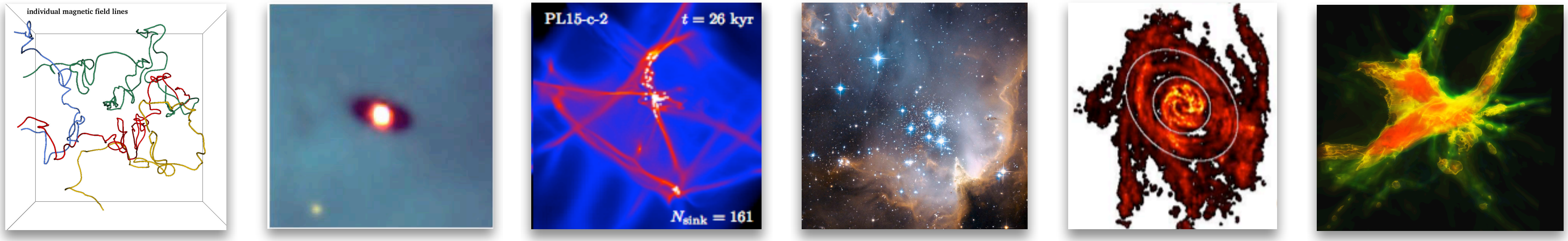
Modeling ISM Dynamics and Star Formation



Ralf Klessen

Universität Heidelberg, Zentrum für Astronomie
Institut für Theoretische Astrophysik

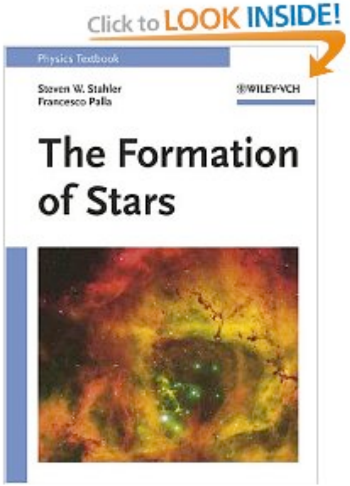
disclaimer

Disclaimer

- I try to cover the field as broadly as possible, however, there will clearly be a bias towards my personal interests and many examples will be from my own work.

literature

Literature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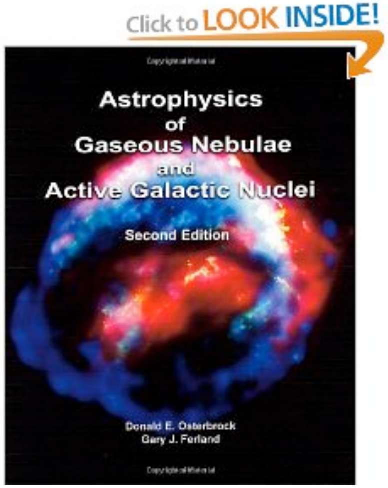
Steven W. Stahler
Francesco Palla
WILEY-VCH
The Formation of Stars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Donald E. Osterbrock
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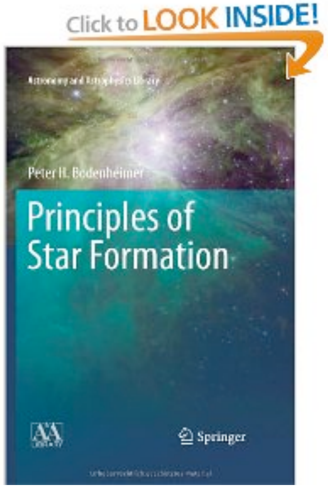
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Principles of Star Formation
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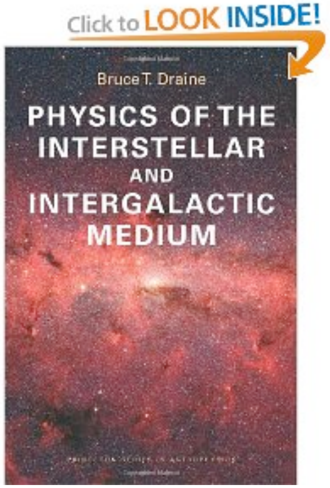
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Bruce T. Draine
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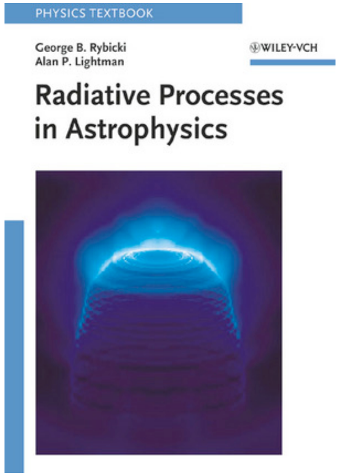
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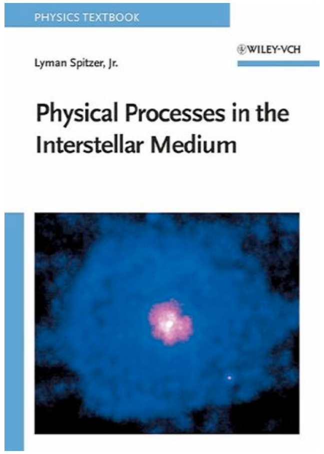
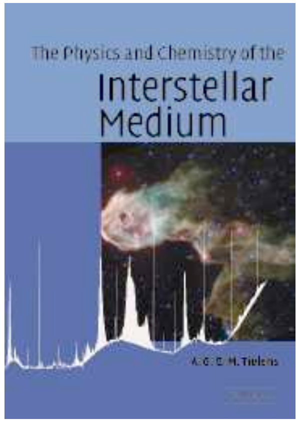
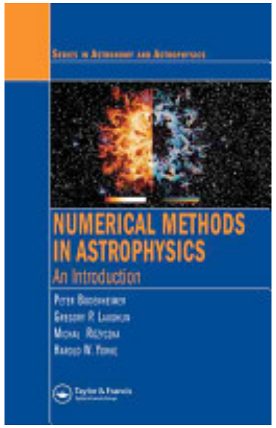

PHYSICS TEXTBOOK
Lyman Spitzer, Jr.
WILEY-VCH
Physical Processes in the Interstellar Medium


The Physics and Chemistry of the Interstellar Medium
A. G. G. M. Tielens


Series in Astronomy and Astrophysics
NUMERICAL METHODS IN ASTROPHYSICS
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Taylor & Francis

- Books
  - Spitzer, L., 1978/2004, Physical Processes in the Interstellar Medium (Wiley-VCH)
  - Rybicki, G.B., & Lightman, A.P., 1979/2004, Radiative Processes in Astrophysics (Wiley-VCH)
  - Stahler, S., & Palla, F., 2004, "The Formation of Stars" (Weinheim: Wiley-VCH)
  - Tielens, A.G.G.M., 2005, The Physics and Chemistry of the Interstellar Medium (Cambridge University Press)
  - Osterbrock, D., & Ferland, G., 2006, "Astrophysics of Gaseous Nebulae & Active Galactic Nuclei, 2nd ed. (Sausalito: Univ. Science Books)
  - Bodenheimer, P., et al., 2007, Numerical Methods in Astrophysics (Taylor & Francis)
  - Draine, B. 2011, "Physics of the Interstellar and Intergalactic Medium" (Princeton Series in Astrophysics)
  - Bodenheimer, P. 2012, "Principles of Star Formation" (Springer Verlag)

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- Review Articles
  - Mac Low, M.-M., Klessen, R.S., 2004, "The control of star formation by supersonic turbulence", Rev. Mod. Phys., 76, 125
  - Elmegreen, B.G., Scalo, J., 2004, "Interstellar Turbulence 1", ARA&A, 42, 211
  - Scalo, J., Elmegreen, B.G., 2004, "Interstellar Turbulence 2", ARA&A, 42, 275
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  - Zinnecker, H., Yorke, McKee, C.F., Ostriker, E.C., 2008, "Toward Understanding Massive Star Formation", ARA&A, 45, 481 - 563
  - McKee, C.F., Ostriker, E.C., 2008, "Theory of Star Formation", ARA&A, 45, 565
  - Kennicutt, R.C., Evans, N.J., 2012, "Star Formation in the Milky Way and Nearby Galaxies", ARA&A, 50, 531

Further resources

- Internet resources
  - Cornelis Dullemond: *Radiative Transfer in Astrophysics*
    http://www.ita.uni-heidelberg.de/~dullemond/lectures/radtrans_2012/index.shtml
  - Cornelis Dullemond: *RADMC-3D: A new multi-purpose radiative transfer tool*
    http://www.ita.uni-heidelberg.de/~dullemond/software/radmc-3d/index.shtml
  - List of molecules in the ISM (wikipedia):
    http://en.wikipedia.org/wiki/List_of_molecules_in_interstellar_space
  - Leiden database of molecular lines (LAMBDA)
    http://home.strw.leidenuniv.nl/~moldata/

Part 2: Dynamics of the ISM

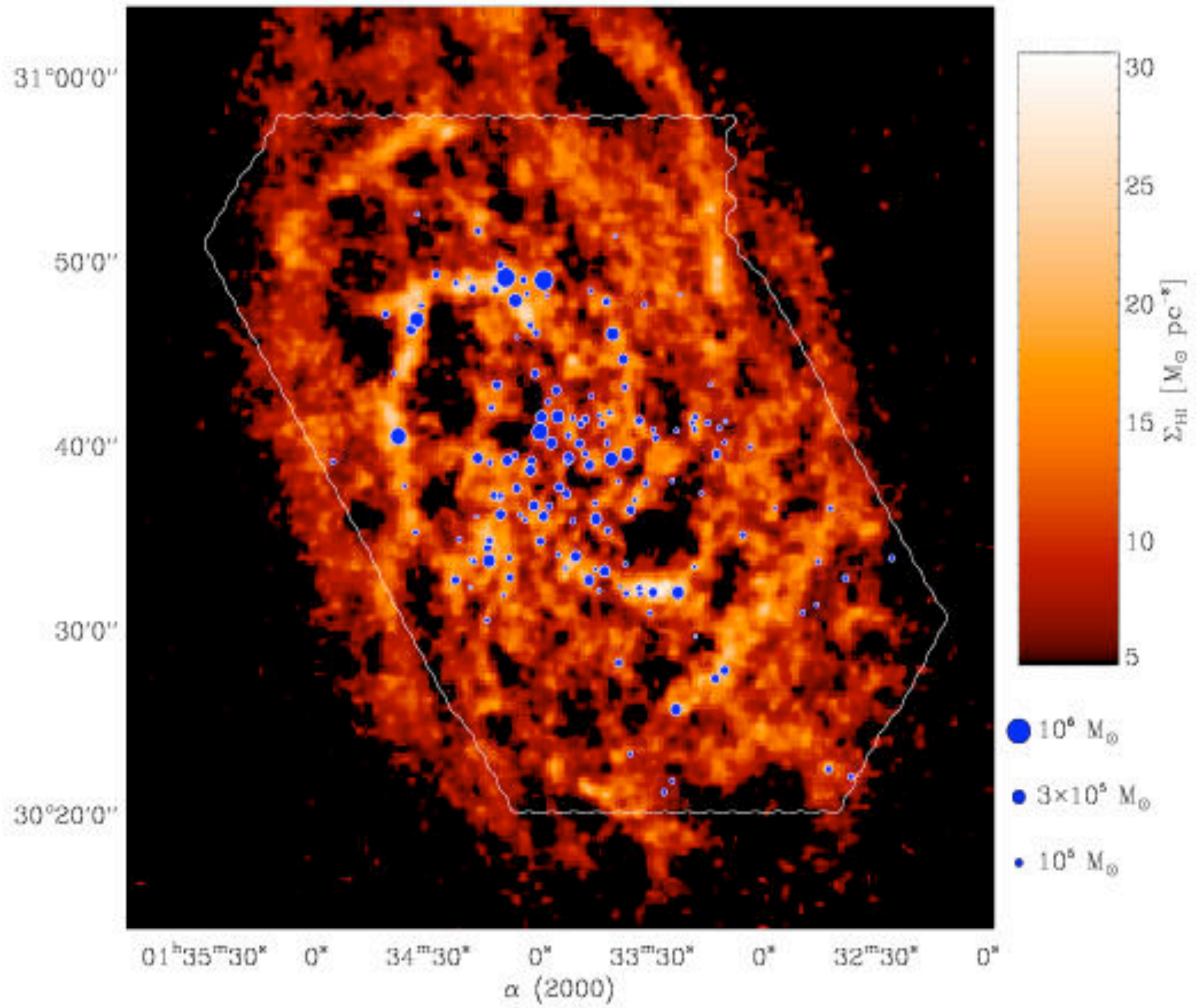
Ralf Klessen

Universität Heidelberg, Zentrum für Astronomie
Institut für Theoretische Astrophysik

molecular cloud formation

Hiroshige - Evening Shower at Atake and the Great Bridge

molecular cloud formation

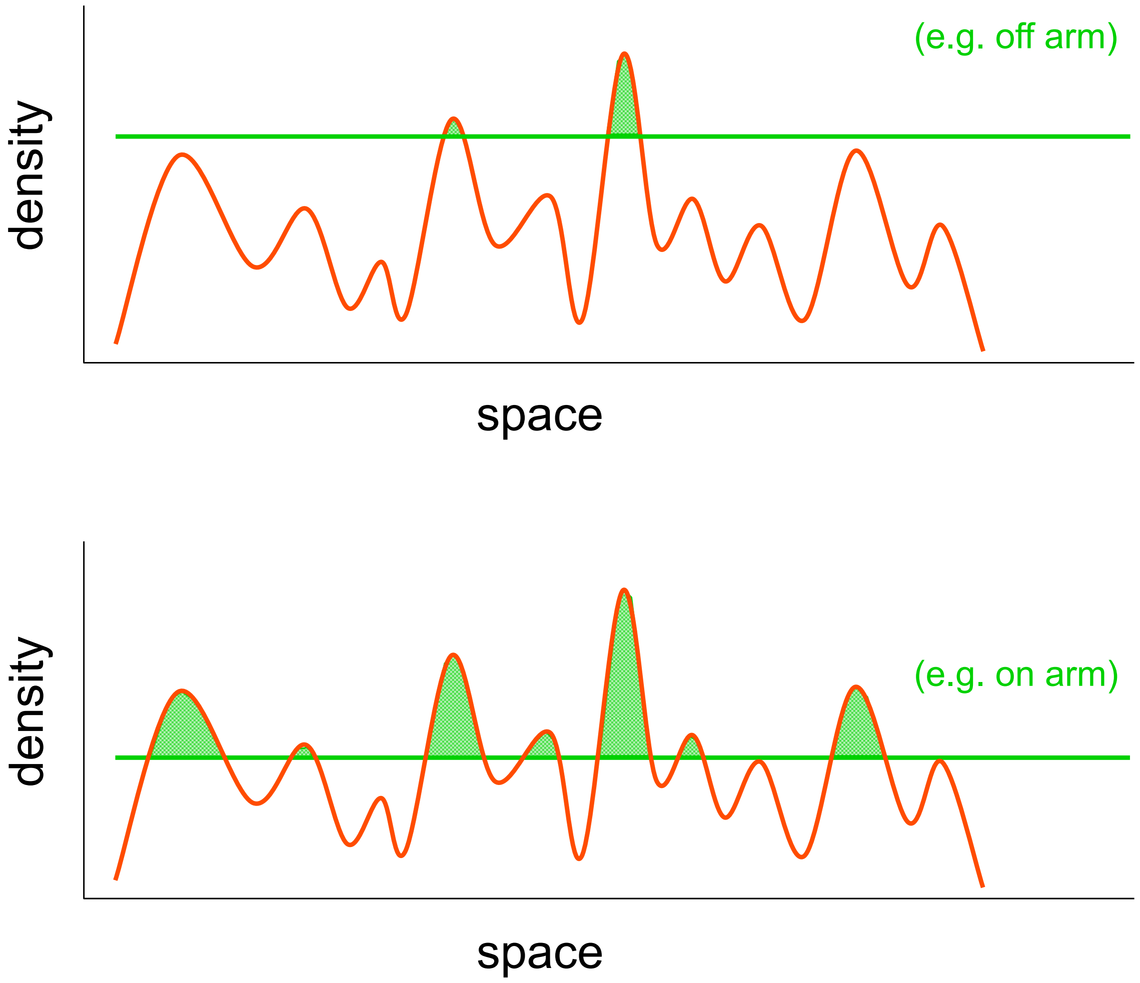


(Deul & van der Hulst 1987, Blitz et al. 2004)

Thesis:

Molecular clouds form at *stagnation points* of large-scale convergent flows, mostly triggered by global (or external) perturbations.

correlation with large-scale perturbations



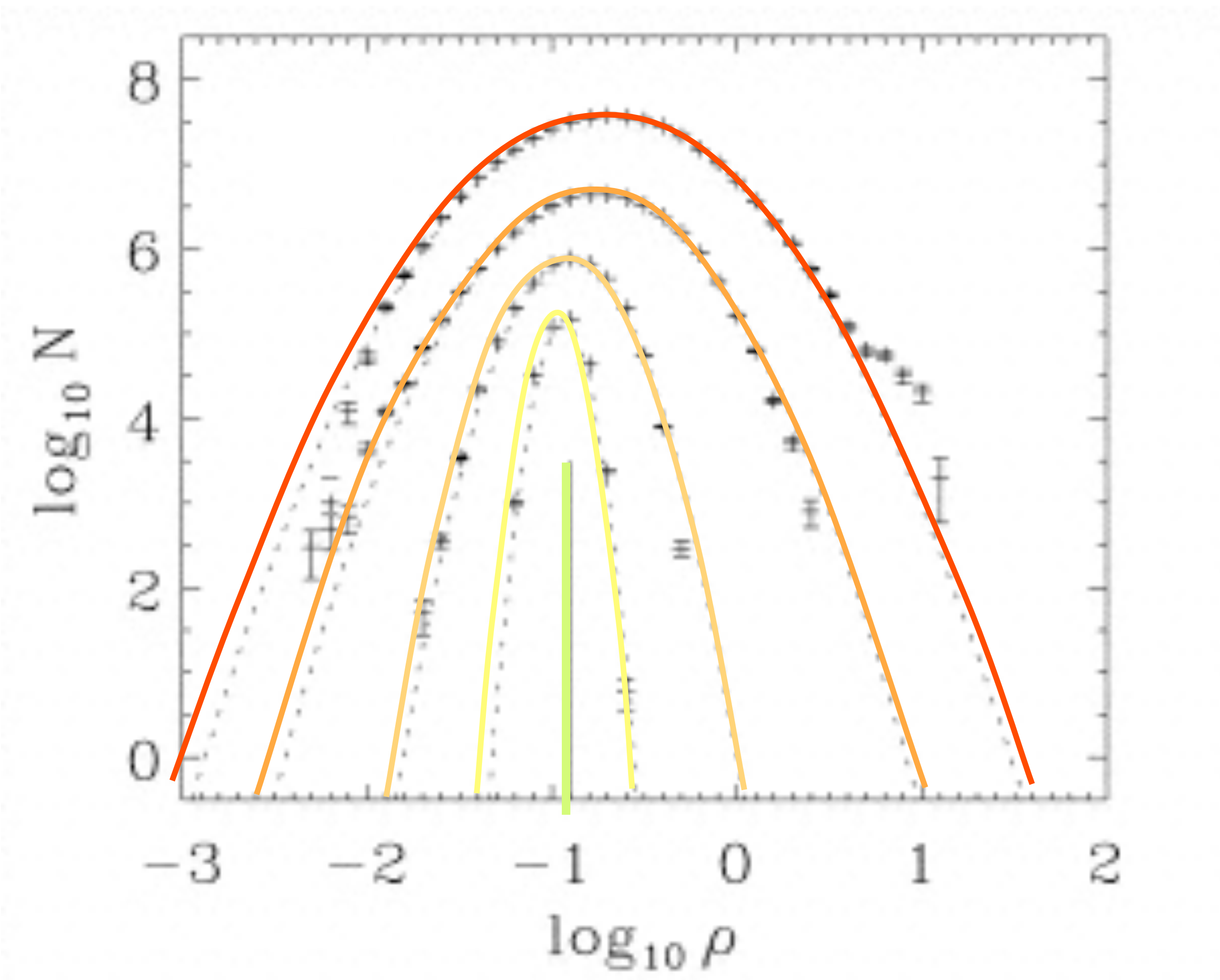
density/temperature fluctuations in warm atomar ISM are caused by *thermal/ gravitational instability* and/ or *supersonic turbulence*

some fluctuations are *dense* enough to *form H_2* within "*reasonable time*"

→ *molecular cloud*

external perturbuations (i.e. potential changes) *increase* likelihood

star formation on *global* scales



probability distribution function of the density (*ρ-pdf)*

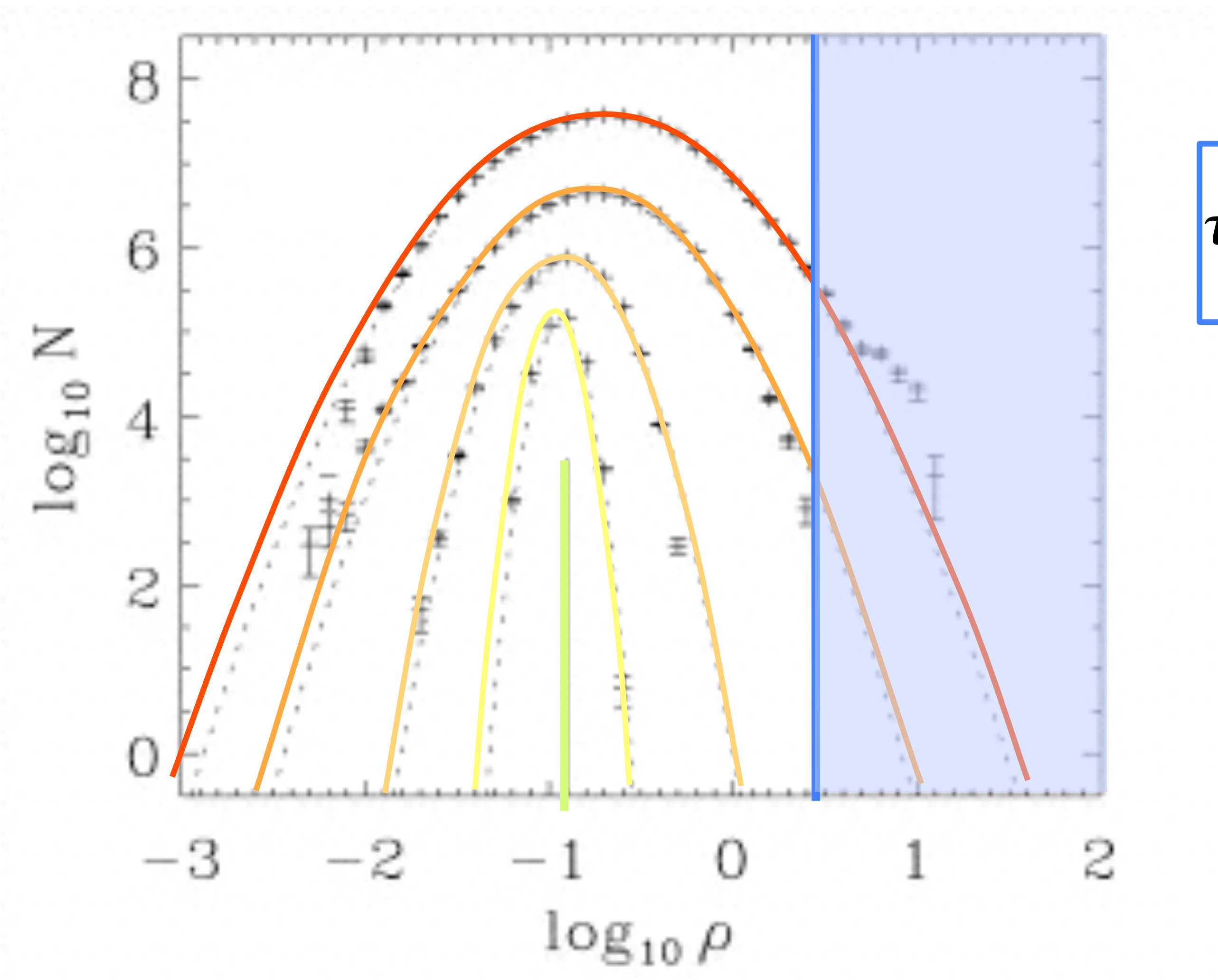
varying rms Mach numbers:

M1 > M2 > M3 > M4 > 0

mass weighted ρ-pdf, each shifted by ΔlogN=1

(from Klessen, 2001; also Gazol et al. 2005, Krumholz & McKee 2005, Glover & Mac Low 2007ab)

star formation on *global* scales



mass weighted ρ-pdf, each shifted by ΔlogN=1

(rate from Hollenback, Werner, & Salpeter 1971)

H_2 formation rate:

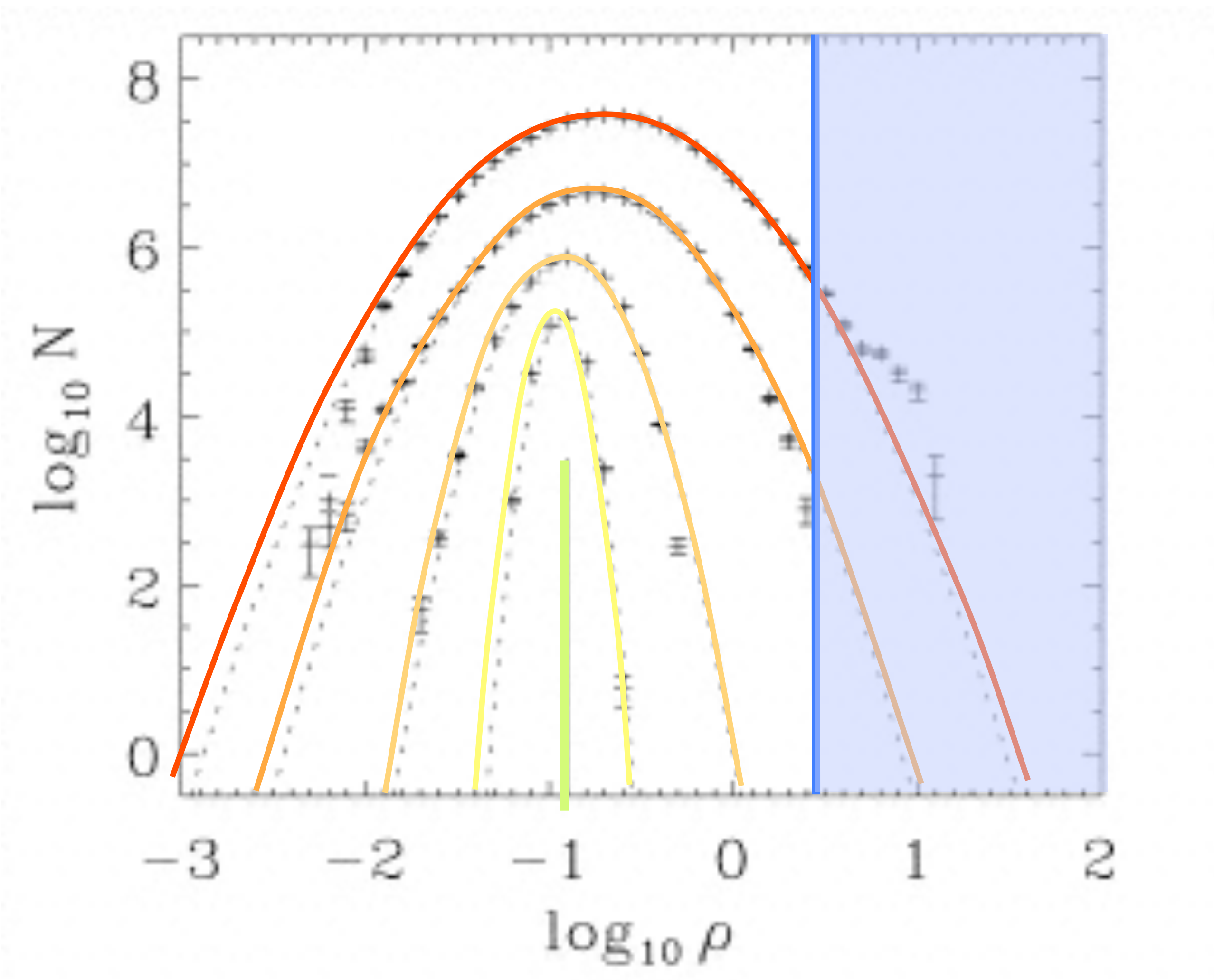
$$\boxed{\tau_{H_2} \approx \frac{1.5\,\mathrm{Gyr}}{n_H / 1\mathrm{cm}^{-3}}}$$

for $n_H \geq 100$ cm^{-3}, H_2 forms within 10 Myr, this is about the lifetime of typical MC's.

in turbulent gas, the H_2 fraction can become very high on short timescale

(for models with coupling between cloud dynamics and time-dependent chemistry, see Glover & Mac Low 2007a,b)

star formation on *global* scales



mass weighted ρ-pdf, each shifted by $\Delta\log N=1$

(rate from Hollenback, Werner, & Salpeter 1971)

BUT: *it doesn’t work*
(at least not so easy):

Chemistry has a memory effect!

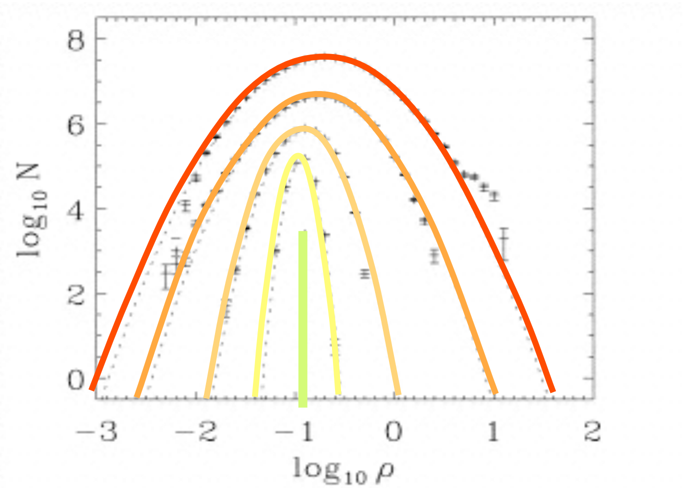
H2 forms more quickly in high-density regions as it gets destroyed in low-density parts.

(for models with coupling between cloud dynamics and time-dependent chemistry, see Glover & Mac Low 2007a,b)

SFR estimates from the PDF

log density PDF:

$$p_s(s) = \frac{1}{\sqrt{2\pi\sigma_s^2}} \exp\left(-\frac{(s-s_0)^2}{2\sigma_s^2}\right)$$



$$s \equiv \ln\left(\rho/\rho_0\right).$$ log density, normalized to the mean

relation between mean density and turbulent Mach number M and magnetic field strength β:

$$s_0 = -\frac{1}{2}\,\sigma_s^2$$

$$\sigma_s^2 = \ln\left(1 + b^2\mathcal{M}^2\frac{\beta}{\beta+1}\right)$$

$$\sigma_s^2 = \ln\left(1 + b^2\mathcal{M}^2\frac{2\mathcal{M}_\mathrm{A}^2}{\mathcal{M}^2 + 2\mathcal{M}_\mathrm{A}^2}\right)$$

e.g. Padoan & Nordlund 2002, Krumholz & McKee 2005, Hennebelle & Chabrier 2009, Federrath & Klessen 2012, Molina et al. 2012

SFR estimates from the PDF

star formation rate (Msun/yr) in terms of the SF efficiency per free-fall time $\mathrm{SFR_{ff}}$

$$\mathrm{SFR} \equiv \frac{M_\mathrm{c}}{t_\mathrm{ff}(\rho_0)}\,\mathrm{SFR_{ff}}\,.$$

$$\mathrm{SFR_{ff}} = \frac{\epsilon}{\phi_t}\int_{s_\mathrm{crit}}^{\infty}\frac{t_\mathrm{ff}(\rho_0)}{t_\mathrm{ff}(\rho)}\,\frac{\rho}{\rho_0}\,p(s)\,\mathrm{d}s\,.$$

SF efficiency per free-fall time

$$t_\mathrm{ff}(\rho) \equiv \left(\frac{3\pi}{32G\rho}\right)^{1/2}$$

free-fall time

e.g. Padoan & Nordlund 2002, Krumholz & McKee 2005, Hennebelle & Chabrier 2009, Federrath & Klessen 2012

SFR estimates from the PDF

comparison and extension of existing models

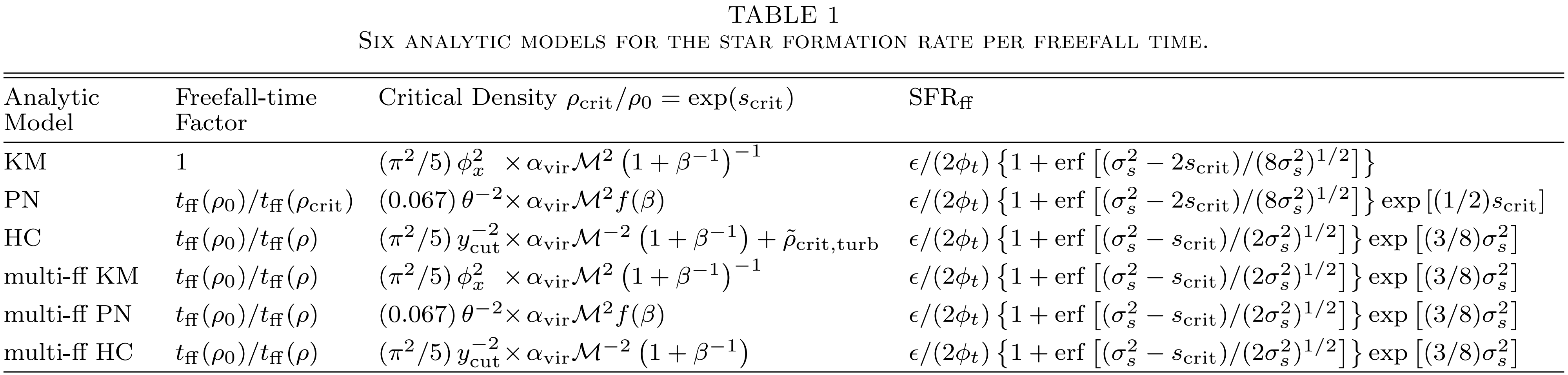


TABLE 1

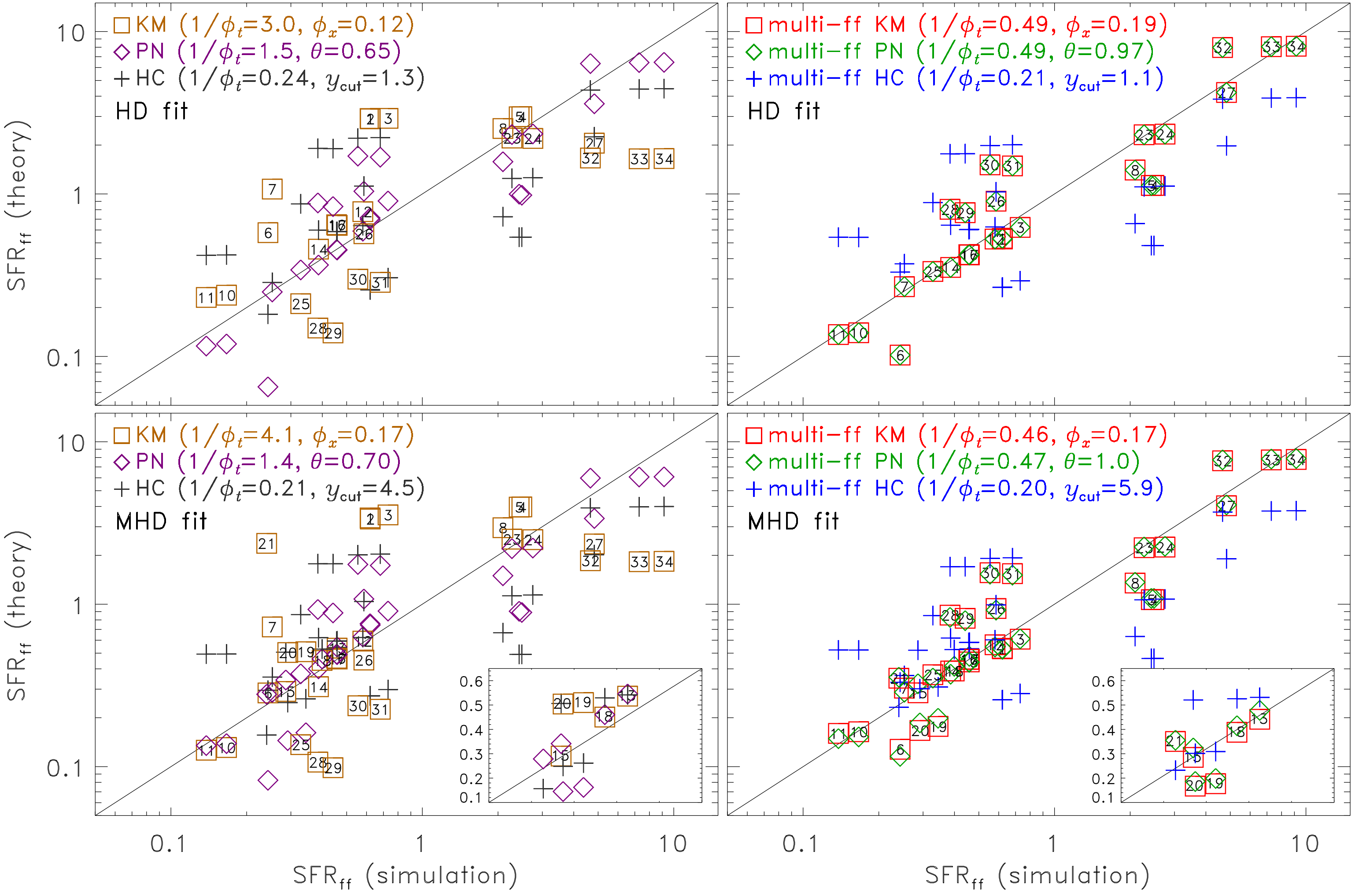
Six analytic models for the star formation rate per freefall time.

Analytic Model	Freefall-time Factor	Critical Density $\rho_{\rm crit}/\rho_0 = \exp(s_{\rm crit})$	$\mathrm{SFR}_{\rm ff}$
KM	1	$(\pi^2/5)\,\phi_x^2 \times \alpha_{\rm vir}\mathcal{M}^2\left(1+\beta^{-1}\right)^{-1}$	$\epsilon/(2\phi_t)\left\{1+\mathrm{erf}\left[(\sigma_s^2-2s_{\rm crit})/(8\sigma_s^2)^{1/2}\right]\right\}$
PN	$t_{\rm ff}(\rho_0)/t_{\rm ff}(\rho_{\rm crit})$	$(0.067)\,\theta^{-2}\times\alpha_{\rm vir}\mathcal{M}^2 f(\beta)$	$\epsilon/(2\phi_t)\left\{1+\mathrm{erf}\left[(\sigma_s^2-2s_{\rm crit})/(8\sigma_s^2)^{1/2}\right]\right\}\exp\left[(1/2)s_{\rm crit}\right]$
HC	$t_{\rm ff}(\rho_0)/t_{\rm ff}(\rho)$	$(\pi^2/5)\,y_{\rm cut}^{-2}\times\alpha_{\rm vir}\mathcal{M}^{-2}\left(1+\beta^{-1}\right)+\tilde{\rho}_{\rm crit,turb}$	$\epsilon/(2\phi_t)\left\{1+\mathrm{erf}\left[(\sigma_s^2-s_{\rm crit})/(2\sigma_s^2)^{1/2}\right]\right\}\exp\left[(3/8)\sigma_s^2\right]$
multi-ff KM	$t_{\rm ff}(\rho_0)/t_{\rm ff}(\rho)$	$(\pi^2/5)\,\phi_x^2 \times \alpha_{\rm vir}\mathcal{M}^2\left(1+\beta^{-1}\right)^{-1}$	$\epsilon/(2\phi_t)\left\{1+\mathrm{erf}\left[(\sigma_s^2-s_{\rm crit})/(2\sigma_s^2)^{1/2}\right]\right\}\exp\left[(3/8)\sigma_s^2\right]$
multi-ff PN	$t_{\rm ff}(\rho_0)/t_{\rm ff}(\rho)$	$(0.067)\,\theta^{-2}\times\alpha_{\rm vir}\mathcal{M}^2 f(\beta)$	$\epsilon/(2\phi_t)\left\{1+\mathrm{erf}\left[(\sigma_s^2-s_{\rm crit})/(2\sigma_s^2)^{1/2}\right]\right\}\exp\left[(3/8)\sigma_s^2\right]$
multi-ff HC	$t_{\rm ff}(\rho_0)/t_{\rm ff}(\rho)$	$(\pi^2/5)\,y_{\rm cut}^{-2}\times\alpha_{\rm vir}\mathcal{M}^{-2}\left(1+\beta^{-1}\right)$	$\epsilon/(2\phi_t)\left\{1+\mathrm{erf}\left[(\sigma_s^2-s_{\rm crit})/(2\sigma_s^2)^{1/2}\right]\right\}\exp\left[(3/8)\sigma_s^2\right]$

Federrath & Klessen (2012)

SFR estimates from the PDF

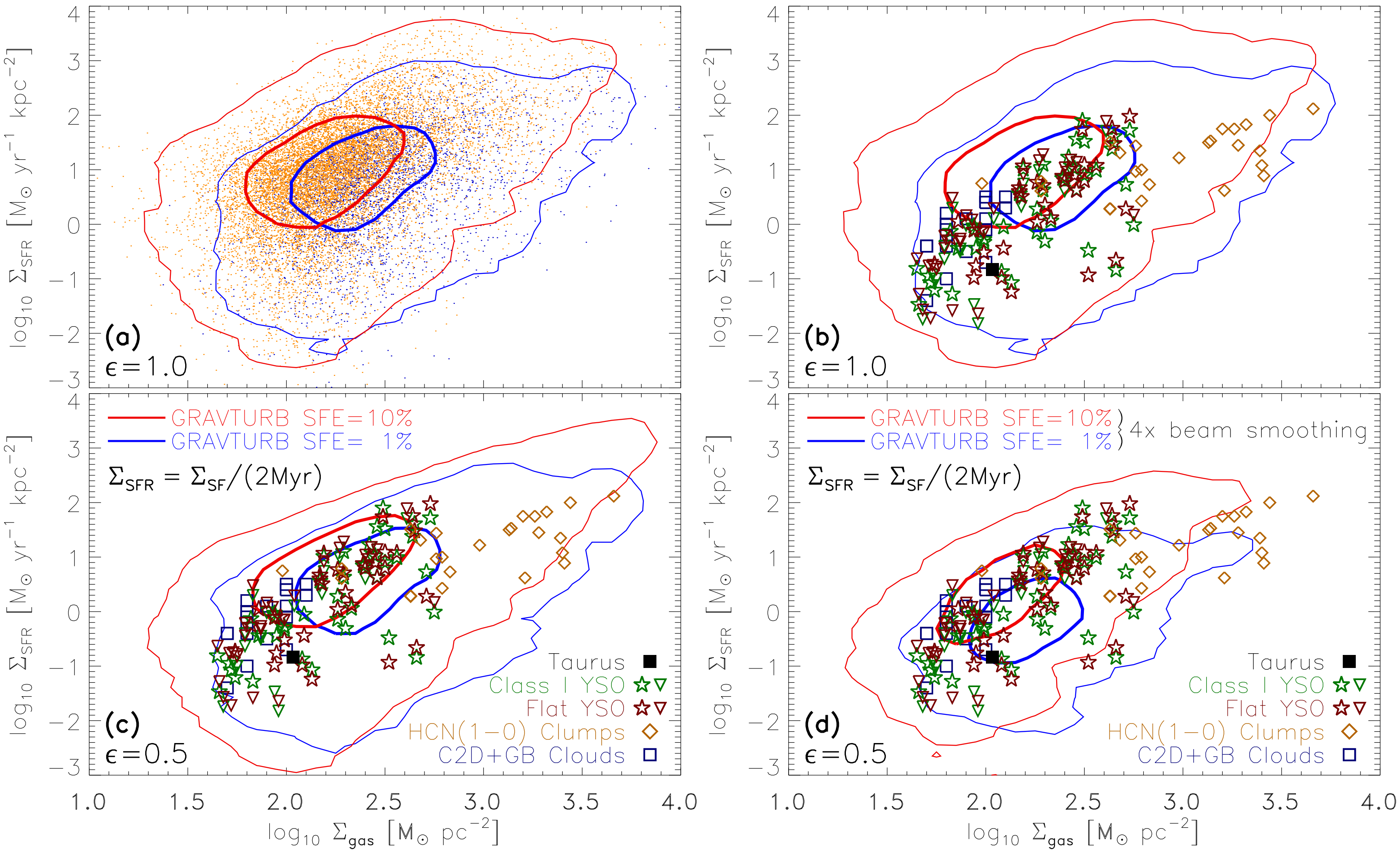
comparison between analytic models and numerical simulations



Federrath & Klessen (2012)

