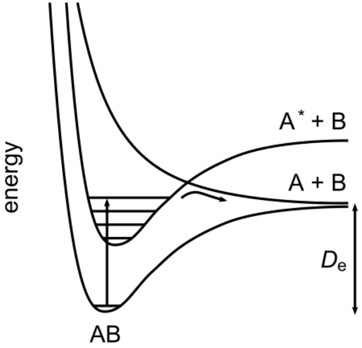
direct photodissociation



- electronic transitions (discussed by Daniele)
- a molecule absorbs a photon into an excited electronic state that is repulsive with respect to the nuclear coordinate.
- spontaneous emission back to the ground state is a slow process ($A \sim 10^9$ s^{-1})
- dissociation times of 10^{13} s^{-1}
- virtually all of the absorptions lead to dissociation of the molecule.

Main processes induced by radiation (2)

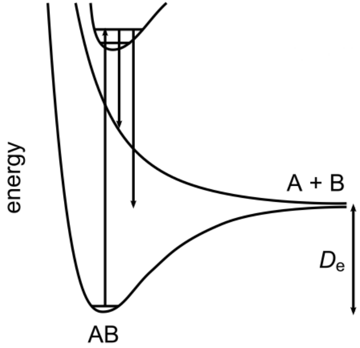
predissociation



- initial absorption occurs into a bound excited electronic state
- non-radiatively interaction with a nearby repulsive electronic state
- e.g. spin-orbit coupling between states of different spin multiplicity (pure quantum mechanics → let's avoid details)

Main processes induced by radiation (2)

spontaneous radiative dissociation



- if the excited bound states are not predissociated
- emission of photons into the continuum of a lower-lying repulsive state
- emission into the vibrational continuum of the ground electronic state

Main processes induced by radiation (2)

rates

1. $k_{ph} = \frac{4\pi}{h}\int_{E_0}^{\infty}\frac{I(E)\sigma(E)}{E}dE$
2. $k_{ph} = \sum_{lines}\frac{\pi e^2}{m_e c^2}\lambda_{line}^2\eta_{line}I(\lambda_{line})$
3. $k_{ph} = a\exp[-bA_\nu]$

- continuum case (direct dissociation)
- discrete case (predissociation& spontaneous radative dissociation)
- already integrated, including optical depth

- molecules like OH, H_2O, CH, CH_2, H_2^+ → direct photodiss. (1)
- CO, H2, N2 → discrete formula (2)
- some of the molecules can go through both processes depending on the radiation:
  - Direct photodissociation in hot radiation fields
  - Predissociation in cool radiation fields

Note: small A_ν optically thin medium, high A_ν optically thick medium. It works as an opacity term (see next slides).

Main processes induced by radiation (2)

H_2 photodissociation

Why H_2 is particular?

- dissociation energy at 4.48 eV
- homonuclear molecule/no dipole-moment

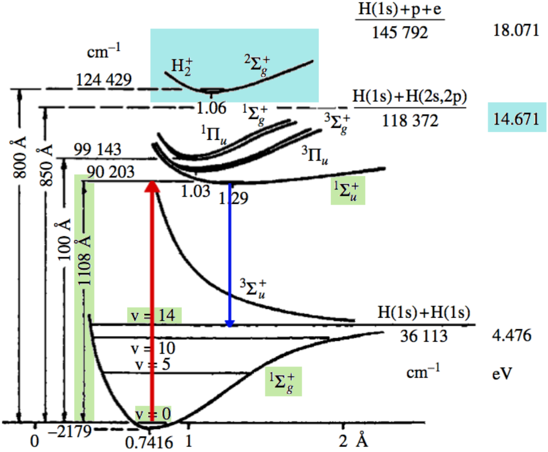
H_2 photodissociation can occur by

1. Direct excitation to the vibrational continuum of the ground electronic state
    - strongly forbidden
    - proceeds at a negligible rate
2. Excitation to the vibrational continuum of an excited electronic state of H2
    - threshold of 14.16 eV for ortho-hydrogen
    - thershold of 14.68 eV for para-hydrogen
    - restricted to HII regions
3. Two-step photodissociation → "Solomon process" (10% of the emission goes into the continuum, Stecher and Williams, 1967)
4. absorptions into the Lyman and Werner bands at 912–1100 Å

Main processes induced by radiation (2)

H_2 Solomon process via Lyman band B→X

$$\mathrm{H_2}(\mathrm{X}^1\Sigma_g^+, v=0) \xrightarrow{\sim 1000\ \text{Å}} \mathrm{H_2}(\mathrm{B}^1\Sigma_u^+, v=v') \rightarrow \mathrm{H_2}(\mathrm{X}^1\Sigma_g^+, v=v''>14) \rightarrow 2\mathrm{H}$$