SFR estimates from the PDF

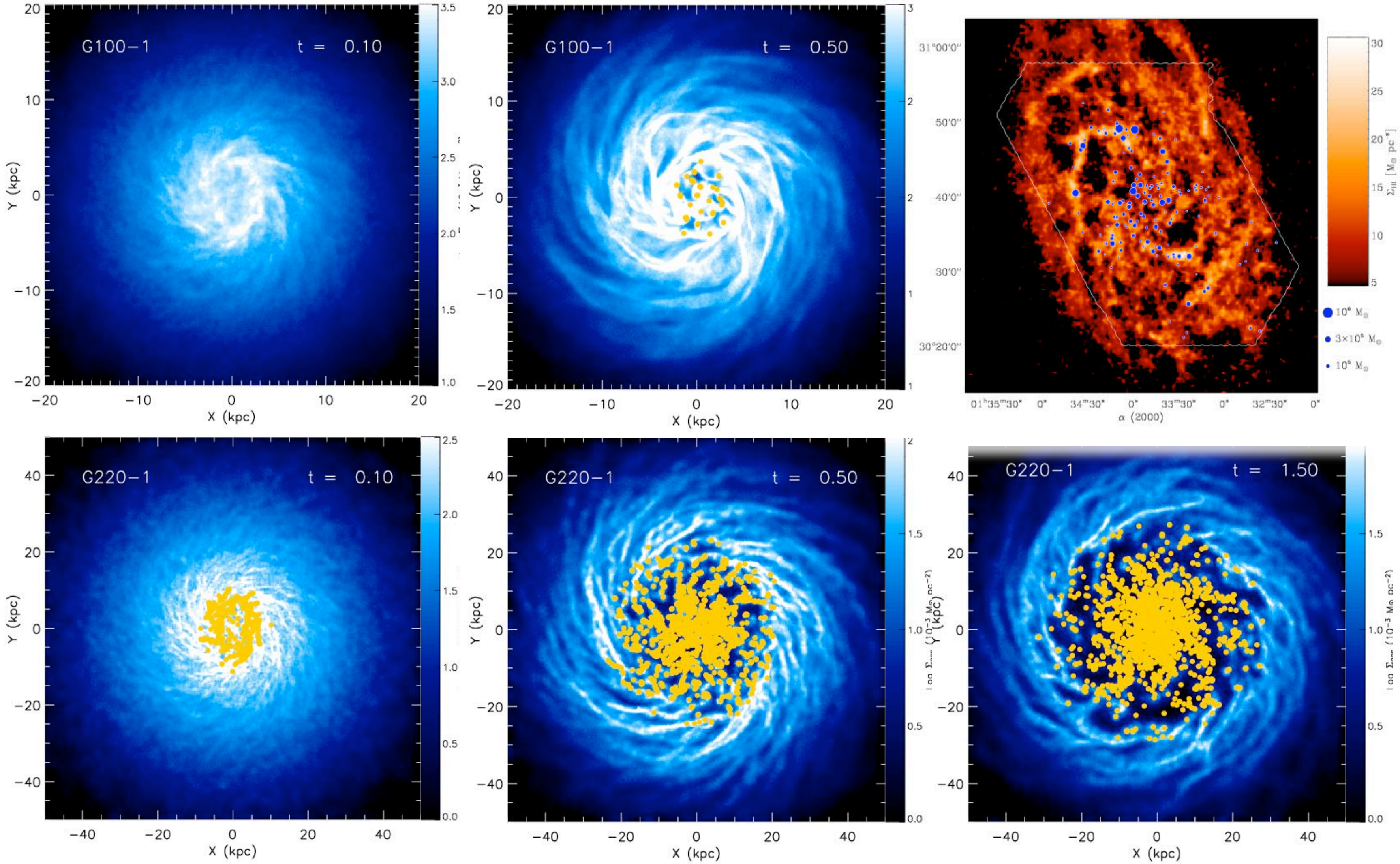
comparison between numerical simulations and observations



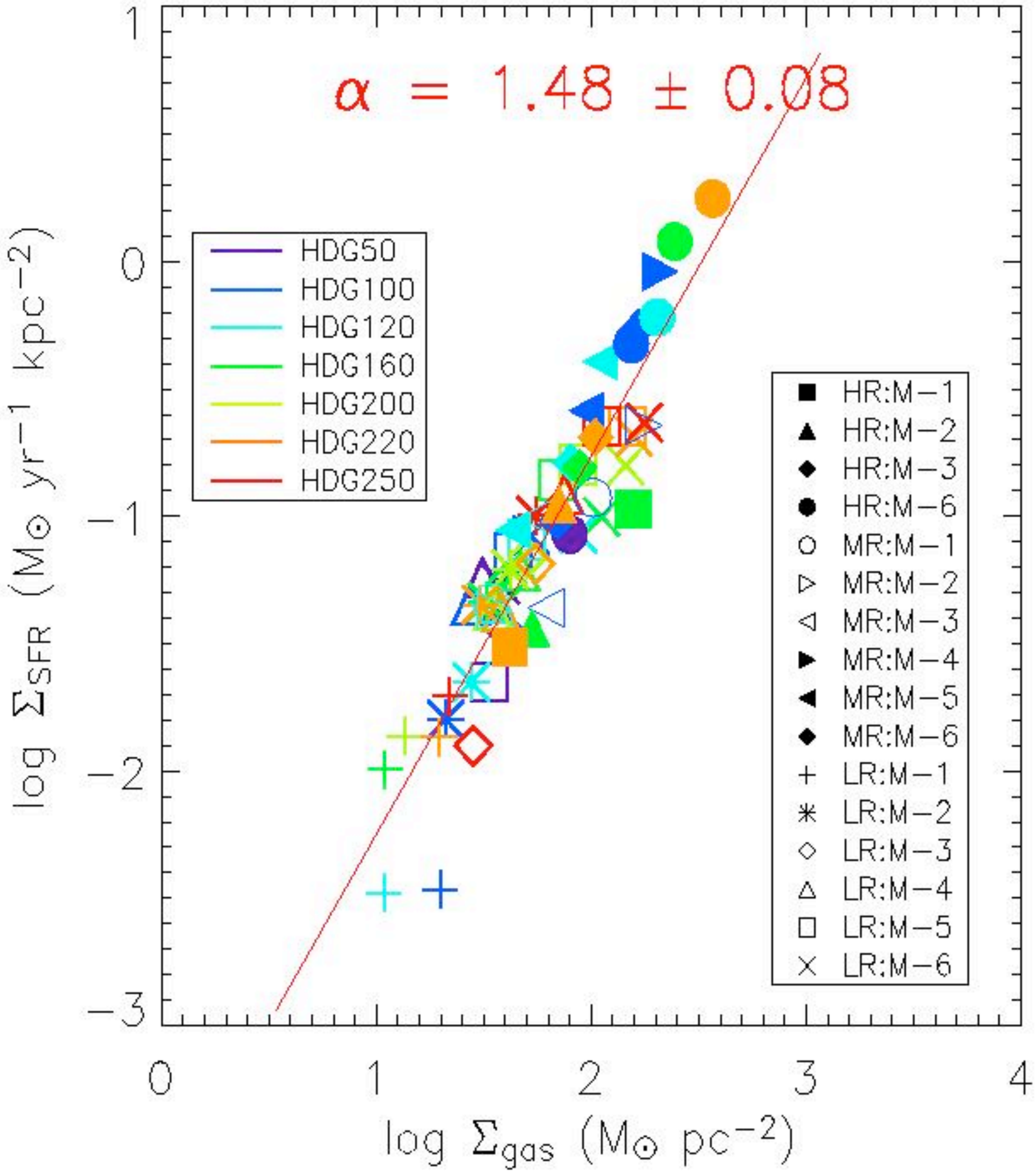
Federrath & Klessen (2012)

modeling galactic SF

SPH calculations of self-gravitating disks of stars and (isothermal) gas in dark-matter potential, sink particles measure local collapse --> star formation



(Li, Mac Low, & Klessen, 2005, ApJ, 620,L19 - L22)



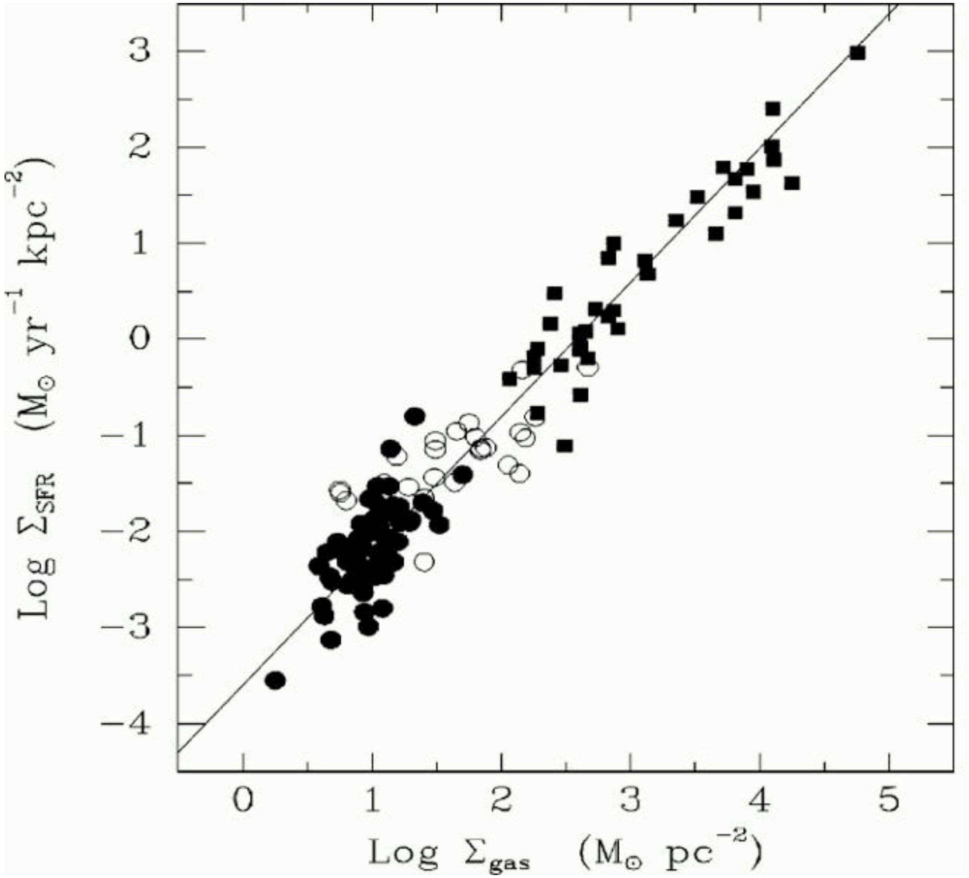
(Li, Mac Low, & Klessen, 2005, ApJ, 620, L19 - L22)

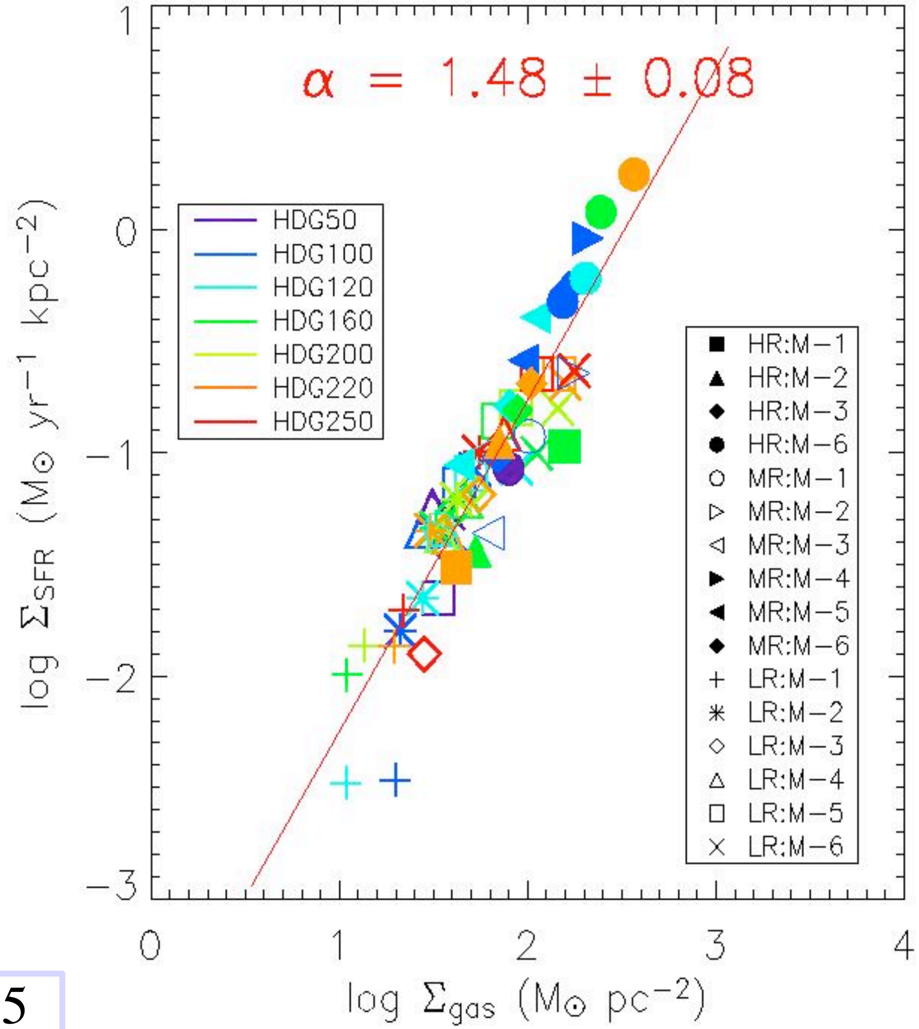
We find correlation between *star formation rate* and *gas surface density:*

$$\Sigma_{\rm SFR} \propto \Sigma_{\rm gas}^{1.5}$$

global Schmidt law

observed Schmidt law



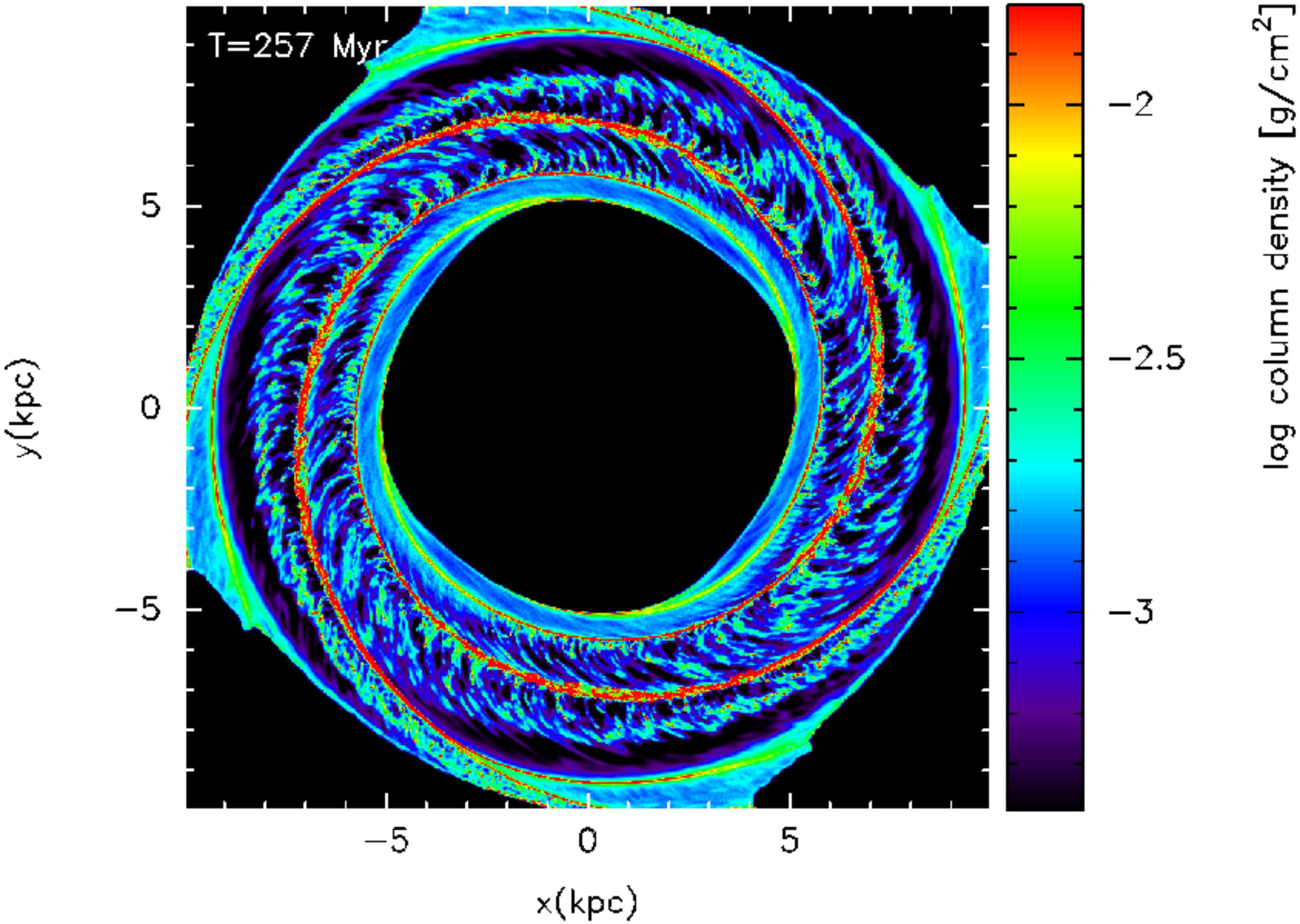


in both cases:

$$\boxed{\Sigma_{SFR} \propto \Sigma_{gas}^{1.5}}$$

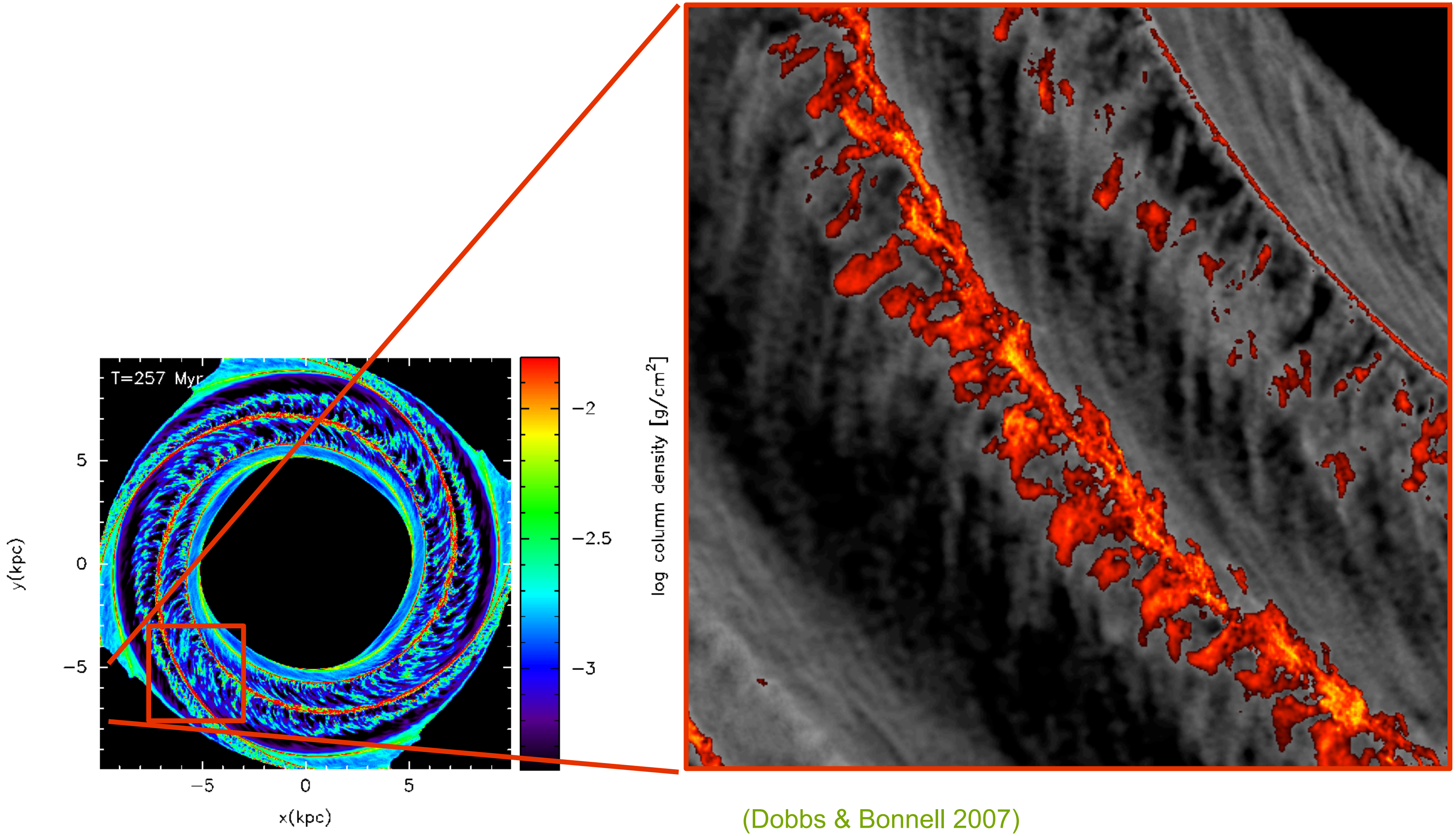
(from Kennicutt 1998)

molecular cloud formation



(from Dobbs et al. 2008)

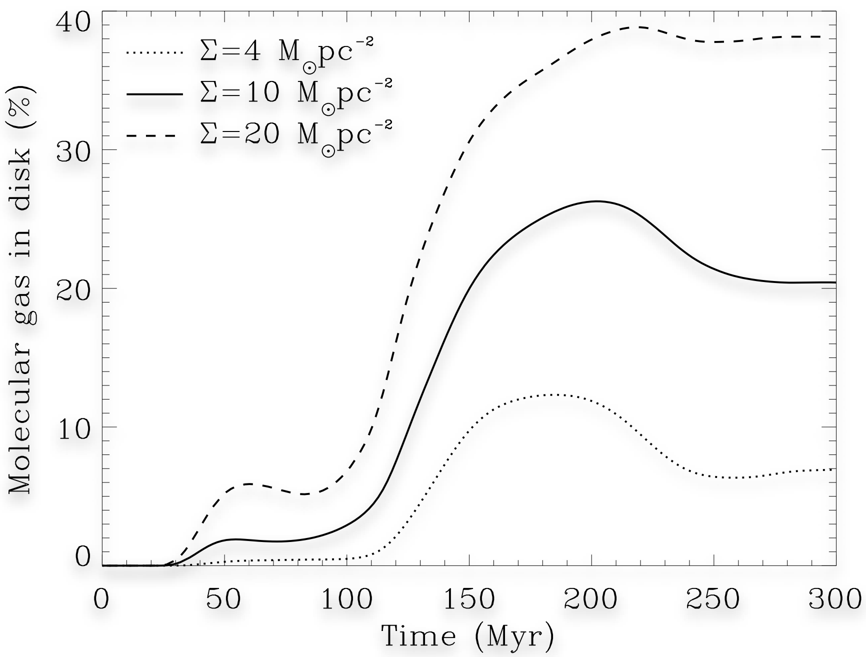
molecular cloud formation



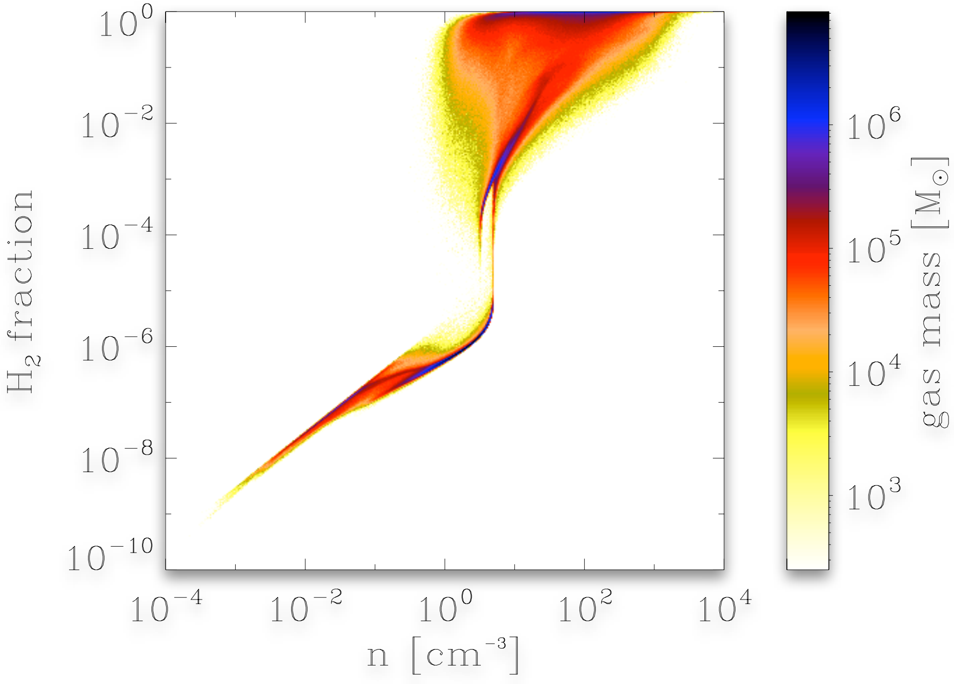
(Dobbs & Bonnell 2007)

molecular cloud formation

molecular gas fraction as function of time



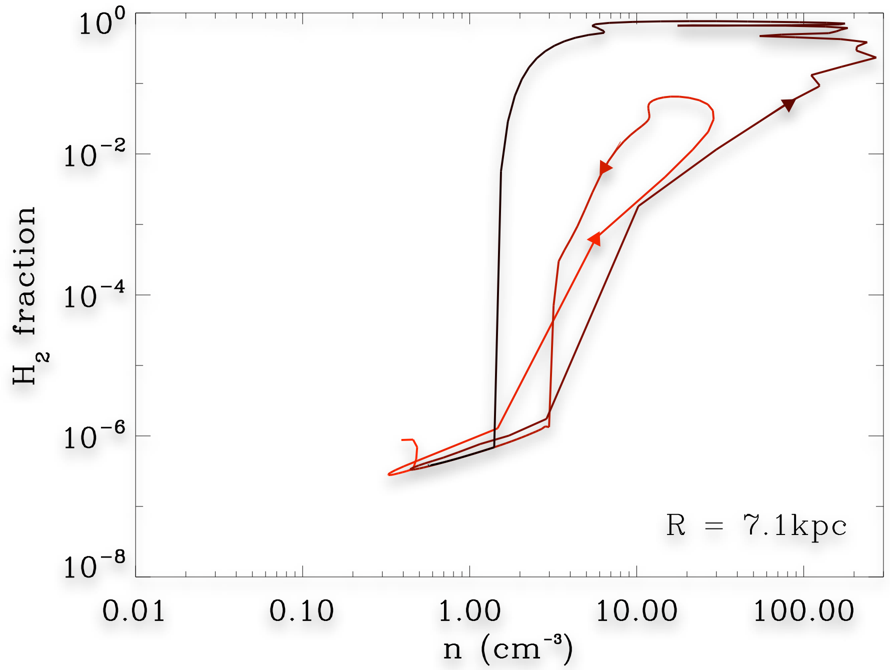
molecular gas fraction as function of density



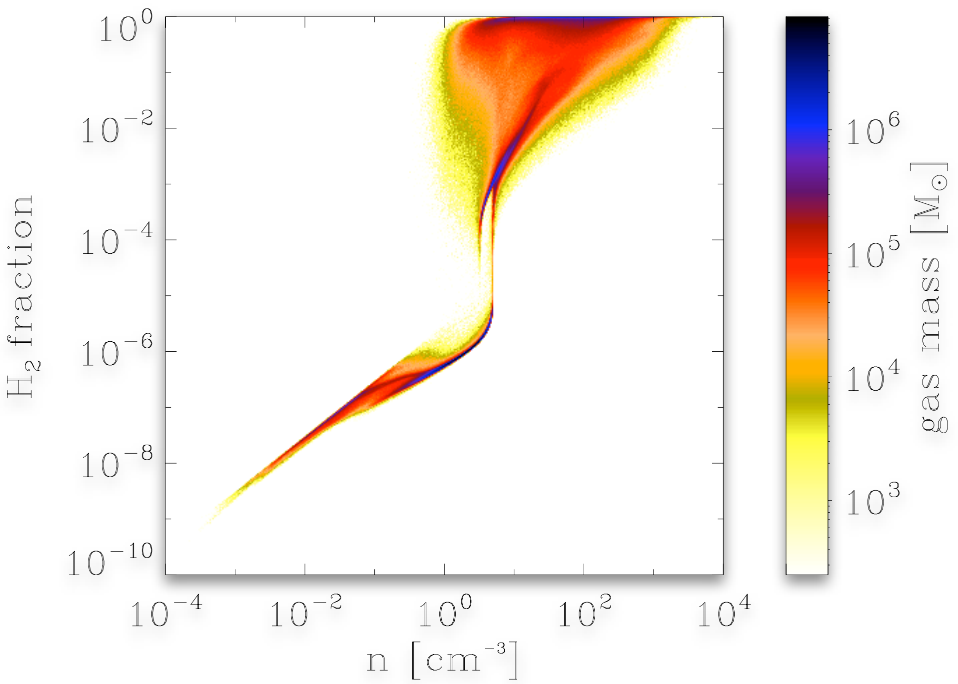
(Dobbs et al. 2008)

molecular cloud formation

molecular gas fraction of fluid element as function of time



molecular gas fraction as function of density



(Dobbs et al. 2008)

models with B-fields

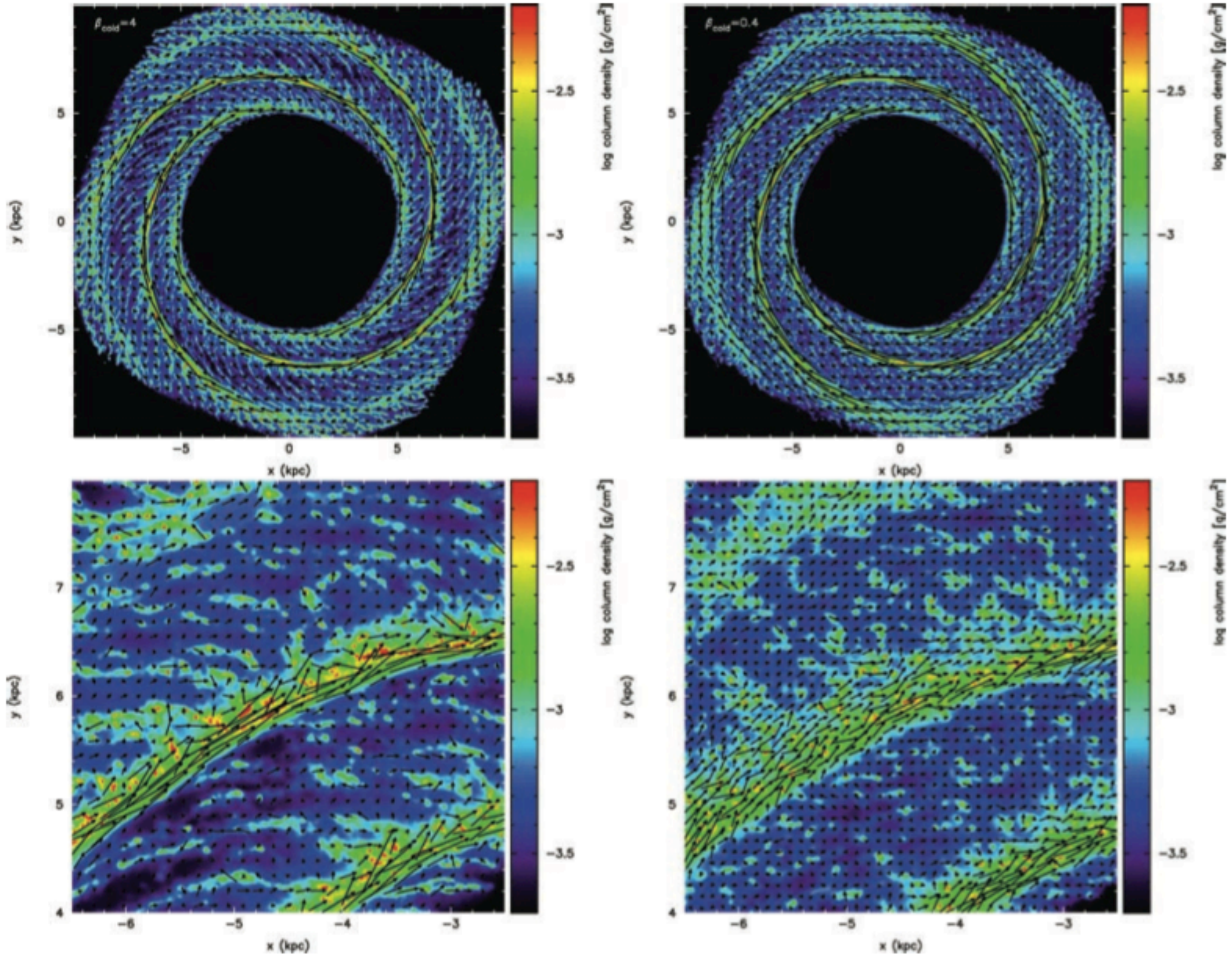
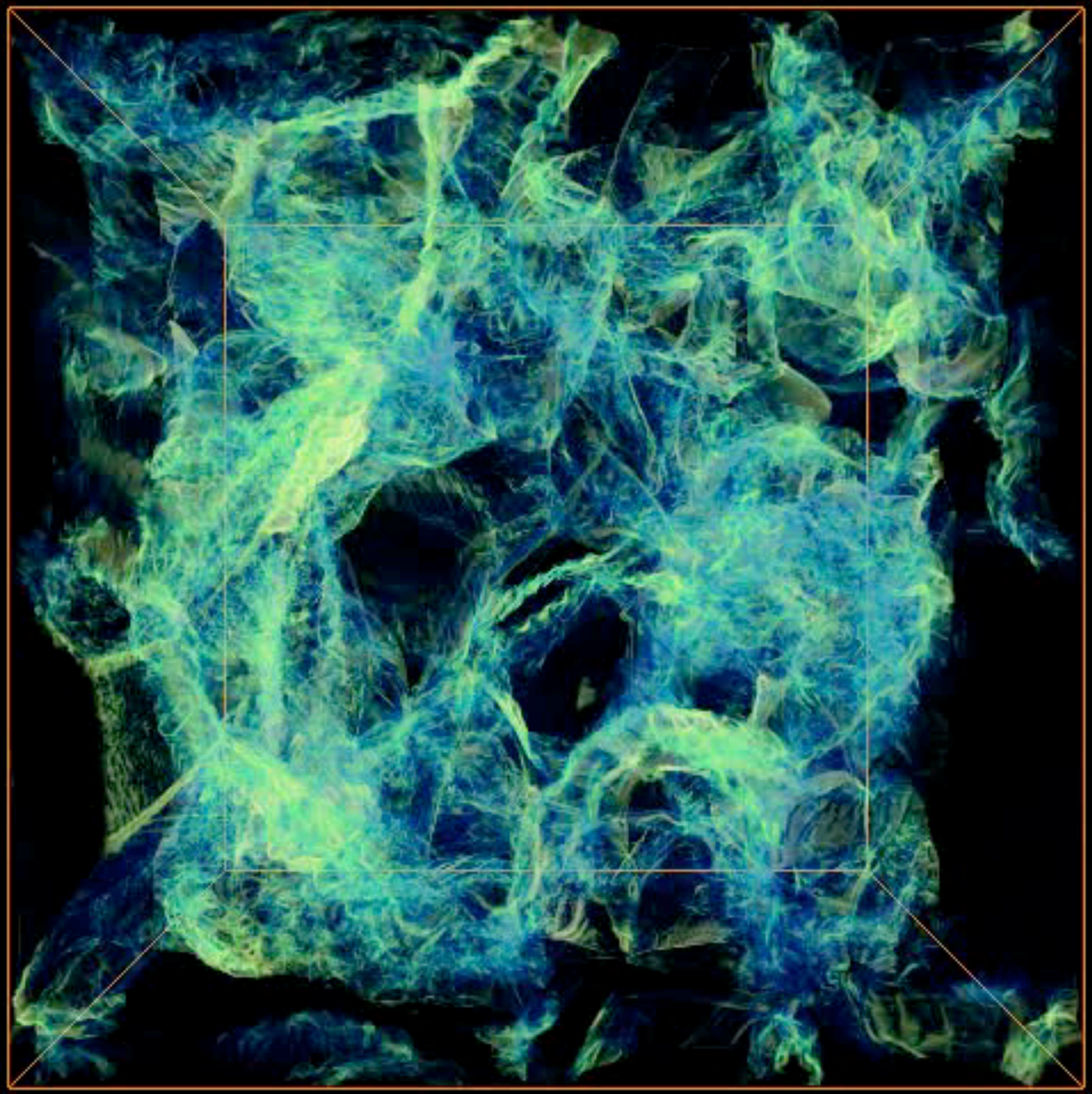


Figure 9. The column density is shown for the two-phase simulations after 250 Myr, for the whole disc (top panel) and a 4 × 4 kpc subsection (bottom panel). The left-hand panels show the case where $\beta_{\mathrm{cold}} = 4$ and the right-hand panels where $\beta_{\mathrm{cold}} = 0.4$. Both the cold and warm phases are shown in the plots, but we show them separately for the case where $\beta_{\mathrm{cold}} = 4$ in Fig. 12. There is more structure in the cold gas when the magnetic field is weaker ($\beta_{\mathrm{cold}} = 4$). The vectors show the magnetic field smoothed over a particular grid size. There is more detailed structure on smaller scales, particularly in the spiral arms which are better resolved.

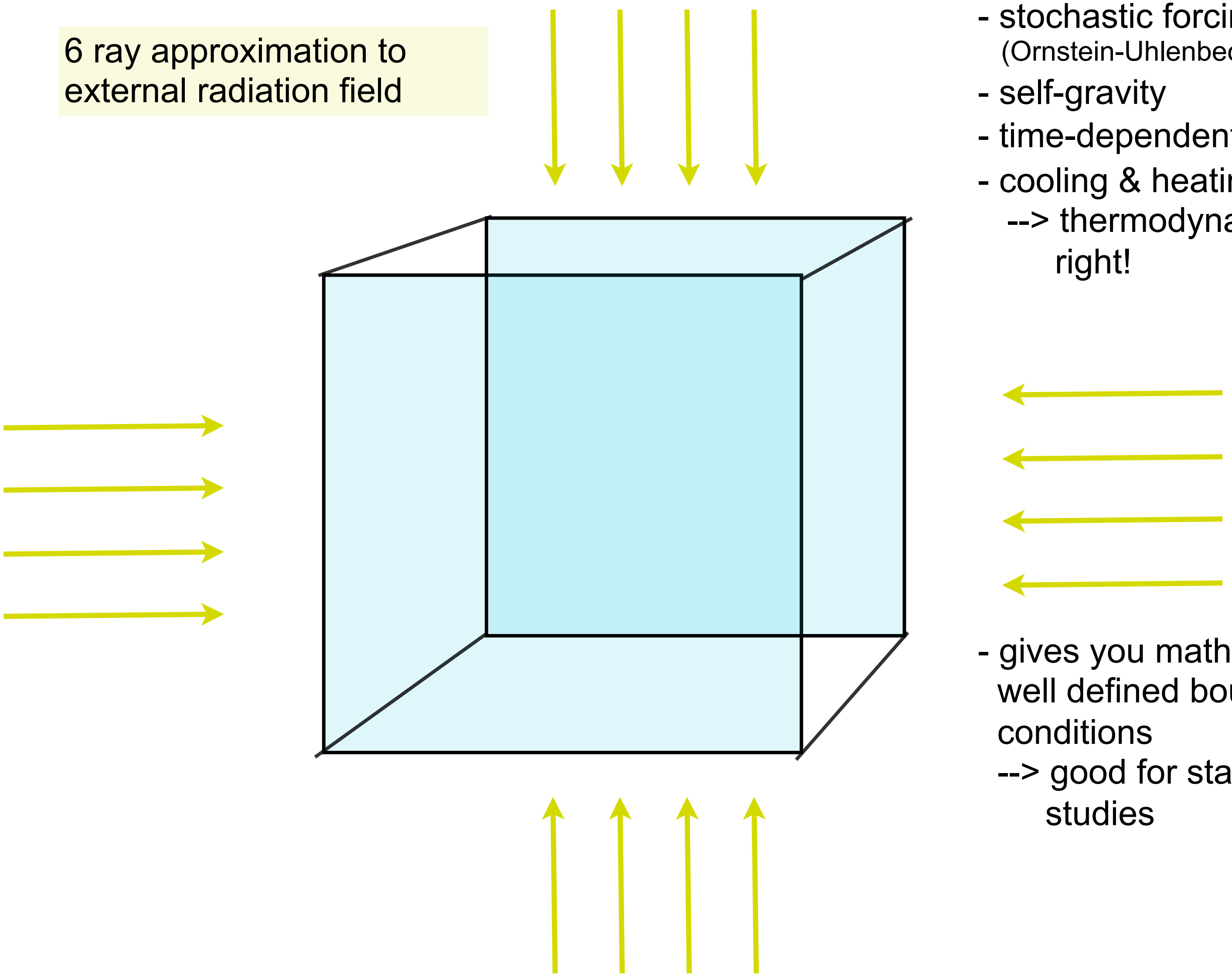
Dobbs & Price (2008), Shetty & Ostriker (2007, 2008)

modeling chemistry



Schmidt et al. (2009, A&A, 494, 127)

experimental set-up



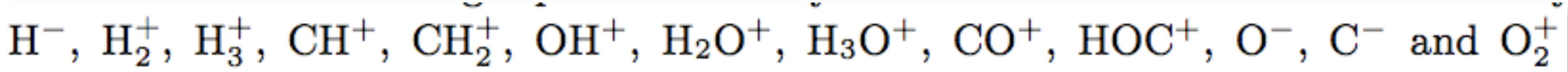
6 ray approximation to external radiation field

- AMR MHD (B = 2 muG)
- stochastic forcing
  (Ornstein-Uhlenbeck)
- self-gravity
- time-dependent chemistry
- cooling & heating processes
  --> thermodynamics done right!

- gives you mathematically well defined boundary conditions
  --> good for statistical studies

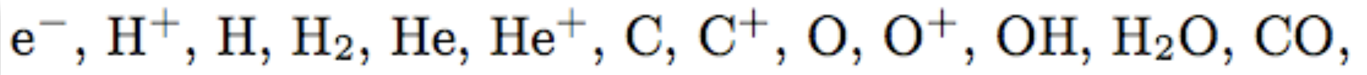
chemical model 0

- 32 chemical species
  - 17 in instantaneous equilibrium:



H^-, H_2^+, H_3^+, CH^+, CH_2^+, OH^+, H_2O^+, H_3O^+, CO^+, HOC^+, O^-, C^- and O_2^+

  - 19 full non-equilibrium evolution



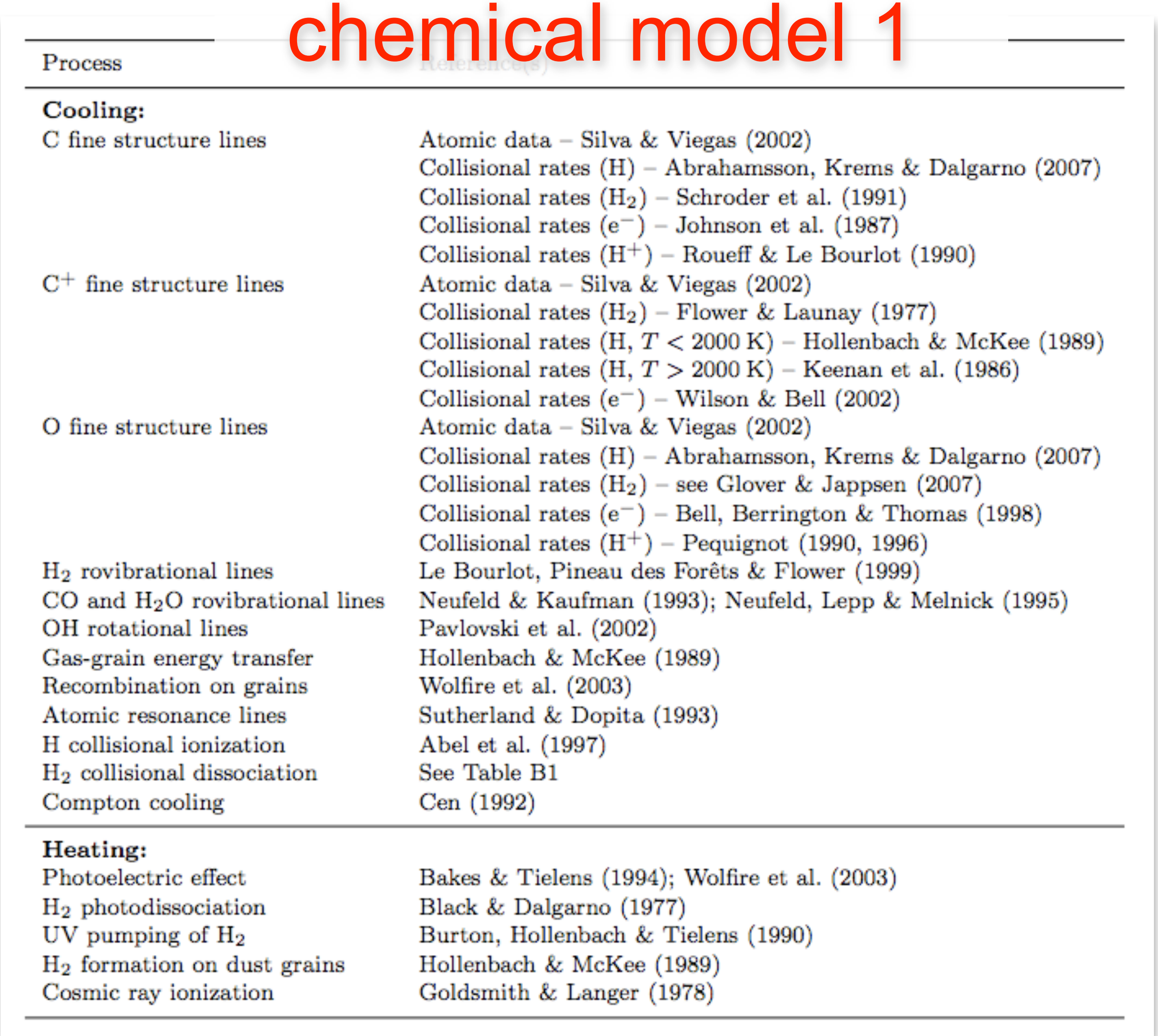
e^-, H^+, H, H_2, He, He^+, C, C^+, O, O^+, OH, H_2O, CO,

C_2, O_2, HCO^+, CH, CH_2 and CH_3^+

- 218 reactions
- various heating and cooling processes

(Glover, Federrath, Mac Low, Klessen, 2010, MNRS, 404, 2)

chemical model 1



Process	Reference(s)
Cooling:	
C fine structure lines	Atomic data – Silva & Viegas (2002)
	Collisional rates (H) – Abrahamsson, Krems & Dalgarno (2007)
	Collisional rates (H_2) – Schroder et al. (1991)
	Collisional rates (e^-) – Johnson et al. (1987)
	Collisional rates (H^+) – Roueff & Le Bourlot (1990)
C^+ fine structure lines	Atomic data – Silva & Viegas (2002)
	Collisional rates (H_2) – Flower & Launay (1977)
	Collisional rates (H, $T < 2000$ K) – Hollenbach & McKee (1989)
	Collisional rates (H, $T > 2000$ K) – Keenan et al. (1986)
	Collisional rates (e^-) – Wilson & Bell (2002)
O fine structure lines	Atomic data – Silva & Viegas (2002)
	Collisional rates (H) – Abrahamsson, Krems & Dalgarno (2007)
	Collisional rates (H_2) – see Glover & Jappsen (2007)
	Collisional rates (e^-) – Bell, Berrington & Thomas (1998)
	Collisional rates (H^+) – Pequignot (1990, 1996)
H_2 rovibrational lines	Le Bourlot, Pineau des Forêts & Flower (1999)
CO and H_2O rovibrational lines	Neufeld & Kaufman (1993); Neufeld, Lepp & Melnick (1995)
OH rotational lines	Pavlovski et al. (2002)
Gas-grain energy transfer	Hollenbach & McKee (1989)
Recombination on grains	Wolfire et al. (2003)
Atomic resonance lines	Sutherland & Dopita (1993)
H collisional ionization	Abel et al. (1997)
H_2 collisional dissociation	See Table B1
Compton cooling	Cen (1992)
Heating:	
Photoelectric effect	Bakes & Tielens (1994); Wolfire et al. (2003)
H_2 photodissociation	Black & Dalgarno (1977)
UV pumping of H_2	Burton, Hollenbach & Tielens (1990)
H_2 formation on dust grains	Hollenbach & McKee (1989)
Cosmic ray ionization	Goldsmith & Langer (1978)

(Glover, Federrath, Mac Low, Klessen, 2010, MNRS, 404, 2)

chemical model 2

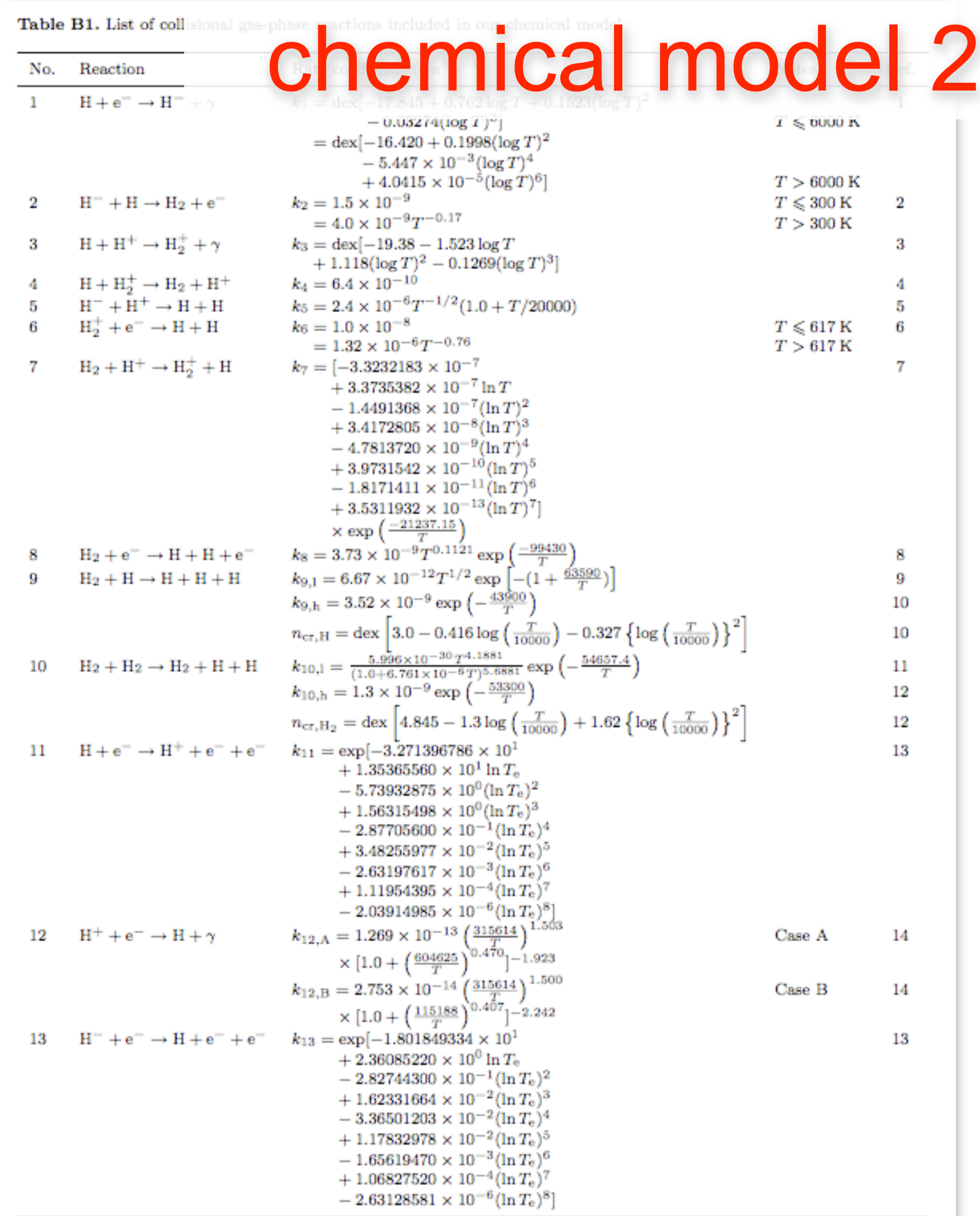


Table B1. List of collisional gas-phase reactions included in our chemical model.

No.	Reaction	Rate coefficient (cm^3 s^{-1})	Notes	Ref.
1	$H + e^- \rightarrow H^- + \gamma$	$k_1 = \mathrm{dex}[-17.845 + 0.762 \log T + 0.1523(\log T)^2 - 0.03274(\log T)^3]$	$T \leqslant 6000$ K	1
		$= \mathrm{dex}[-16.420 + 0.1998(\log T)^2 - 5.447 \times 10^{-3}(\log T)^4 + 4.0415 \times 10^{-5}(\log T)^6]$	$T > 6000$ K	
2	$H^- + H \rightarrow H_2 + e^-$	$k_2 = 1.5 \times 10^{-9}$	$T \leqslant 300$ K	2
		$= 4.0 \times 10^{-9} T^{-0.17}$	$T > 300$ K	
3	$H + H^+ \rightarrow H_2^+ + \gamma$	$k_3 = \mathrm{dex}[-19.38 - 1.523 \log T + 1.118(\log T)^2 - 0.1269(\log T)^3]$		3
4	$H + H_2^+ \rightarrow H_2 + H^+$	$k_4 = 6.4 \times 10^{-10}$		4
5	$H^- + H^+ \rightarrow H + H$	$k_5 = 2.4 \times 10^{-6} T^{-1/2}(1.0 + T/20000)$		5
6	$H_2^+ + e^- \rightarrow H + H$	$k_6 = 1.0 \times 10^{-8}$	$T \leqslant 617$ K	6
		$= 1.32 \times 10^{-6} T^{-0.76}$	$T > 617$ K	
7	$H_2 + H^+ \rightarrow H_2^+ + H$	$k_7 = [-3.3232183 \times 10^{-7} + 3.3735382 \times 10^{-7} \ln T - 1.4491368 \times 10^{-7}(\ln T)^2 + 3.4172805 \times 10^{-8}(\ln T)^3 - 4.7813720 \times 10^{-9}(\ln T)^4 + 3.9731542 \times 10^{-10}(\ln T)^5 - 1.8171411 \times 10^{-11}(\ln T)^6 + 3.5311932 \times 10^{-13}(\ln T)^7] \times \exp\left(\frac{-21237.15}{T}\right)$		7
8	$H_2 + e^- \rightarrow H + H + e^-$	$k_8 = 3.73 \times 10^{-9} T^{0.1121} \exp\left(\frac{-99430}{T}\right)$		8
9	$H_2 + H \rightarrow H + H + H$	$k_{9,l} = 6.67 \times 10^{-12} T^{1/2} \exp\left[-(1 + \frac{63590}{T})\right]$		9
		$k_{9,h} = 3.52 \times 10^{-9} \exp\left(-\frac{43900}{T}\right)$		10
		$n_{cr,H} = \mathrm{dex}\left[3.0 - 0.416 \log\left(\frac{T}{10000}\right) - 0.327 \left\{\log\left(\frac{T}{10000}\right)\right\}^2\right]$		10
10	$H_2 + H_2 \rightarrow H_2 + H + H$	$k_{10,l} = \frac{5.996 \times 10^{-30} T^{4.1881}}{(1.0 + 6.761 \times 10^{-6} T)^{5.6881}} \exp\left(-\frac{54657.4}{T}\right)$		11
		$k_{10,h} = 1.3 \times 10^{-9} \exp\left(-\frac{53300}{T}\right)$		12
		$n_{cr,H_2} = \mathrm{dex}\left[4.845 - 1.3 \log\left(\frac{T}{10000}\right) + 1.62 \left\{\log\left(\frac{T}{10000}\right)\right\}^2\right]$		12
11	$H + e^- \rightarrow H^+ + e^- + e^-$	$k_{11} = \exp[-3.271396786 \times 10^1 + 1.35365560 \times 10^1 \ln T_e - 5.73932875 \times 10^0 (\ln T_e)^2 + 1.56315498 \times 10^0 (\ln T_e)^3 - 2.87705600 \times 10^{-1}(\ln T_e)^4 + 3.48255977 \times 10^{-2}(\ln T_e)^5 - 2.63197617 \times 10^{-3}(\ln T_e)^6 + 1.11954395 \times 10^{-4}(\ln T_e)^7 - 2.03914985 \times 10^{-6}(\ln T_e)^8]$		13
12	$H^+ + e^- \rightarrow H + \gamma$	$k_{12,A} = 1.269 \times 10^{-13} \left(\frac{315614}{T}\right)^{1.503} \times \left[1.0 + \left(\frac{604625}{T}\right)^{0.470}\right]^{-1.923}$	Case A	14
		$k_{12,B} = 2.753 \times 10^{-14} \left(\frac{315614}{T}\right)^{1.500} \times \left[1.0 + \left(\frac{115188}{T}\right)^{0.407}\right]^{-2.242}$	Case B	14
13	$H^- + e^- \rightarrow H + e^- + e^-$	$k_{13} = \exp[-1.801849334 \times 10^1 + 2.36085220 \times 10^0 \ln T_e - 2.82744300 \times 10^{-1}(\ln T_e)^2 + 1.62331664 \times 10^{-2}(\ln T_e)^3 - 3.36501203 \times 10^{-2}(\ln T_e)^4 + 1.17832978 \times 10^{-2}(\ln T_e)^5 - 1.65619470 \times 10^{-3}(\ln T_e)^6 + 1.06827520 \times 10^{-4}(\ln T_e)^7 - 2.63128581 \times 10^{-6}(\ln T_e)^8]$		13

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chemical model 2

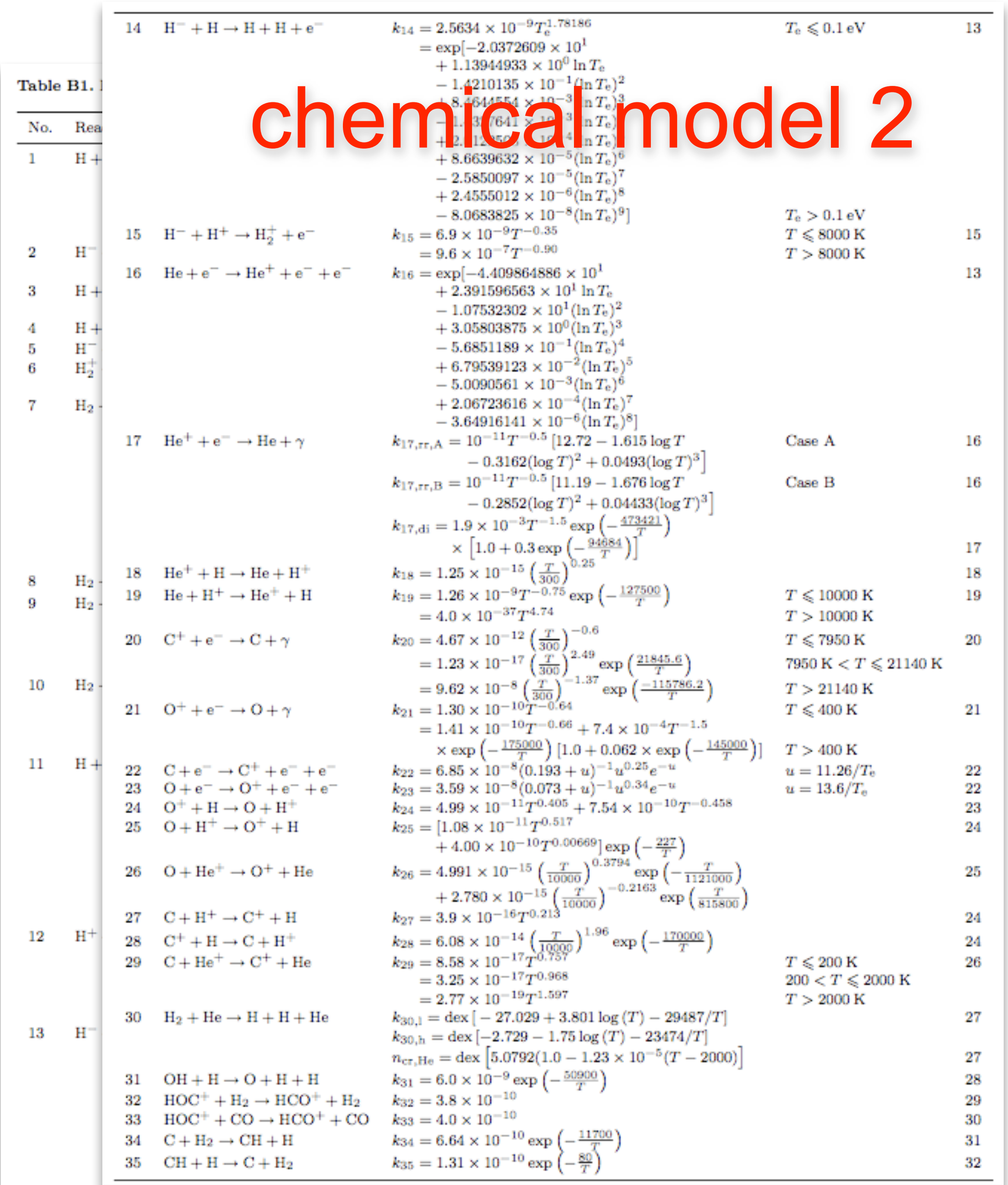

Table B1.

No.	Rea
1	H +
2	H^-
3	H +
4	H +
5	H^-
6	H_2^+
7	H_2
8	H_2
9	H_2
10	H_2
11	H +
12	H^+
13	H^-

14	$H^- + H \rightarrow H + H + e^-$	$k_{14} = 2.5634 \times 10^{-9} T_e^{1.78186}$ $= \exp[-2.0372609 \times 10^{1}$ $+ 1.13944933 \times 10^{0} \ln T_e$ $- 1.4210135 \times 10^{-1} (\ln T_e)^2$ $+ 8.4644554 \times 10^{-3} (\ln T_e)^3$ $- 1.$[illegible]$7641 \times 10^{-3} (\ln T_e)^4$ $+ 2.$[illegible]$\times 10^{-4} (\ln T_e)^5$ $+ 8.6639632 \times 10^{-5} (\ln T_e)^6$ $- 2.5850097 \times 10^{-5} (\ln T_e)^7$ $+ 2.4555012 \times 10^{-6} (\ln T_e)^8$ $- 8.0683825 \times 10^{-8} (\ln T_e)^9]$	$T_e \leqslant 0.1$ eV $T_e > 0.1$ eV	13
15	$H^- + H^+ \rightarrow H_2^+ + e^-$	$k_{15} = 6.9 \times 10^{-9} T^{-0.35}$ $= 9.6 \times 10^{-7} T^{-0.90}$	$T \leqslant 8000$ K $T > 8000$ K	15
16	$He + e^- \rightarrow He^+ + e^- + e^-$	$k_{16} = \exp[-4.409864886 \times 10^{1}$ $+ 2.391596563 \times 10^{1} \ln T_e$ $- 1.07532302 \times 10^{1} (\ln T_e)^2$ $+ 3.05803875 \times 10^{0} (\ln T_e)^3$ $- 5.6851189 \times 10^{-1} (\ln T_e)^4$ $+ 6.79539123 \times 10^{-2} (\ln T_e)^5$ $- 5.0090561 \times 10^{-3} (\ln T_e)^6$ $+ 2.06723616 \times 10^{-4} (\ln T_e)^7$ $- 3.64916141 \times 10^{-6} (\ln T_e)^8]$		13
17	$He^+ + e^- \rightarrow He + \gamma$	$k_{17,rr,A} = 10^{-11} T^{-0.5} [12.72 - 1.615 \log T$ $- 0.3162 (\log T)^2 + 0.0493 (\log T)^3]$ $k_{17,rr,B} = 10^{-11} T^{-0.5} [11.19 - 1.676 \log T$ $- 0.2852 (\log T)^2 + 0.04433 (\log T)^3]$ $k_{17,di} = 1.9 \times 10^{-3} T^{-1.5} \exp\left(-\frac{473421}{T}\right)$ $\times \left[1.0 + 0.3 \exp\left(-\frac{94684}{T}\right)\right]$	Case A Case B	16 16 17
18	$He^+ + H \rightarrow He + H^+$	$k_{18} = 1.25 \times 10^{-15} \left(\frac{T}{300}\right)^{0.25}$		18
19	$He + H^+ \rightarrow He^+ + H$	$k_{19} = 1.26 \times 10^{-9} T^{-0.75} \exp\left(-\frac{127500}{T}\right)$ $= 4.0 \times 10^{-37} T^{4.74}$	$T \leqslant 10000$ K $T > 10000$ K	19
20	$C^+ + e^- \rightarrow C + \gamma$	$k_{20} = 4.67 \times 10^{-12} \left(\frac{T}{300}\right)^{-0.6}$ $= 1.23 \times 10^{-17} \left(\frac{T}{300}\right)^{2.49} \exp\left(\frac{21845.6}{T}\right)$ $= 9.62 \times 10^{-8} \left(\frac{T}{300}\right)^{-1.37} \exp\left(\frac{-115786.2}{T}\right)$	$T \leqslant 7950$ K $7950 \text{ K} < T \leqslant 21140$ K $T > 21140$ K	20
21	$O^+ + e^- \rightarrow O + \gamma$	$k_{21} = 1.30 \times 10^{-10} T^{-0.64}$ $= 1.41 \times 10^{-10} T^{-0.66} + 7.4 \times 10^{-4} T^{-1.5}$ $\times \exp\left(-\frac{175000}{T}\right) [1.0 + 0.062 \times \exp\left(-\frac{145000}{T}\right)]$	$T \leqslant 400$ K $T > 400$ K	21
22	$C + e^- \rightarrow C^+ + e^- + e^-$	$k_{22} = 6.85 \times 10^{-8} (0.193 + u)^{-1} u^{0.25} e^{-u}$	$u = 11.26/T_e$	22
23	$O + e^- \rightarrow O^+ + e^- + e^-$	$k_{23} = 3.59 \times 10^{-8} (0.073 + u)^{-1} u^{0.34} e^{-u}$	$u = 13.6/T_e$	22
24	$O^+ + H \rightarrow O + H^+$	$k_{24} = 4.99 \times 10^{-11} T^{0.405} + 7.54 \times 10^{-10} T^{-0.458}$		23
25	$O + H^+ \rightarrow O^+ + H$	$k_{25} = [1.08 \times 10^{-11} T^{0.517}$ $+ 4.00 \times 10^{-10} T^{0.00669}] \exp\left(-\frac{227}{T}\right)$		24
26	$O + He^+ \rightarrow O^+ + He$	$k_{26} = 4.991 \times 10^{-15} \left(\frac{T}{10000}\right)^{0.3794} \exp\left(-\frac{T}{1121000}\right)$ $+ 2.780 \times 10^{-15} \left(\frac{T}{10000}\right)^{-0.2163} \exp\left(\frac{T}{815800}\right)$		25
27	$C + H^+ \rightarrow C^+ + H$	$k_{27} = 3.9 \times 10^{-16} T^{0.213}$		24
28	$C^+ + H \rightarrow C + H^+$	$k_{28} = 6.08 \times 10^{-14} \left(\frac{T}{10000}\right)^{1.96} \exp\left(-\frac{170000}{T}\right)$		24
29	$C + He^+ \rightarrow C^+ + He$	$k_{29} = 8.58 \times 10^{-17} T^{0.757}$ $= 3.25 \times 10^{-17} T^{0.968}$ $= 2.77 \times 10^{-19} T^{1.597}$	$T \leqslant 200$ K $200 < T \leqslant 2000$ K $T > 2000$ K	26
30	$H_2 + He \rightarrow H + H + He$	$k_{30,l} = \text{dex}[-27.029 + 3.801 \log(T) - 29487/T]$ $k_{30,h} = \text{dex}[-2.729 - 1.75 \log(T) - 23474/T]$ $n_{cr,He} = \text{dex}\left[5.0792(1.0 - 1.23 \times 10^{-5}(T - 2000)\right]$		27 27
31	$OH + H \rightarrow O + H + H$	$k_{31} = 6.0 \times 10^{-9} \exp\left(-\frac{50900}{T}\right)$		28
32	$HOC^+ + H_2 \rightarrow HCO^+ + H_2$	$k_{32} = 3.8 \times 10^{-10}$		29
33	$HOC^+ + CO \rightarrow HCO^+ + CO$	$k_{33} = 4.0 \times 10^{-10}$		30
34	$C + H_2 \rightarrow CH + H$	$k_{34} = 6.64 \times 10^{-10} \exp\left(-\frac{11700}{T}\right)$		31
35	$CH + H \rightarrow C + H_2$	$k_{35} = 1.31 \times 10^{-10} \exp\left(-\frac{80}{T}\right)$		32

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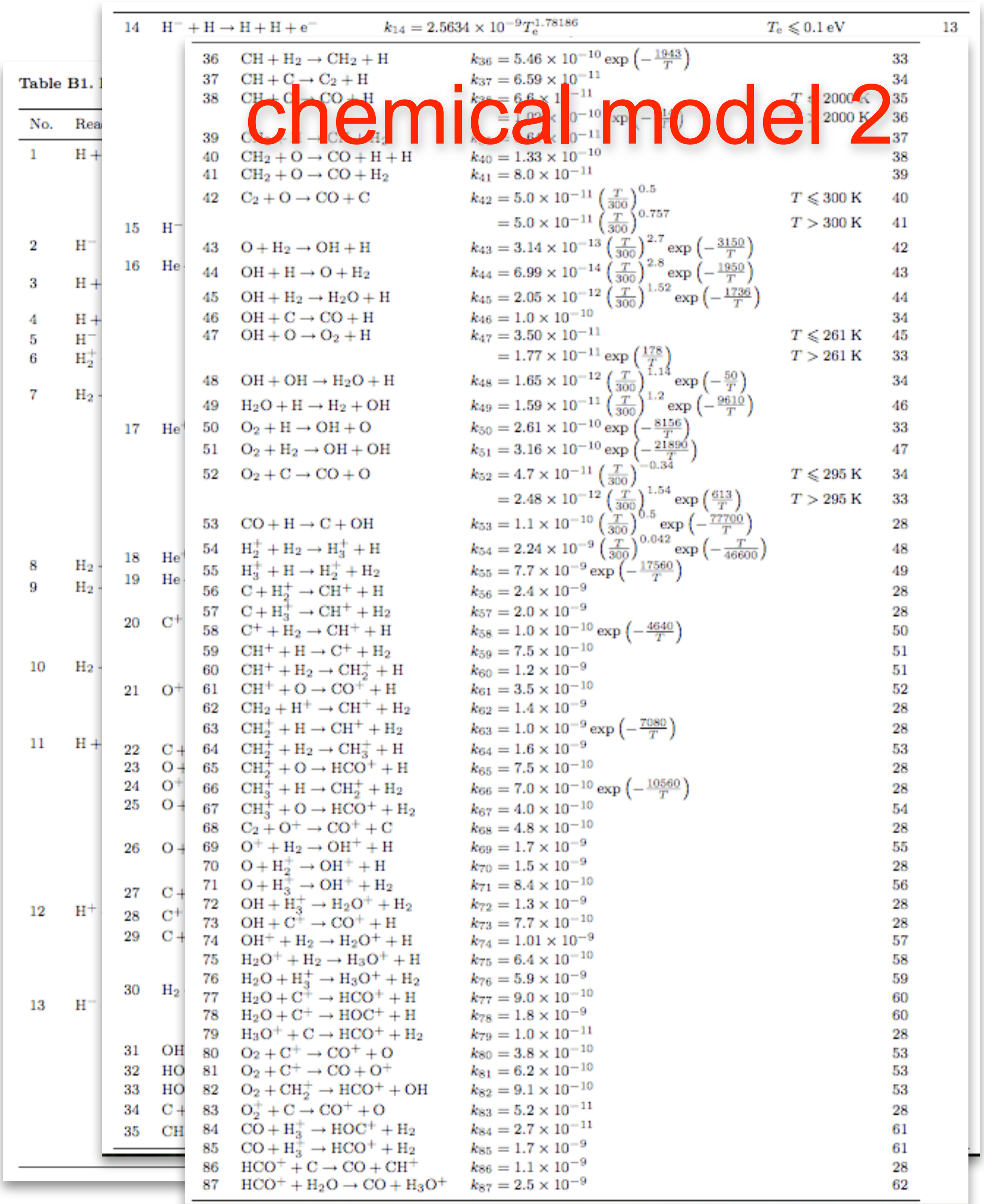
chemical model 2



14	$H^- + H \rightarrow H + H + e^-$	$k_{14} = 2.5634 \times 10^{-9} T_e^{1.78186}$	$T_e \leqslant 0.1$ eV	13

36	$CH + H_2 \rightarrow CH_2 + H$	$k_{36} = 5.46 \times 10^{-10} \exp\left(-\frac{1943}{T}\right)$		33
37	$CH + C \rightarrow C_2 + H$	$k_{37} = 6.59 \times 10^{-11}$		34
38	$CH + O \rightarrow CO + H$	$k_{38} = 6.6 \times 10^{-11}$	$T \leqslant 2000$ K	35
		= [illegible] $\times 10^{-10} \exp$ [illegible]	$T > 2000$ K	36
39	[illegible] $\rightarrow$ [illegible] $+ H_2$	[illegible] $\times 10^{-11}$		37
40	$CH_2 + O \rightarrow CO + H + H$	$k_{40} = 1.33 \times 10^{-10}$		38
41	$CH_2 + O \rightarrow CO + H_2$	$k_{41} = 8.0 \times 10^{-11}$		39
42	$C_2 + O \rightarrow CO + C$	$k_{42} = 5.0 \times 10^{-11} \left(\frac{T}{300}\right)^{0.5}$	$T \leqslant 300$ K	40
		$= 5.0 \times 10^{-11} \left(\frac{T}{300}\right)^{0.757}$	$T > 300$ K	41
43	$O + H_2 \rightarrow OH + H$	$k_{43} = 3.14 \times 10^{-13} \left(\frac{T}{300}\right)^{2.7} \exp\left(-\frac{3150}{T}\right)$		42
44	$OH + H \rightarrow O + H_2$	$k_{44} = 6.99 \times 10^{-14} \left(\frac{T}{300}\right)^{2.8} \exp\left(-\frac{1950}{T}\right)$		43
45	$OH + H_2 \rightarrow H_2O + H$	$k_{45} = 2.05 \times 10^{-12} \left(\frac{T}{300}\right)^{1.52} \exp\left(-\frac{1736}{T}\right)$		44
46	$OH + C \rightarrow CO + H$	$k_{46} = 1.0 \times 10^{-10}$		34
47	$OH + O \rightarrow O_2 + H$	$k_{47} = 3.50 \times 10^{-11}$	$T \leqslant 261$ K	45
		$= 1.77 \times 10^{-11} \exp\left(\frac{178}{T}\right)$	$T > 261$ K	33
48	$OH + OH \rightarrow H_2O + H$	$k_{48} = 1.65 \times 10^{-12} \left(\frac{T}{300}\right)^{1.14} \exp\left(-\frac{50}{T}\right)$		34
49	$H_2O + H \rightarrow H_2 + OH$	$k_{49} = 1.59 \times 10^{-11} \left(\frac{T}{300}\right)^{1.2} \exp\left(-\frac{9610}{T}\right)$		46
50	$O_2 + H \rightarrow OH + O$	$k_{50} = 2.61 \times 10^{-10} \exp\left(-\frac{8156}{T}\right)$		33
51	$O_2 + H_2 \rightarrow OH + OH$	$k_{51} = 3.16 \times 10^{-10} \exp\left(-\frac{21890}{T}\right)$		47
52	$O_2 + C \rightarrow CO + O$	$k_{52} = 4.7 \times 10^{-11} \left(\frac{T}{300}\right)^{-0.34}$	$T \leqslant 295$ K	34
		$= 2.48 \times 10^{-12} \left(\frac{T}{300}\right)^{1.54} \exp\left(\frac{613}{T}\right)$	$T > 295$ K	33
53	$CO + H \rightarrow C + OH$	$k_{53} = 1.1 \times 10^{-10} \left(\frac{T}{300}\right)^{0.5} \exp\left(-\frac{77700}{T}\right)$		28
54	$H_2^+ + H_2 \rightarrow H_3^+ + H$	$k_{54} = 2.24 \times 10^{-9} \left(\frac{T}{300}\right)^{0.042} \exp\left(-\frac{T}{46600}\right)$		48
55	$H_3^+ + H \rightarrow H_2^+ + H_2$	$k_{55} = 7.7 \times 10^{-9} \exp\left(-\frac{17560}{T}\right)$		49
56	$C + H_2^+ \rightarrow CH^+ + H$	$k_{56} = 2.4 \times 10^{-9}$		28
57	$C + H_3^+ \rightarrow CH^+ + H_2$	$k_{57} = 2.0 \times 10^{-9}$		28
58	$C^+ + H_2 \rightarrow CH^+ + H$	$k_{58} = 1.0 \times 10^{-10} \exp\left(-\frac{4640}{T}\right)$		50
59	$CH^+ + H \rightarrow C^+ + H_2$	$k_{59} = 7.5 \times 10^{-10}$		51
60	$CH^+ + H_2 \rightarrow CH_2^+ + H$	$k_{60} = 1.2 \times 10^{-9}$		51
61	$CH^+ + O \rightarrow CO^+ + H$	$k_{61} = 3.5 \times 10^{-10}$		52
62	$CH_2 + H^+ \rightarrow CH^+ + H_2$	$k_{62} = 1.4 \times 10^{-9}$		28
63	$CH_2^+ + H \rightarrow CH^+ + H_2$	$k_{63} = 1.0 \times 10^{-9} \exp\left(-\frac{7080}{T}\right)$		28
64	$CH_2^+ + H_2 \rightarrow CH_3^+ + H$	$k_{64} = 1.6 \times 10^{-9}$		53
65	$CH_2^+ + O \rightarrow HCO^+ + H$	$k_{65} = 7.5 \times 10^{-10}$		28
66	$CH_3^+ + H \rightarrow CH_2^+ + H_2$	$k_{66} = 7.0 \times 10^{-10} \exp\left(-\frac{10560}{T}\right)$		28
67	$CH_3^+ + O \rightarrow HCO^+ + H_2$	$k_{67} = 4.0 \times 10^{-10}$		54
68	$C_2 + O^+ \rightarrow CO^+ + C$	$k_{68} = 4.8 \times 10^{-10}$		28
69	$O^+ + H_2 \rightarrow OH^+ + H$	$k_{69} = 1.7 \times 10^{-9}$		55
70	$O + H_2^+ \rightarrow OH^+ + H$	$k_{70} = 1.5 \times 10^{-9}$		28
71	$O + H_3^+ \rightarrow OH^+ + H_2$	$k_{71} = 8.4 \times 10^{-10}$		56
72	$OH + H_3^+ \rightarrow H_2O^+ + H_2$	$k_{72} = 1.3 \times 10^{-9}$		28
73	$OH + C^+ \rightarrow CO^+ + H$	$k_{73} = 7.7 \times 10^{-10}$		28
74	$OH^+ + H_2 \rightarrow H_2O^+ + H$	$k_{74} = 1.01 \times 10^{-9}$		57
75	$H_2O^+ + H_2 \rightarrow H_3O^+ + H$	$k_{75} = 6.4 \times 10^{-10}$		58
76	$H_2O + H_3^+ \rightarrow H_3O^+ + H_2$	$k_{76} = 5.9 \times 10^{-9}$		59
77	$H_2O + C^+ \rightarrow HCO^+ + H$	$k_{77} = 9.0 \times 10^{-10}$		60
78	$H_2O + C^+ \rightarrow HOC^+ + H$	$k_{78} = 1.8 \times 10^{-9}$		60
79	$H_3O^+ + C \rightarrow HCO^+ + H_2$	$k_{79} = 1.0 \times 10^{-11}$		28
80	$O_2 + C^+ \rightarrow CO^+ + O$	$k_{80} = 3.8 \times 10^{-10}$		53
81	$O_2 + C^+ \rightarrow CO + O^+$	$k_{81} = 6.2 \times 10^{-10}$		53
82	$O_2 + CH_2^+ \rightarrow HCO^+ + OH$	$k_{82} = 9.1 \times 10^{-10}$		53
83	$O_2^+ + C \rightarrow CO^+ + O$	$k_{83} = 5.2 \times 10^{-11}$		28
84	$CO + H_3^+ \rightarrow HOC^+ + H_2$	$k_{84} = 2.7 \times 10^{-11}$		61
85	$CO + H_3^+ \rightarrow HCO^+ + H_2$	$k_{85} = 1.7 \times 10^{-9}$		61
86	$HCO^+ + C \rightarrow CO + CH^+$	$k_{86} = 1.1 \times 10^{-9}$		28
87	$HCO^+ + H_2O \rightarrow CO + H_3O^+$	$k_{87} = 2.5 \times 10^{-9}$		62

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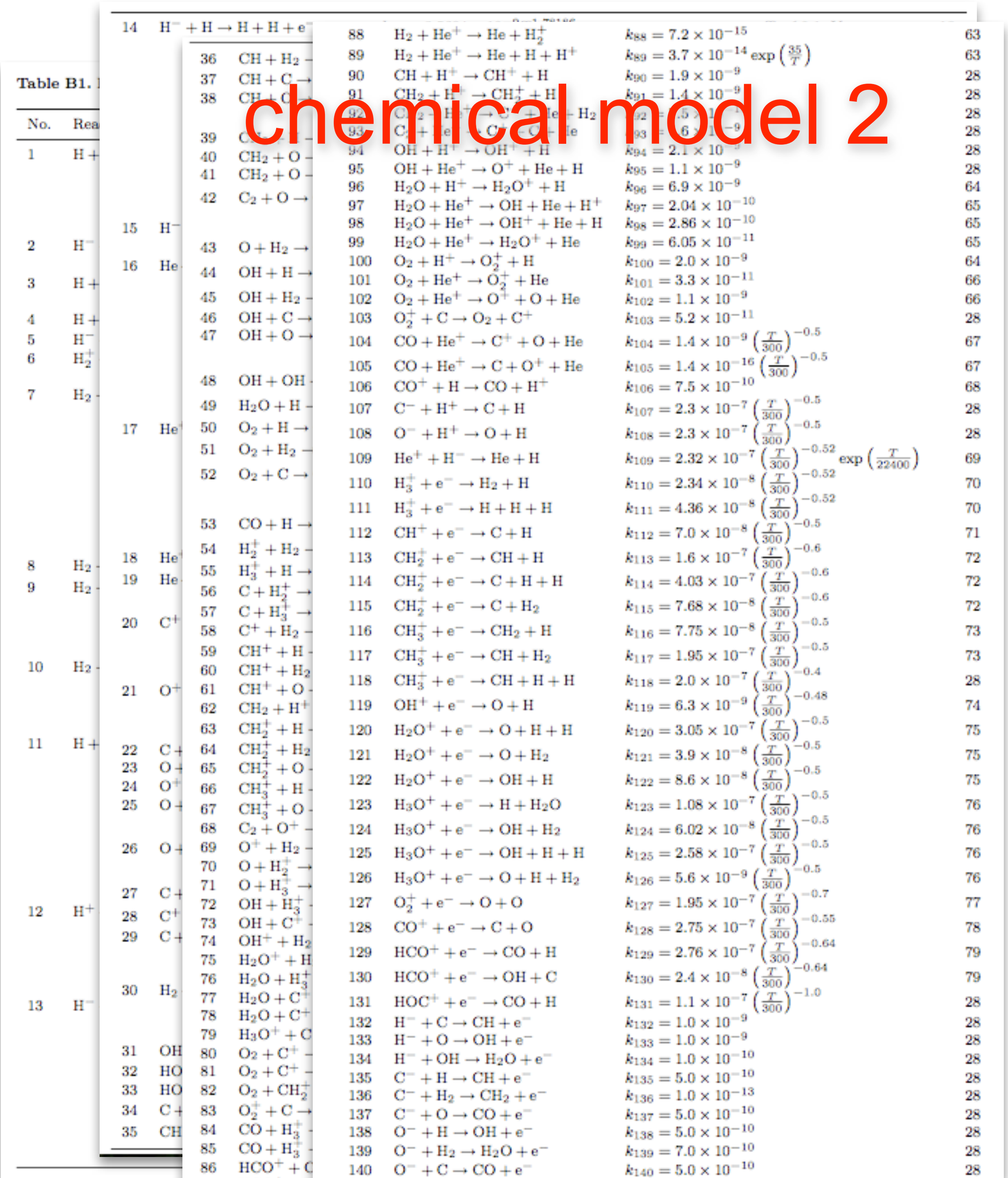
chemical model 2



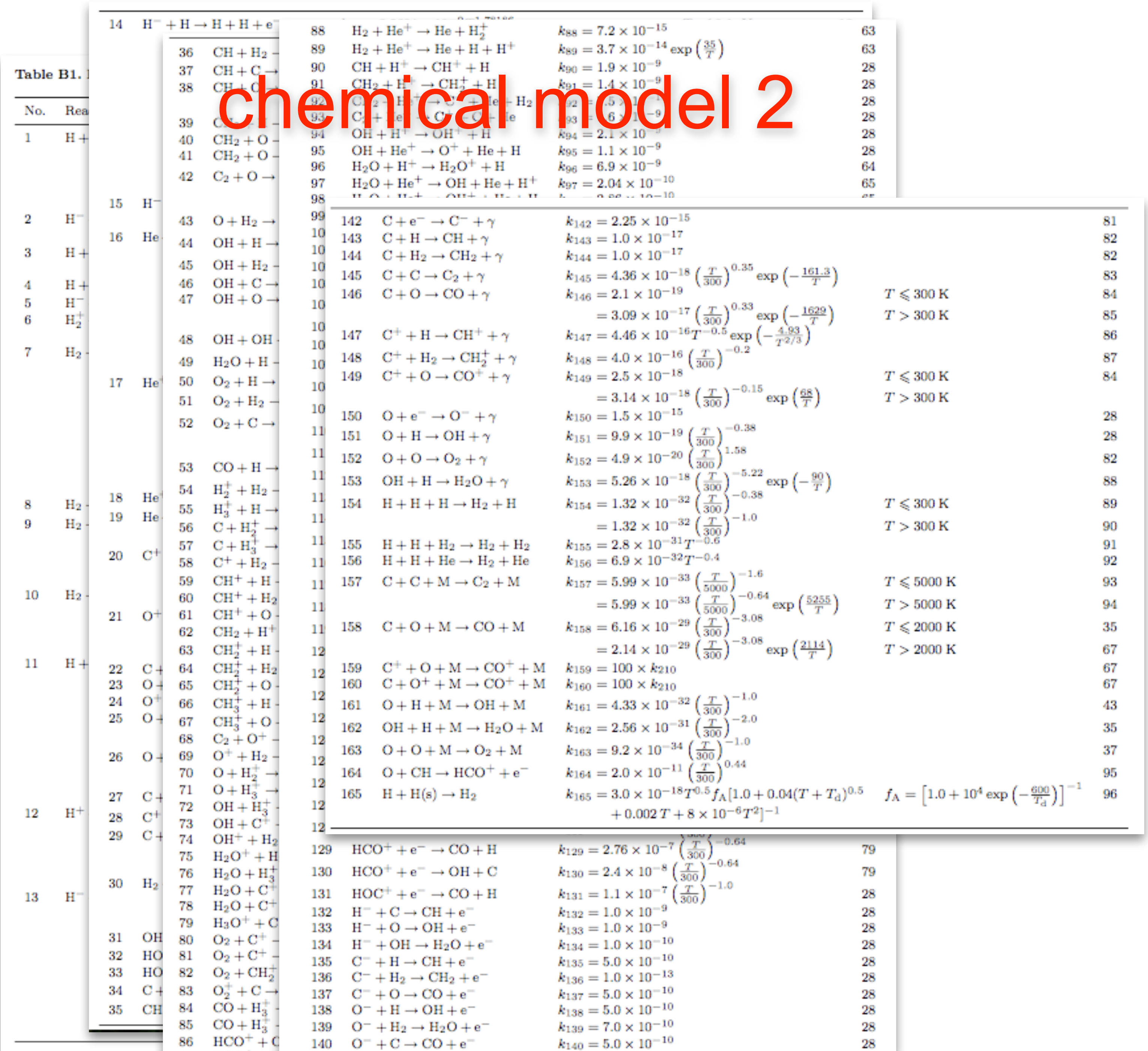
88	$H_2 + He^+ \rightarrow He + H_2^+$	$k_{88} = 7.2 \times 10^{-15}$	63
89	$H_2 + He^+ \rightarrow He + H + H^+$	$k_{89} = 3.7 \times 10^{-14} \exp\left(\frac{35}{T}\right)$	63
90	$CH + H^+ \rightarrow CH^+ + H$	$k_{90} = 1.9 \times 10^{-9}$	28
91	$CH_2 + H^+ \rightarrow CH_2^+ + H$	$k_{91} = 1.4 \times 10^{-9}$	28
92	$CH_2 + He^+ \rightarrow C^+ + He + H_2$	$k_{92} =$ [illegible]	28
93	$C_2 + He^+ \rightarrow C^+ + C + He$	$k_{93} =$ [illegible] $\times 10^{-9}$	28
94	$OH + H^+ \rightarrow OH^+ + H$	$k_{94} = 2.1 \times 10^{-9}$	28
95	$OH + He^+ \rightarrow O^+ + He + H$	$k_{95} = 1.1 \times 10^{-9}$	28
96	$H_2O + H^+ \rightarrow H_2O^+ + H$	$k_{96} = 6.9 \times 10^{-9}$	64
97	$H_2O + He^+ \rightarrow OH + He + H^+$	$k_{97} = 2.04 \times 10^{-10}$	65
98	$H_2O + He^+ \rightarrow OH^+ + He + H$	$k_{98} = 2.86 \times 10^{-10}$	65
99	$H_2O + He^+ \rightarrow H_2O^+ + He$	$k_{99} = 6.05 \times 10^{-11}$	65
100	$O_2 + H^+ \rightarrow O_2^+ + H$	$k_{100} = 2.0 \times 10^{-9}$	64
101	$O_2 + He^+ \rightarrow O_2^+ + He$	$k_{101} = 3.3 \times 10^{-11}$	66
102	$O_2 + He^+ \rightarrow O^+ + O + He$	$k_{102} = 1.1 \times 10^{-9}$	66
103	$O_2^+ + C \rightarrow O_2 + C^+$	$k_{103} = 5.2 \times 10^{-11}$	28
104	$CO + He^+ \rightarrow C^+ + O + He$	$k_{104} = 1.4 \times 10^{-9} \left(\frac{T}{300}\right)^{-0.5}$	67
105	$CO + He^+ \rightarrow C + O^+ + He$	$k_{105} = 1.4 \times 10^{-16} \left(\frac{T}{300}\right)^{-0.5}$	67
106	$CO^+ + H \rightarrow CO + H^+$	$k_{106} = 7.5 \times 10^{-10}$	68
107	$C^- + H^+ \rightarrow C + H$	$k_{107} = 2.3 \times 10^{-7} \left(\frac{T}{300}\right)^{-0.5}$	28
108	$O^- + H^+ \rightarrow O + H$	$k_{108} = 2.3 \times 10^{-7} \left(\frac{T}{300}\right)^{-0.5}$	28
109	$He^+ + H^- \rightarrow He + H$	$k_{109} = 2.32 \times 10^{-7} \left(\frac{T}{300}\right)^{-0.52} \exp\left(\frac{T}{22400}\right)$	69
110	$H_3^+ + e^- \rightarrow H_2 + H$	$k_{110} = 2.34 \times 10^{-8} \left(\frac{T}{300}\right)^{-0.52}$	70
111	$H_3^+ + e^- \rightarrow H + H + H$	$k_{111} = 4.36 \times 10^{-8} \left(\frac{T}{300}\right)^{-0.52}$	70
112	$CH^+ + e^- \rightarrow C + H$	$k_{112} = 7.0 \times 10^{-8} \left(\frac{T}{300}\right)^{-0.5}$	71
113	$CH_2^+ + e^- \rightarrow CH + H$	$k_{113} = 1.6 \times 10^{-7} \left(\frac{T}{300}\right)^{-0.6}$	72
114	$CH_2^+ + e^- \rightarrow C + H + H$	$k_{114} = 4.03 \times 10^{-7} \left(\frac{T}{300}\right)^{-0.6}$	72
115	$CH_2^+ + e^- \rightarrow C + H_2$	$k_{115} = 7.68 \times 10^{-8} \left(\frac{T}{300}\right)^{-0.6}$	72
116	$CH_3^+ + e^- \rightarrow CH_2 + H$	$k_{116} = 7.75 \times 10^{-8} \left(\frac{T}{300}\right)^{-0.5}$	73
117	$CH_3^+ + e^- \rightarrow CH + H_2$	$k_{117} = 1.95 \times 10^{-7} \left(\frac{T}{300}\right)^{-0.5}$	73
118	$CH_3^+ + e^- \rightarrow CH + H + H$	$k_{118} = 2.0 \times 10^{-7} \left(\frac{T}{300}\right)^{-0.4}$	28
119	$OH^+ + e^- \rightarrow O + H$	$k_{119} = 6.3 \times 10^{-9} \left(\frac{T}{300}\right)^{-0.48}$	74
120	$H_2O^+ + e^- \rightarrow O + H + H$	$k_{120} = 3.05 \times 10^{-7} \left(\frac{T}{300}\right)^{-0.5}$	75
121	$H_2O^+ + e^- \rightarrow O + H_2$	$k_{121} = 3.9 \times 10^{-8} \left(\frac{T}{300}\right)^{-0.5}$	75
122	$H_2O^+ + e^- \rightarrow OH + H$	$k_{122} = 8.6 \times 10^{-8} \left(\frac{T}{300}\right)^{-0.5}$	75
123	$H_3O^+ + e^- \rightarrow H + H_2O$	$k_{123} = 1.08 \times 10^{-7} \left(\frac{T}{300}\right)^{-0.5}$	76
124	$H_3O^+ + e^- \rightarrow OH + H_2$	$k_{124} = 6.02 \times 10^{-8} \left(\frac{T}{300}\right)^{-0.5}$	76
125	$H_3O^+ + e^- \rightarrow OH + H + H$	$k_{125} = 2.58 \times 10^{-7} \left(\frac{T}{300}\right)^{-0.5}$	76
126	$H_3O^+ + e^- \rightarrow O + H + H_2$	$k_{126} = 5.6 \times 10^{-9} \left(\frac{T}{300}\right)^{-0.5}$	76
127	$O_2^+ + e^- \rightarrow O + O$	$k_{127} = 1.95 \times 10^{-7} \left(\frac{T}{300}\right)^{-0.7}$	77
128	$CO^+ + e^- \rightarrow C + O$	$k_{128} = 2.75 \times 10^{-7} \left(\frac{T}{300}\right)^{-0.55}$	78
129	$HCO^+ + e^- \rightarrow CO + H$	$k_{129} = 2.76 \times 10^{-7} \left(\frac{T}{300}\right)^{-0.64}$	79
130	$HCO^+ + e^- \rightarrow OH + C$	$k_{130} = 2.4 \times 10^{-8} \left(\frac{T}{300}\right)^{-0.64}$	79
131	$HOC^+ + e^- \rightarrow CO + H$	$k_{131} = 1.1 \times 10^{-7} \left(\frac{T}{300}\right)^{-1.0}$	28
132	$H^- + C \rightarrow CH + e^-$	$k_{132} = 1.0 \times 10^{-9}$	28
133	$H^- + O \rightarrow OH + e^-$	$k_{133} = 1.0 \times 10^{-9}$	28
134	$H^- + OH \rightarrow H_2O + e^-$	$k_{134} = 1.0 \times 10^{-10}$	28
135	$C^- + H \rightarrow CH + e^-$	$k_{135} = 5.0 \times 10^{-10}$	28
136	$C^- + H_2 \rightarrow CH_2 + e^-$	$k_{136} = 1.0 \times 10^{-13}$	28
137	$C^- + O \rightarrow CO + e^-$	$k_{137} = 5.0 \times 10^{-10}$	28
138	$O^- + H \rightarrow OH + e^-$	$k_{138} = 5.0 \times 10^{-10}$	28
139	$O^- + H_2 \rightarrow H_2O + e^-$	$k_{139} = 7.0 \times 10^{-10}$	28
140	$O^- + C \rightarrow CO + e^-$	$k_{140} = 5.0 \times 10^{-10}$	28