Optical depth

understanding from a PDR

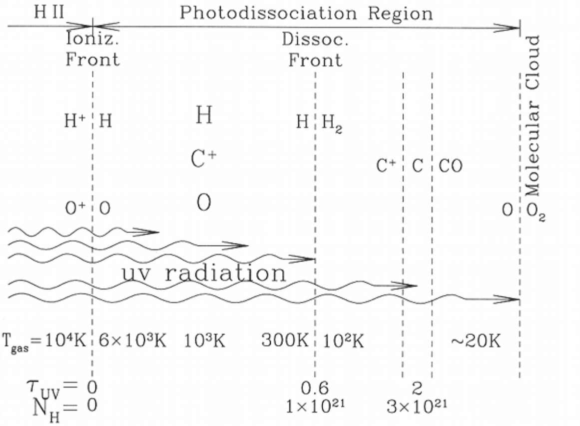


Figure 31.2 Structure of a PDR at the interface between an H II region and a dense molecular cloud.

Optical depth

understanding from a PDR

optically thin

$$k_{phi} = \frac{4\pi}{h}\int_{E_0}^{\infty}\frac{I(E)\sigma(E)}{E}dE$$

optically thick

$$k_{ph} = \frac{4\pi}{h}\int_{E_0}^{\infty}\frac{I(E)\sigma(E)}{E}e^{-\tau(E,n)}dE$$

- optical depth
- $\tau(E,n) = \sum_i \sigma_i N_i$
  - $\sigma_i \rightarrow$ cross-section
  - $N_i \rightarrow$ column density (see Tommaso's talk)

limiting cases

- $\lim_{\tau\rightarrow 0} e^{-\tau} = 1 \Longrightarrow$ medium optically thin
- $\lim_{\tau\rightarrow\infty} e^{-\tau} = 0 \Longrightarrow$ medium optically thick

Optical depth

understanding from a PDR

- $\lim_{\tau \to 0} e^{-\tau} = 1$
- $\lim_{\tau \to \infty} e^{-\tau} = 0$
- HII regions optically thin
- HI region optically thick

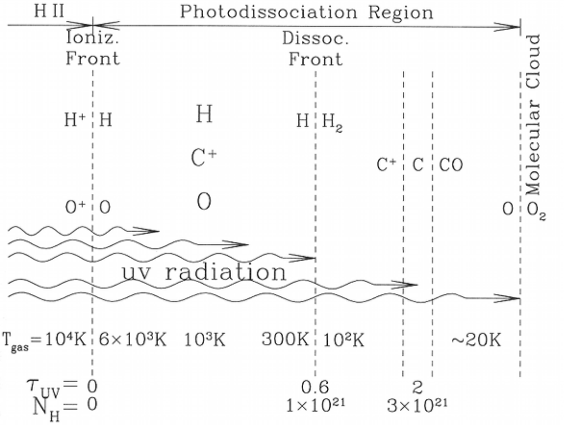


Figure 31.2 Structure of a PDR at the interface between an H II region and a dense molecular cloud.

Main processes induced by radiation (3)

photoheating

The photodissociation and photoionization induced by FUV radiation generate an excess of energy which can go into heating ($h\nu - E_0$).

Photoheating is mainly caused by

- atoms photoionizations in HII regions ($h\nu > 13.6$ eV)
- photo-ionization of large molecules and small dust grains in HI regions ($h\nu < 13.6$ eV)
- molecules photodissociation in molecular regions

$$H_{ph}[\mathrm{erg\ s}^{-1}] = \frac{4\pi}{h}\int_{E_0}^{\infty}\frac{I(E)\sigma(E)}{E}(E-E_0)\eta(E)e^{-\tau}dE \qquad (1)$$

$\eta(E)$ is an efficiency factor that determines the amount of energy released into the gas. The effective photoheating is

$$\Gamma_{ph} = H_{ph}n_X \qquad (2)$$

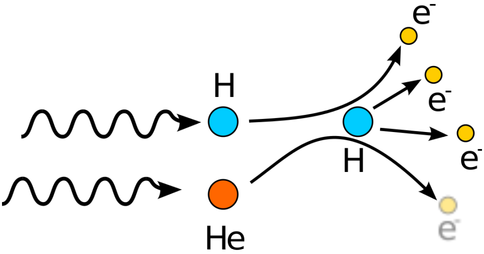
in erg s^{-1} cm^{-3}.