87	$HCO^+ + H_2O \rightarrow CO + H_3O^+$	$k_{87} = 2.5 \times 10^{-9}$	62

(Glover, Federrath, Mac Low, Klessen, 2010, MNRS, 404, 2)

chemical model 2

(Glover, Federrath, Mac Low, Klessen, 2010, MNRS, 404, 2)



87	$HCO^+ + H_2O \rightarrow CO + H_3O^+$	$k_{87} = 2.5 \times 10^{-9}$	62
88	$H_2 + He^+ \rightarrow He + H_2^+$	$k_{88} = 7.2 \times 10^{-15}$	63
89	$H_2 + He^+ \rightarrow He + H + H^+$	$k_{89} = 3.7 \times 10^{-14} \exp\left(\frac{35}{T}\right)$	63
90	$CH + H^+ \rightarrow CH^+ + H$	$k_{90} = 1.9 \times 10^{-9}$	28
91	$CH_2 + H^+ \rightarrow CH_2^+ + H$	$k_{91} = 1.4 \times 10^{-9}$	28
92	[illegible]	[illegible]	28
93	[illegible]	[illegible]	28
94	$OH + H^+ \rightarrow OH^+ + H$	$k_{94} = 2.1 \times 10^{-9}$	28
95	$OH + He^+ \rightarrow O^+ + He + H$	$k_{95} = 1.1 \times 10^{-9}$	28
96	$H_2O + H^+ \rightarrow H_2O^+ + H$	$k_{96} = 6.9 \times 10^{-9}$	64
97	$H_2O + He^+ \rightarrow OH + He + H^+$	$k_{97} = 2.04 \times 10^{-10}$	65
129	$HCO^+ + e^- \rightarrow CO + H$	$k_{129} = 2.76 \times 10^{-7} \left(\frac{T}{300}\right)^{-0.64}$	79
130	$HCO^+ + e^- \rightarrow OH + C$	$k_{130} = 2.4 \times 10^{-8} \left(\frac{T}{300}\right)^{-0.64}$	79
131	$HOC^+ + e^- \rightarrow CO + H$	$k_{131} = 1.1 \times 10^{-7} \left(\frac{T}{300}\right)^{-1.0}$	28
132	$H^- + C \rightarrow CH + e^-$	$k_{132} = 1.0 \times 10^{-9}$	28
133	$H^- + O \rightarrow OH + e^-$	$k_{133} = 1.0 \times 10^{-9}$	28
134	$H^- + OH \rightarrow H_2O + e^-$	$k_{134} = 1.0 \times 10^{-10}$	28
135	$C^- + H \rightarrow CH + e^-$	$k_{135} = 5.0 \times 10^{-10}$	28
136	$C^- + H_2 \rightarrow CH_2 + e^-$	$k_{136} = 1.0 \times 10^{-13}$	28
137	$C^- + O \rightarrow CO + e^-$	$k_{137} = 5.0 \times 10^{-10}$	28
138	$O^- + H \rightarrow OH + e^-$	$k_{138} = 5.0 \times 10^{-10}$	28
139	$O^- + H_2 \rightarrow H_2O + e^-$	$k_{139} = 7.0 \times 10^{-10}$	28
140	$O^- + C \rightarrow CO + e^-$	$k_{140} = 5.0 \times 10^{-10}$	28

142	$C + e^- \rightarrow C^- + \gamma$	$k_{142} = 2.25 \times 10^{-15}$		81
143	$C + H \rightarrow CH + \gamma$	$k_{143} = 1.0 \times 10^{-17}$		82
144	$C + H_2 \rightarrow CH_2 + \gamma$	$k_{144} = 1.0 \times 10^{-17}$		82
145	$C + C \rightarrow C_2 + \gamma$	$k_{145} = 4.36 \times 10^{-18} \left(\frac{T}{300}\right)^{0.35} \exp\left(-\frac{161.3}{T}\right)$		83
146	$C + O \rightarrow CO + \gamma$	$k_{146} = 2.1 \times 10^{-19}$	$T \leqslant 300$ K	84
		$= 3.09 \times 10^{-17} \left(\frac{T}{300}\right)^{0.33} \exp\left(-\frac{1629}{T}\right)$	$T > 300$ K	85
147	$C^+ + H \rightarrow CH^+ + \gamma$	$k_{147} = 4.46 \times 10^{-16} T^{-0.5} \exp\left(-\frac{4.93}{T^{2/3}}\right)$		86
148	$C^+ + H_2 \rightarrow CH_2^+ + \gamma$	$k_{148} = 4.0 \times 10^{-16} \left(\frac{T}{300}\right)^{-0.2}$		87
149	$C^+ + O \rightarrow CO^+ + \gamma$	$k_{149} = 2.5 \times 10^{-18}$	$T \leqslant 300$ K	84
		$= 3.14 \times 10^{-18} \left(\frac{T}{300}\right)^{-0.15} \exp\left(\frac{68}{T}\right)$	$T > 300$ K	
150	$O + e^- \rightarrow O^- + \gamma$	$k_{150} = 1.5 \times 10^{-15}$		28
151	$O + H \rightarrow OH + \gamma$	$k_{151} = 9.9 \times 10^{-19} \left(\frac{T}{300}\right)^{-0.38}$		28
152	$O + O \rightarrow O_2 + \gamma$	$k_{152} = 4.9 \times 10^{-20} \left(\frac{T}{300}\right)^{1.58}$		82
153	$OH + H \rightarrow H_2O + \gamma$	$k_{153} = 5.26 \times 10^{-18} \left(\frac{T}{300}\right)^{-5.22} \exp\left(-\frac{90}{T}\right)$		88
154	$H + H + H \rightarrow H_2 + H$	$k_{154} = 1.32 \times 10^{-32} \left(\frac{T}{300}\right)^{-0.38}$	$T \leqslant 300$ K	89
		$= 1.32 \times 10^{-32} \left(\frac{T}{300}\right)^{-1.0}$	$T > 300$ K	90
155	$H + H + H_2 \rightarrow H_2 + H_2$	$k_{155} = 2.8 \times 10^{-31} T^{-0.6}$		91
156	$H + H + He \rightarrow H_2 + He$	$k_{156} = 6.9 \times 10^{-32} T^{-0.4}$		92
157	$C + C + M \rightarrow C_2 + M$	$k_{157} = 5.99 \times 10^{-33} \left(\frac{T}{5000}\right)^{-1.6}$	$T \leqslant 5000$ K	93
		$= 5.99 \times 10^{-33} \left(\frac{T}{5000}\right)^{-0.64} \exp\left(\frac{5255}{T}\right)$	$T > 5000$ K	94
158	$C + O + M \rightarrow CO + M$	$k_{158} = 6.16 \times 10^{-29} \left(\frac{T}{300}\right)^{-3.08}$	$T \leqslant 2000$ K	35
		$= 2.14 \times 10^{-29} \left(\frac{T}{300}\right)^{-3.08} \exp\left(\frac{2114}{T}\right)$	$T > 2000$ K	67
159	$C^+ + O + M \rightarrow CO^+ + M$	$k_{159} = 100 \times k_{210}$		67
160	$C + O^+ + M \rightarrow CO^+ + M$	$k_{160} = 100 \times k_{210}$		67
161	$O + H + M \rightarrow OH + M$	$k_{161} = 4.33 \times 10^{-32} \left(\frac{T}{300}\right)^{-1.0}$		43
162	$OH + H + M \rightarrow H_2O + M$	$k_{162} = 2.56 \times 10^{-31} \left(\frac{T}{300}\right)^{-2.0}$		35
163	$O + O + M \rightarrow O_2 + M$	$k_{163} = 9.2 \times 10^{-34} \left(\frac{T}{300}\right)^{-1.0}$		37
164	$O + CH \rightarrow HCO^+ + e^-$	$k_{164} = 2.0 \times 10^{-11} \left(\frac{T}{300}\right)^{0.44}$		95
165	$H + H(s) \rightarrow H_2$	$k_{165} = 3.0 \times 10^{-18} T^{0.5} f_A [1.0 + 0.04 (T + T_d)^{0.5} + 0.002\, T + 8 \times 10^{-6} T^2]^{-1}$	$f_A = \left[1.0 + 10^4 \exp\left(-\frac{600}{T_d}\right)\right]^{-1}$	96

chemical model 2

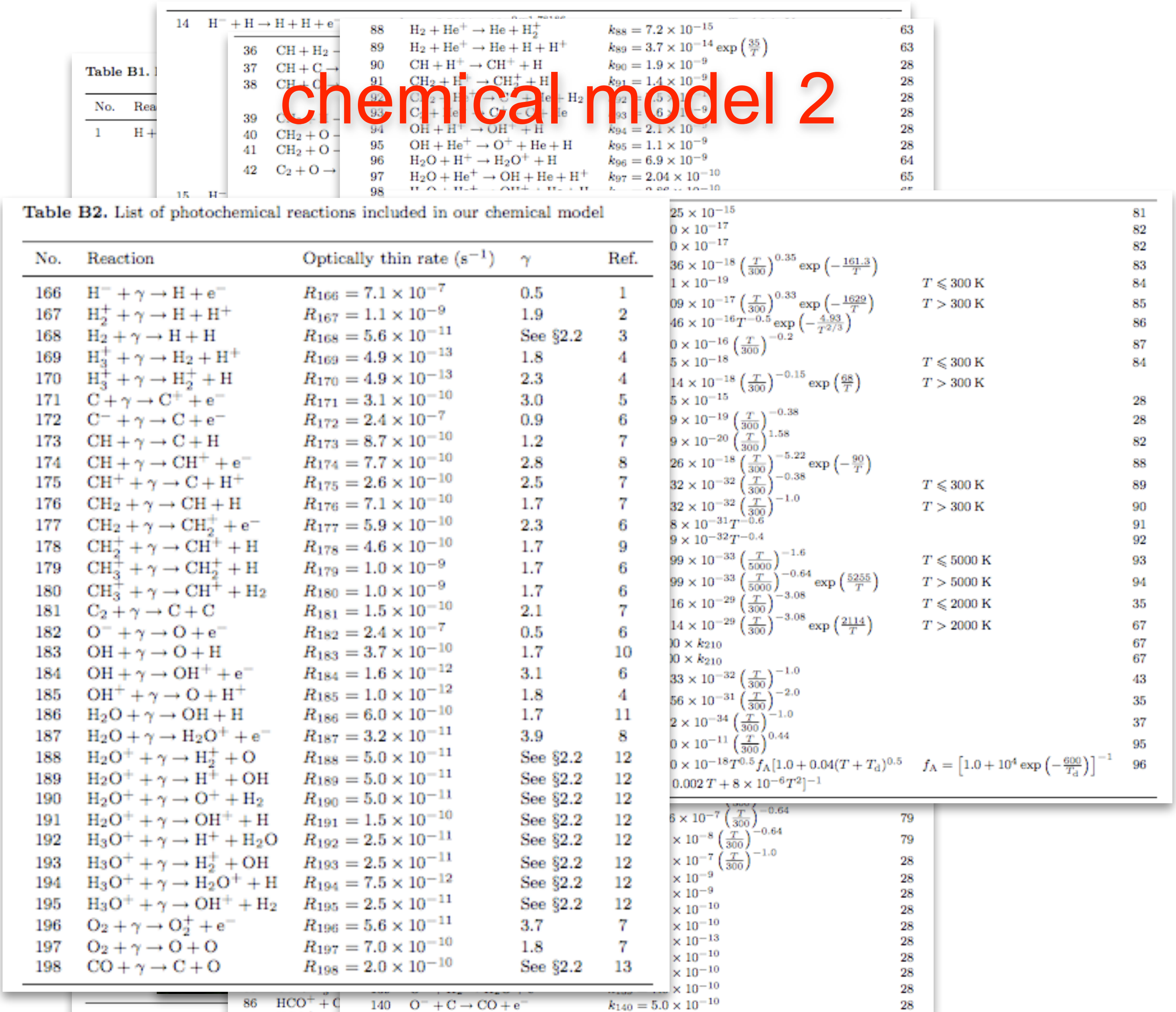


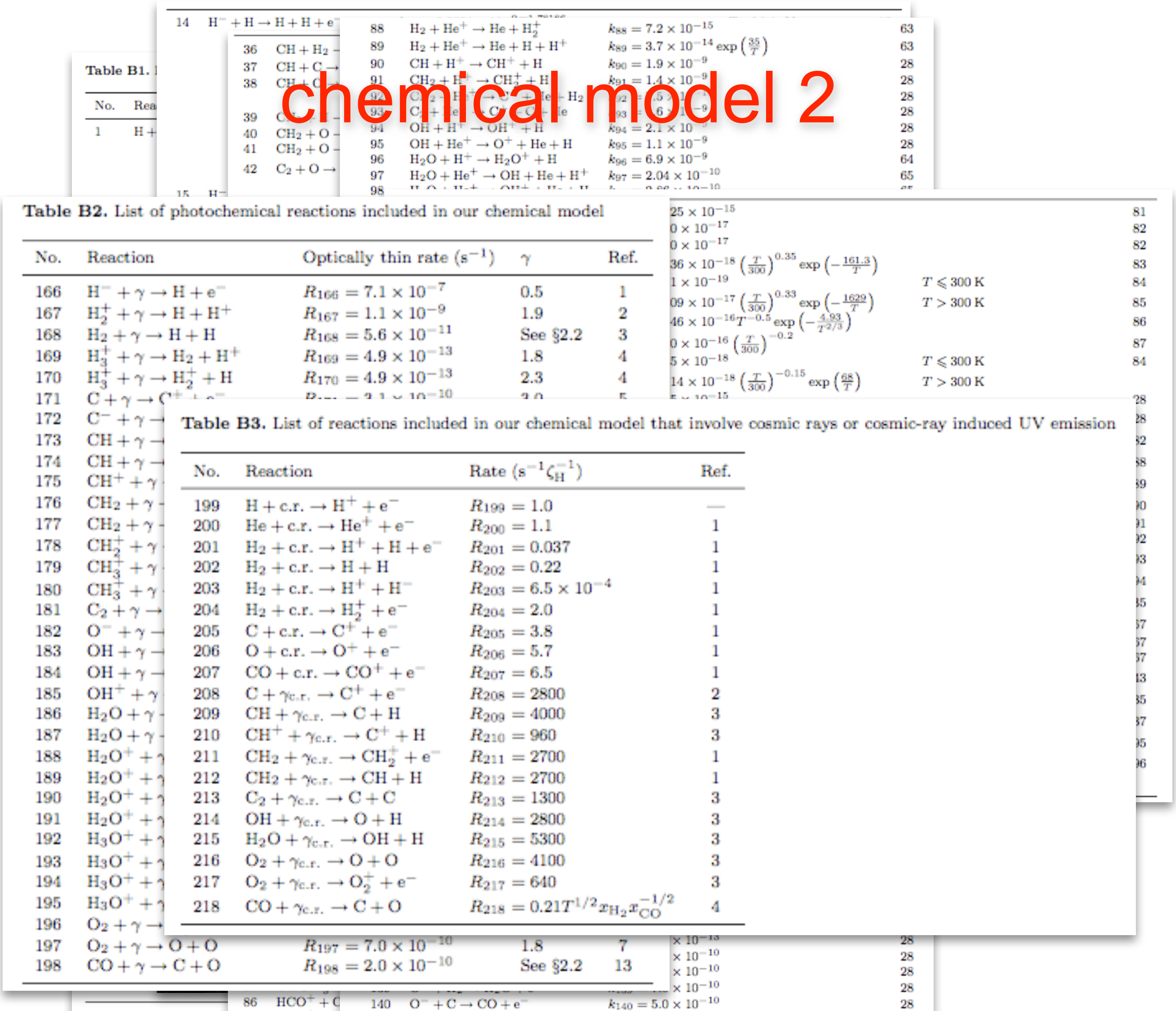
Table B2. List of photochemical reactions included in our chemical model

No.	Reaction	Optically thin rate (s^{-1})	γ	Ref.
166	$H^- + \gamma \rightarrow H + e^-$	$R_{166} = 7.1 \times 10^{-7}$	0.5	1
167	$H_2^+ + \gamma \rightarrow H + H^+$	$R_{167} = 1.1 \times 10^{-9}$	1.9	2
168	$H_2 + \gamma \rightarrow H + H$	$R_{168} = 5.6 \times 10^{-11}$	See §2.2	3
169	$H_3^+ + \gamma \rightarrow H_2 + H^+$	$R_{169} = 4.9 \times 10^{-13}$	1.8	4
170	$H_3^+ + \gamma \rightarrow H_2^+ + H$	$R_{170} = 4.9 \times 10^{-13}$	2.3	4
171	$C + \gamma \rightarrow C^+ + e^-$	$R_{171} = 3.1 \times 10^{-10}$	3.0	5
172	$C^- + \gamma \rightarrow C + e^-$	$R_{172} = 2.4 \times 10^{-7}$	0.9	6
173	$CH + \gamma \rightarrow C + H$	$R_{173} = 8.7 \times 10^{-10}$	1.2	7
174	$CH + \gamma \rightarrow CH^+ + e^-$	$R_{174} = 7.7 \times 10^{-10}$	2.8	8
175	$CH^+ + \gamma \rightarrow C + H^+$	$R_{175} = 2.6 \times 10^{-10}$	2.5	7
176	$CH_2 + \gamma \rightarrow CH + H$	$R_{176} = 7.1 \times 10^{-10}$	1.7	7
177	$CH_2 + \gamma \rightarrow CH_2^+ + e^-$	$R_{177} = 5.9 \times 10^{-10}$	2.3	6
178	$CH_2^+ + \gamma \rightarrow CH^+ + H$	$R_{178} = 4.6 \times 10^{-10}$	1.7	9
179	$CH_3^+ + \gamma \rightarrow CH_2^+ + H$	$R_{179} = 1.0 \times 10^{-9}$	1.7	6
180	$CH_3^+ + \gamma \rightarrow CH^+ + H_2$	$R_{180} = 1.0 \times 10^{-9}$	1.7	6
181	$C_2 + \gamma \rightarrow C + C$	$R_{181} = 1.5 \times 10^{-10}$	2.1	7
182	$O^- + \gamma \rightarrow O + e^-$	$R_{182} = 2.4 \times 10^{-7}$	0.5	6
183	$OH + \gamma \rightarrow O + H$	$R_{183} = 3.7 \times 10^{-10}$	1.7	10
184	$OH + \gamma \rightarrow OH^+ + e^-$	$R_{184} = 1.6 \times 10^{-12}$	3.1	6
185	$OH^+ + \gamma \rightarrow O + H^+$	$R_{185} = 1.0 \times 10^{-12}$	1.8	4
186	$H_2O + \gamma \rightarrow OH + H$	$R_{186} = 6.0 \times 10^{-10}$	1.7	11
187	$H_2O + \gamma \rightarrow H_2O^+ + e^-$	$R_{187} = 3.2 \times 10^{-11}$	3.9	8
188	$H_2O^+ + \gamma \rightarrow H_2^+ + O$	$R_{188} = 5.0 \times 10^{-11}$	See §2.2	12
189	$H_2O^+ + \gamma \rightarrow H^+ + OH$	$R_{189} = 5.0 \times 10^{-11}$	See §2.2	12
190	$H_2O^+ + \gamma \rightarrow O^+ + H_2$	$R_{190} = 5.0 \times 10^{-11}$	See §2.2	12
191	$H_2O^+ + \gamma \rightarrow OH^+ + H$	$R_{191} = 1.5 \times 10^{-10}$	See §2.2	12
192	$H_3O^+ + \gamma \rightarrow H^+ + H_2O$	$R_{192} = 2.5 \times 10^{-11}$	See §2.2	12
193	$H_3O^+ + \gamma \rightarrow H_2^+ + OH$	$R_{193} = 2.5 \times 10^{-11}$	See §2.2	12
194	$H_3O^+ + \gamma \rightarrow H_2O^+ + H$	$R_{194} = 7.5 \times 10^{-12}$	See §2.2	12
195	$H_3O^+ + \gamma \rightarrow OH^+ + H_2$	$R_{195} = 2.5 \times 10^{-11}$	See §2.2	12
196	$O_2 + \gamma \rightarrow O_2^+ + e^-$	$R_{196} = 5.6 \times 10^{-11}$	3.7	7
197	$O_2 + \gamma \rightarrow O + O$	$R_{197} = 7.0 \times 10^{-10}$	1.8	7
198	$CO + \gamma \rightarrow C + O$	$R_{198} = 2.0 \times 10^{-10}$	See §2.2	13

88	$H_2 + He^+ \rightarrow He + H_2^+$	$k_{88} = 7.2 \times 10^{-15}$	63
89	$H_2 + He^+ \rightarrow He + H + H^+$	$k_{89} = 3.7 \times 10^{-14} \exp\left(\frac{35}{T}\right)$	63
90	$CH + H^+ \rightarrow CH^+ + H$	$k_{90} = 1.9 \times 10^{-9}$	28
91	$CH_2 + H^+ \rightarrow CH_2^+ + H$	$k_{91} = 1.4 \times 10^{-9}$	28
92	[illegible] H_2	[illegible]	28
93	[illegible]	[illegible]	28
94	$OH + H^+ \rightarrow OH^+ + H$	$k_{94} = 2.1 \times 10^{-9}$	28
95	$OH + He^+ \rightarrow O^+ + He + H$	$k_{95} = 1.1 \times 10^{-9}$	28
96	$H_2O + H^+ \rightarrow H_2O^+ + H$	$k_{96} = 6.9 \times 10^{-9}$	64
97	$H_2O + He^+ \rightarrow OH + He + H^+$	$k_{97} = 2.04 \times 10^{-10}$	65

(Glover, Federrath, Mac Low, Klessen, 2010, MNRS, 404, 2)

chemical model 2



88	$H_2 + He^+ \rightarrow He + H_2^+$	$k_{88} = 7.2 \times 10^{-15}$	63
89	$H_2 + He^+ \rightarrow He + H + H^+$	$k_{89} = 3.7 \times 10^{-14} \exp\left(\frac{35}{T}\right)$	63
90	$CH + H^+ \rightarrow CH^+ + H$	$k_{90} = 1.9 \times 10^{-9}$	28
91	$CH_2 + H^+ \rightarrow CH_2^+ + H$	$k_{91} = 1.4 \times 10^{-9}$	28
92	[illegible]	[illegible]	28
93	[illegible]	[illegible]	28
94	$OH + H^+ \rightarrow OH^+ + H$	$k_{94} = 2.1 \times 10$	28
95	$OH + He^+ \rightarrow O^+ + He + H$	$k_{95} = 1.1 \times 10^{-9}$	28
96	$H_2O + H^+ \rightarrow H_2O^+ + H$	$k_{96} = 6.9 \times 10^{-9}$	64
97	$H_2O + He^+ \rightarrow OH + He + H^+$	$k_{97} = 2.04 \times 10^{-10}$	65

	25×10^{-15}		81
	0×10^{-17}		82
	0×10^{-17}		82
	$36 \times 10^{-18} \left(\frac{T}{300}\right)^{0.35} \exp\left(-\frac{161.3}{T}\right)$		83
	1×10^{-19}	$T \leqslant 300$ K	84
	$09 \times 10^{-17} \left(\frac{T}{300}\right)^{0.33} \exp\left(-\frac{1629}{T}\right)$	$T > 300$ K	85
	$46 \times 10^{-16} T^{-0.5} \exp\left(-\frac{4.93}{T^{2/3}}\right)$		86
	$0 \times 10^{-16} \left(\frac{T}{300}\right)^{-0.2}$		87
	5×10^{-18}	$T \leqslant 300$ K	84
	$14 \times 10^{-18} \left(\frac{T}{300}\right)^{-0.15} \exp\left(\frac{68}{T}\right)$	$T > 300$ K	

Table B2. List of photochemical reactions included in our chemical model

No.	Reaction	Optically thin rate (s^{-1})	γ	Ref.
166	$H^- + \gamma \rightarrow H + e^-$	$R_{166} = 7.1 \times 10^{-7}$	0.5	1
167	$H_2^+ + \gamma \rightarrow H + H^+$	$R_{167} = 1.1 \times 10^{-9}$	1.9	2
168	$H_2 + \gamma \rightarrow H + H$	$R_{168} = 5.6 \times 10^{-11}$	See §2.2	3
169	$H_3^+ + \gamma \rightarrow H_2 + H^+$	$R_{169} = 4.9 \times 10^{-13}$	1.8	4
170	$H_3^+ + \gamma \rightarrow H_2^+ + H$	$R_{170} = 4.9 \times 10^{-13}$	2.3	4
171	$C + \gamma \rightarrow$			
172	$C^- + \gamma \rightarrow$			
173	$CH + \gamma \rightarrow$			
174	$CH + \gamma \rightarrow$			
175	$CH^+ + \gamma$			
176	$CH_2 + \gamma$			
177	$CH_2 + \gamma$			
178	$CH_2^+ + \gamma$			
179	$CH_3^+ + \gamma$			
180	$CH_3^+ + \gamma$			
181	$C_2 + \gamma \rightarrow$			
182	$O^- + \gamma \rightarrow$			
183	$OH + \gamma \rightarrow$			
184	$OH + \gamma \rightarrow$			
185	$OH^+ + \gamma$			
186	$H_2O + \gamma$			
187	$H_2O + \gamma$			
188	$H_2O^+ + \gamma$			
189	$H_2O^+ + \gamma$			
190	$H_2O^+ + \gamma$			
191	$H_2O^+ + \gamma$			
192	$H_3O^+ + \gamma$			
193	$H_3O^+ + \gamma$			
194	$H_3O^+ + \gamma$			
195	$H_3O^+ + \gamma$			
196	$O_2 + \gamma \rightarrow$			
197	$O_2 + \gamma \rightarrow O + O$	$R_{197} = 7.0 \times 10^{-10}$	1.8	7
198	$CO + \gamma \rightarrow C + O$	$R_{198} = 2.0 \times 10^{-10}$	See §2.2	13

Table B3. List of reactions included in our chemical model that involve cosmic rays or cosmic-ray induced UV emission

No.	Reaction	Rate ($s^{-1}\zeta_H^{-1}$)	Ref.
199	$H + c.r. \rightarrow H^+ + e^-$	$R_{199} = 1.0$	—
200	$He + c.r. \rightarrow He^+ + e^-$	$R_{200} = 1.1$	1
201	$H_2 + c.r. \rightarrow H^+ + H + e^-$	$R_{201} = 0.037$	1
202	$H_2 + c.r. \rightarrow H + H$	$R_{202} = 0.22$	1
203	$H_2 + c.r. \rightarrow H^+ + H^-$	$R_{203} = 6.5 \times 10^{-4}$	1
204	$H_2 + c.r. \rightarrow H_2^+ + e^-$	$R_{204} = 2.0$	1
205	$C + c.r. \rightarrow C^+ + e^-$	$R_{205} = 3.8$	1
206	$O + c.r. \rightarrow O^+ + e^-$	$R_{206} = 5.7$	1
207	$CO + c.r. \rightarrow CO^+ + e^-$	$R_{207} = 6.5$	1
208	$C + \gamma_{c.r.} \rightarrow C^+ + e^-$	$R_{208} = 2800$	2
209	$CH + \gamma_{c.r.} \rightarrow C + H$	$R_{209} = 4000$	3
210	$CH^+ + \gamma_{c.r.} \rightarrow C^+ + H$	$R_{210} = 960$	3
211	$CH_2 + \gamma_{c.r.} \rightarrow CH_2^+ + e^-$	$R_{211} = 2700$	1
212	$CH_2 + \gamma_{c.r.} \rightarrow CH + H$	$R_{212} = 2700$	1
213	$C_2 + \gamma_{c.r.} \rightarrow C + C$	$R_{213} = 1300$	3
214	$OH + \gamma_{c.r.} \rightarrow O + H$	$R_{214} = 2800$	3
215	$H_2O + \gamma_{c.r.} \rightarrow OH + H$	$R_{215} = 5300$	3
216	$O_2 + \gamma_{c.r.} \rightarrow O + O$	$R_{216} = 4100$	3
217	$O_2 + \gamma_{c.r.} \rightarrow O_2^+ + e^-$	$R_{217} = 640$	3
218	$CO + \gamma_{c.r.} \rightarrow C + O$	$R_{218} = 0.21 T^{1/2} x_{H_2} x_{CO}^{-1/2}$	4

140 $O^- + C \rightarrow CO + e^-$ $k_{140} = 5.0 \times 10^{-10}$ 28

87 $HCO^+ + H_2O \rightarrow CO + H_3O^+$ $k_{87} = 2.5 \times 10^{-9}$ 62

(Glover, Federrath, Mac Low, Klessen, 2010, MNRS, 404, 2)

HI to H2 conversion rate

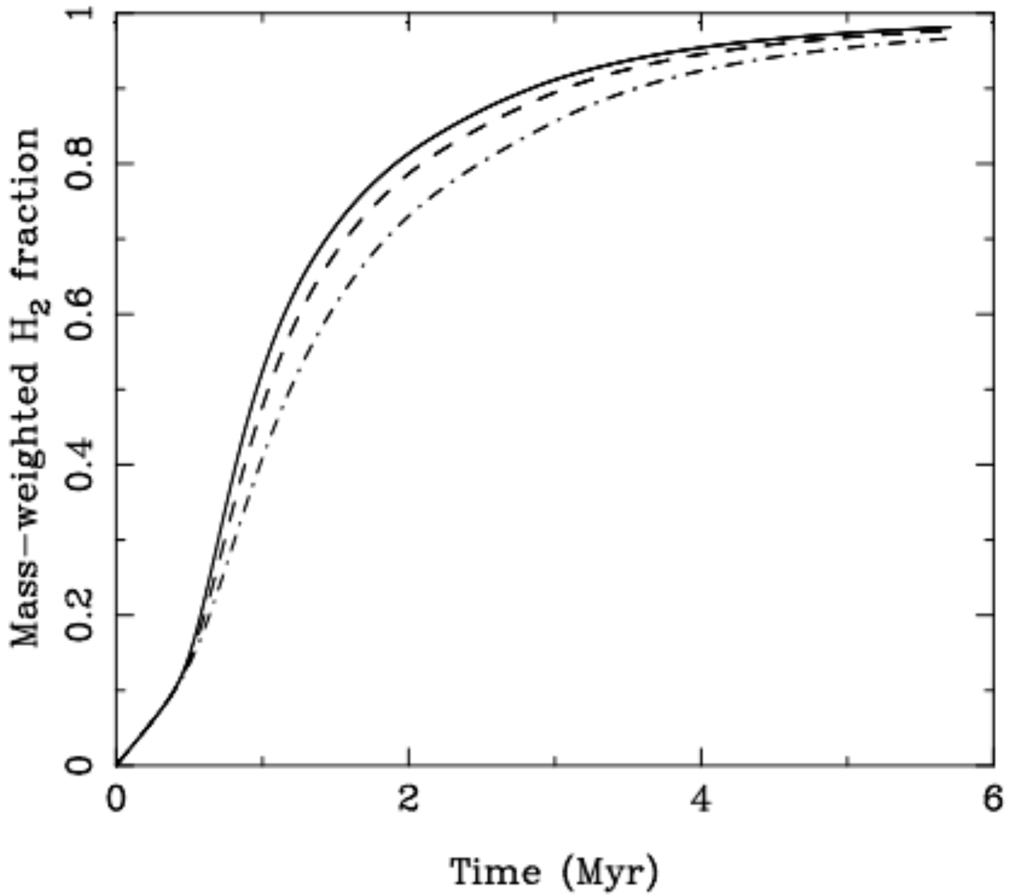
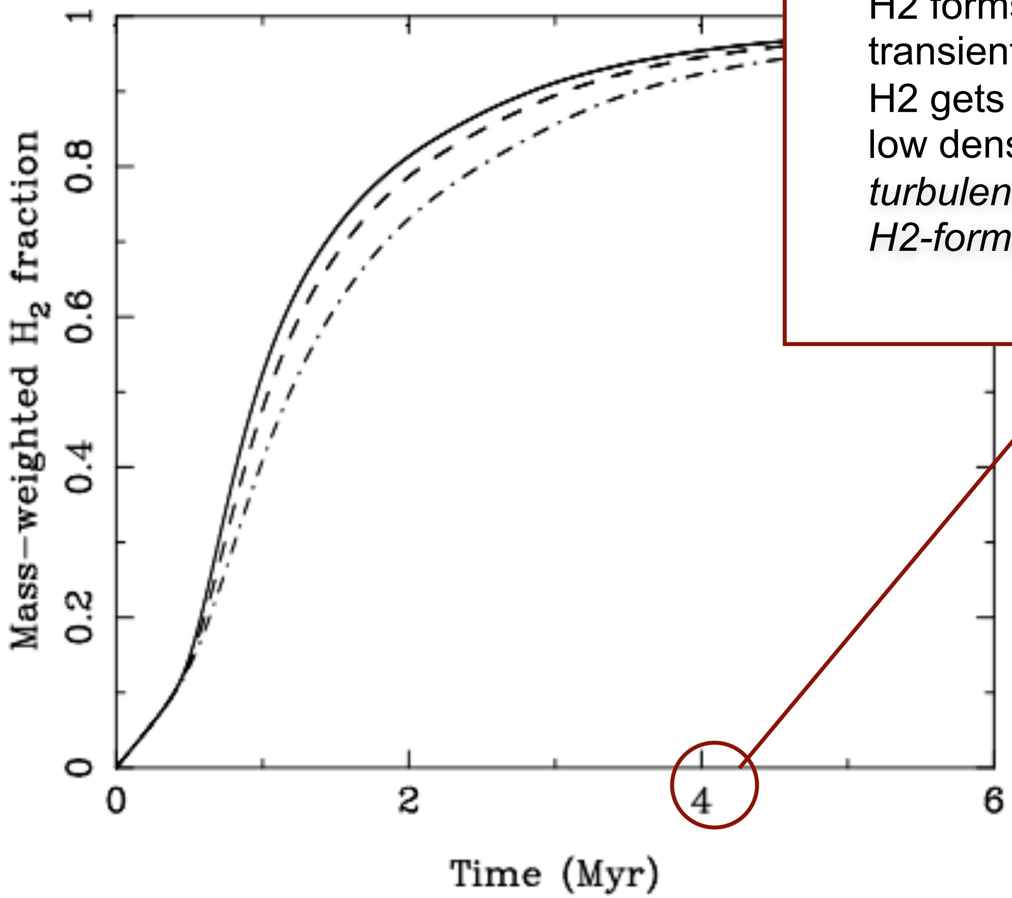


Figure 4. Time evolution of the mass-weighted H_2 abundance in simulations R1, R2 and R3, which have numerical resolutions of 64^3 zones (dot-dashed), 128^3 zones (dashed) and 256^3 zones (solid), respectively.

(Glover, Federrath, Mac Low, Klessen, 2010)

HI to H2 conversion rate

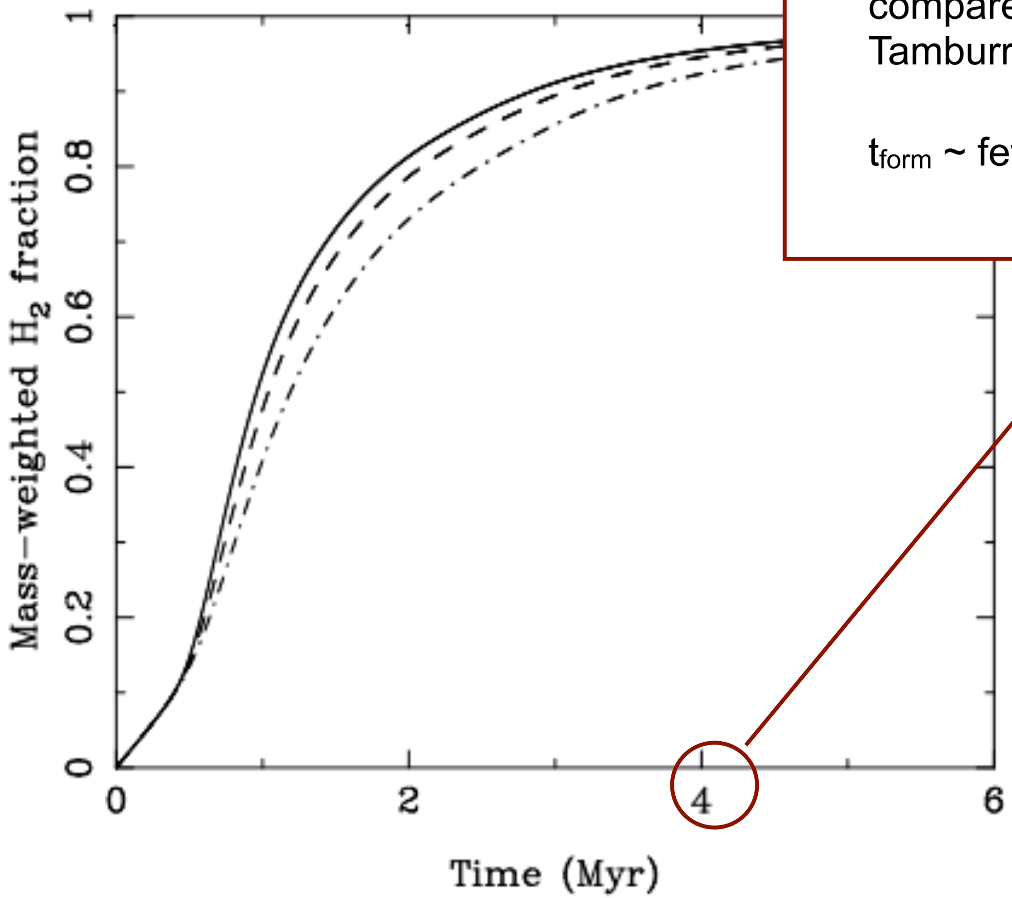


H2 forms rapidly in shocks / transient density fluctuations / H2 gets destroyed slowly in low density regions / *result: turbulence greatly enhances H2-formation rate*

Figure 4. Time evolution of the mass-weighted H_2 abundance in simulations R1, R2 and R3, which have numerical resolutions of 64^3 zones (dot-dashed), 128^3 zones (dashed) and 256^3 zones (solid), respectively.

(Glover, Federrath, Mac Low, Klessen, 2010)

HI to H2 conversion rate



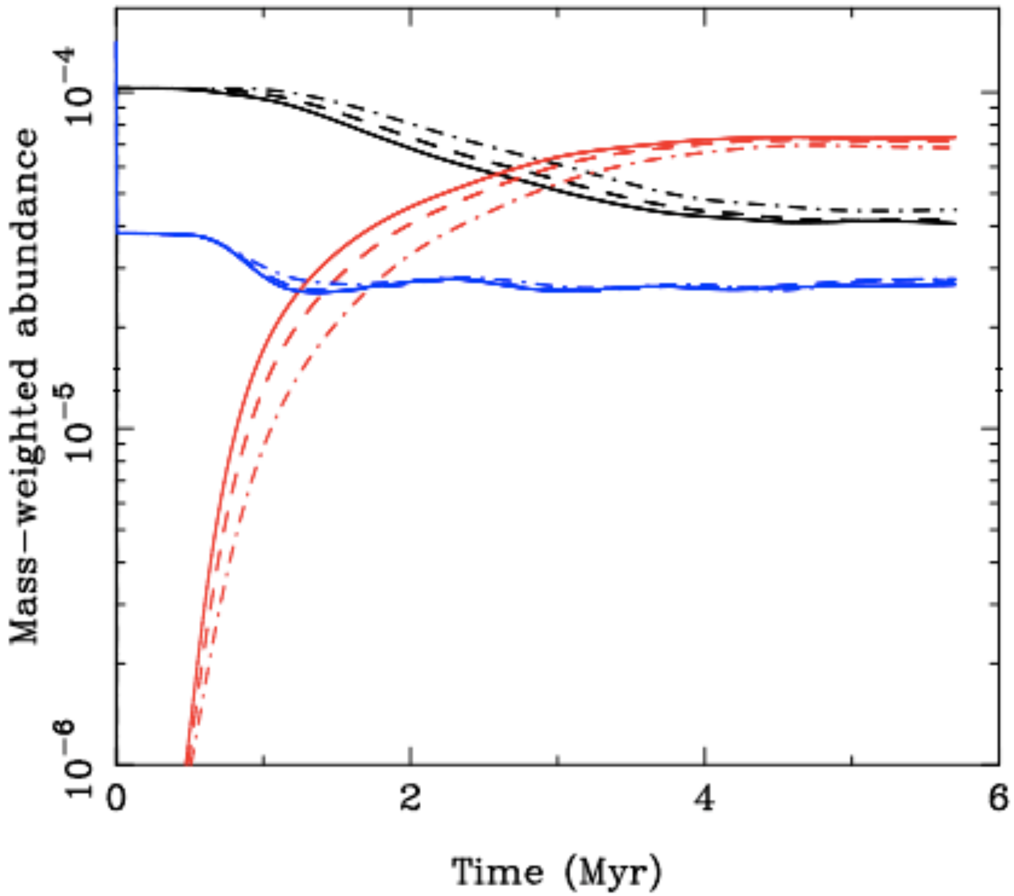
compare to data from Tamburro et al. (2008) study:

t_{form} ~ few x 10^6 years

Figure 4. Time evolution of the mass-weighted H_2 abundance in simulations R1, R2 and R3, which have numerical resolutions of 64^3 zones (dot-dashed), 128^3 zones (dashed) and 256^3 zones (solid), respectively.

(Glover, Federrath, Mac Low, Klessen, 2010)

CO, C$^+$ formation rates



CO

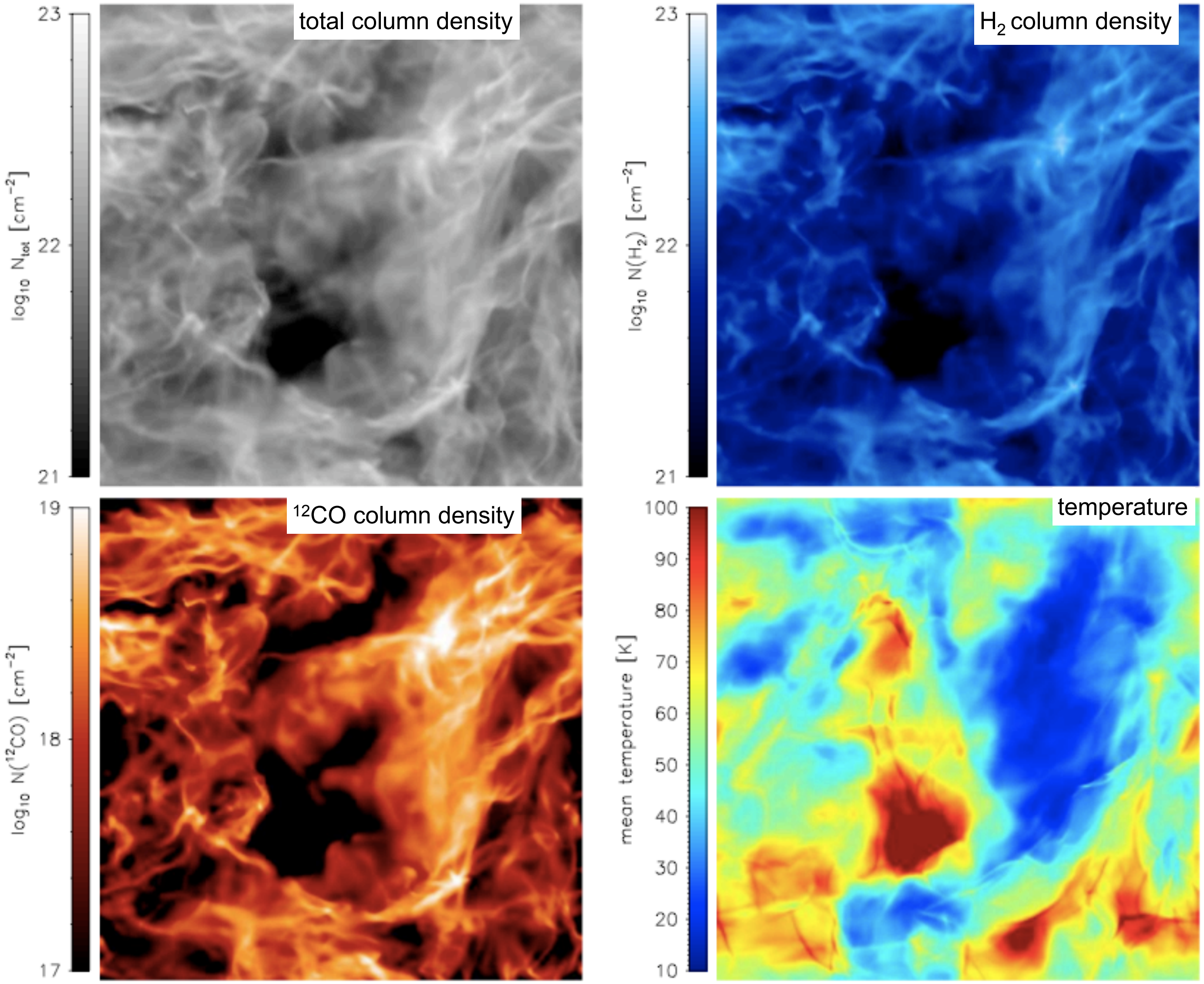
C

C$^+$

Figure 5. Time evolution of the mass-weighted abundances of atomic carbon (black lines), CO (red lines), and C$^+$ (blue lines) in simulations with numerical resolutions of 64^3 zones (dot-dashed), 128^3 zones (dashed) and 256^3 zones (solid).

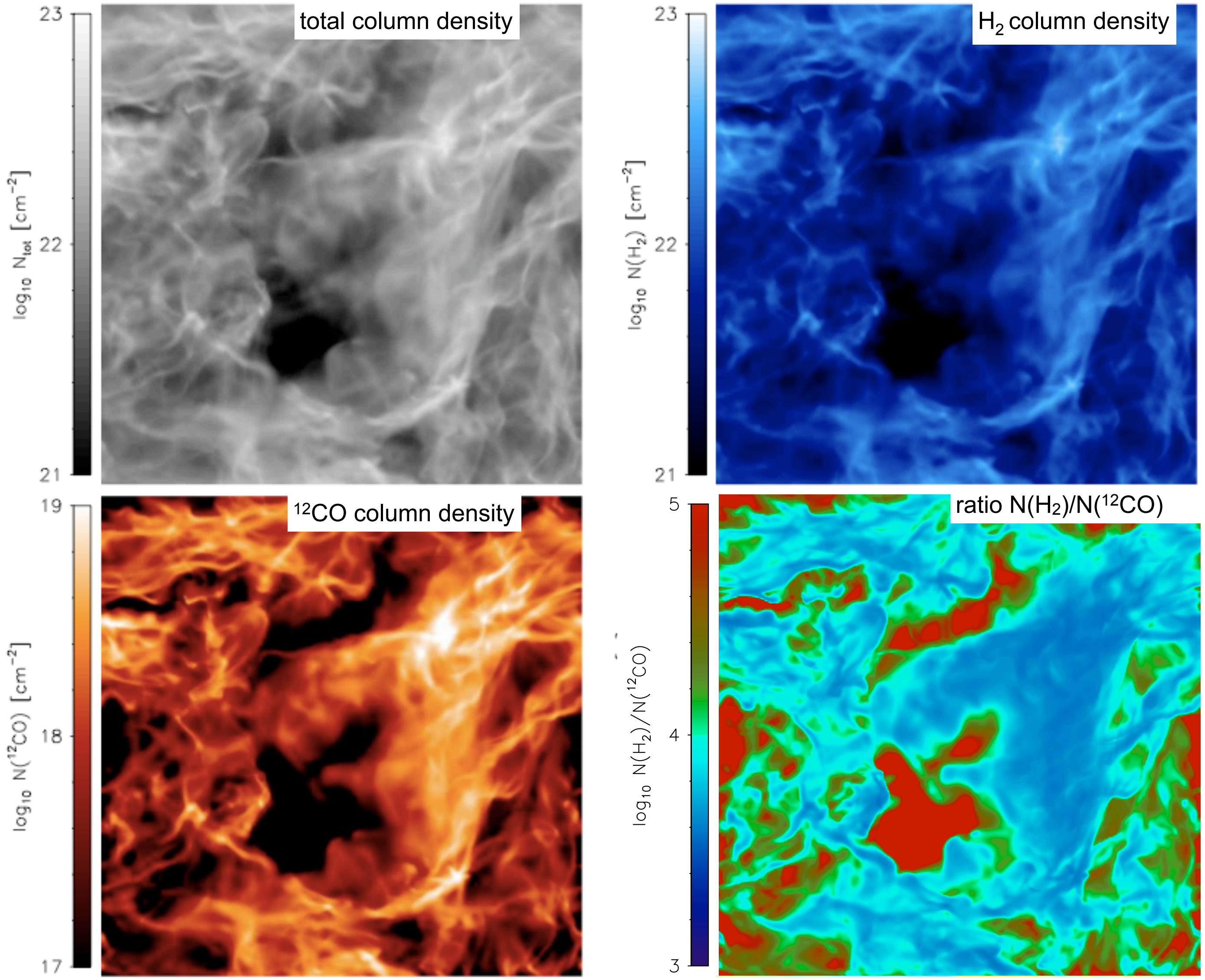
(Glover, Federrath, Mac Low, Klessen, 2010)

effects of chemistry 1



(Glover, Federrath, Mac Low, Klessen, 2010)

effects of chemistry 2



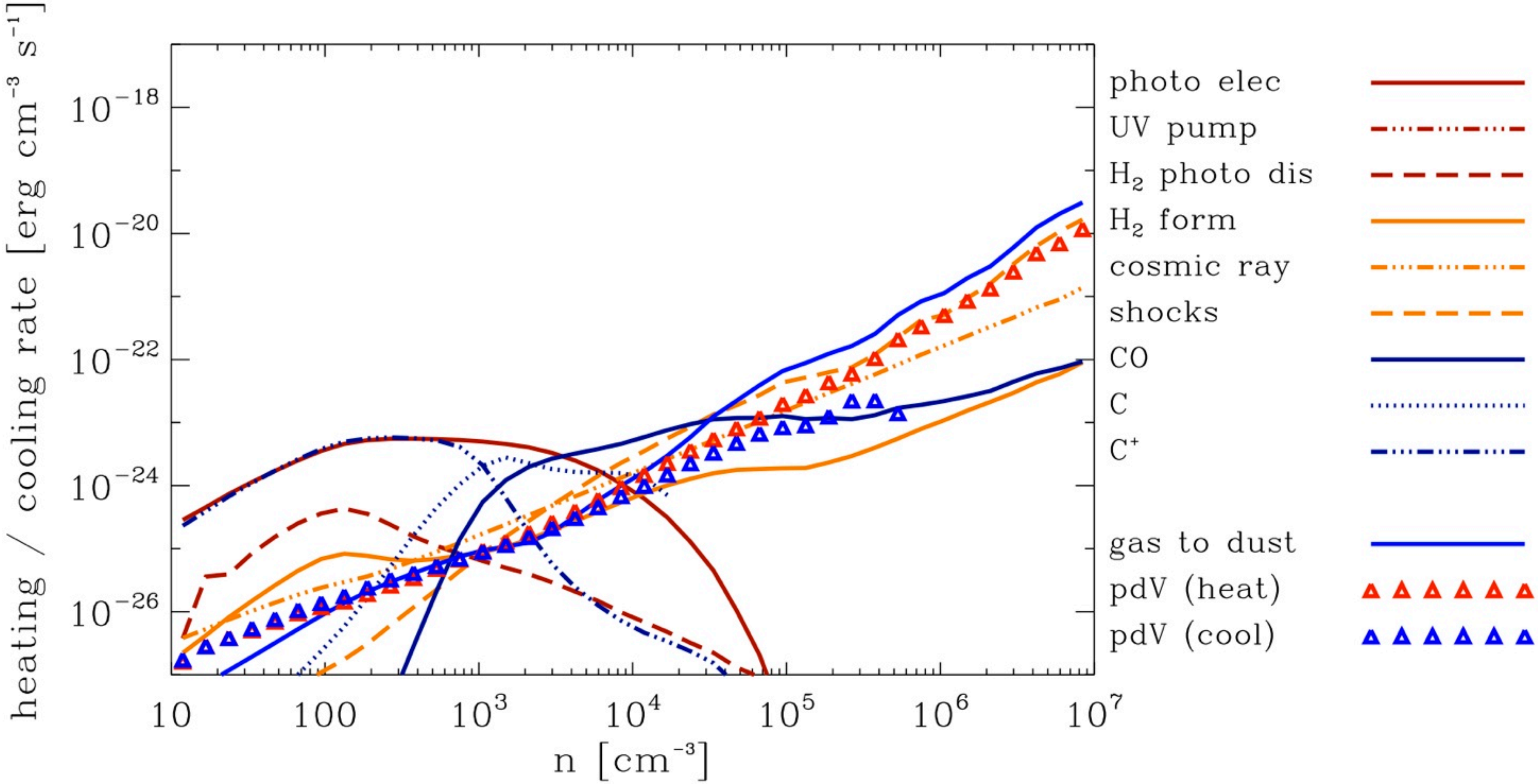
(Glover, Federrath, Mac Low, Klessen, 2010)

are molecules needed to form stars?

- it has been proposed that molecule formation (H_2, CO, etc.) is a prerequisite for star formation
  (e.g. Schaye 2004; Krumholz & McKee 2005; Elmegreen 2007; Krumholz et al. 2009)
- the idea is that CO is a necessary coolant for collapse
- however, also C+ is a very efficient coolant!
  (Glover & Clark 2011)

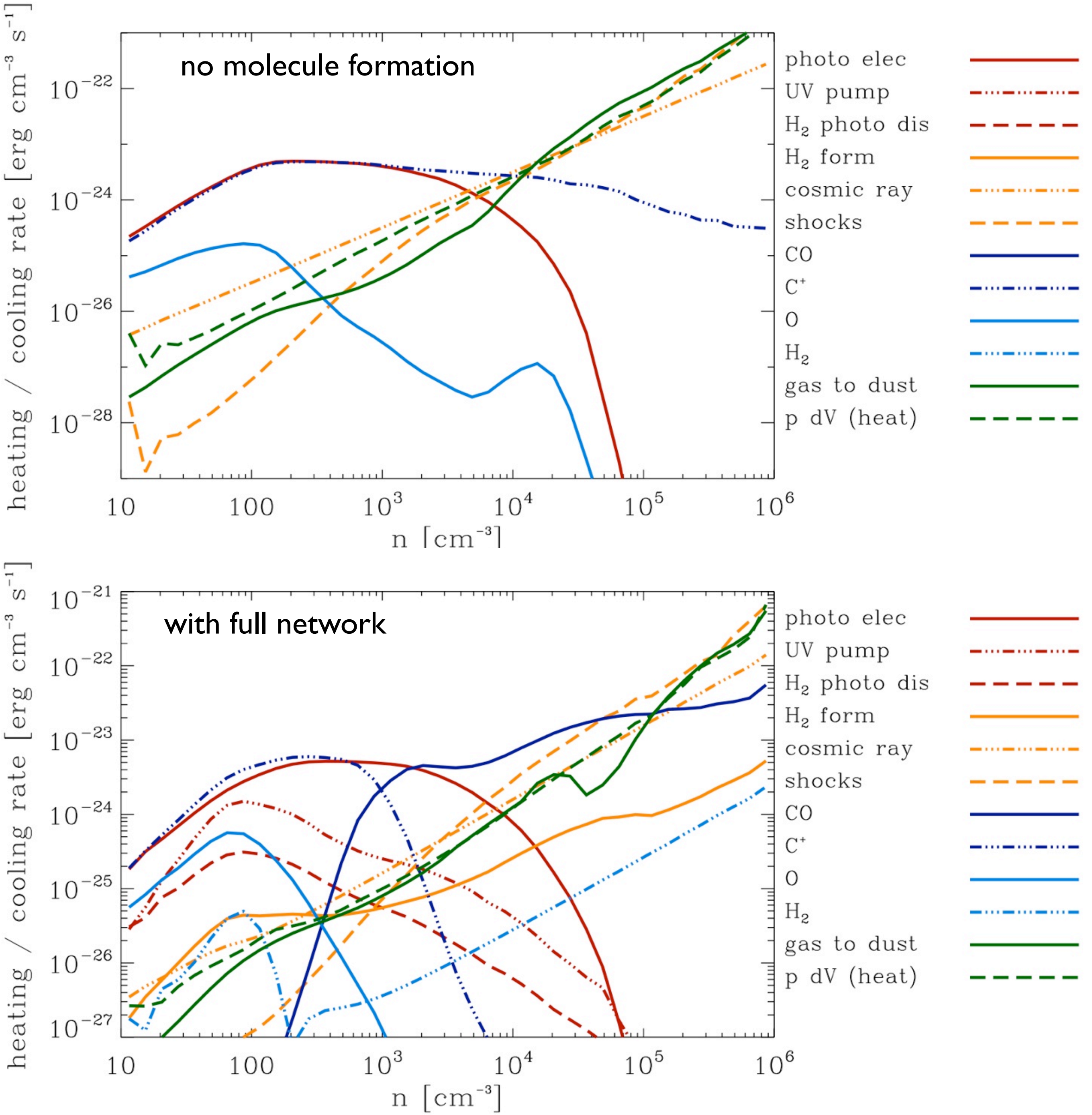
- to address this question, we performed dedicated simulations in Heidelberg

are molecules needed to form stars?



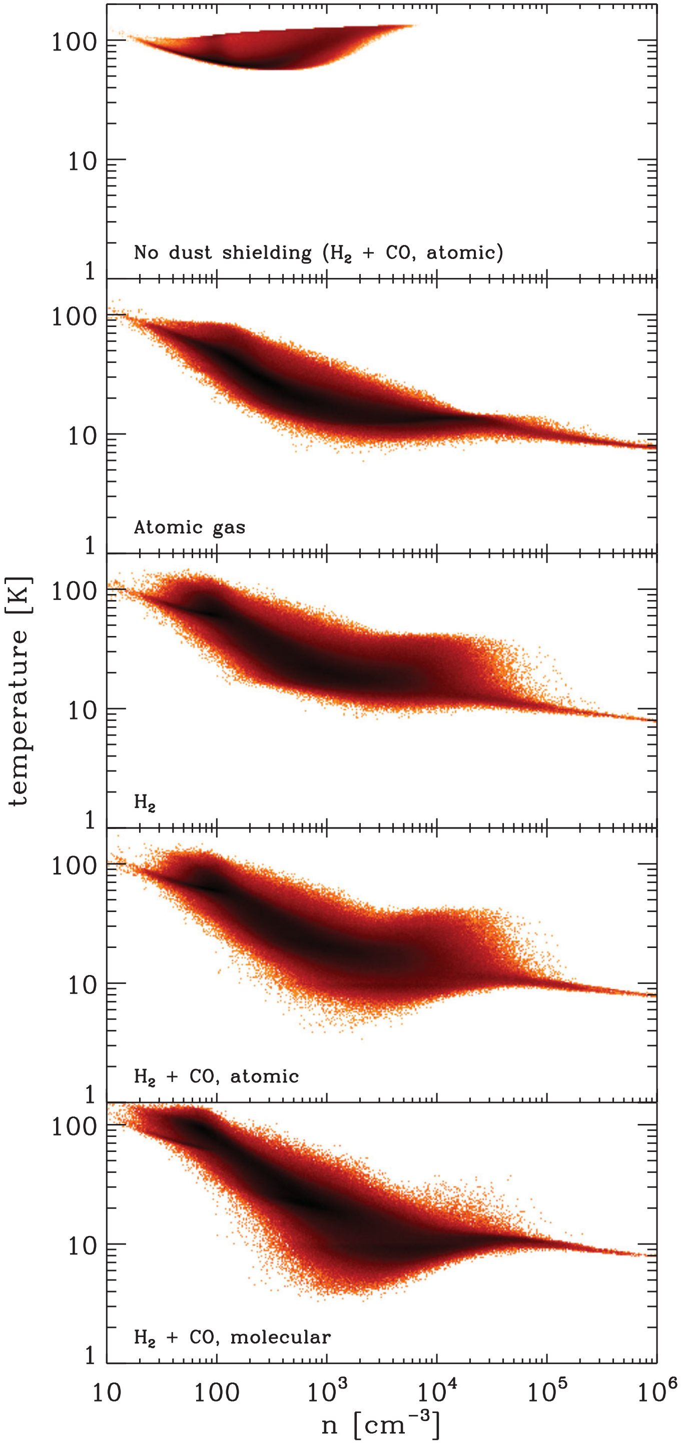
NO! CII, CI, provide equal amounts of cooling to CO . . .

image from Simon Glover



cooling rates for different species

Glover & Clark (2011, MNRAS, 421, 9)



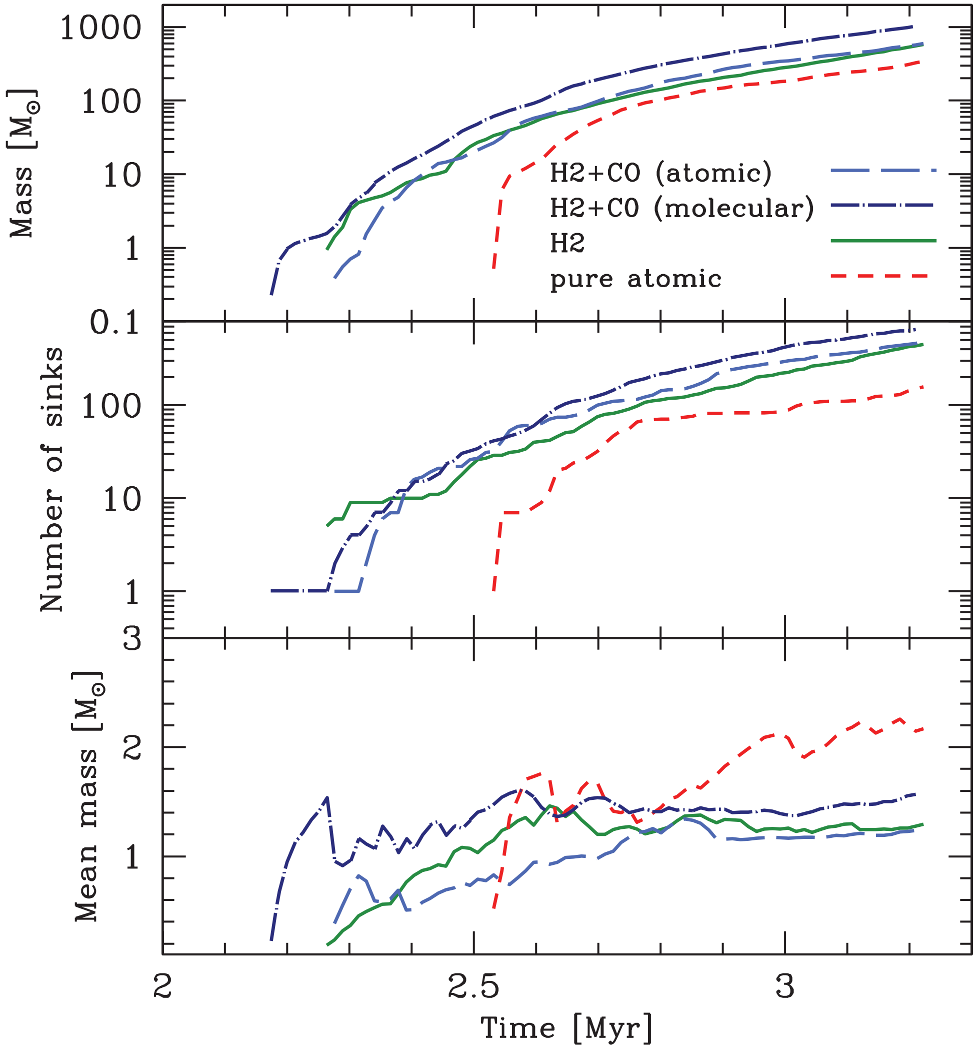
resulting temperatures

RESULTS:

- presence of molecular gas has only very minor influence on ability of cloud to form stars
- C^+ is equally efficient coolant in atomic phase as CO in molecular
- what is crucial is the ability of cloud to shield itself from interstellar radiation field
- but clouds that are big/dense enough to shield themselves will be molecular!

this suggests that the correlation between H_2 and star formation is a coincidence

Glover & Clark (2011, MNRAS, 421, 9)



collapse and star formation

RESULTS:

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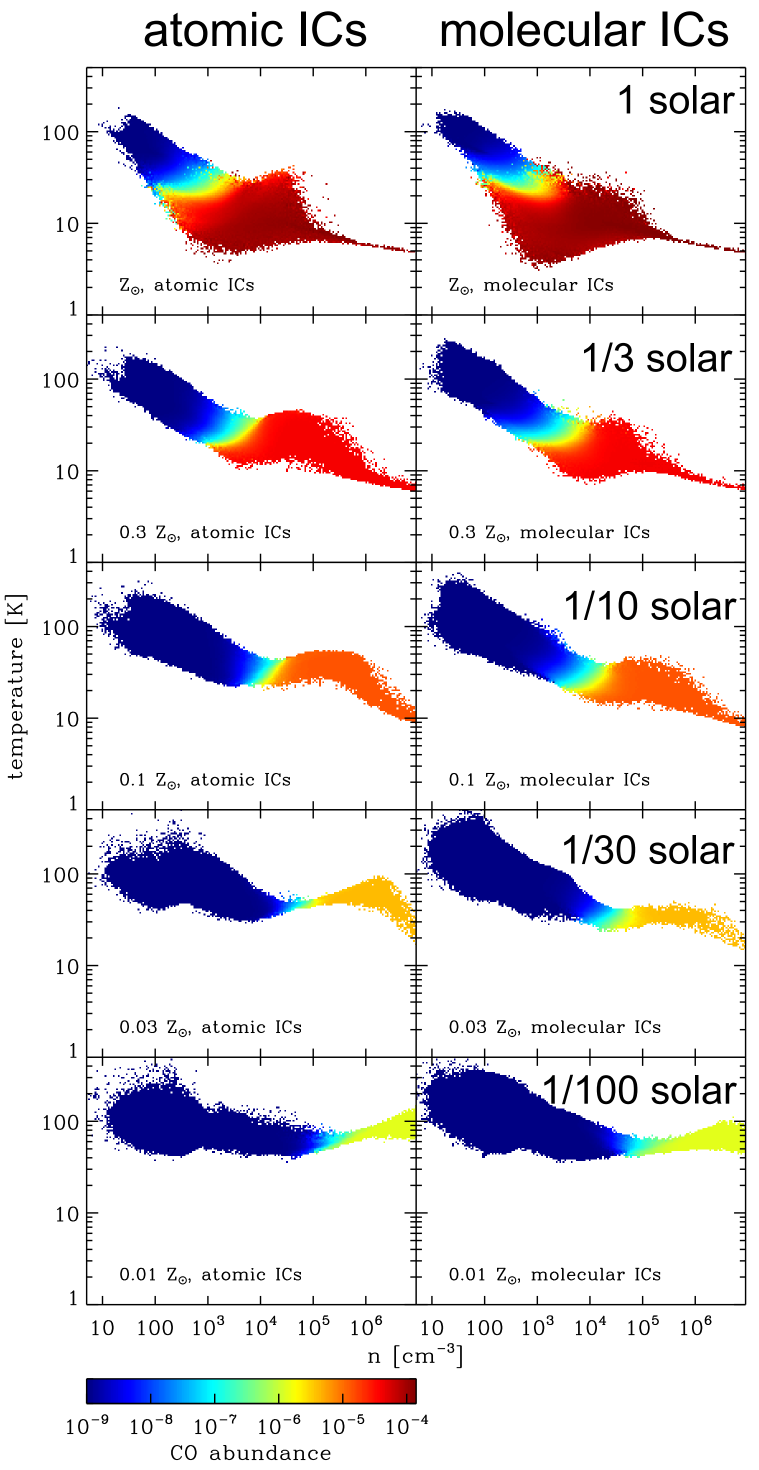
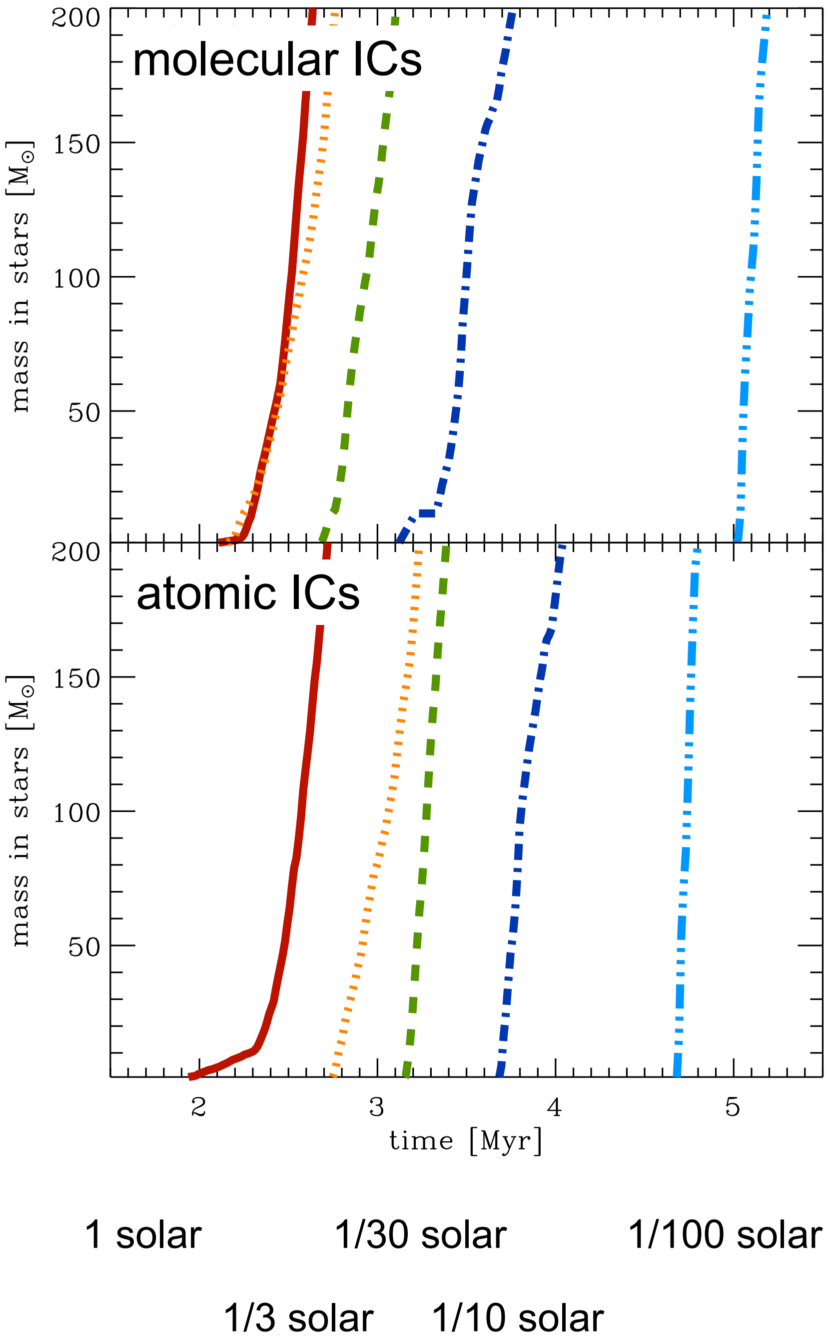


extensions to low metallicity

- how does the overall cooling process depend on metallicity?
- how does this influence star formation?

Glover & Clark (2012, MNRAS, 426, 377)

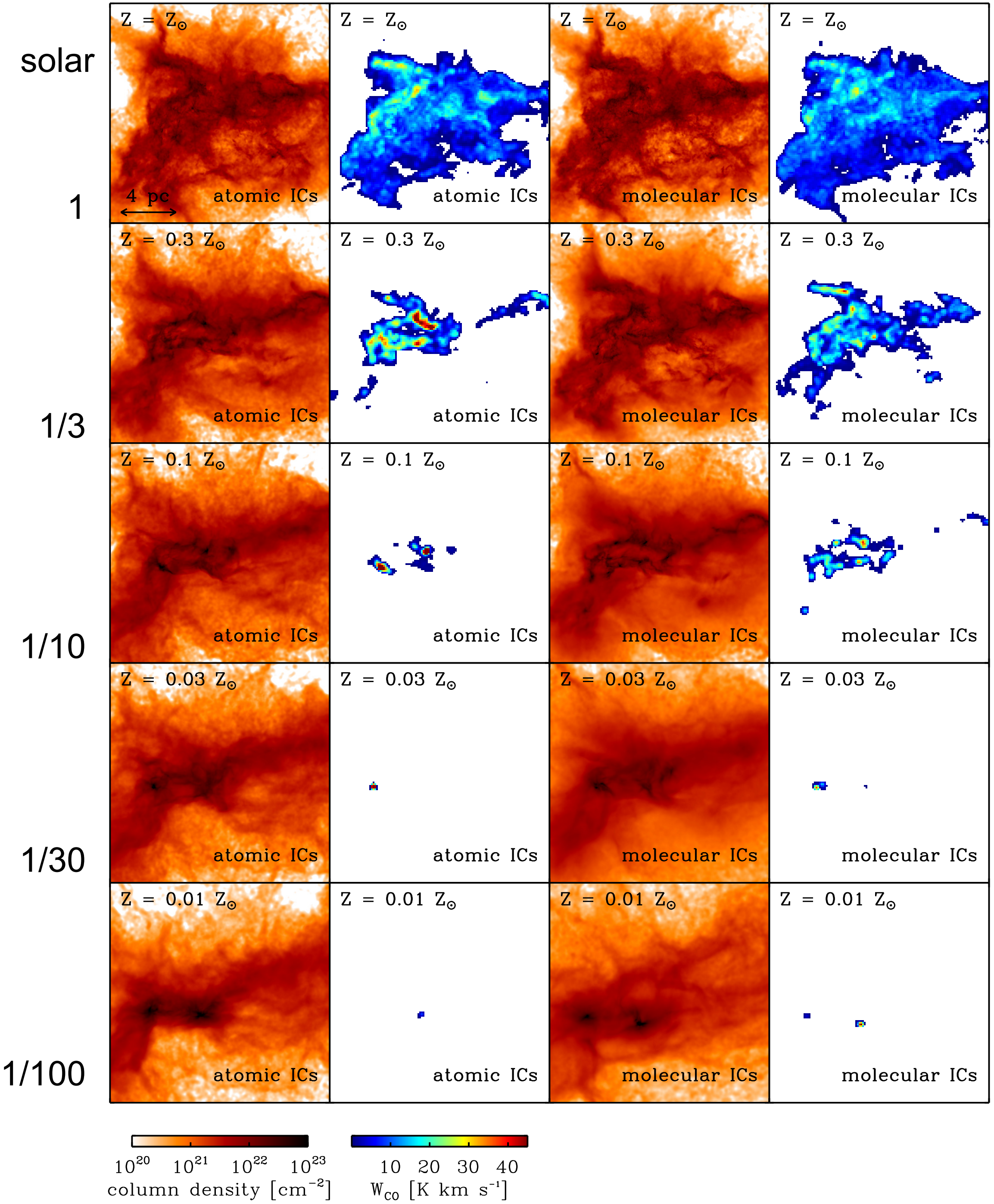
extensions to low metallicity



- how does the overall cooling process depend on metallicity?
- how does this influence star formation?

- all the model clouds form stars
- some delays due to larger temperatures

Glover & Clark (2012, MNRAS, 426, 377)



extensions to low metallicity

- how does the overall cooling process depend on metallicity?
- how does this influence star formation?

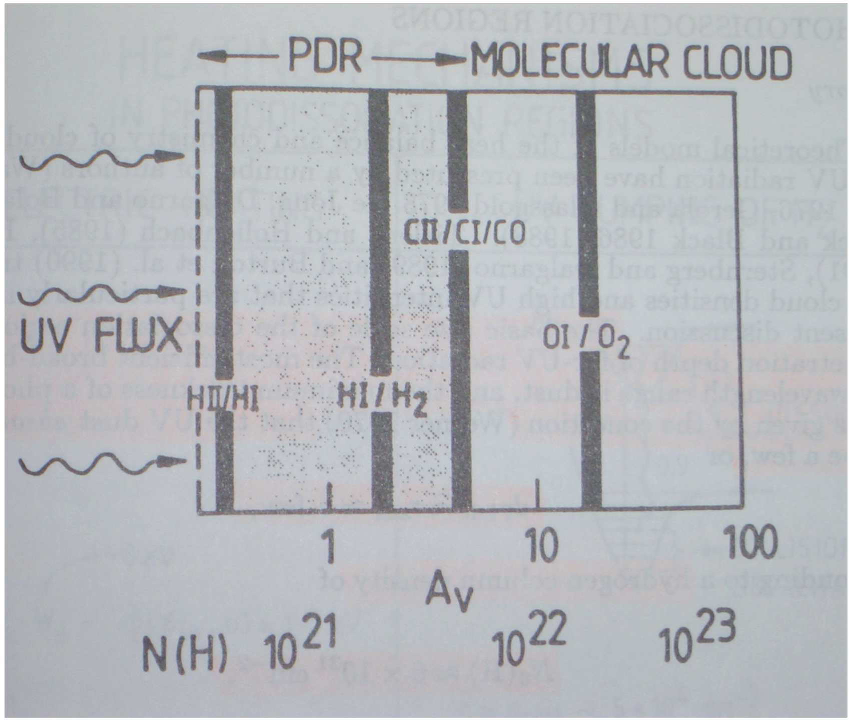
- all the model clouds form stars
- some delays due to larger temperatures

- important difference: only very high density gas is traced by CO emission at low metallicities!
- better correlation between CO and star formation at low metallicities.

Glover & Clark (2012)

do clouds have long invisible phases?

- there is a proposal that (at least) half of the Galactic H_2 is not traced by CO emission, that it is *invisible* (e.g. Pringle et al. 2001, MNRAS, 327, 663)
- the idea is that H_2 is in a tenuous phase where self-shielding is sufficient to sustain H_2, but dust shielding is insufficient to prevent the photo-destruction of CO



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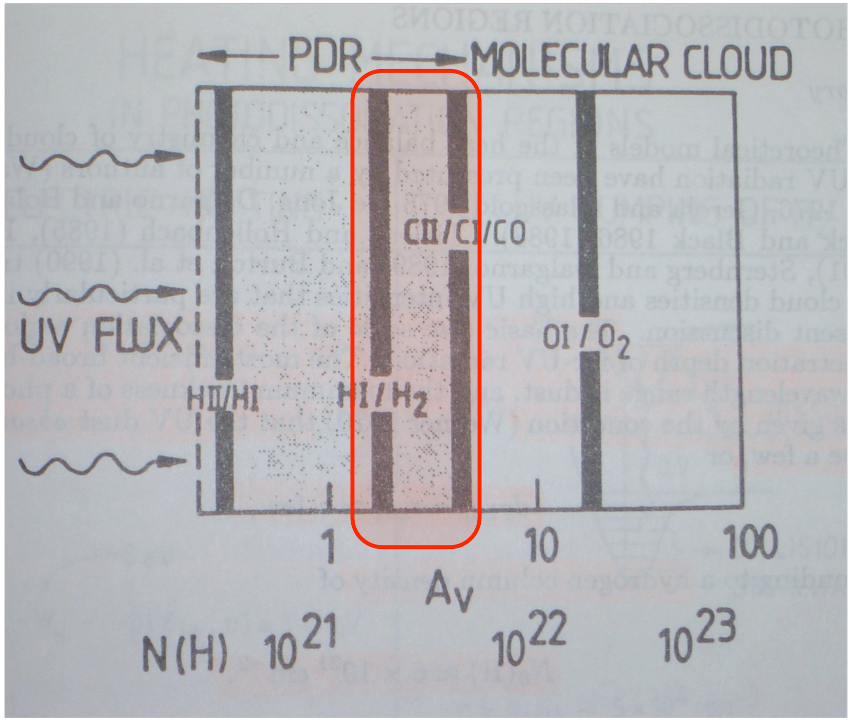

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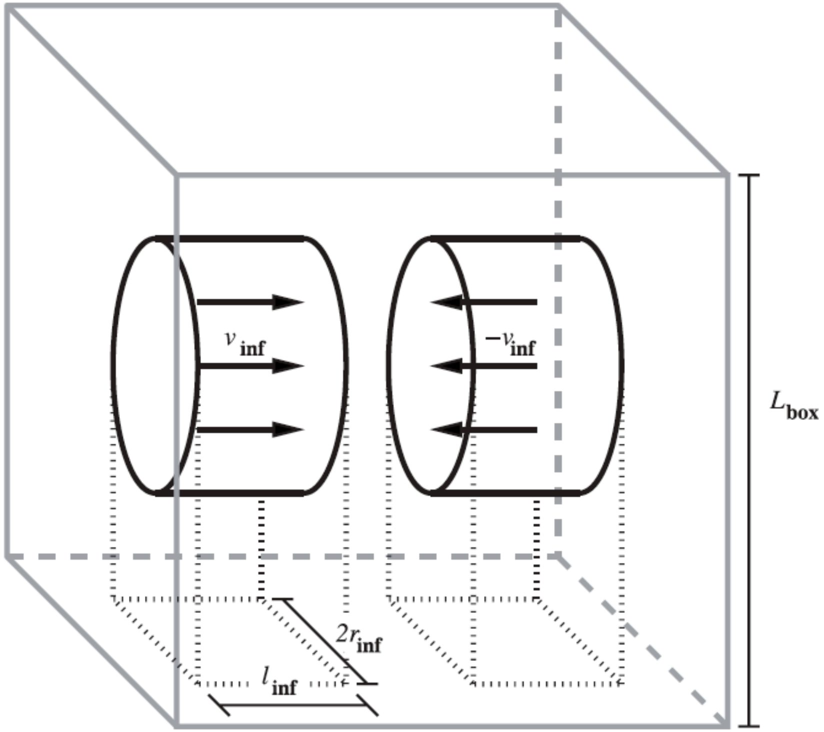
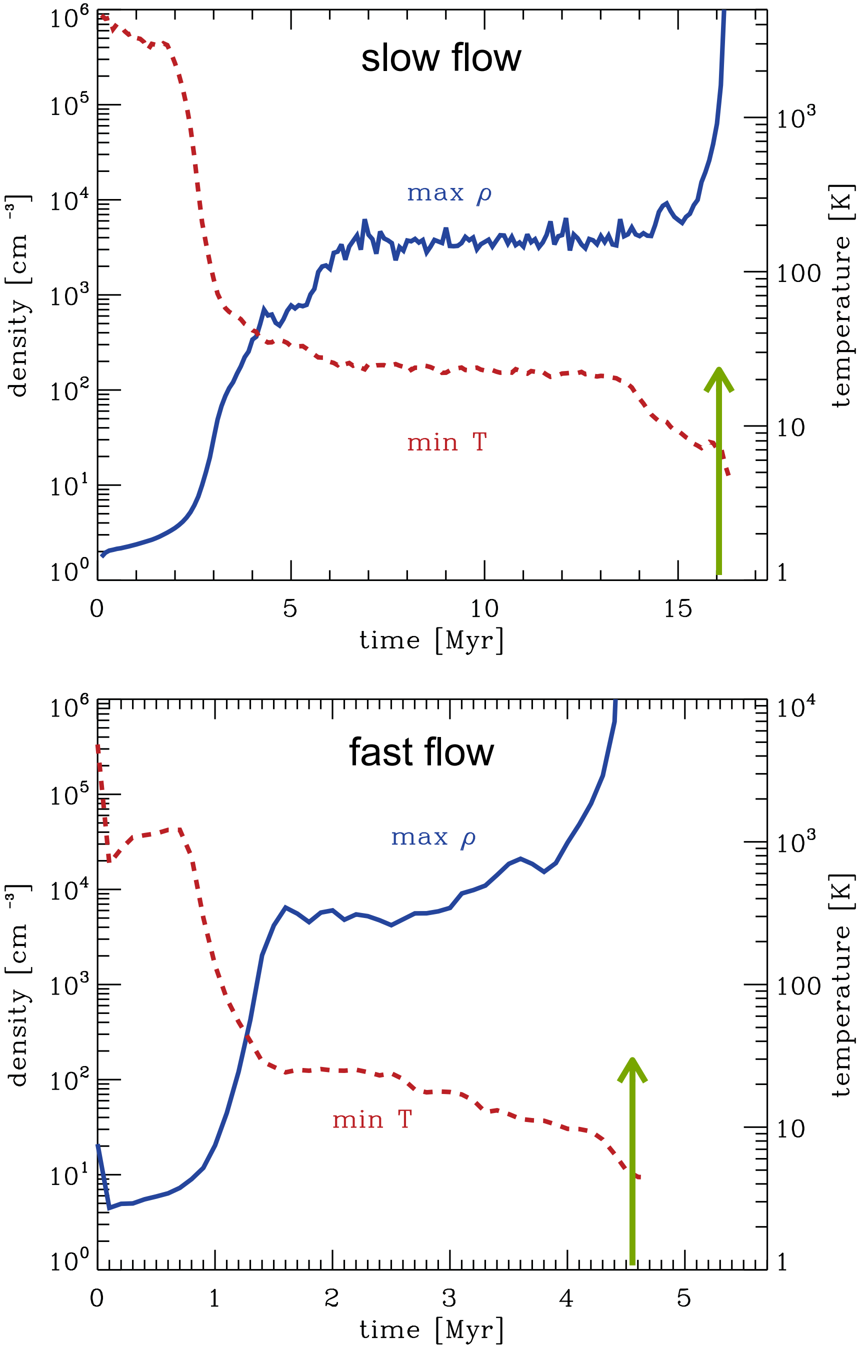


- test this hypothesis in ***colliding flow simulations***
- try fast and slow flow