Main processes induced by radiation (4)

X-rays photons

Xrays photons (2-10 keV)

- a typical X-ray photon is far more likely to be absorbed by HeI rather than HI.
- generate energetic photoelectrons which cause secondary ionizations
- the ejected photoelectron, however, will ionize many more HI atoms than HeI, as HI is more abundant



Courtesy of T. Grassi

Shull+1985,Wolfire+1995,Ricotti+2002,Ricotti+2004,2005,Furlanetto+2010

Main processes induced by radiation (4)

X-rays photons

$$\zeta^i_{tot} = \zeta^i_p + \sum_{j=\mathrm{H,He}} \frac{n_j}{n_i} \zeta^j_p \langle \phi^i \rangle$$

- total primary + secondary ionization rate

Main processes induced by radiation (4)

X-rays photons

$$\zeta^i_{tot} = \zeta^i_p + \sum_{j=\mathrm{H,He}} \frac{n_j}{n_i}\zeta^j_p \langle\phi^i\rangle$$

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Main processes induced by radiation (4)

X-rays photons

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- total primary + secondary ionization rate
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- number of secondary ionization per primary ionization

Main processes induced by radiation (4)

X-rays photons

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- total primary + secondary ionization rate
- primary photoionization rate
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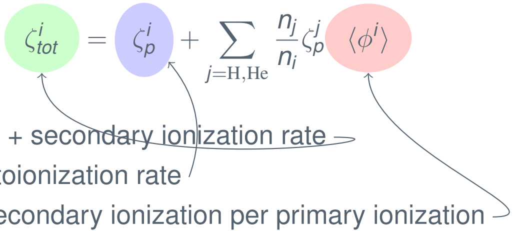
- $\phi^H(E, x_e) = \left(\frac{E}{13.6\ \mathrm{eV}} - 1\right) 0.3908(1 - x_e^{0.4092})^{1.7592}$

Main processes induced by radiation (4)

X-rays photons



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- $\phi^{He}(E, x_e) = \left(\frac{E}{24.6\ \mathrm{eV}} - 1\right) 0.0554(1 - x_e^{0.4614})^{1.666}$

Main processes induced by radiation (4)

X-rays photons

$$\zeta^i_{tot} = \zeta^i_p + \sum_{j=\mathrm{H,He}} \frac{n_j}{n_i} \zeta^j_p \langle \phi^i \rangle$$

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- $\langle \phi^i \rangle = \frac{\int I_X(E) \phi^i(E, x_e) dE}{\int I_X(E) dE}$

Main processes induced by radiation (4)

X-rays photons

$$\zeta^i_{tot} = \zeta^i_p + \sum_{j=\mathrm{H,He}} \frac{n_j}{n_i} \zeta^j_p \langle \phi^i \rangle$$

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- primary photoionization rate
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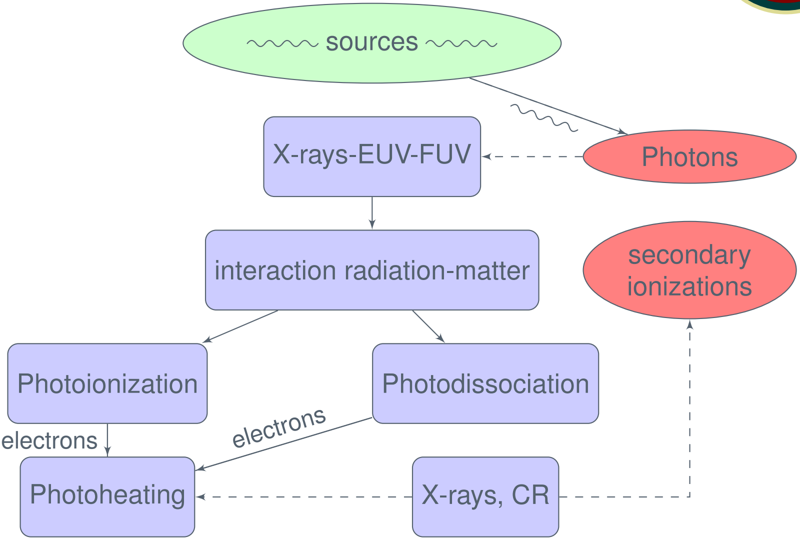
- $\langle \phi^i \rangle = \frac{\int I_X(E) \phi^i(E, x_e) dE}{\int I_X(E) dE}$
- → see Latif's talk for an application

Interaction radiation-matter

a schematic summary



Additional info

References:

- T. P. Stecher & D.A. Williams, ApJL, 149, L29, 1967
- J. M. Shull & M.E. Van Stenberg, ApJ, 298, 268, 1985
- D. A. Verner & G. J. Ferland, ApJS, 103, 647, 1996
- J. Dyson, D. A. Williams, "The physics of the interstellar medium", 1997
- S. C. O. Glover & P. W. J. L. Brand, MNRAS, 321, 385, 2001
- A. Tielens "The Physics and Chemistry of the Interstellar Medium", 2005
- H. Bradt "Astrophysics processes", 2008
- B. T. Draine "Physics of the Interstellar and Intergalactic Medium", 2011
- E. F. van Dishoeck & R. Visser, eprint arXiv:1106.3917, 2011
- `http://home.strw.leidenuniv.nl/~ewine/photo/`

www.kromepackage.org

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