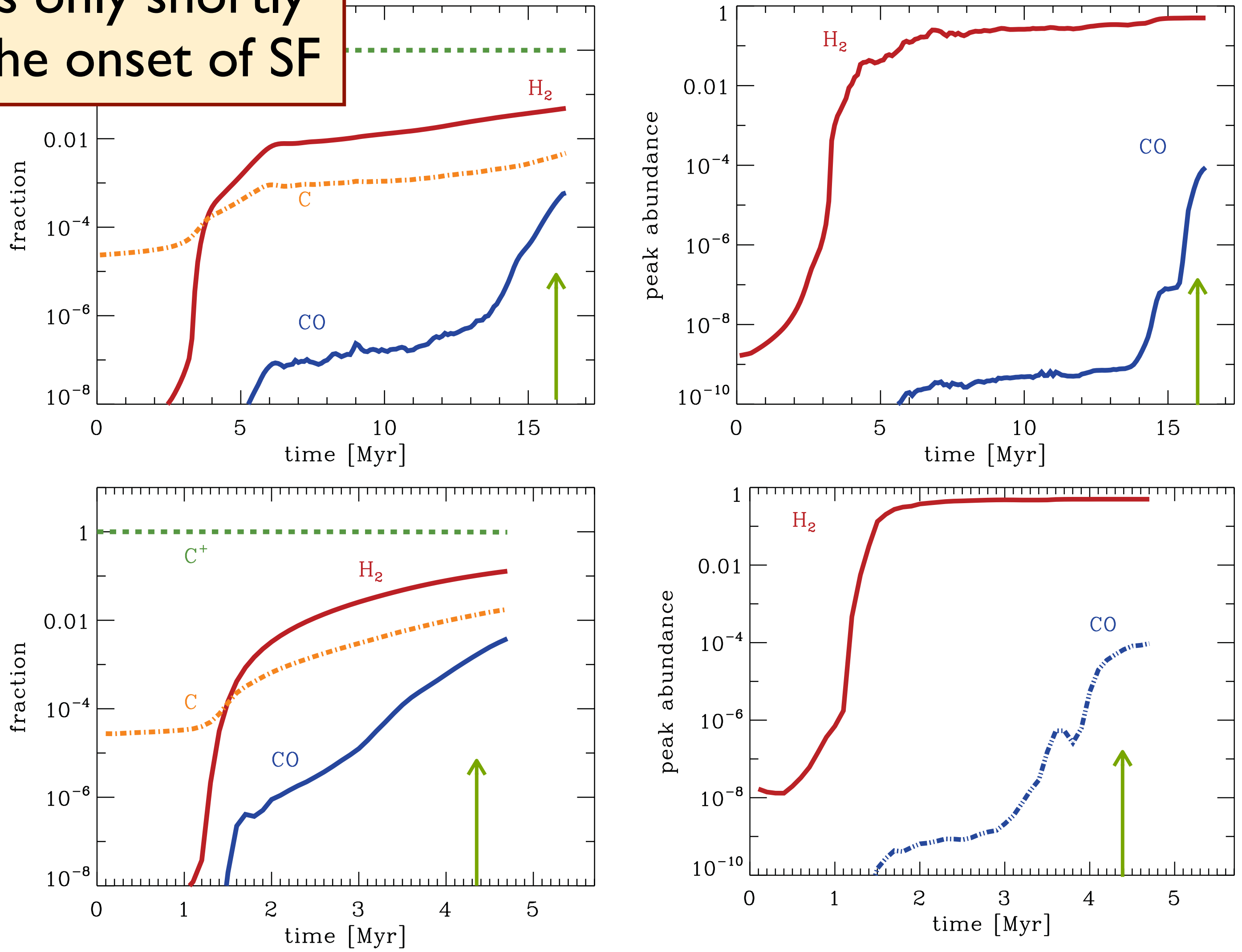
long phase of ram pressure confinement

- test this hypothesis in ***colliding flow simulations***
- all 'clouds" go through a phase of gas accumulation at constant ρ_{max} where they are held together by ram pressure
- this phase lasts between 2 to 10 Myr
- only then collapse and star cluster formation sets in



Clark (2012, MNRAS, 424, 2599)

CO rises only shortly before the onset of SF



slow flow

fast flow

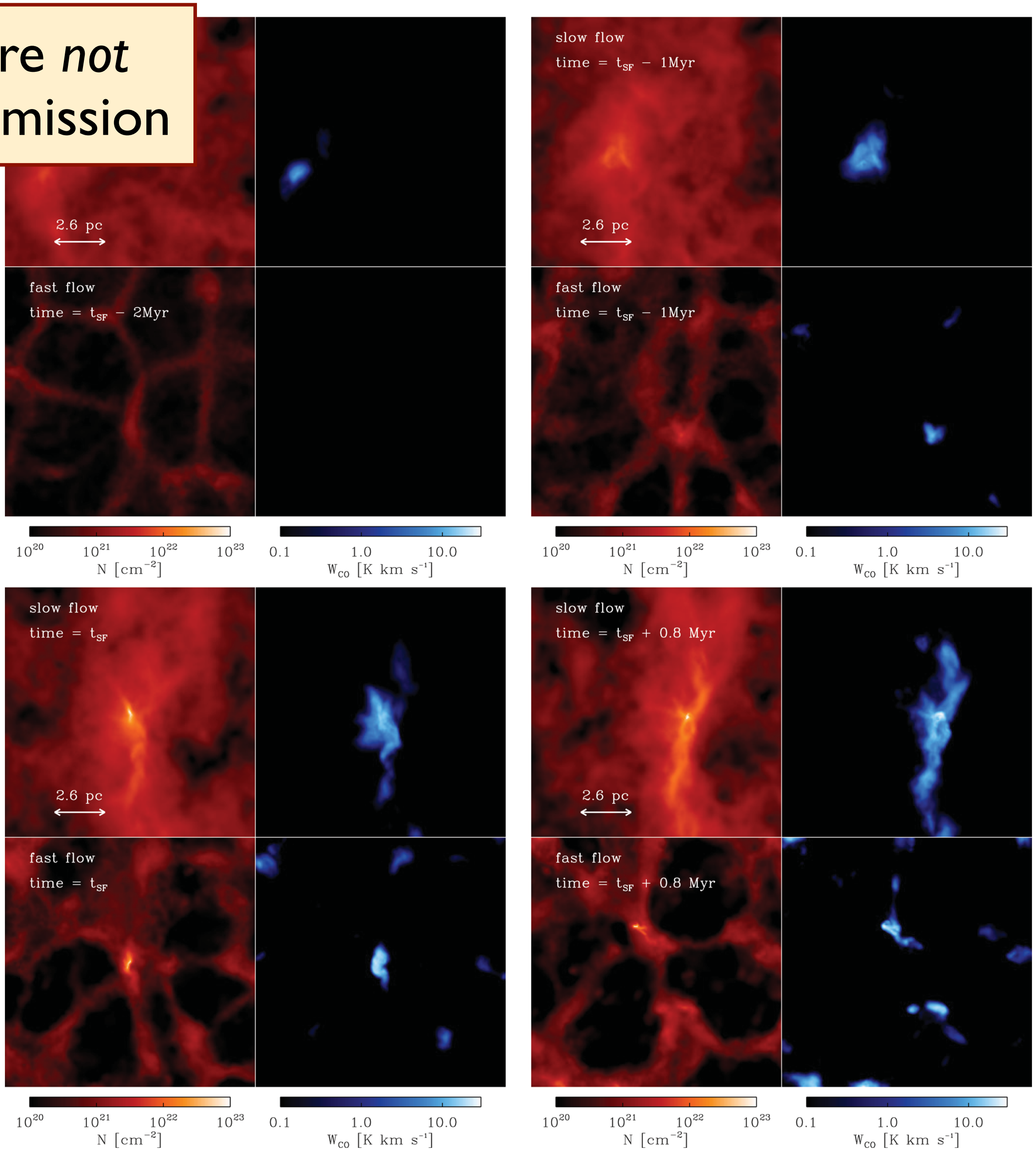
Figure 6. Chemical evolution of the gas in the flow. In the left-hand column, we show the time evolution of the fraction of the total mass of hydrogen that is in the form of H_2 (red solid line) for the 6.8 km s^{-1} flow (upper panel) and the 13.6 km s^{-1} flow (lower panel). We also show the time evolution of the fraction of the total mass of carbon that is in the form of C^+ (green dashed line), C (orange dot–dashed line) and CO (blue double-dot–dashed line). In the right-hand column, we show the peak values of the fractional abundances of H_2 and CO. These are computed relative to the total number of hydrogen nuclei, and so the maximum fractional abundances of H_2 and CO are 0.5 and 1.4×10^{-4}, respectively. Again, we show results for the 6.8 km s^{-1} flow in the upper panel and the 13.6 km s^{-1} flow in the lower panel. Note that the scale of the horizontal axis differs between the upper and lower panels.

Clark (2012, MNRAS, 424, 2599)

large columns are *not* traced by CO emission

red: total column

blue: CO lines



slow flow

fast flow

slow flow

fast flow

Figure 9. The images show the evolution of the column number density, N, and the velocity-integrated intensity in the $J = 1$–0 line of ^{12}CO, W_{CO} (1–0), for the region in which the first star forms in each of the flows. Four times are shown: 2 Myr prior to star formation (upper left-hand panels), 1 Myr prior to star formation (upper right-hand panels), the point of star formation (lower left-hand panels) and 0.8 Myr after the onset of star formation (lower right-hand panels). The CO-integrated intensity map is obtained via a radiative transfer calculation performed with the RADMC-3D code and uses the large velocity gradient approximation to compute the CO level populations.

Clark (2012, MNRAS, 424, 2599)

Different Physics - Heating and cooling balance...

Heating

photoelectric emission
(Bakes & Tielens 1994; Wolfire et al 2003)

Heating by H2 formation on dust grains
(Duley & Williams 1993; Glover 2009)

Excitation and photodissociation of H2
(Black & Dalgarno 1977; Draine & Bertoldi 1996)

Cosmic ray ionisation
(Goldsmith & Langer 1978)

Heating of the dust by the interstellar radiation field
(Mathis et al 1983; Black 1994; Ossenkopf & Henning 1994).

Shock heating

Cooling

Molecular line cooling from H2 (Le Bourlot et al 1999), CO and H_2O
(Neufeld & Kaufmann 1993; Neufeld, Lepp & Melnick 1995; Glover & Clark *in prep*).

Fine-structure atomic line cooling from CI, CII, OI, SiI, SiI I
(Glover & Mac Low 2007a).

Both

pdV from gas dynamics.

Accurate treatment of the adiabatic index
(Boley et al 2007).

Energy transfer between the gas and dust (Hollenbach & McKee 1979)

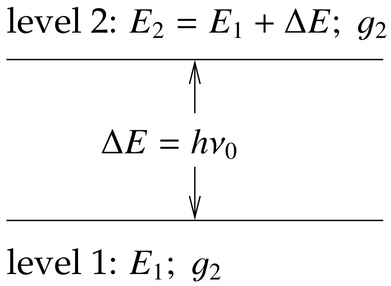
2-level system

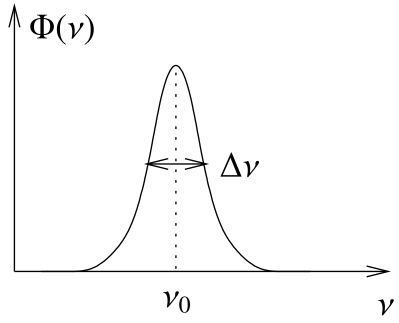
2-level system 1

Einstein considered three processes in the 2-level system

- **spontaneous emission**
  A_{21} = probability per unit time for spontaneous transition 2 → 1
- **absorption**
  $B_{21}I_\nu$ = transition probability per unit time for absorption of a photon of frequency ν leading to 1 → 2
- **stimulated emission**
  $B_{21}I_\nu$ = transition probability per unit time for stimulated emission of photon ν
- I_ν is the intensity, A_{21}, $B_{12}I_\nu$, and $B_{21}I_\nu$ have units of 1/s.
- A_{21}, B_{12}, and B_{21} are the **Einstein coefficients**
- in reality, the transition 1 → 2 requires a certain time Δt leading to an uncertainty in the line width Δν; we introduce the line profile function φ(ν), which is normalized to $$\int_0^\infty \varphi(\nu)\, d\nu = 1$$
- we replace I_ν by $\bar{I}_\nu = \int_0^\infty I_\nu\, \varphi(\nu)\, d\nu$

the statistical weight g indicates the degeneracy of the energy level;





2-level system 2

- in thermodynamic equilibrium the number of transition 2 → 1 are equal to 1 → 2, this is called detailed balance

$$N_1 B_{12} \bar{I}_\nu = N_2 A_{21} + N_2 B_{21} \bar{I}_\nu$$

- we get $\bar{I}_\nu = \dfrac{A_{21}/B_{21}}{(N_1/N_2)(B_{12}/B_{21}) - 1}$

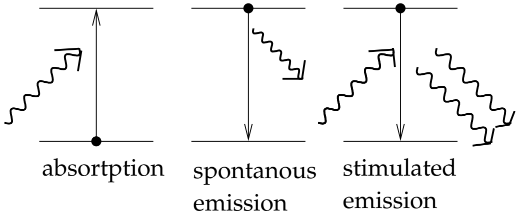
- in thermodynamic equilibrium, we have the additional relation

$$\frac{N_1}{N_2} = \frac{g_1 \exp(-E_1 / kT)}{g_2 \exp(-E_2 / kT)} = \frac{g_1}{g_2} \exp\left(\frac{h\nu}{kT}\right)$$

- and both together give

$$\bar{I}_\nu = \frac{A_{21}/B_{21}}{(g_1 B_{12} / g_2 B_{21}) \exp(h\nu / kT) - 1}$$

stimulated emission takes place in exactly the same photon state (direction and frequency) as the photon that stimulated the emission; both are precisely coherent;



2-level system 3

- because in thermodynamic equilibrium we have $\bar{I}_\nu = B_\nu(T)$, meaning that the intensity follows the Planck function

$$B_\nu(T) = \frac{2h\nu^3/c^2}{\exp(h\nu/kT) - 1}$$

we get the following relations between the Einstein coefficients:

$$\begin{aligned} g_1 B_{12} &= g_2 B_{21} \\ A_{21} &= \frac{2h\nu^3}{c^2} B_{21} \end{aligned}$$

- although this was derived for thermodynamic equilibrium, these relations always hold, because the coefficients depend on fundamental atomic quantities only

2-level system 4

- we get the following relations between the Einstein coefficients:

$$\begin{aligned} g_1 B_{12} &= g_2 B_{21} \\ A_{21} &= \frac{2h\nu^3}{c^2} B_{21} \end{aligned}$$

- we can express the Einstein coefficients in terms of the oscillator strength f_{21}

$$B_{21} = \frac{4\pi}{h\nu_{21}} \frac{\pi e}{m_e c} f_{21}$$

  where m_e is the electron mass and e the electron charge; the oscillator strength "counts" the number of classical oscillators involved in the transition; for constant f_{21} the spontaneous transition rate is proportional to ν^3

- example: electric dipole transition

$$B_{21} = \frac{32\pi^4 e^2}{3h^2 c} \mu_{21}^2$$

  where μ_{21} is the dipole matrix element

2-level system 5

- relation between emissivity and Einstein's A_{21} coefficient:

$$j_\nu = \frac{h\nu\varphi(\nu)}{4\pi} n_2 A_{21}$$

- relation between absorption coefficient and Einstein's B_{21} coefficient:

$$\alpha_\nu = \frac{h\nu\varphi(\nu)}{4\pi} n_1 B_{12}$$

- when including stimulated emission (laser, maser), this reads as

$$\alpha_\nu = \frac{h\nu\varphi(\nu)}{4\pi} (n_1 B_{12} - n_2 B_{21})$$

2-level system 6

- recall the equation of radiative transfer

$$\frac{dI_\nu}{dl} = -\alpha_\nu I_\nu + j_\nu$$

- this equation describes the change of intensity I_ν along a ray of light at frequency ν; l is the distance traveled along the ray, α_ν is the absorption coefficient at frequency ν, and j_ν is the emissivity

- with the Einstein coefficients this reads

$$\frac{dI_\nu}{dl} = -\frac{h\nu\varphi(\nu)}{4\pi}\left(n_1 B_{12} - n_2 B_{21}\right) I_\nu + \frac{h\nu\varphi(\nu)}{4\pi} n_2 A_{12}$$

- the source function reads as

$$S_\nu = \frac{j_\nu}{\alpha_\nu} = \frac{n_2 A_{21}}{n_1 B_{12} - n_2 B_{21}}$$

2-level system 6

- with Einstein's relations we can write

$$
\begin{aligned}
\alpha_\nu &= \frac{h\nu\varphi(\nu)}{4\pi} n_1 B_{12}\left(1-\frac{g_1 n_2}{g_2 n_1}\right) \\
S_\nu &= \frac{2h\nu^3}{c^2}\left(\frac{g_2 n_1}{g_1 n_2}-1\right)^{-1}
\end{aligned}
$$

where n_1 and n_2 is the number density of the states 1 and 2, and g_1 and g_2 are their statistical weights

- in **LTE** *(local thermodynamic equilibrium)* we have $\frac{n_1}{n_2} = \frac{g_1}{g_2}\exp\left(\frac{h\nu}{kT}\right)$

which leads to

$$
\begin{aligned}
\alpha_\nu &= \frac{h\nu\varphi(\nu)}{4\pi} n_1 B_{12}\left[1-\exp\left(-\frac{h\nu}{kT}\right)\right] \\
S_\nu &= B_\nu(T)
\end{aligned}
$$

- non-thermal emission covers all cases with $\frac{n_1}{n_2} \neq \frac{g_1}{g_2}\exp\left(\frac{h\nu}{kT}\right)$

- and population inversion (laser, maser) corresponds to $\frac{n_1}{g_1} < \frac{n_2}{g_2}$

thermodynamics of dust

thermodynamics of dust

Importance of dust for the thermal balance in the ISM:

- dust temperature is relatively insensitive to the strength of the radiation field
- dust acts as a thermostat in the ISM
- above a certain density, dust and gas are thermally coupled (by collisions)

- dust absorbs radiation a high frequencies and re-emits this energy as thermal radiation at IR wavelengths

radiative dust heating 1

- dust heating by absorption of radiation

$$\left(\frac{dE}{dt}\right)_{\rm abs} = \int \frac{u_\nu d\nu}{h\nu} \times c \times h\nu \times Q_{\rm abs}(\nu)\pi a^2 \ .$$

where $u_\nu d\nu / h\nu$ is the number density of photons in frequency range $[\nu, \nu + d\nu]$; the photons move with speed of light *c* and carry the energy *hν*, the dust grain has the frequency-dependent absorption cross section $Q_{\rm abs}(\nu)\pi a^2$

- it is useful to define the spectrum-averaged absorption cross section

$$\langle Q_{\rm abs}\rangle_\star \equiv \frac{\int d\nu\ u_{\star\nu} Q_{\rm abs}(\nu)}{u_\star} \quad , \quad u_\star \equiv \int d\nu\ u_{\star\nu} \quad ,$$

the index ★ is used because the dominant source of radiation is star light

- then $\left(\frac{dE}{dt}\right)_{\rm abs} = \langle Q_{\rm abs}\rangle_\star \pi a^2 u_\star c$

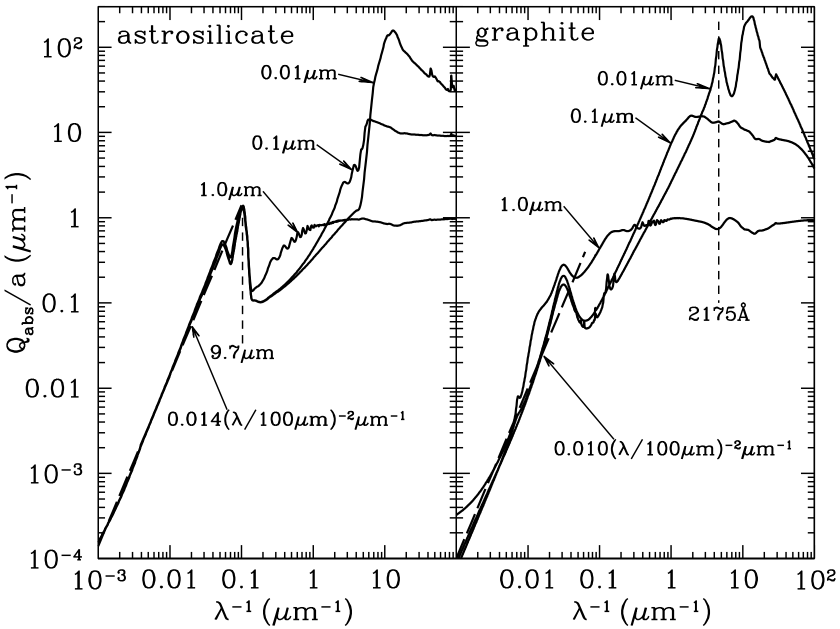


Figure 24.1 Absorption efficiency $Q_{\rm abs}(\lambda)$ divided by grain radius a for spheres of amorphous silicate (left) and graphite (right). Also shown are power-laws that provide a reasonable approximation to the opacity for $\lambda \gtrsim 20\,\mu$m.

Draine: Physics of the ISM and IGM (Princeton University Press)

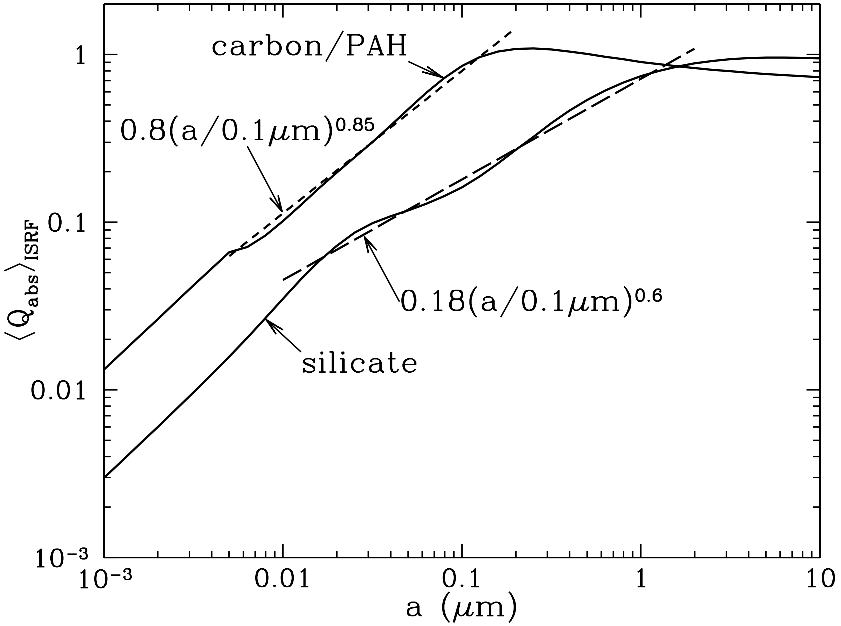
radiative dust heating 2

- it is useful to define the spectrum-averaged absorption cross section

$$\langle Q_{\rm abs}\rangle_\star \equiv \frac{\int d\nu\; u_{\star\nu} Q_{\rm abs}(\nu)}{u_\star} \quad , \quad u_\star \equiv \int d\nu\; u_{\star\nu} \quad ,$$

- we then have $$\left(\frac{dE}{dt}\right)_{\rm abs} = \langle Q_{\rm abs}\rangle_\star \pi a^2 u_\star c$$

- with typical values of



$$\langle Q\rangle_{\rm ISRF} \approx 0.18(a/0.1\,\mu{\rm m})^{0.6} \quad , \quad \text{for silicate}, 0.01 \lesssim a \lesssim 1\,\mu{\rm m}\ ,$$

$$\approx 0.8(a/0.1\,\mu{\rm m})^{0.85} \quad , \quad \text{for graphite}, 0.005 \lesssim a \lesssim 0.15\,\mu{\rm m}\ .$$

Draine: Physics of the ISM and IGM (Princeton University Press)

relation between gas and dust 1

- dust grains can also be heated by collisions with gas.
- at low densities, the gas temperature is higher than the dust temperature
  → ***GAS COOLING***
- the net energy transfer (heating of the dust) is

$$\left(\frac{dE}{dt}\right)_{\mathrm{gas}} = \sum_i n_i \left(\frac{8kT_{\mathrm{gas}}}{\pi m_i}\right)^{1/2} \pi a^2 \times \alpha_i \times 2k(T_{\mathrm{gas}} - T_{\mathrm{dust}})$$

  where the sum is over the different gas species i, n_i is the number density, and the sqrt-term simply is the mean velocity of the species i
- note the energy is $2kT$, which is larger than the kinetic energy $3/2kT$ because it takes into account that more energetic particles collide more frequently
- the parameter α_i measures the efficiency of energy transfer; $0 \leq \alpha_i \leq 1$, with $\alpha_i = 0$ denoting fully elastic collisions, if particles stick to the surface for more than 10^{-12} s then $\alpha_i \sim 1$
- for the cold neutral medium, collisional heating is not important:

$$\frac{(dE/dt)_{\mathrm{gas}}}{(dE/dt)_{\mathrm{abs}}} = \frac{n_{\mathrm{H}}(8kT/\pi m_{\mathrm{H}})^{1/2} 2\alpha_{\mathrm{H}} kT}{\langle Q_{\mathrm{abs}}\rangle_\star u_\star c} \times 1.05$$

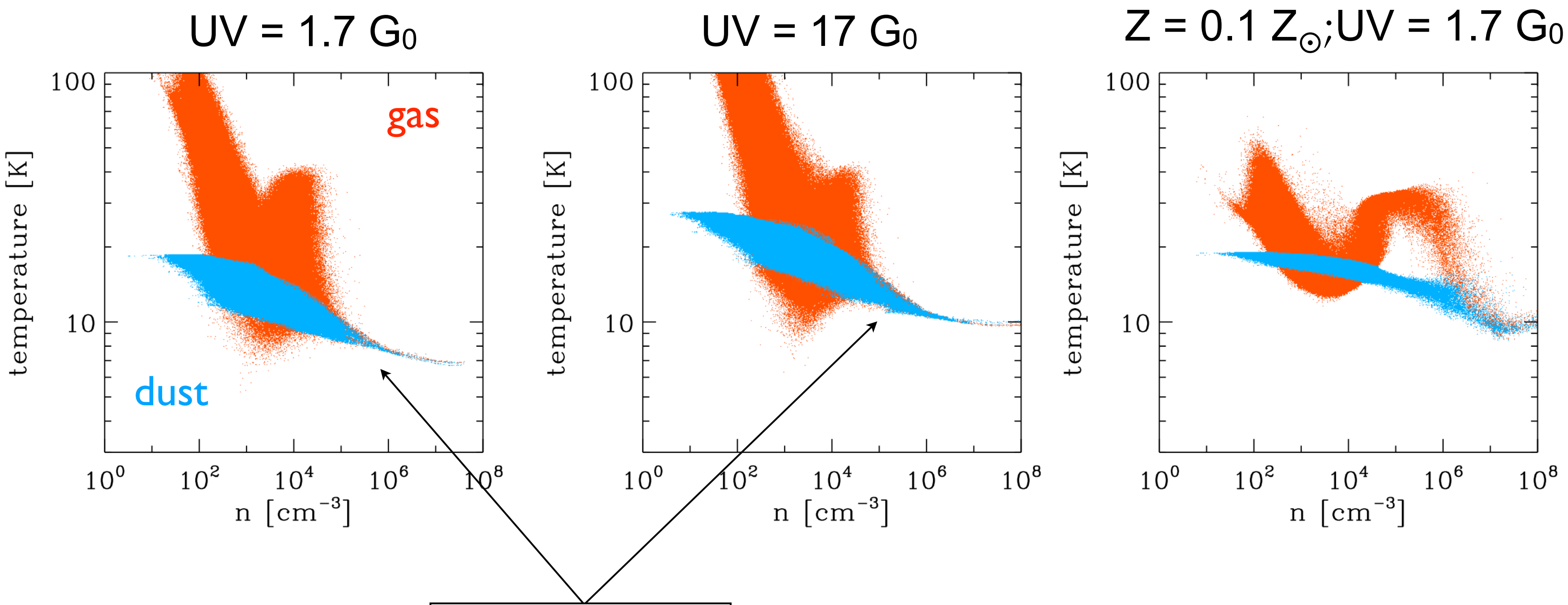
$$= \frac{3.8 \times 10^{-6}}{U} \frac{\alpha_{\mathrm{H}}}{\langle Q_{\mathrm{abs}}\rangle_\star} \left(\frac{n_{\mathrm{H}}}{30\,\mathrm{cm}^{-3}}\right) \left(\frac{T_{\mathrm{gas}}}{10^2\,\mathrm{K}}\right)^{3/2}$$

Draine: Physics of the ISM and IGM (Princeton University Press)

relation between gas and dust 2

- → ***GAS COOLING***
- the net energy transfer (heating of the dust) is

$$\left(\frac{dE}{dt}\right)_{\rm gas} = \sum_i n_i \left(\frac{8kT_{\rm gas}}{\pi m_i}\right)^{1/2} \pi a^2 \times \alpha_i \times 2k(T_{\rm gas} - T_{\rm dust})$$



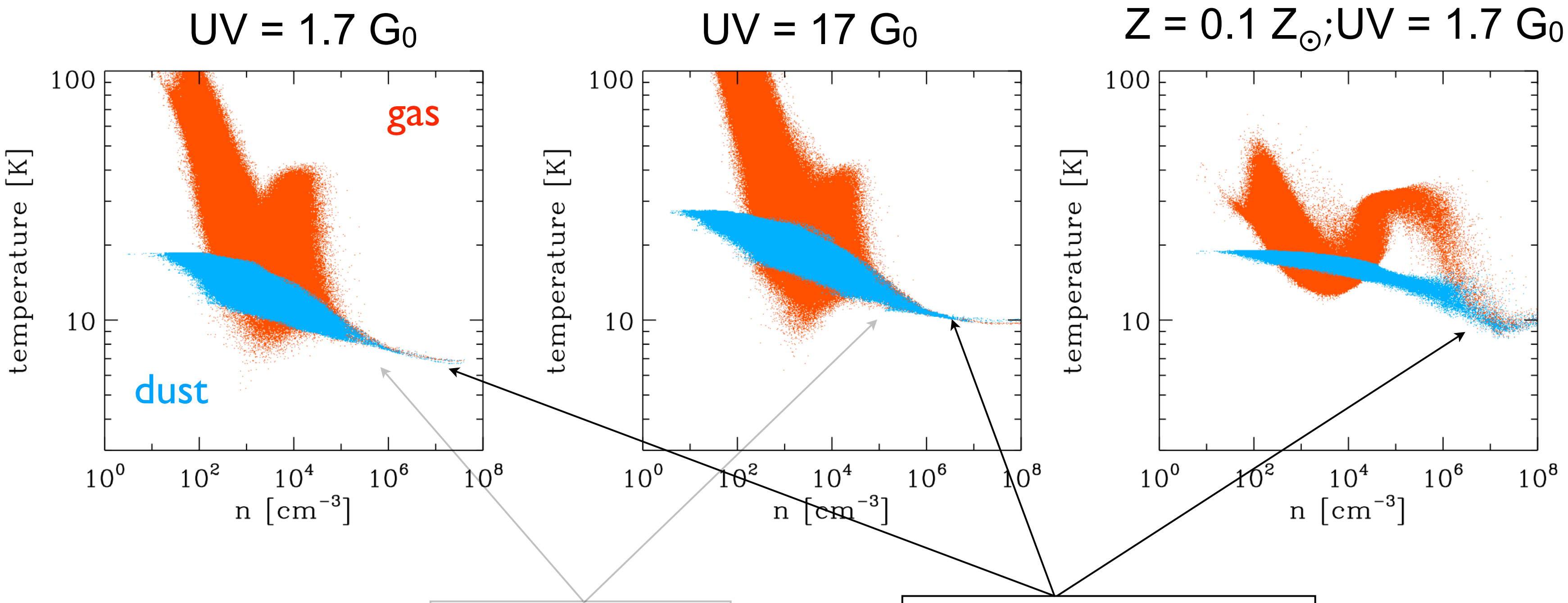
dust is very insensitive to the radiation field

calculation by Clark & Glover (Heidelberg)

relation between gas and dust 3

- → ***GAS COOLING***
- the net energy transfer (heating of the dust) is

$$\left(\frac{dE}{dt}\right)_{\rm gas} = \sum_i n_i \left(\frac{8kT_{\rm gas}}{\pi m_i}\right)^{1/2} \pi a^2 \times \alpha_i \times 2k(T_{\rm gas} - T_{\rm dust})$$



dust is very insensitive to the radiation field

above some density gas couples to dust, this depends on metallicity

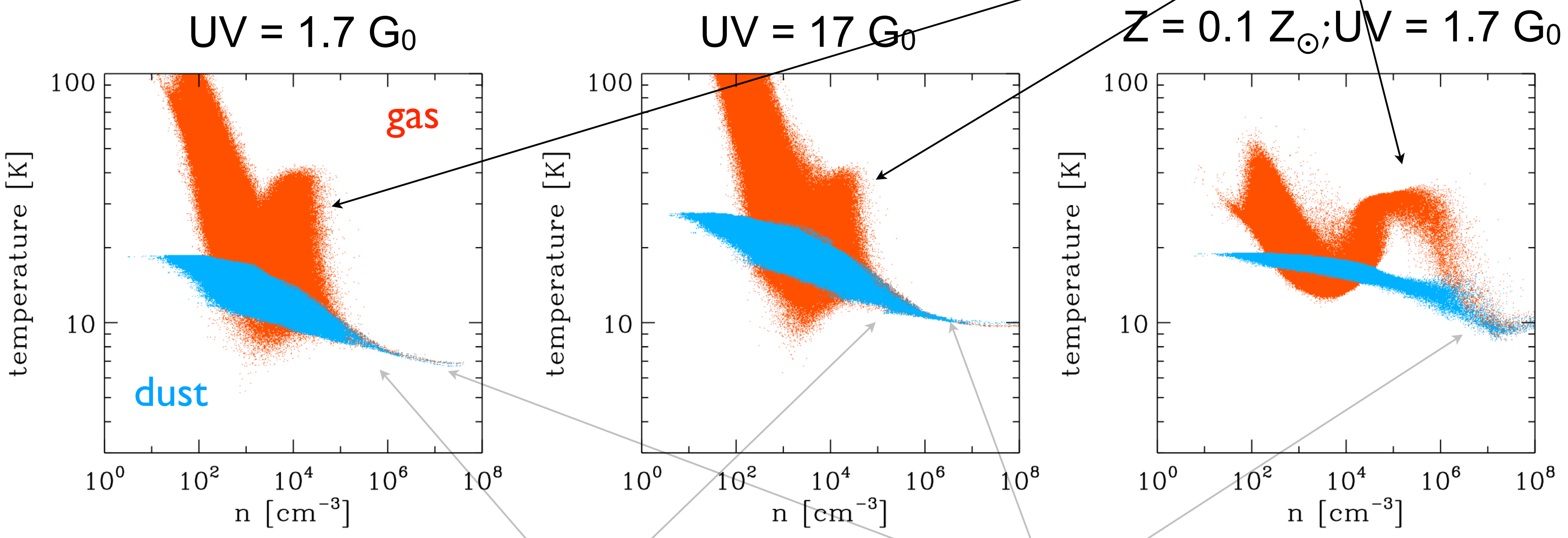
calculation by Clark & Glover (Heidelberg)

relation between gas and dust 4

- → ***GAS COOLING***
- the net energy transfer (heating of the dust) is

$$\left(\frac{dE}{dt}\right)_{\rm gas} = \sum_i n_i \left(\frac{8kT_{\rm gas}}{\pi m_i}\right)^{1/2} \pi a^2 \times \alpha_i \times 2k(T_{\rm gas} - T_{\rm dust})$$

H2 formation on dust grains produces warm ‘bump’ at n ~10^4 cm^{-3}



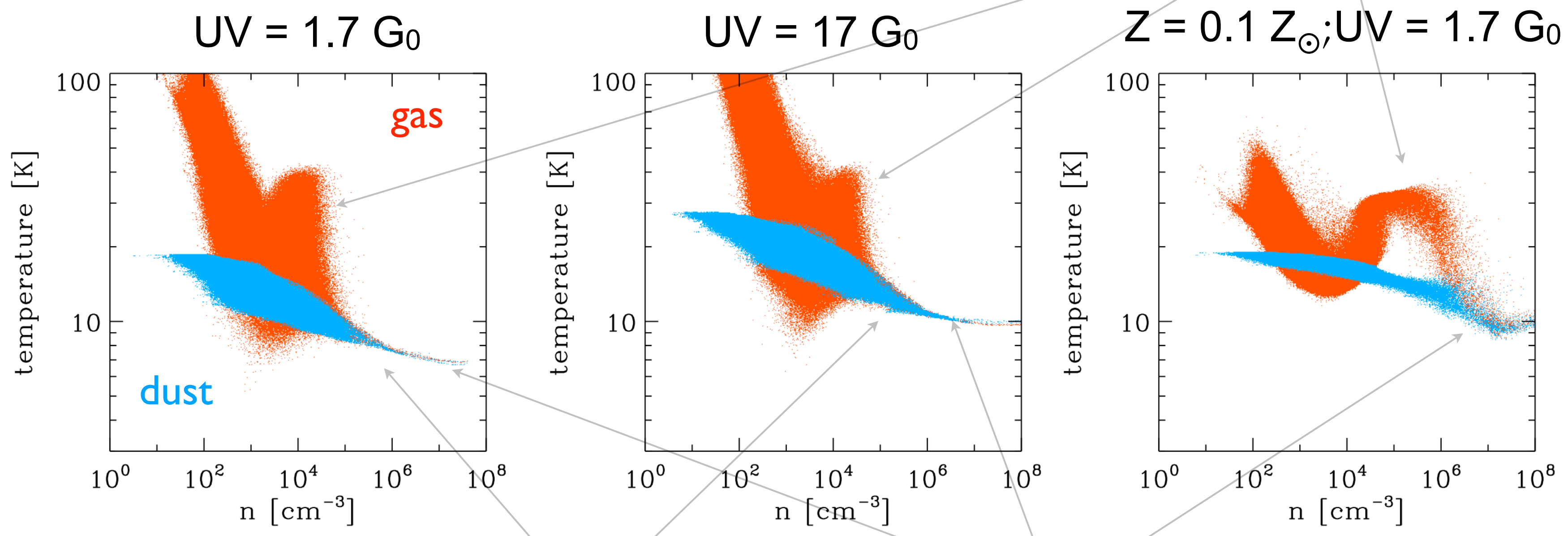
dust is very insensitive to the radiation field

above some density gas couples to dust, this depends on metallicity

calculation by Clark & Glover (Heidelberg)

relation between gas and dust 5

the ISM is far FAR from isothermal, at low densities it is hot, at high densities it becomes cold



H2 formation on dust grains produces warm 'bump' at n ~10^4 cm^{-3}

dust is very insensitive to the radiation field

above some density gas couples to dust, this depends on metallicity

calculation by Clark & Glover (Heidelberg)

radiative dust cooling 1

- dust grains release energy by thermal radiation, typically at IR wavelength

$$\left(\frac{dE}{dt}\right)_{\rm emiss.} = \int d\nu\ 4\pi B_\nu(T_d) C_{\rm abs}(\nu) = 4\pi a^2 \langle Q_{\rm abs}\rangle_{T_d} \sigma T_d^4$$

- where σ is the Stefan-Boltzmann constant, and the Planck averaged emission coefficient is defined as

$$\langle Q_{\rm abs}\rangle_T \equiv \frac{\int d\nu B_\nu(T) Q_{\rm abs}(\nu)}{\int d\nu B_\nu(T)}$$

- if $Q_{\rm abs}(\nu)$ can be approximated by a power-law in frequency

$$Q_{\rm abs}(\nu) = Q_0\,(\nu/\nu_0)^\beta = Q_0\,(\lambda/\lambda_0)^{-\beta}$$

then the Planck mean has a power-law dependency on the temperature

$$\langle Q\rangle = \frac{15}{\pi^4}\Gamma(4+\beta)\zeta(4+\beta)Q_0\left(\frac{kT}{h\nu_0}\right)^\beta$$

Draine: Physics of the ISM and IGM (Princeton University Press)

radiative dust cooling 2

- with $$Q_{\rm abs} \approx 1.4 \times 10^{-3} \left(\frac{a}{0.1\,\mu{\rm m}}\right)\left(\frac{\lambda}{100\,\mu{\rm m}}\right)^{-2}, \quad {\rm silicate}, \lambda \gtrsim 20\,\mu{\rm m},$$ $$\approx 1.0 \times 10^{-3} \left(\frac{a}{0.1\,\mu{\rm m}}\right)\left(\frac{\lambda}{100\,\mu{\rm m}}\right)^{-2}, \quad {\rm graphite}, \lambda \gtrsim 30\,\mu{\rm m}.$$
- we get $$\langle Q_{\rm abs}\rangle_T \approx 1.3 \times 10^{-6} (a/0.1\,\mu{\rm m})(T/\,{\rm K})^2 \quad ({\rm silicate})$$ $$\approx 8 \times 10^{-7} (a/0.1\,\mu{\rm m})(T/\,{\rm K})^2 \quad ({\rm graphite})$$
- with agrees well with the measurements for temperatures below about 100 K

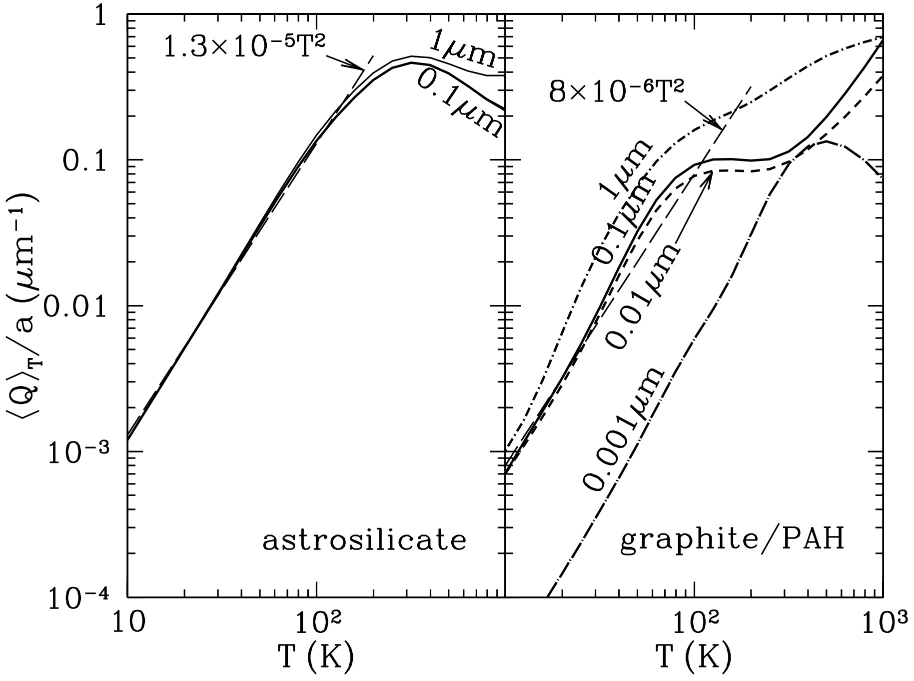


Figure 24.3 Planck-averaged absorption efficiency divided by grain radius as a function of grain temperature T for spheres of amorphous silicate (left) and graphite/PAH (right).

Draine: Physics of the ISM and IGM (Princeton University Press)

equilibrium temperature 1

- taken together, we obtain for the dust temperature in steady state (in equilibrium) in an ambient radiation field $u_\star$:

$$\boxed{4\pi a^2 \langle Q_{\rm abs} \rangle_{T_{\rm ss}} \sigma T_{\rm ss}^4 = \pi a^2 \langle Q_{\rm abs} \rangle_\star u_\star \, c}$$

thermal emission

radiative absorption

- for $Q_{\rm abs} = Q_0 (\lambda / \lambda_0)^{-\beta}$ we get

$$T_{\rm ss} = \left(\frac{h\nu_0}{k} \right)^{\beta/(4+\beta)} \left[\frac{\pi^4 \langle Q_{\rm abs} \rangle_\star \, c}{60 \Gamma(4+\beta) \zeta(4+\beta) Q_0 \sigma} \right]^{1/(4+\beta)} u_\star^{1/(4+\beta)}$$

- for the local ISRF $U = 1.7\ G_0$ we get

$$T_{\rm ss} \approx 16.4 \, (a/0.1\,\mu{\rm m})^{-1/15}\, U^{1/6}\,{\rm K} \ , \ \ {\rm silicate}, 0.01 \lesssim a \lesssim 1\,\mu{\rm m}$$

$$\approx 22.3 \, (a/0.1\,\mu{\rm m})^{-1/40}\, U^{1/6}\,{\rm K} \ , \ \ {\rm graphite}, 0.005 \lesssim a \lesssim 0.15\,\mu{\rm m}$$

Draine: Physics of the ISM and IGM (Princeton University Press)

equilibrium temperature 2

- for the local ISRF $U = 1.7\, G_0$ we get

$$T_{\rm ss} \approx 16.4\, (a/0.1\,\mu{\rm m})^{-1/15}\, U^{1/6}\,{\rm K}\ \ ,\ \ {\rm silicate}, 0.01 \lesssim a \lesssim 1\,\mu{\rm m}$$

$$\approx 22.3\, (a/0.1\,\mu{\rm m})^{-1/40}\, U^{1/6}\,{\rm K}\ \ ,\ \ {\rm graphite}, 0.005 \lesssim a \lesssim 0.15\,\mu{\rm m}$$

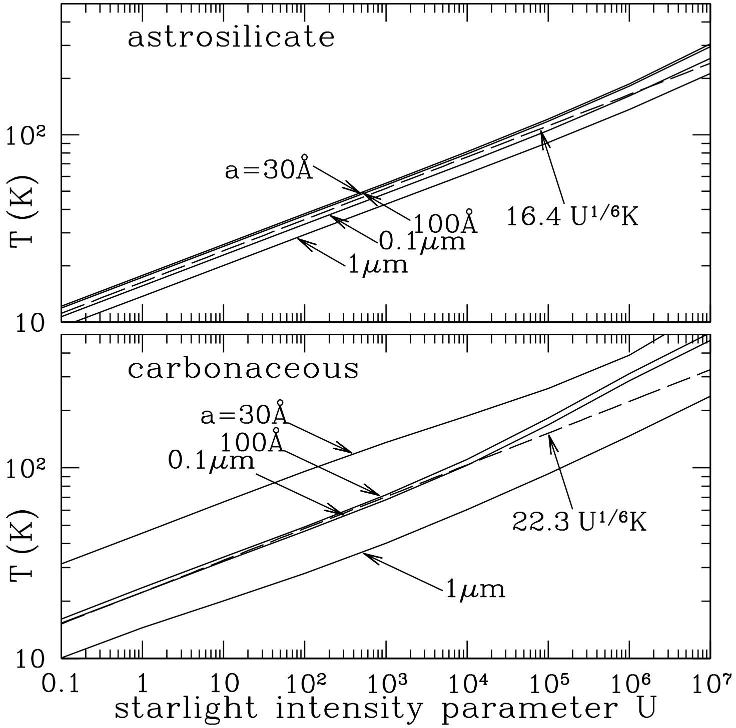


Figure 24.4 Equilibrium temperature for astrosilicate and carbonaceous grains heated by starlight with the spectrum of the local radiation field, and intensity U times the local intensity. Also shown are the power-laws $T = 16.4U^{1/6}$ K and $T = 22.3U^{1/6}$ for $a = 0.1\,\mu$m from Eqs. (24.19 and 24.20).

Draine: Physics of the ISM and IGM (Princeton University Press)

equilibrium temperature 3

- for the local ISRF $U = 1.7\,G_0$ we get

$$T_{\rm ss} \approx 16.4\,(a/0.1\,\mu{\rm m})^{-1/15}\,U^{1/6}\,{\rm K}$$

$$\approx 22.3\,(a/0.1\,\mu{\rm m})^{-1/40}\,U^{1/6}\,{\rm K}$$

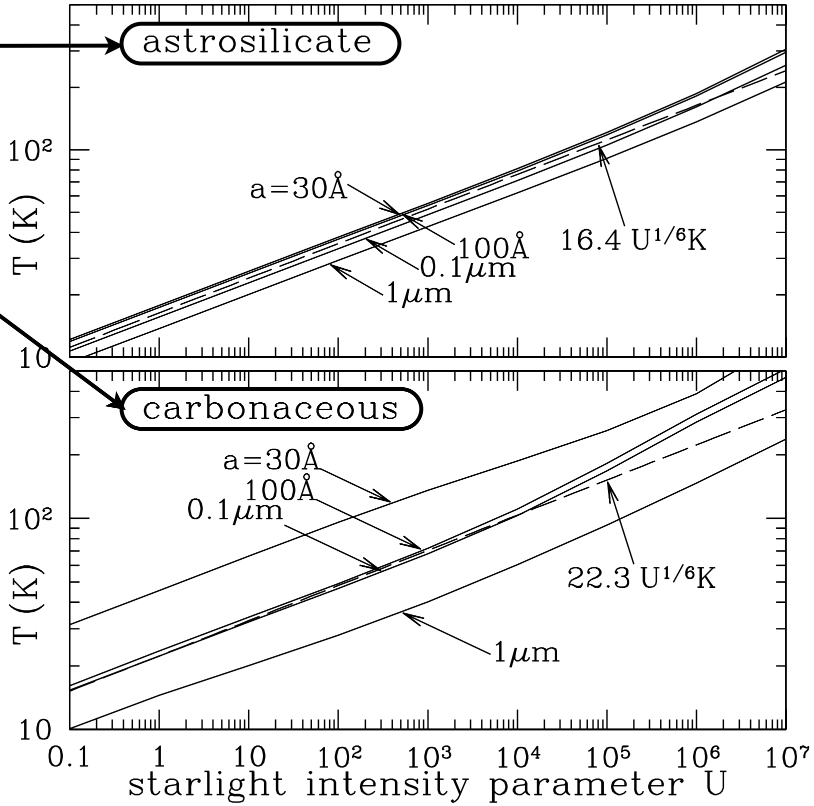


Figure 24.4 Equilibrium temperature for astrosilicate and carbonaceous grains heated by starlight with the spectrum of the local radiation field, and intensity U times the local intensity. Also shown are the power-laws $T = 16.4U^{1/6}$ K and $T = 22.3U^{1/6}$ for $a = 0.1\,\mu$m from Eqs. (24.19 and 24.20).

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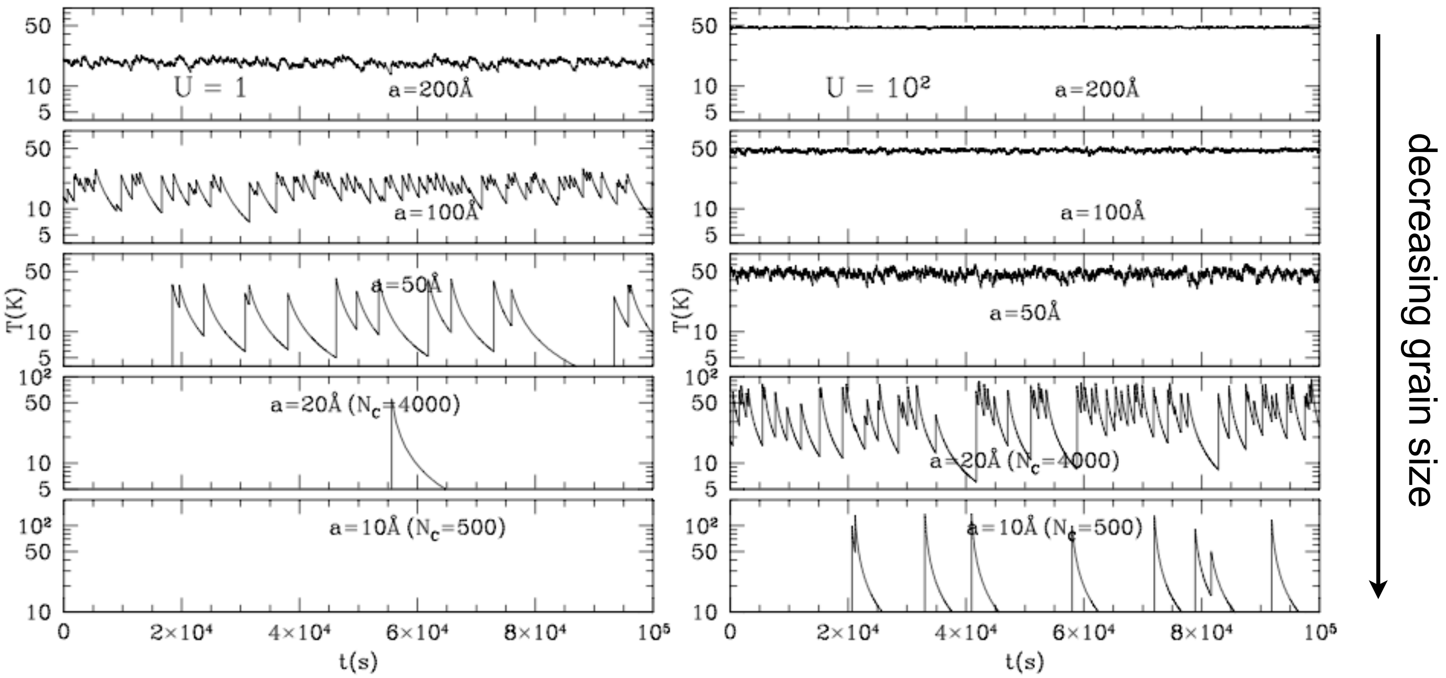
note on stochasticity

- if the grains are very small, then individual heating events (absorption of a photon, or a collision with a gas particle) can lead to large temperature spikes



decreasing grain size

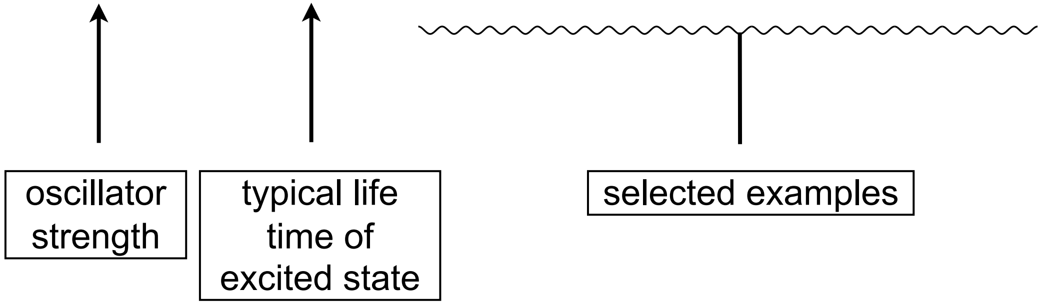
Figure 24.5 Temperature versus time during 10^5 s (~ 1 day) for five carbonaceous grains in two radiation fields: the local starlight intensity ($U = 1$; left panel) and 10^2 times the local starlight intensity ($U = 10^2$; right panel). The importance of quantized stochastic heating is evident for the smaller sizes.

Draine: Physics of the ISM and IGM (Princeton University Press)

gas cooling processes

gas cooling

Type of transition	$f_{\rm ul}$	$A_{\rm ul}(\mathrm{s}^{-1})$	Example	λ	$A_{\rm ul}(\mathrm{s}^{-1})$
Electric dipole					
UV	1	10^9	Lyα	1216 Å	2.40×10^8
Optical	1	10^7	Hα	6563 Å	6.00×10^6
Vibrational	10^{-5}	10^2	CO	4.67 μm	34.00
Rotational	10^{-6}	3×10^{-6}	CS^b	6.1 mm	1.70×10^{-6}
Forbidden					
Optical (Electric quadrupole)	10^{-8}	1	[OIII]	4363 Å	1.7
Optical (Magnetic dipole)	2×10^{-5}	2×10^2	[OIII]	5007 Å	2.00×10^{-2}
Far-IR fine structure	$\frac{2\times10^{-7}}{\lambda(\mu\mathrm{m})}$	$\frac{10}{\lambda^3(\mu\mathrm{m})}$	[OIII]	52 μm	9.80×10^{-5}
Hyperfine			HI	21 cm	2.90×10^{-15}



oscillator strength

typical life time of excited state

selected examples

A. Tielens: Physics and Chemistry of the ISM (Cambridge University Press)

electronic transitions

	Electric dipole “allowed”	Magnetic dipole “forbidden”	Electric quadrupole “forbidden”
1	$\Delta J = 0, \pm 1$ $0 \nleftrightarrow 0$	$\Delta J = 0, \pm 1$ $0 \nleftrightarrow 0$	$\Delta J = 0, \pm 1, \pm 2$ $0 \nleftrightarrow 0,\ 1/2 \nleftrightarrow 1/2,\ 0 \nleftrightarrow 1$
2	$\Delta M = 0, \pm 1$ $0 \nleftrightarrow 0$ when $\Delta J = 0$	$\Delta M = 0, \pm 1$ $0 \nleftrightarrow 0$ when $\Delta J = 0$	$\Delta M = 0, \pm 1, \pm 2$
3	Parity change	No parity change	No parity change
4[b]	One electron jumping $\Delta l = \pm 1$, Δn arbitrary	For all electrons $\Delta l = 0$, $\Delta n = 0$	One electron jumping with $\Delta l = 0, \pm 2$, Δn arbitrary or for all electrons $\Delta l = 0$, $\Delta n = 0$
5[c]	$\Delta S = 0$	$\Delta S = 0$	$\Delta S = 0$
6[c]	$\Delta L = 0, \pm 1$ $0 \nleftrightarrow 0$	$\Delta L = 0$, $\Delta J = \pm 1$	$\Delta L = 0, \pm 1, \pm 2$ $0 \nleftrightarrow 0, 0 \nleftrightarrow 1$

[a] A short summary of six selection rules describing electric dipole and quadrupole and magnetic dipole transitions.

[b] With negligible configuration interaction.

[c] For *LS* coupling only.

A. Tielens: Physics and Chemistry of the ISM (Cambridge University Press)

electronic transitions

- Grotrian diagram:
  example of the α transitions
  (note that the 2s level is metastable)

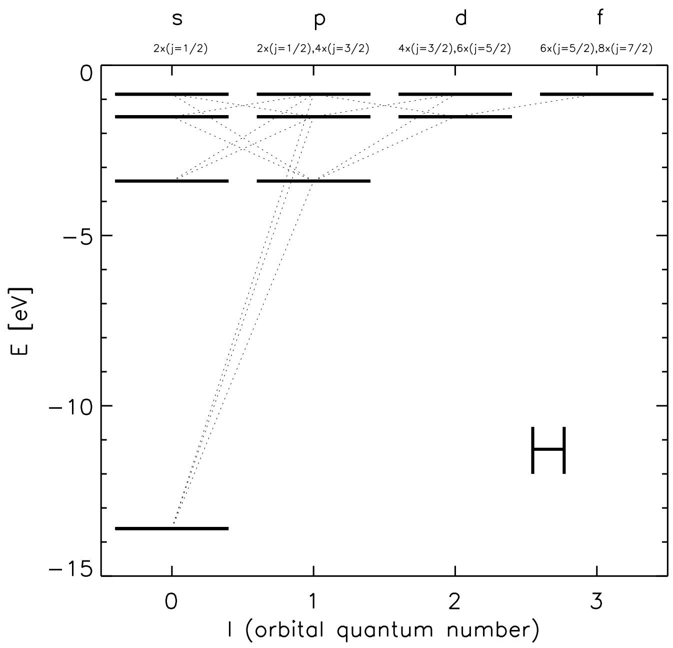
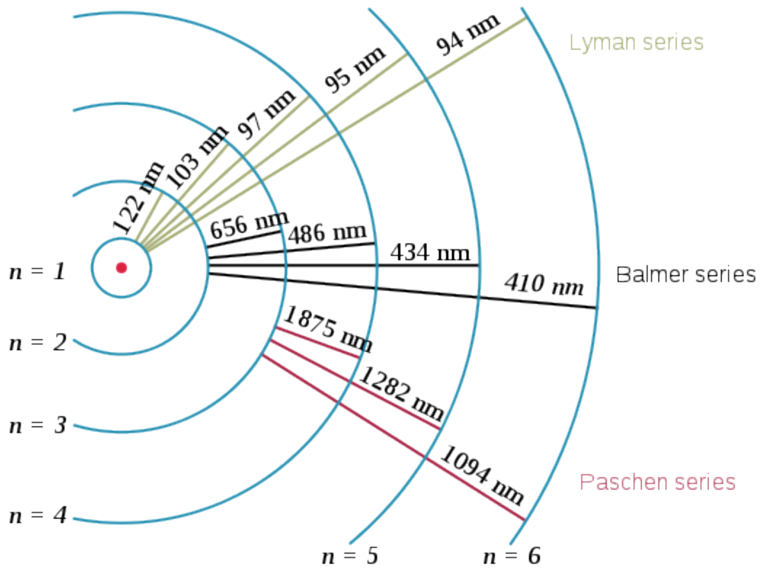
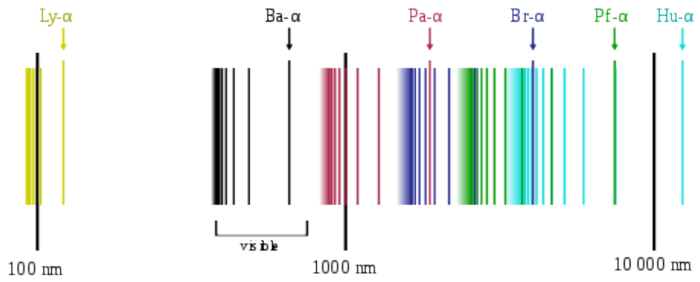


image courtesy of Cornelis Dullemond





hydrogen lines

Lyman: *n’=1*
Balmer: to *n’=2*
Paschen: to *n’=3*
Bracket: to *n’=4*
Pfund: to *n’=5*
etc.

wavelength:

$$\frac{1}{\lambda} = R\left(\frac{1}{(n')^2} - \frac{1}{n^2}\right)$$

with

$$R = 1.097373 \times 10^7\ \mathrm{m}^{-1}$$

images: wikipedia

vibrational transitions

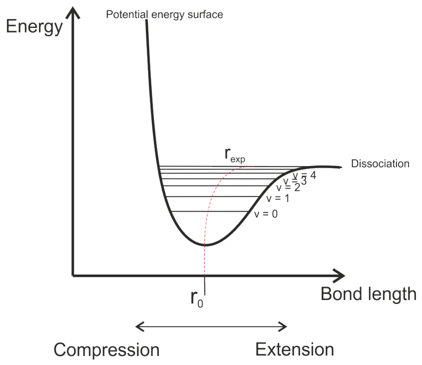
- atoms in a molecule can vibrate, i.e. the can oscillate with respect to each other
- to good approximation, this can be described as harmonic oscillator with energy

$$E_v = h\nu_0 (v + \frac{1}{2})$$

- that means, all transitions with $\Delta v = \pm 1$ (1→0, 2→1, 3→2, etc.) have the same transition energy

$$\Delta E_{ij} = h\nu_{ij} = h\nu_0 (v_i - v_j)$$

- $\Delta v = \pm 1$ is called fundamental transition, $\Delta v = \pm 2$, $\Delta v = \pm 3$, etc. give rise to overtone transitions
- diatomic molecules are simple, however more complex molecules can have very complicated spectra



from: http://chemtube3d.com

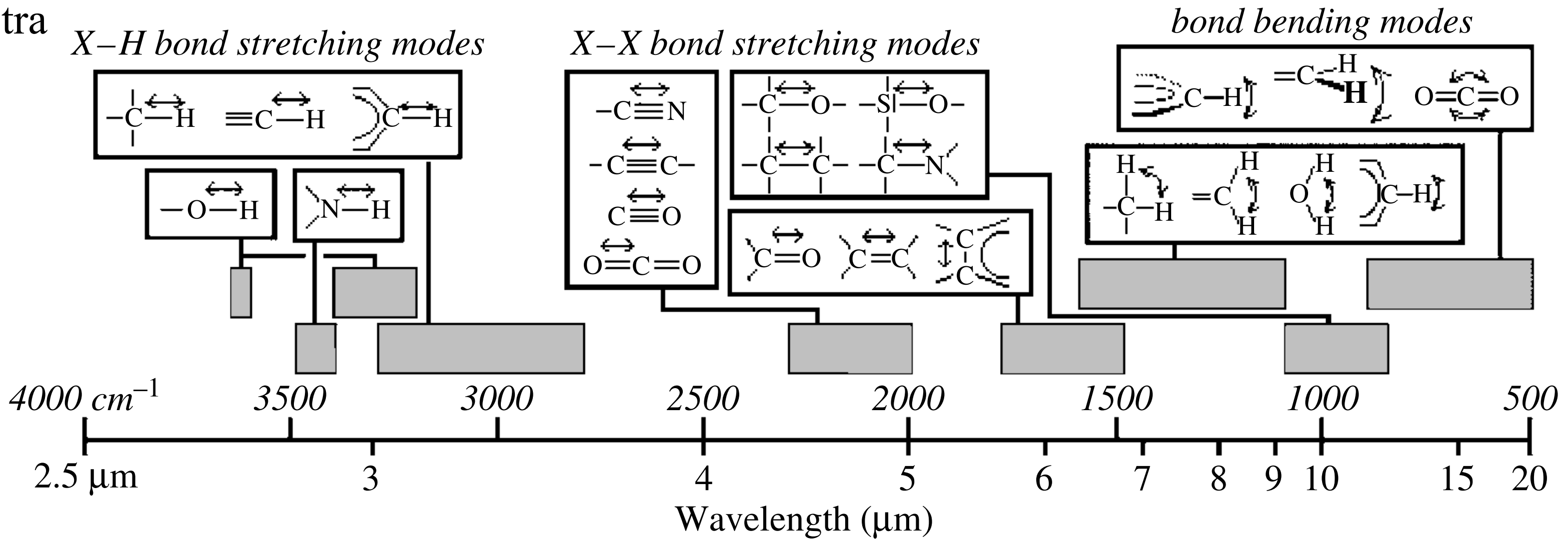


figure from A. Tielens: Physics and Chemistry of the ISM (Cambridge University Press)

rotational transitions

- for diatomic and linear molecules, the rotational levels depend on rotational quantum number J

$$E = \frac{\hbar^2}{2I} J(J+1)$$

- with moment of inertia

$$I = \sum_k m_k r_k^2$$

(note that I can change as the molecule stretches when it rotates faster)

- statistical weight is $g = 2J + 1$
- selection rule $\Delta J = \pm 1$ → the frequencies of transitions (J+1) to J grow *linearly* with J

$$\boxed{h\nu = \frac{\hbar^2}{2I}[J(J+1) - (J-1)J] = \frac{\hbar^2}{I} J}$$

this leads to the *rotational ladder* (a very simply spectrum)

- example CO:

i	j	Name	λ [μm]	A_{ij} [s^{-1}]
2	1	J=1→0	2600.7576	7.203×10^{-8}
3	2	J=2→1	1300.4037	6.910×10^{-7}
4	3	J=3→2	866.96337	2.497×10^{-6}
5	4	J=4→3	650.25151	6.126×10^{-6}

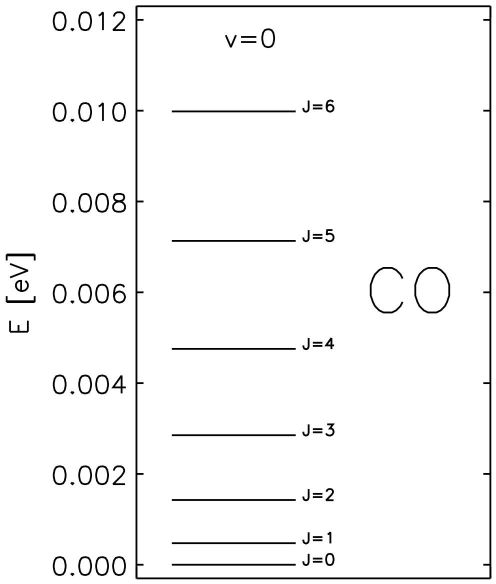


image courtesy of Cornelis Dullemond

rotational transitions

- further examples

Species	Transition	ν_{ul}(GHz)	E_u(K)	A_{ul} (s^{-1})	n_{cr} (cm^{-3})
CO	1–0	115.3	5.5	7.2×10^{-8}	1.1×10^{3}
	2–1	230.8	16.6	6.9×10^{-7}	6.7×10^{3}
	3–2	346.0	33.2	2.5×10^{-6}	2.1×10^{4}
	4–3	461.5	55.4	6.1×10^{-6}	4.4×10^{4}
	5–4	576.9	83.0	1.2×10^{-5}	7.8×10^{4}
	6–5	691.2	116.3	2.1×10^{-5}	1.3×10^{5}
	7–6	806.5	155.0	3.4×10^{-5}	2.0×10^{5}
CS	1–0	49.0	2.4	1.8×10^{-6}	4.6×10^{4}
	2–1	98.0	7.1	1.7×10^{-5}	3.0×10^{5}
	3–2	147.0	14.0	6.6×10^{-5}	1.3×10^{6}
	5–4	244.9	35.0	3.1×10^{-4}	8.8×10^{6}
	7–6	342.9	66.0	1.0×10^{-3}	2.8×10^{7}
	10–9	489.8	129.0	2.6×10^{-3}	1.2×10^{8}
HCO^+	1–0	89.2	4.3	3.0×10^{-5}	1.7×10^{5}
	3–2	267.6	26.0	1.0×10^{-3}	4.2×10^{6}
	4–3	356.7	43.0	2.5×10^{-3}	9.7×10^{6}
HCN	1–0	88.6	4.3	2.4×10^{-5}	2.6×10^{6}
	3–2	265.9	26.0	8.4×10^{-4}	7.8×10^{7}
	4–3	354.5	43.0	2.1×10^{-3}	1.5×10^{8}
H_2CO	2_{12}–1_{11}	140.8	6.8	5.4×10^{-5}	1.1×10^{6}
	3_{13}–2_{12}	211.2	17	2.3×10^{-4}	5.6×10^{6}
	4_{14}–3_{13}	281.5	30	6.0×10^{-4}	9.7×10^{6}
	5_{15}–4_{14}	351.8	47	1.2×10^{-3}	2.6×10^{7}
NH_3	(1,1) inversion	23.7	1.1	1.7×10^{-7}	1.8×10^{3}
	(2,2) inversion	23.7	42	2.3×10^{-7}	2.1×10^{3}
H_2	2–0	1.06×10^{4} [a]	510	2.9×10^{-11}	10
	3–1	1.76×10^{4} [b]	1015	4.8×10^{-10}	300

[a] $\lambda = 28.2\,\mu m$.

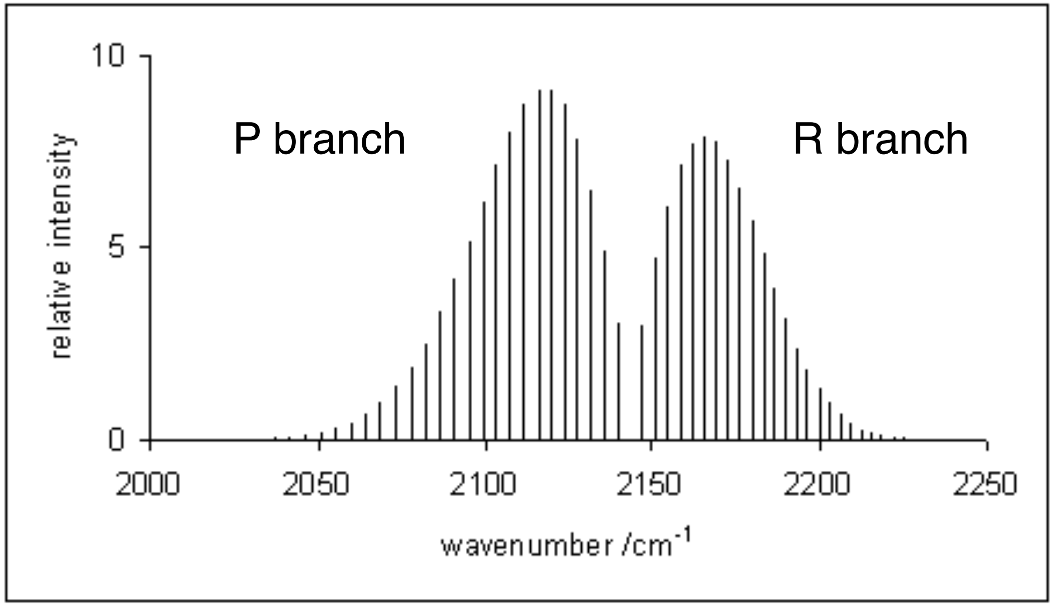
[b] $\lambda = 17.0\,\mu m$.

table from A. Tielens: Physics and Chemistry of the ISM (Cambridge University Press)

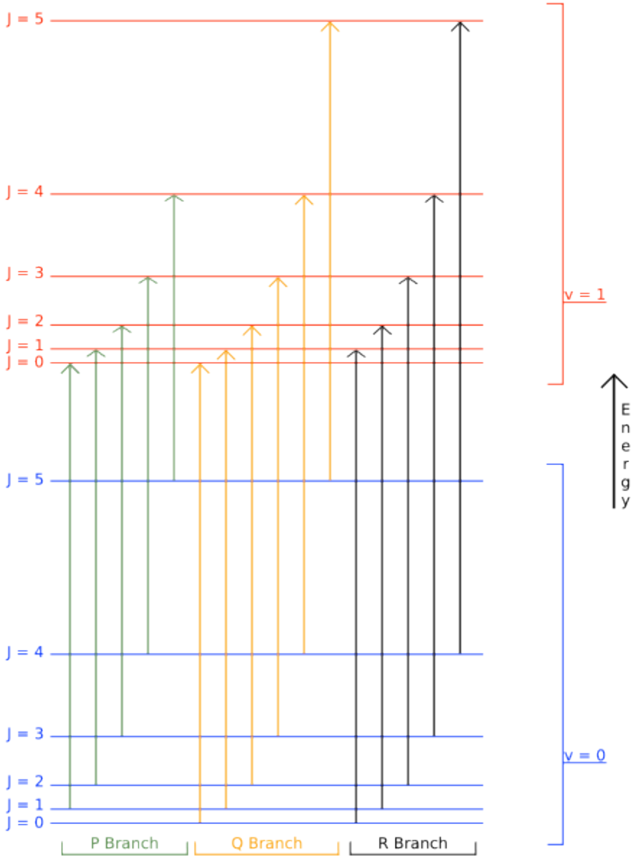
ro-vibrational transitions

- often molecules do both, vibrate as well as rotate
- the selection rules of the combined transitions are that any Δv is possible, but that ΔJ can only change by +1 (R branch), 0 (Q branch), and -1 (P branch)
- the energies of the combined levels are

$$E_{vJ} = h\nu_0(v + \frac{1}{2}) + \frac{\hbar^2}{2I} J(J+1)$$



synthetic specrum of $^{12}C^{16}O$

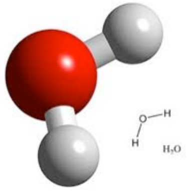


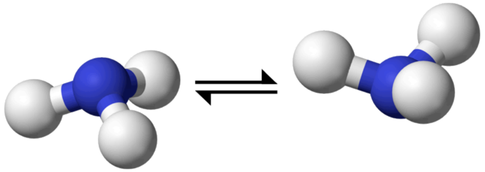
images: wikipedia.org

ro-vibrational transitions

- more complex molecules can have many more possible modes of configurational oscillations and rotations

- some examples
  - symmetric diatomic molecules (quadrupole transitions)
  - symmetric top molecules (two different axes of rotation, $I_A = I_B < I_C$ disk shape $I_A < I_B = I_C$ cigar shape)
  - asymmetric top molecules ($I_A < I_B < I_C$)
  - inversion of ammonia
  - etc.





images: wikipedia.org

gas cooling rates

cooling rate: principles 1

- what is the cooling power provided by a transition $i \rightarrow j$?

$$\boxed{n^2 \Lambda_x(\nu_{ij}) = n_i A_{ij}\, h\nu_{ij}\, \beta(\tau_{ij}) \frac{S_x(\nu_{ij}) - P_x(\nu_{ij})}{S_x(\nu_{ij})} \qquad \text{in } \mathbf{erg/cm^3\, s^{-1}}}$$

- here x denotes the species, n_i is the population density of level i, A_{ij} is the spontaneous emission probability, $h\nu_{ij}$ is the energy different between levels i and j ; the parameter $\beta(\tau_{ij})$ describes the probability of the emitted photon to escape the cloud given an optical depth of τ_{ij} averaged over the line ν_{ij} ;
- the source function of the emission is given by

$$S_x(\nu_{ij}) = \frac{2h\nu_{ij}}{c^2} \left(\frac{g_i n_j}{g_j n_i} - 1 \right)^{-1}$$

  where g_i and g_j are again the statistical weights of the levels i and j;
- there is one additional term that takes the environment into account; $P_x(\nu_{ij})$ typically includes several terms; in its most simple form it includes the contribution from the cosmic microwave background and the local dust emission

$$P_x(\nu_{ij}) = B_{\nu_{ij}}(T = 2.7\,\mathrm{K}) + \tau_{\mathrm{dust}}(\nu_{ij}) B_{\nu_{ij}}(T_{\mathrm{dust}})$$

cooling rate: principles 2

- the level populations follow from detailed balance, it states that in statistical equilibrium all reactions that populate a level and that de-populate a level exactly balance; for altogether N energy levels, it reads for level i

$$n_i \sum_{k \neq i}^{N} R_{ik} = \sum_{i \neq k}^{N} n_k R_{ki}$$

- here the rates R_{ik} denote all "forward" (loss) reactions $i \longrightarrow k$ and the rates R_{ki} the "backward" (gain) reactions $k \longrightarrow i$ that affect the level i
- these reaction can be radiative or collisional; we distinguish between reaction down and up the energy scale

$$R_{ik} = A_{ik}\beta(\tau_{ik})(1 + Q_{ik}) \,+\, C_{ik} \quad \text{for } E_i > E_k$$

$$R_{ik} = \frac{g_k}{g_i} A_{ik}\beta(\tau_{ik})\, Q_{ik} \,+\, C_{ik} \quad \text{for } E_i < E_k$$

again A_{ik} is the Einstein coefficient for spontaneous emission and C_{ij} is the collisional rate for a transition from level i to level k

cooling rate: principles 3

- the background radiation field is contained in the parameter Q_{ik}, which reads

$$Q_{ik} = \frac{c^2}{2h\nu_{ik}} P(\nu_{ik})$$

  it is this term, that carries most of the complexity, because it links the local chemistry to the overall radiation field, which is an intrinsically non-local quantity (see discussion of radiative transfer processes)
- the N equations are not independent, there is in addition the equation of mass conservation for the species x, which for the different levels k reads

$$n_x = \sum_{k=0}^{N} n_k$$

  typically one of the balance equations is replaced by the conservation equation.
- note that special care needs to be taken when solving the advection equation numerically on a computer

- the above needs to be done in a coupled way for each species in the chemical network

application to 2-level system

- as a start, let us assume optically thin conditions (photon escape probability $\beta = 1$) and no ambient radiation field ($P = 0$)
- we assume collisional excitation and collisional as well as radiative de-excitation

$$n_1 n C_{12} = n_2 n C_{21} + n_2 A_{21}$$

where $n = n_1 + n_2$ is the total number density, and the collisional rates are C_{12} and C_{21}, and the rate A_{21} for spontaneous emission

- we assume detailed balance between the collisional rate and get

$$C_{12} = \frac{g_2}{g_1} C_{21} \exp\left(-E_{21}/kT\right)$$

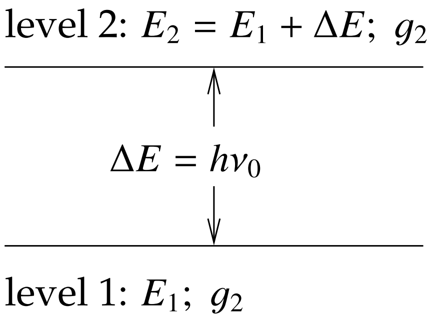
with the statistical weights g_1 and g_2

- we can now solve for the ratio of the level populations n_2/n_1

$$\frac{n_2}{n_1} = \frac{g_2}{g_1} \frac{\exp\left(-E_{21}/kT\right)}{1 + n_{\rm cr}/n}$$

where we introduce the critical density

$$n_{\rm cr} = \frac{A_{21}}{C_{21}}$$



level 2: $E_2 = E_1 + \Delta E;\ g_2$

$\Delta E = h\nu_0$

level 1: $E_1;\ g_2$

application to 2-level system

- the critical density is $n_{\rm cr} = A_{21}/C_{21}$

- note: this can easily be extended to ***multi-level systems***; the critical density now compares the sum of all radiative transitions to the available lower levels to the collisional rates to all levels

$$n_{\rm cr} = \frac{\sum_{j<i} A_{ij}}{\sum_{j\neq i} C_{ij}}$$

- for $n > n_{\rm cr}$ the de-excitation process is dominated by collisions, the system is in local thermodynamic equilibrium (LTE) and the level populations follow the Boltzmann distribution with the kinetic temperature of the gas $T_{\rm gas}$

- for $n < n_{\rm cr}$ radiative transitions dominate the transition to the ground level, in this case T in the Boltzmann term is the radiation temperature; if $T_{\rm rad} \neq T_{\rm gas}$ then the system is not in LTE, this defines the excitation temperature $T_{\rm exc}$

$$T_{\rm exc} = \frac{E_{21}}{k} \left[\ln \left(\frac{n_1 g_2}{n_2 g_1} \right) \right]^{-1}$$

excitation temperature

- combining $T_{\rm exc} = \frac{E_{21}}{k}\left[\ln\left(\frac{n_1 g_2}{n_2 g_1}\right)\right]^{-1}$ with $\frac{n_2}{n_1} = \frac{g_2}{g_1}\frac{\exp\left(-E_{21}/kT\right)}{1+n_{\rm cr}/n}$

  gives an estimate for the ratio between the gas temperature and the excitation temperature $T_{\rm exc}$

$$\frac{T}{T_{\rm exc}} = 1 + \frac{kT}{E_{21}}\ln\left(1+\frac{n_{\rm cr}}{n}\right)$$

- as expected for $n_{\rm cr} \gg n$ we get $T_{\rm exc} \approx T$

- for low densities $n_{\rm cr} \ll n$ $T_{\rm exc}$ will typically be much less than T
- if $kT \ll E_{21}$ then $T_{\rm exc} \approx T$ is also possible, but in this case the upper level 2 will hardly be populated and the transition will be weak anyway

collisional rates

- typical collisional de-excitation rates can be computed as

$$C_{21} = 4\pi \left(\frac{\mu}{2\pi kT}\right)^{3/2} \int_0^\infty \sigma_{21}(v) v^3 \exp\left(-\frac{\mu v^2}{2kT}\right) dv$$

where μ is the reduced mass of the collision partners, $\sigma_{21}(v)$ is the collision cross section, depending on the relative velocity v of the collision partners

- typically $C_{21} \propto T^{1/2}$ for neutral-neutral collisions that are regulated by short-range van der Waals interaction
- electron-neutral interaction often involve spin change (e.g. through the exchange of the colliding electron with a previously bound electron); these collisions involve induced dipoles and are therefore stronger with larger rate coefficients
- electron-ion interactions involve Coulomb forces; they favor low relative velocities ($\sigma \propto v^{-2}$); because of focussing effects between species with opposite charges the cross sections are usually very large, with corresponding large rate coefficients at low T

Table 2.5 *Typical de-excitation rate coefficients*

Collision partners	$< \sigma_{\rm ul} >$ (10^{-15} cm^2)	$\gamma_{\rm ul}$ (cm^3 s^{-1})
Neutral–neutral	2	$3 \times 10^{-11}\, T^{1/2}$
Electron–neutral	30	1×10^{-9}
Electron–ion	$2 \times 10^4/T$	$1 \times 10^{-5}\, T^{-1/2}$

table from A. Tielens: Physics and Chemistry of the ISM (Cambridge University Press)

cooling rate 4

- recall the general form of the cooling strength (for the 2-level species x with transition from 2 → 1):

$$n^2\Lambda_x(\nu_{21}) = n_2 A_{21}\, h\nu_{21}\, \beta(\tau_{21}) \frac{S_x(\nu_{21}) - P_x(\nu_{21})}{S_x(\nu_{21})}$$

- without external radiation field $P_x(\nu_{21})$ and optically thin conditions ($\beta = 1$) the we get

$$\boxed{n^2\Lambda_x(\nu_{21}) = n_2 A_{21}\, h\nu_{21} = \frac{g_2/g_1 \exp[-h\nu_{21}/kT]}{1 + n_{\rm cr}/n + g_2/g_1 \exp[-h\nu_{21}/kT]}\, \chi_x n A_{21} h\nu_{21}}$$

- where we introduce the relative abundance of species x via $\chi_x n = n_2 + n_1$

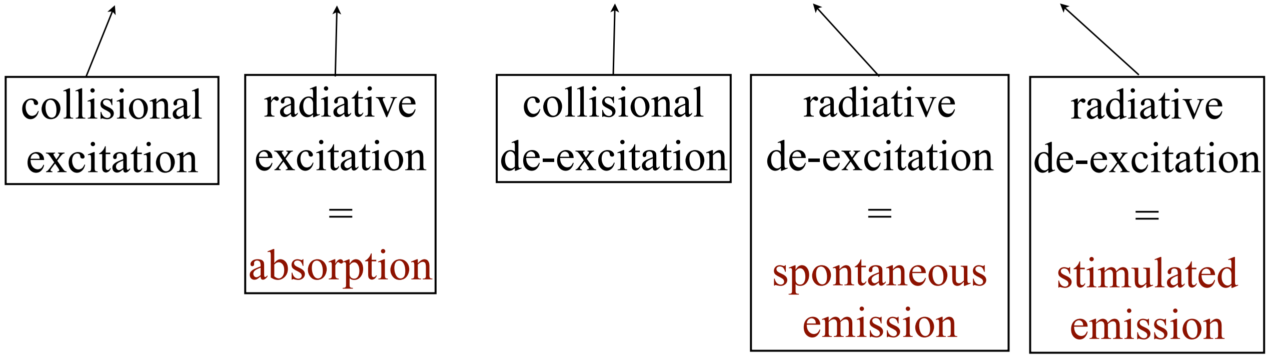
- ***high-density limit*** $n_{\rm cr} \gg n$: we obtain the equations for ***LTE*** (as expected) and we see that in this limit the cooling strength scales *linearly* with density n and temperature T; the resulting intensity in the cooling line scales as the column density (the LOS integral of n)
- ***low-density limit*** $n_{\rm cr} \ll n$: every upward collision eventually results in the emission of a photon; the cooling strength scales as the *density squared* n^2 (and the intensity scales as the density times the column density)

$$\boxed{n^2\Lambda_x(\nu_{21}) = n^2\chi_x\, C_{21} h\nu_{21}}$$

2-level system with optical depth

- let us consider again the simple 2-level system, but now we include the effects of finite optical depth
- taking the interaction with the ambient radiation field $J_{21} = J_{\nu_{21}}$ at the frequency ν_{21} into account, the equation of detailed balance now reads

$$n_1 n C_{12} + n_1 B_{12} J_{21} = n_2 n C_{21} + n_2 A_{21} + n_2 B_{21} J_{21}$$



collisional excitation

radiative excitation = absorption

collisional de-excitation

radiative de-excitation = spontaneous emission

radiative de-excitation = stimulated emission

- PROBLEM: this is now are strongly coupled non-linear problem! the level populations depend on the radiation field, while the radiation field depends on the level population everywhere in the cloud
- calculation of level populations is coupled to the radiative transfer problem
  ↳ computationally extremely demanding!

simplification

- we can make *two simplifications* to make the problem of computing the level population local again

- introduce ***local escape probability***: photons produced locally can only be absorbed locally
  ↳ large velocity gradient approximation ⟷ Sobolev approximation
- for calculating the optical depth, we assume that the ***local*** level population holds ***globally***

- these two assumptions decouple the calculation of the level population from solving the global radiative transfer problem

- we say that the net number of photon absorption events (corrected for stimulated emission) is equal to the number of photons that do not escape the local volume (say computational cell)

$$(n_1 B_{12} J_{21} - n_2 B_{21}) J_{21} = [1 - \beta(\tau_{21})]\, n_2 A_{21}$$

where $\beta(\tau)$ is the probability of a photon formed at optical depth τ escapes from the region of interest (computational cell)

2-level system with escape probability

- combining $n_1 n C_{12} + n_1 B_{12} J_{21} = n_2 n C_{21} + n_2 A_{21} + n_2 B_{21} J_{21}$

  with $(n_1 B_{12} J_{21} - n_2 B_{21}) J_{21} = [1 - \beta(\tau_{21})]\, n_2 A_{21}$

  leads to a ***fully local equation*** (no dependence on J_{21}) for the level populations:

$$\boxed{n_1 n C_{12} = n_2 n C_{21} + \beta(\tau_{21})\, n_2 A_{21}}$$

- this is identical to the optically thin case discussed before, except that $n_2 \rightarrow \beta(\tau_{21})\, n_2$
- we recover the same formal solution for the ratio of the level populations

$$\frac{n_2}{n_1} = \frac{g_2}{g_1} \frac{\exp\left(-E_{21}/kT\right)}{1 + n_{\rm cr}/n}$$

  with $n_{\rm cr} = \beta(\tau_{21}) A_{21} / C_{21}$

- thus, including local photon trapping *effectively **lowers** the critical density* for reaching LTE; a fraction of the emitted photons become absorbed again; this excited state has another chance to de-excite via a collision and give back the energy to the gas before it emits a new photon which might escape and carry away the energy

2-level system with escape probability

- hot to calculate $\beta(\tau_{21})$?
- large velocity gradient (LVG) or Sobolev approximation:

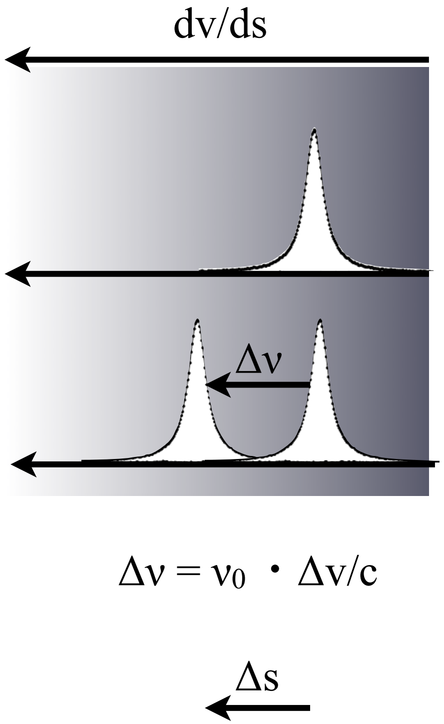
  if there is a *large velocity gradient* across the local region of interest, then we quickly have a significant Doppler shift between the emitted photon and all possible absorbers

  once the photon has managed to escape the local region, then it can no longer be absorbed by other regions of the cloud

- we can write the corresponding optical depth

$$\tau_{21} = \frac{A_{21} c^3}{8\pi \nu_{21}^3} \frac{n2}{|dv/ds|} \left(\frac{n_1 g_2}{n_2 g_1} - 1 \right)$$

- for simple geometries $\beta(\tau_{21})$ can be calculated analytically



the line is Doppler shifted away over the small distance Δs

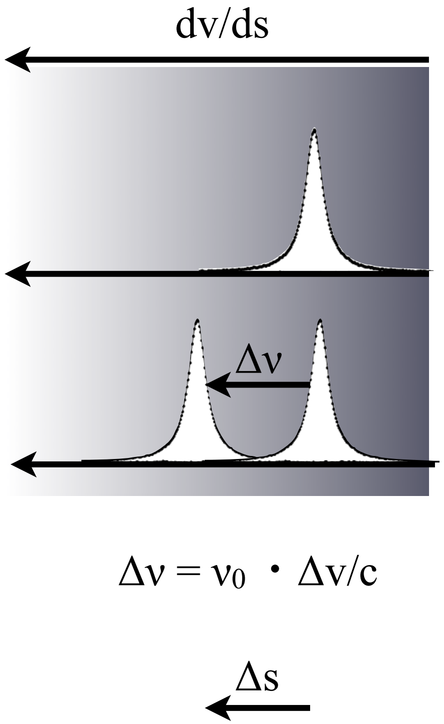
2-level system with escape probability

- for simple geometries $\beta(\tau_{21})$ can be calculated analytically
- example: infinite slab of gas with dv/ds gives

$$\beta(\tau) = \frac{1 - \exp(-2.34\tau)}{4.68\tau} \qquad \tau < 7$$

and

$$\beta(\tau) = \left[4\,\tau \left(\ln\left(\frac{\tau}{\sqrt{\pi}}\right)\right)^{1/2}\right]^{-1} \qquad \tau > 7$$



$\Delta\nu = \nu_0 \cdot \Delta v/c$

the line is Doppler shifted away over the small distance Δs

cooling in ionized gas 1

- in ionized gas (T ~ 10^4 K) the most important cooling mechanism is the excitation of low lying electronic states of trace species such as O^{++} or N^+
- these states are excited by collisions with free electrons in the ionized gas with rates

$$C_{21} = \left(\frac{2\pi}{kT}\right)^{1/2} \frac{\Omega_{21}}{g_2} \approx \frac{8.6 \times 10^{-6}}{T^{1/2}} \frac{\Omega_{21}}{g_2}\,\mathrm{cm}^3\mathrm{s}^{-1}$$

  with $\Omega_{21} \sim 1$ being the collision strength and g_2 the statistical weight of the upper state
- these transition connect states with the same electron configuration and are thus dipole-forbidden transitions
- however, the density in HII regions is typically much below the critical density for collisional de-excitation, so these lines are effective coolants
- because they are forbidden transitions and because HII regions are usually small, optical depth effects play no role and the emission is typically optically thin

cooling in ionized gas 2

- some line data:

$$n^2\Lambda_x(\nu_{21}) = n_2 A_{21}\, h\nu_{21} = \frac{g_2/g_1 \exp[-h\nu_{21}/kT]}{1 + n_{\rm cr}/n + g_2/g_1 \exp[-h\nu_{21}/kT]}\,\chi_x n A_{21} h\nu_{21}$$

$$n_{\rm cr} = \beta(\tau_{21}) A_{21}/C_{21}$$

$$\chi_x n = n_2 + n_1$$

Ion	u	l	$\lambda_{\rm ul}$(Å)	$E_{\rm ul}$(K)	$A_{\rm ul}$(s)	$\Omega_{\rm ul}$ (cm^{-3})	$n_{\rm cr}$(u)
O^+	$^2D_{5/2}$	$^4S_{3/2}$	3 728.8	3.9×10^4	3.8×10^{-5}	0.82	1.3×10^3
O^+	$^2P_{1/2}$	$^2D_{5/2}$	7 318.8	2.0×10^4	6.1×10^{-2}	0.30	4.3×10^6
O^+	$^2P_{1/2}$	$^2D_{3/2}$	7 329.6	2.0×10^4	1.0×10^{-1}	0.28	4.3×10^6
						.14	4.3×10^6
						.74	6.3×10^6
						.41	6.3×10^6
						.28	6.3×10^6
N^+	$^3P_1$	$^3P_0$	2 040 000.0	7.0×10^1	2.1×10^{-6}	0.41	4.5×10^1
N^+	$^3P_2$	$^3P_1$	1 220 000.0	1.2×10^2	7.5×10^{-6}	1.12	2.8×10^2
N^+	$^1D_2$	$^3P_2$	6 583.4	2.2×10^4	3.0×10^{-3}	1.47	8.6×10^4
N^+	$^1D_2$	$^3P_1$	6 548.1	2.2×10^4	1.0×10^{-3}	0.88	8.6×10^4
N^+	$^1S_0$	$^1D_2$	5 754.6	2.5×10^4	1.0	0.83	1.1×10^7
N^+	$^1S_0$	$^3P_1$	3 062.8	4.7×10^4	3.3×10^{-2}	0.10	1.1×10^7
S^+	$^2D_{3/2}$	$^4S_{3/2}$	6 730.8	2.1×10^4	8.8×10^{-4}	2.76	3.6×10^3
S^+	$^2D_{5/2}$	$^4S_{3/2}$	6 716.4	2.1×10^4	2.6×10^{-4}	4.14	1.3×10^3
S^+	$^2P_{1/2}$	$^2D_{5/2}$	10 370.5	1.4×10^4	7.8×10^{-2}	2.20	9.8×10^5
S^+	$^2P_{1/2}$	$^2D_{3/2}$	10 336.4	1.4×10^4	1.6×10^{-1}	1.79	9.8×10^5
S^+	$^2P_{1/2}$	$^4S_{3/2}$	4 076.4	3.5×10^4	9.1×10^{-2}	1.17	9.8×10^5
S^+	$^2P_{3/2}$	$^2D_{5/2}$	10 320.5	1.4×10^4	1.8×10^{-1}	4.99	5.7×10^6
S^+	$^2P_{3/2}$	$^2D_{3/2}$	10 286.7	1.4×10^4	1.3×10^{-1}	3.00	5.7×10^6
S^+	$^2P_{3/2}$	$^4S_{3/2}$	4 068.6	3.5×10^4	2.2×10^{-1}	2.35	5.7×10^6
O^{++}	$^3P_1$	$^3P_0$	884 000.0	1.6×10^2	2.7×10^{-5}	0.54	5.0×10^2
O^{++}	$^3P_2$	$^3P_1$	518 000.0	2.8×10^2	9.8×10^{-5}	1.29	3.4×10^3
O^{++}	$^1D_2$	$^3P_2$	5 006.9	2.9×10^4	2.0×10^{-2}	1.27	6.9×10^5
O^{++}	$^1D_2$	$^3P_1$	4 958.9	2.9×10^4	7.0×10^{-3}	0.76	6.9×10^5
O^{++}	$^1S_0$	$^1D_2$	4 363.2	3.3×10^4	1.7	0.58	2.4×10^7
O^{++}	$^1S_0$	$^3P_1$	2 321.4	6.2×10^4	2.3×10^{-1}	0.10	2.4×10^7

table from A. Tielens: Physics and Chemistry of the ISM (Cambridge University Press)

cooling in atomic gas 1

- as the ionized gas, the cooling of atomic gas is done through the excitation of low-lying electronic transitions
- because the temperatures are typically low, cooling by fine-structure lines with $\Delta T < 1000$ K is generally most efficient
- we need to distinguish between excitation by
  - collisions with H, and
  - collisions with electrons and ions (like C, S, Si)
  - collisions with molecular hydrogen (becomes relevant only at very high densities)
- there are always some free electrons by ionization of trace species with small ionization energy, and by the normal cosmic ray flux

- example: cooling by C^+, in the low density limit the [CII] line at 158 μm provides the following cooling rate

$$n^2\Lambda_{[\mathrm{CII}]} \approx 3\times 10^{-27} n^2 \left(\frac{\chi_{\mathrm{C}}}{1.4\times 10^{-4}}\right)\left[1+0.42\left(\frac{x}{10^{-3}}\right)\right]\exp\left(-\frac{92\mathrm{K}}{T}\right)\,\mathrm{erg\,cm^{-3}\,s^{-1}}$$

where we have assume that C is fully ionized and that H has an ionization degree of x

cooling in atomic gas 2

- note, that optical depth effects can be important

$$N(\tau = 1) \approx 6.8 \times 10^{21}\mathrm{cm}^{-2} \left(\frac{10^{-5}}{A_{21}}\right)\left(\frac{10^{-4}}{\chi}\right)\left(\frac{100\mu\mathrm{m}}{\lambda_{21}}\right)^3 \left(\frac{\sigma}{1\,\mathrm{km\,s^{-1}}}\right)$$

  where χ is again the fractional abundance of the species under consideration

- note this roughly corresponds to an $A_\mathrm{v} \sim 1$ which is also the value for self-shielding of H_2 to become important

cooling in atomic gas 3

- some line data:

						p, e collisions[a]		H collisions			
Species	u	l	$\lambda_{\rm ul}$(Å)	$E_{\rm ul}$(K)	$A_{\rm ul}$(s)	$\gamma^b_{\rm ul}$ (cm^3 s^{-1})	$n^b_{\rm cr}$ (cm^{-3})	α^b (cm^3 s^{-1})	β^b (cm^{-3})	$n^b_{\rm cr}$ (cm^{-2})	N_τ
C$^+$	$^2P_{3/2}$	$^2P_{1/2}$	1 577 000	92	2.4 (−6)	3.8 (−7)	6.3 (0)	8.9 (−10)	0.02	2.7 (3)	1.2 (21)
C	$^3P_1$	$^3P_0$	6 092 000	23.6	7.9 (−8)	3.0 (−9)	2.6 (1)	1.6 (−10)	0.14	4.9 (2)	4.2 (20)
C	$^3P_2$	$^3P_1$	3 690 000	38.9	2.7 (−7)	1.5 (−8)	1.8 (1)	2.9 (−10)	0.26	9.3 (2)	1.0 (21)
C	$^3P_2$	$^3P_0$	230	62.5	2.0 (−14)	5.0 (−9)	—	9.2 (−11)	0.26	—	1.9 (28)
O	$^3P_1$	$^3P_2$	632 000	228	8.95 (−5)	1.4 (−8)	6.4 (3)	9.2 (−11)	0.67	9.7 (5)	1.0 (21)
O	$^3P_0$	$^3P_1$	1 456 000	98	1.7 (−5)	5.0 (−9)	3.4 (3)	1.1 (−10)	0.44	1.5 (5)	7.8 (20)
O	$^3P_0$	$^3P_2$	440 000	326	1.0 (−10)	1.4 (−8)	—	4.4 (−11)	0.80	—	8.0 (27)
O	$^1D_2$	$^3P_2$	6 300.3	2.3(4)	6.3 (−3)	2.5 (−9)[c]	2.4 (6)[c]	—	—	—	—
O	$^1D_2$	$^3P_1$	6 363.8	2.3(4)	2.1 (−3)	1.5 (−9)[c]	1.4 (6)[c]	—	—	—	—
Si$^+$	$^2P_{3/2}$	$^2P_{1/2}$	348 000	414	2.2 (−4)	4.3 (−7)	5.1 (2)	6.5 (−10)	—	3.4 (5)	4.6 (23)
S	$^3P_2$	$^3P_1$	252 000	571	1.4 (−3)	3.3 (−8)	4.2 (4)	7.5 (−10)	0.17	1.8 (6)	6.4 (22)
S	$^3P_0$	$^3P_1$	566 000	255	3.0 (−4)	1.2 (−8)	2.5 (4)	4.2 (−10)	0.17	7.1 (5)	4.7 (22)
S[d]	$^3P_2$	$^3P_0$	174 000	826	6.7 (−8)	3.3 (−8)	—	7.1 (−10)	0.17	—	1.2 (28)
Fe	$^5D_3$	$^5D_4$	242 000	595	2.5 (−3)	1.2 (−7)	2.1 (4)	8.0 (−10)	0.17	3.1 (6)	9.9 (23)
Fe	$^5D_2$	$^5D_3$	347 000	415	1.6 (−3)	9.3 (−8)	1.7 (4)	5.3 (−10)	0.17	3.0 (6)	3.7 (21)
Fe	$^5D_4$	$^5D_2$	143 000	1010	1.0 (−9)	1.2 (−7)	—	6.9 (−10)	0.17	—	1.7 (32)
Fe$^+$	$^6D_{7/2}$	$^6D_{9/2}$	260 000	554	2.1 (−3)	1.8 (−6)	6.0 (2)	9.5 (−10)	—	2.2 (6)	9.1 (23)
Fe$^+$	$^6D_{5/2}$	$^6D_{7/2}$	354 000	407	1.6 (−3)	8.7 (−7)	1.8 (3)	4.7 (−10)	—	3.3 (6)	5.2 (23)
Fe$^+$	$^6D_{5/2}$	$^6D_{9/2}$	150 000	961	1.5 (−9)	1.8 (−6)	—	5.7 (−10)	—	—	9.0 (30)

[a] Electron collision rates for ions (these have a $T^{-0.5}$ dependence), proton collision rates for neutrals.

[b] De-excitation collisional rate coefficient and critical density evaluated at 100 K, unless otherwise noted.

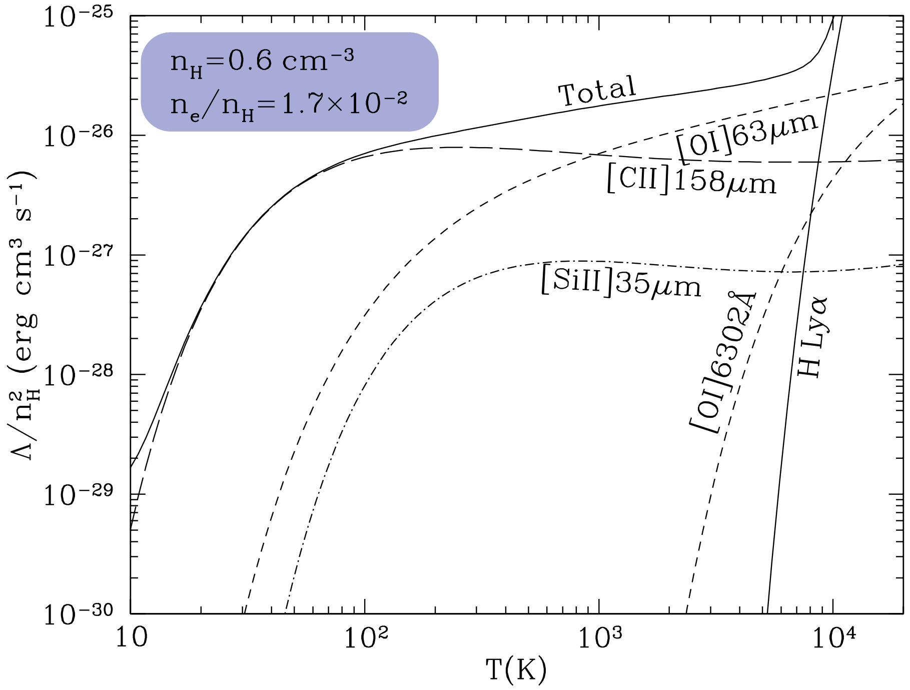
[c] Evaluated at 10 000 K. Scales with $T^{0.6}$.

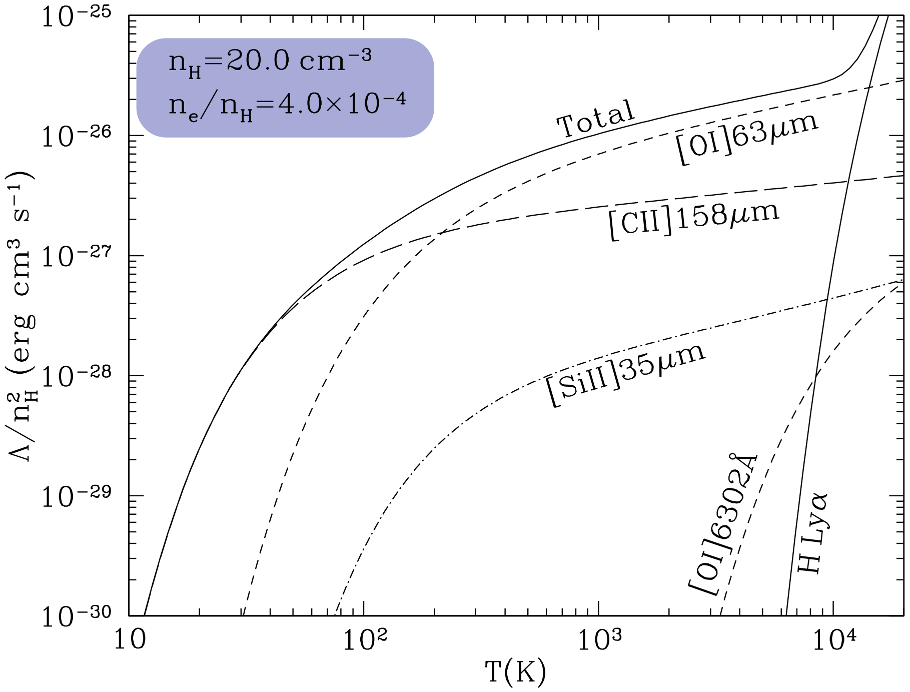
[d] The cooling parameters of S$^+$ are given in Table 2.6.

table from A. Tielens: Physics and Chemistry of the ISM (Cambridge University Press)

cooling in atomic gas 4

- some representative cooling curves:





- for temperature range $10 \lesssim T \lesssim 2 \times 10^4$ K and two different fractional ionizations

- cooling is dominated by two fine-structure lines, [CII] at 158 μm and [OI] at 63 μm for T < 10^4 K

Draine: Physics of the ISM and IGM (Princeton University Press)

cooling in molecular gas 1

- molecular gas has many very efficient pathways for cooling
- molecular vibrational and rotational levels are easily excited and can efficiently remove energy from the system

- under typical conditions, cooling is dominated by CO lines, but also H_2O can be come important at high densities and temperatures
- the coupling between gas and dust is important for high densities
- optical depth effects become important

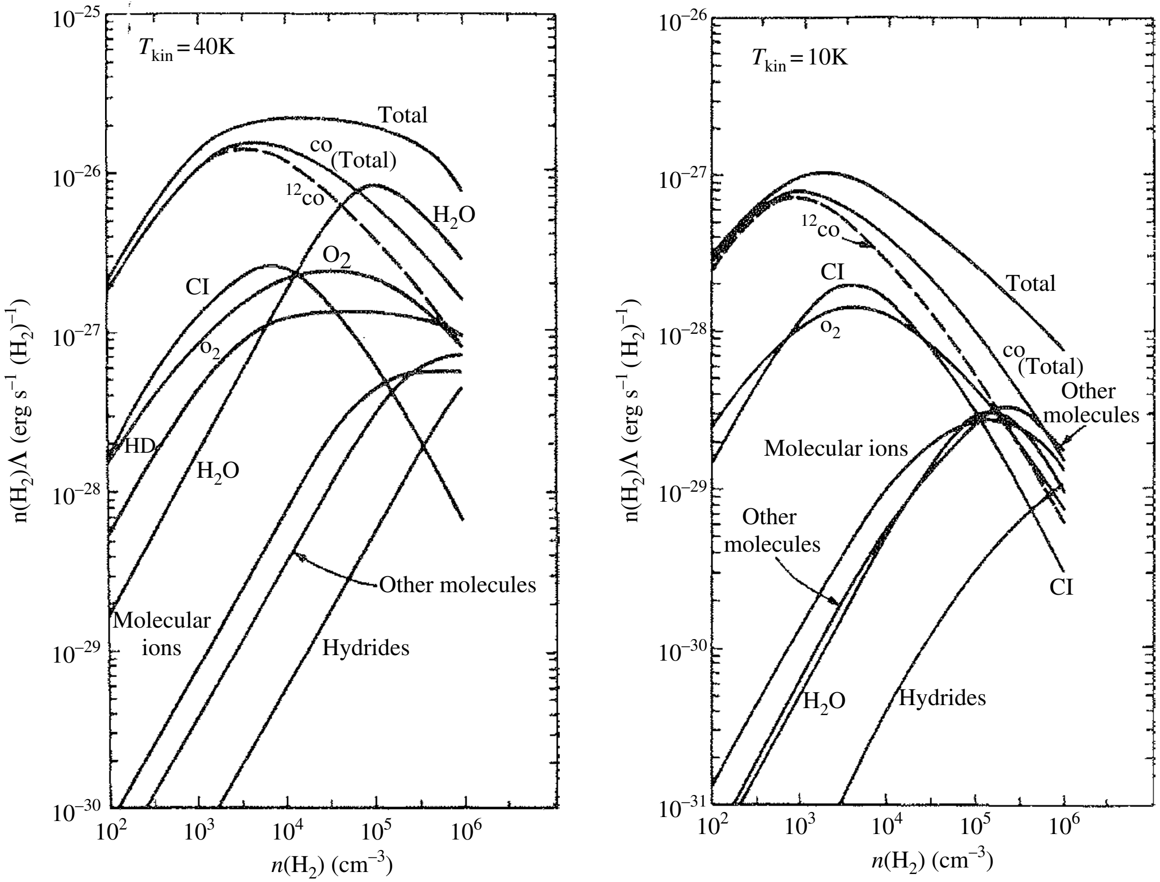


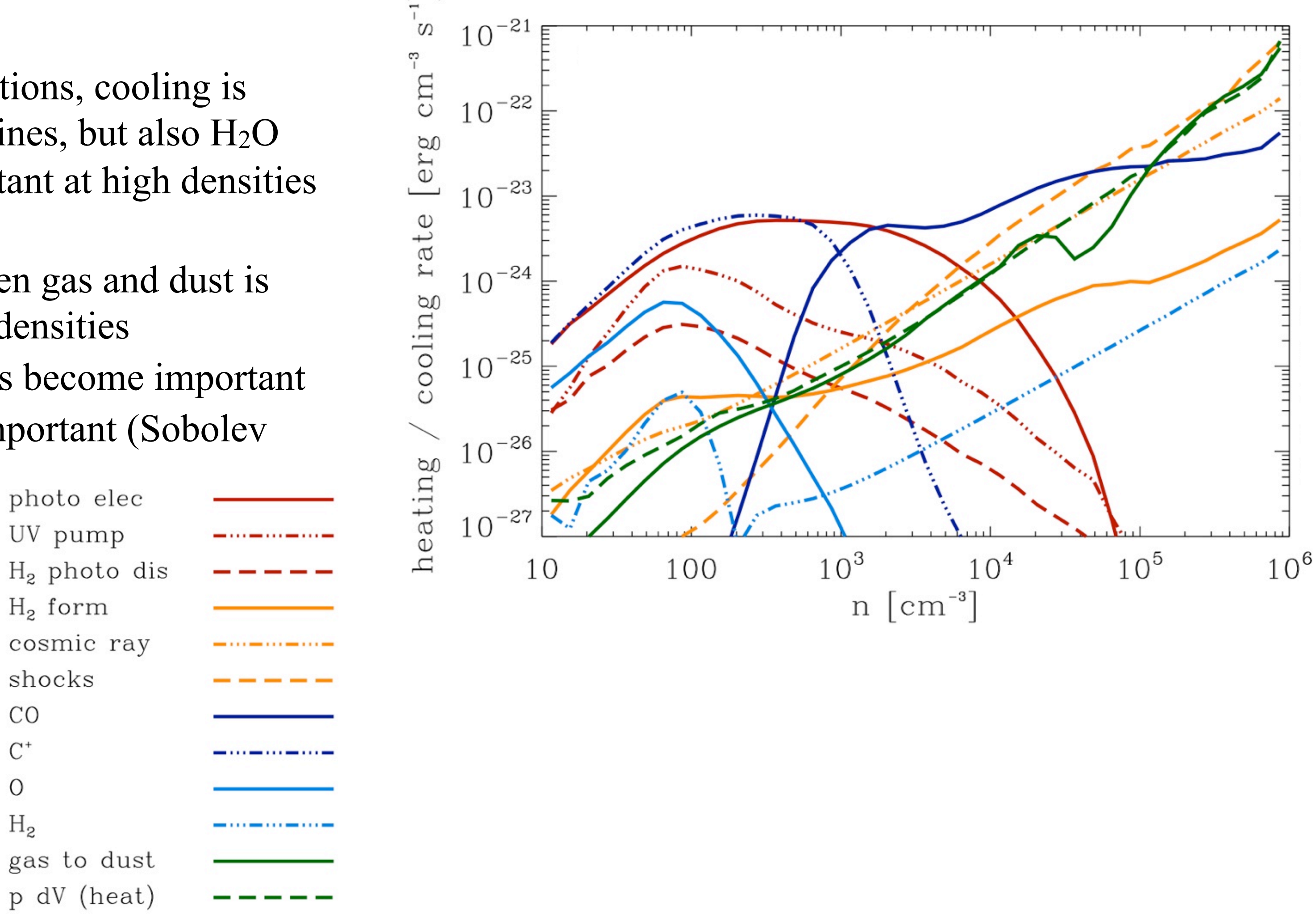
Figure 2.11 The calculated cooling rate per H_2 molecule for 10 and 40 K molecular gas as a function of density.

figure from A. Tielens: Physics and Chemistry of the ISM (Cambridge University Press)

cooling in molecular gas 2

- molecular gas has many very efficient pathways for cooling
- molecular vibrational and rotational levels are easily excited and can efficiently remove energy from the system

- under typical conditions, cooling is dominated by CO lines, but also H_2O can be come important at high densities and temperatures
- the coupling between gas and dust is important for high densities
- optical depth effects become important
- dynamics is also important (Sobolev approximation)



Glover & Clark (2011, MNRAS, 421, 9)

heating rates

photo-electric heating 1

- this is the most important heating mechanism in the neutral ISM
- when a photon hits a PAH or a small dust grain it may release an electron
- this electron may diffuse through the grain and eventually leave the grain

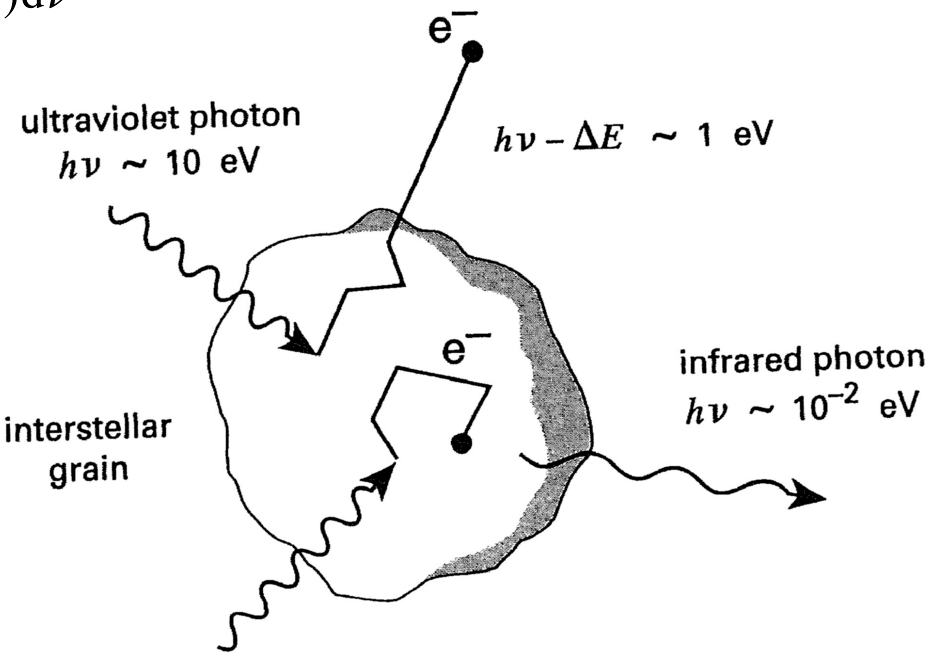
- typical energy gain per event:

$$\frac{3}{2}kT_{\mathrm{grain}} = \frac{\int_{\nu_i}^{\nu_\mathrm{H}} \mathcal{N}(\nu)\alpha_{\mathrm{grain}}(\nu)E_{\mathrm{kin}}\mathrm{d}\nu}{\int_{\nu_i}^{\nu_\mathrm{H}} \mathcal{N}(\nu)\alpha_{\mathrm{grain}}(\nu)\mathrm{d}\nu}$$

- with
  α_{grain} = ionization cross section of the grains
  E_{kin} = kinetic energy of the photo-electron
  $\nu_i = (W + \Phi)/h$ = photon energy required for ionization
  W = work function for diffusion inside grain
  Φ = Coulomb barrier if grain is positively charged

- average energy per ionization event

$$\overline{E}_{\mathrm{kin}}/k \simeq 50\,000\,\mathrm{K}$$



A. Tielens: Physics and Chemistry of the ISM (Cambridge University Press)

photo-electric heating 2

- calculating the photo-electric heating rate in detail is very complex
- the result is

$$n\Gamma_{\rm pe} = 10^{-24} \epsilon n G_0 \, {\rm erg \, cm^{-3} \, s^{-1}}$$

with the heating efficiency $$\epsilon = \frac{4.87 \times 10^{-2}}{1 + 4 \times 10^{-3} \gamma^{0.73}} + \frac{3.65 \times 10^{-2} (T/10^4)^{0.7}}{1 + 2 \times 10^{-4} \gamma}$$

and $\gamma = G_0 T^{1/2} / n_{\rm e}$

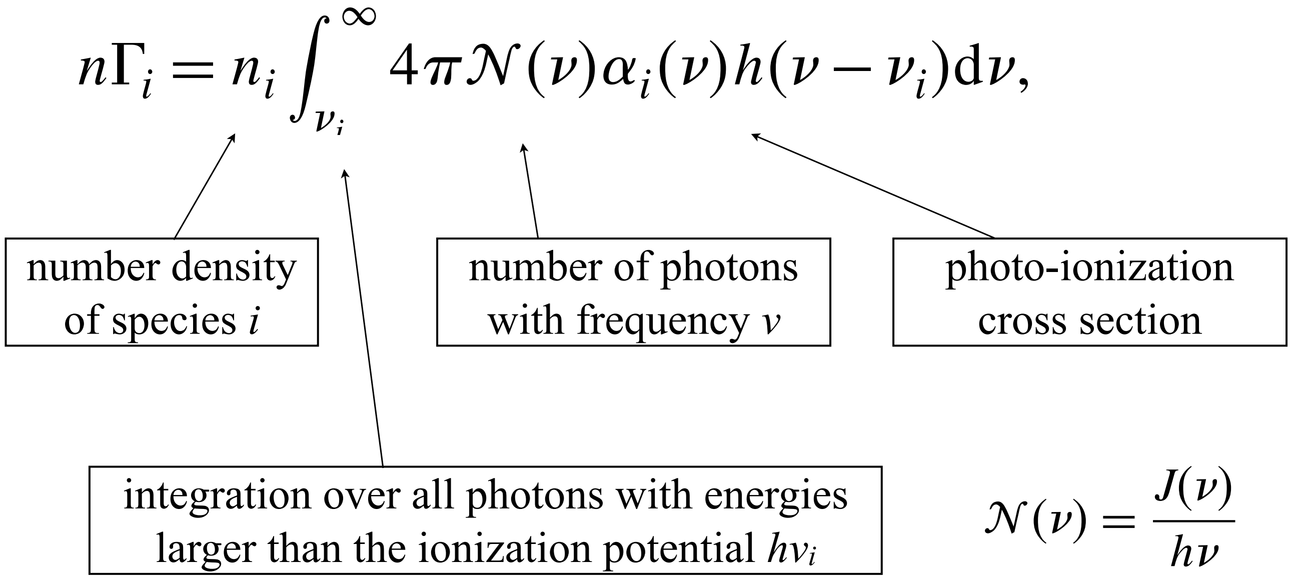
(recall that G_0 is the Habing field)

A. Tielens: Physics and Chemistry of the ISM (Cambridge University Press)

photo-ionization 1

- when a photon ionizes an atom the photon energy minus the ionization potential goes into kinetic energy of the free electron; this energy can quickly be shared by the surrounding gas particles

- heating rate for element *i* is



$$n\Gamma_i = n_i \int_{\nu_i}^{\infty} 4\pi \mathcal{N}(\nu)\alpha_i(\nu)h(\nu-\nu_i)\mathrm{d}\nu,$$

number density of species *i*

number of photons with frequency ν

photo-ionization cross section

integration over all photons with energies larger than the ionization potential $h\nu_i$

$$\mathcal{N}(\nu) = \frac{J(\nu)}{h\nu}$$

A. Tielens: Physics and Chemistry of the ISM (Cambridge University Press)

photo-ionization 2

- when a photon ionizes an atom the photon energy minus the ionization potential goes into kinetic energy of the free electron; this energy can quickly be shared by the surrounding gas particles

- we can define the average energy 1.5 kT_i carried away by the photo electron (i.e the average kinetic energy produced per ionization event) can be defined as

$$\frac{3}{2}kT_i = \frac{\int_{\nu_i}^{\infty} \mathcal{N}(\nu)\alpha_i(\nu)h(\nu-\nu_i)\mathrm{d}\nu}{\int_{\nu_i}^{\infty} \mathcal{N}(\nu)\alpha_i(\nu)\mathrm{d}\nu}$$

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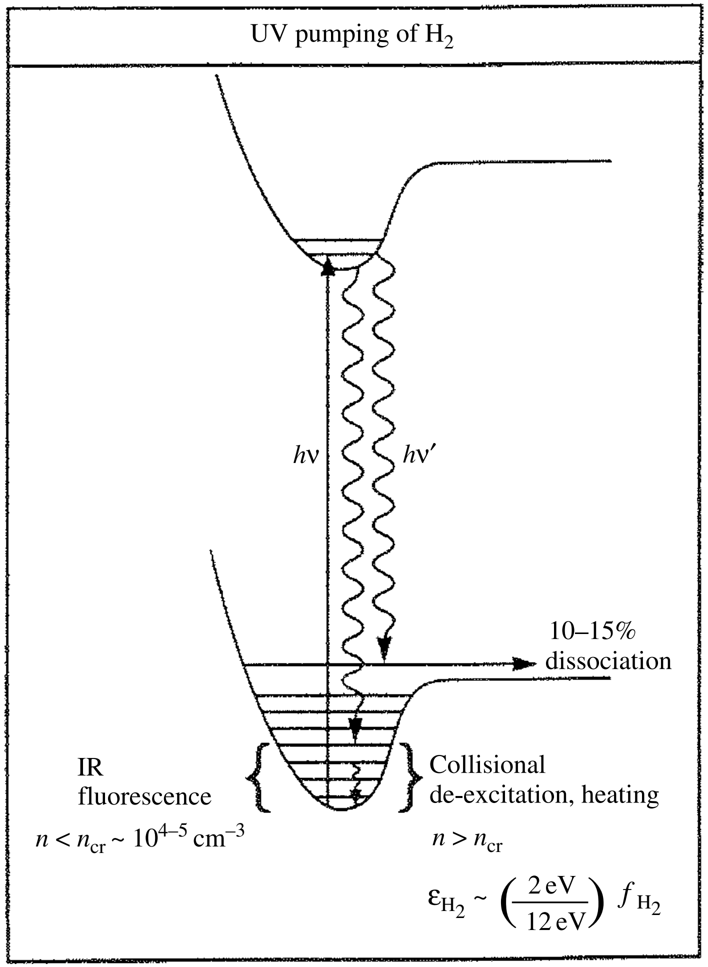
photo heating by H_2 1

- photodissociation of a molecule will heat the gas: the fragments carry away some of the energy
- however, also the ***reformation*** of the molecule will heat the gas:
  - often the newly formed species is in an excited state (typically in an vibrationally excited state)
  - collisional decay leads to heating
- because of the large abundance, photo heating of H_2 will most important photo heating process



$$\varepsilon_{H_2} \sim \left(\frac{2\,\mathrm{eV}}{12\,\mathrm{eV}}\right) f_{H_2}$$

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photo heating by H_2 2

H_2 absorbs FUV photon from ground-electronic state to excited electronic state

10% decays back to the vibrational continuum of the ground electronic state → the molecule dissociates

this delivers 0.25 eV directly

heating rate:

$$n\Gamma_{\rm pd} = 4 \times 10^{-14} n({\rm H_2}) k_{\rm pump}\,{\rm erg\,cm^{-3}\,s^{-1}}$$

with pumping rate

$$k_{\rm pump} = 3.4 \times 10^{-10} \beta(\tau) G_0 \exp[-2.6\,A_v]\,{\rm s^{-1}}$$

attenuation of the ambient radiation field enters via β(τ) for self-shielding and via the exponential factor taking dust extinction into account

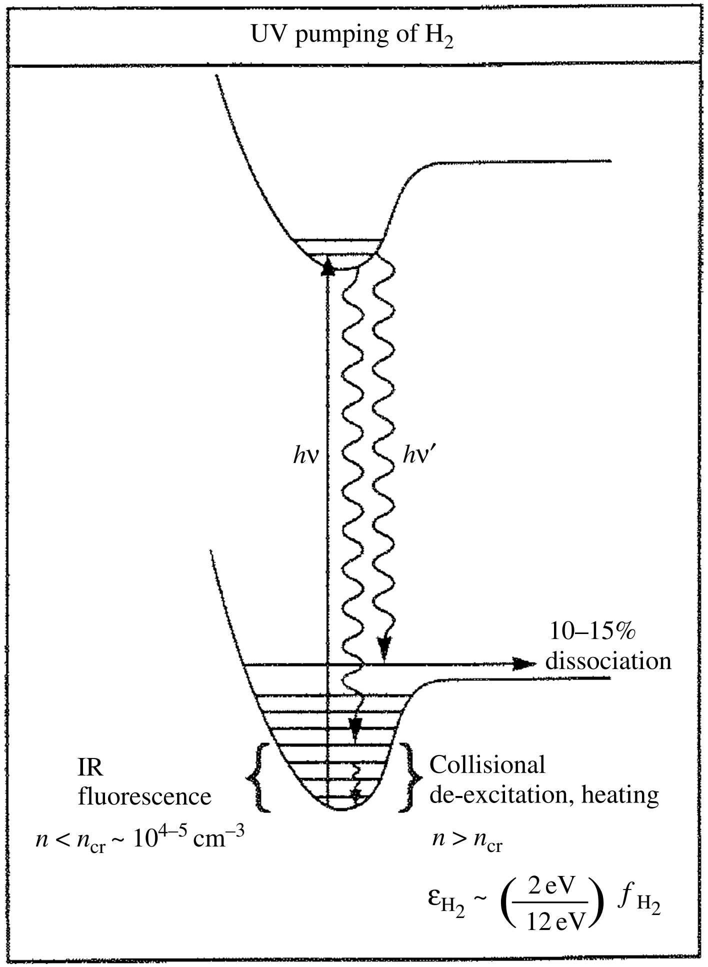

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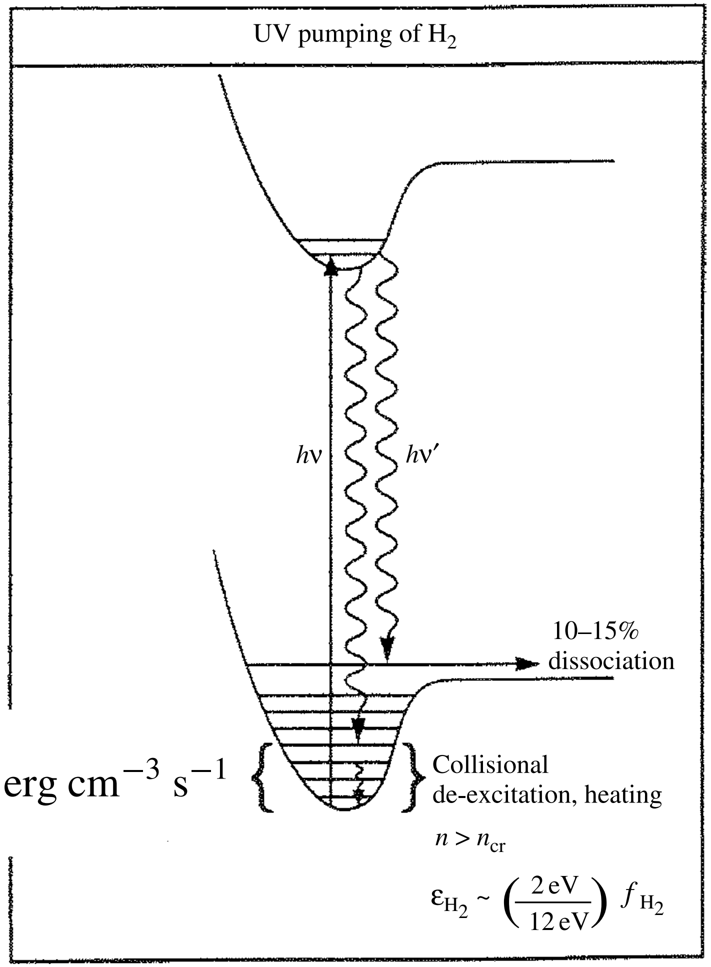
photo heating by H_2 3

H_2 absorbs FUV photon from ground-electronic state to excited electronic state

most H2 molecules decay back into bound vibrational states of ground electronic state

the molecule then slowly go down further either via the emission of IR photons or via collisions

efficiency of process depends on density (number of collisions) and vibrational level population + extinction + shielding



$$n\Gamma_{H_2} \simeq 2.9\times10^{-11} n n_H k_d \left[1+\left(\frac{n_{cr}}{n}\right)+\frac{4.4\times10^2\,G_0}{n\,T^{1/2}\exp[-1000/T]}\right]^{-1} \mathrm{erg\ cm^{-3}\ s^{-1}}$$

at edge of a warm ($T \sim 1000$ K) cloud, $A_v = 0$ and $\beta(\tau=0)=1$

$$n_{cr} = A/\gamma \simeq 10^5/T^{0.5}\exp[-1000/T]\,\mathrm{cm^{-3}}$$

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H_2 formation heating (on dust)

- also when H_2 forms on dust, the binding energy (~ 4.5 eV) is available
- the newly formed molecule is in highly excited vibrational and rotational state on the grain surface
- some of this energy may be transferred to the grain, but if the H2 molecule is ejected quickly a fraction of this energy is carried away and available to heat the gas

$$n\Gamma_{\rm chem} = 7.2 \times 10^{-12} \frac{n_{\rm H} n k_{\rm d}}{1 + n_{\rm cr}/n} \epsilon_{\rm chem} \, {\rm erg\ cm^{-3}\ s^{-1}}$$

with $\epsilon_{\rm chem}$ being small (maybe ~0.2)

- side remark: 3-body H_2 formation in the gas phase is important heat source at high densities during primordial star formation

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gas-dust coupling

- we have seen before that dust acts as a thermostat and that collisions couple gas and dust together
- if dust is warmer than gas (e.g. in the envelope of a protostar) it provides heating to the gas

$$n\Gamma_{\mathrm{g-d}} = n n_{\mathrm{d}} \sigma_{\mathrm{d}} \left(\frac{8kT}{\pi m} \right)^{1/2} (2kT_{\mathrm{d}} - 2kT) \alpha_{\mathrm{a}}$$

- with experimental and numerical data this turns into

$$n\Gamma_{\mathrm{g-d}} \simeq 10^{-33} n^2 T^{1/2} (T_{\mathrm{d}} - T) \, \mathrm{erg\ cm^{-3}\ s^{-1}}$$

- at lower densities (diffuse ISM) dust provides cooling rather than acts as a heat source

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cosmic ray heating

- cosmic rays can ionize gas particles, as cosmic rays are very energetic, the products of the primary ionization event can ionize further particles (secondary ionization)

- ionization rate

$$n\xi_{\rm CR} = n\zeta_{\rm CR}[1 + \phi^{\rm H}(E, x_{\rm e}) + \phi^{\rm He}(E, x_{\rm e})]$$

x_e = electron fraction, $\Phi^i(E, x_e)$ = average number of secondary ionizations

- the heating rate is

$$n\Gamma_{\rm CR} = n\zeta_{\rm CR} E_{\rm h}(E, x_{\rm e})$$

- typical values are $\zeta_{CR} \sim 2 \times 10^{-16}$ s^{-1} and $\xi_{CR} \sim 3 \times 10^{-16}$ s^{-1} and $E_h(E,x_e) \sim 7$ eV which leads to

$$n\Gamma_{\rm CR} = 3 \times 10^{-27} n \left[\frac{\zeta_{\rm CR}}{2 \times 10^{-16}}\right] \,{\rm erg\,cm^{-3}\,s^{-1}}$$

- this provides a primary heating source in the inner well-shielded parts of dense cloud cores, where all other heating sources are no longer effective
  → sets a lower temperature floor of ~ 7 K in dense starless cores

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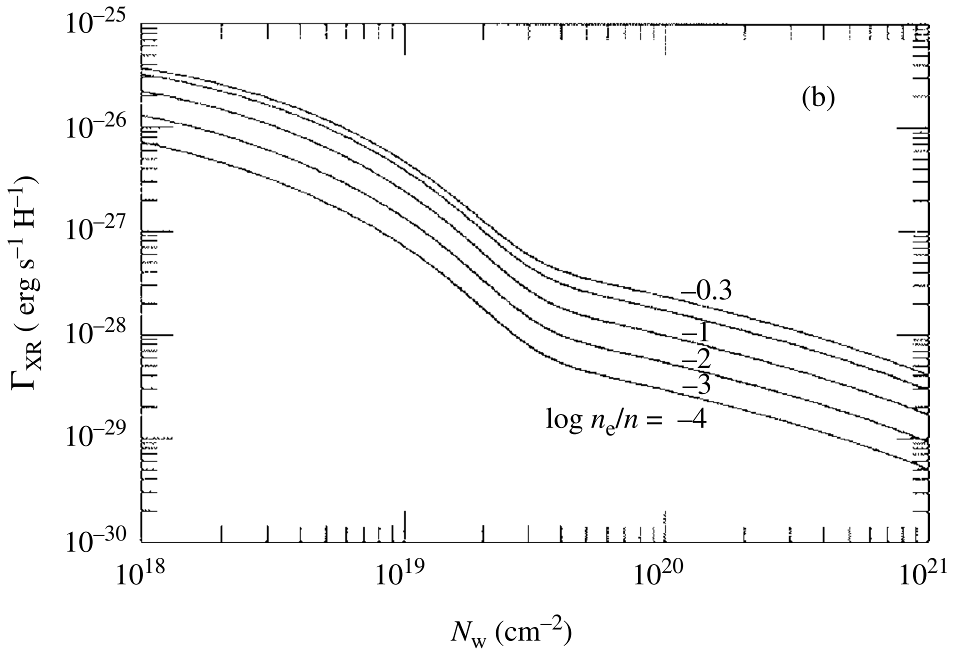
x-ray heating

- x-ray ionization rate

$$n\zeta_{\mathrm{XR}} = 4\pi \underset{\text{density}}{\underset{\uparrow}{n}} \int \underset{\text{x-ray mean photon intensity}}{\underset{\uparrow}{\mathcal{N}_{\mathrm{XR}}}}(\nu)\, e^{-\sigma(\nu)\underset{\text{column density}}{\underset{\uparrow}{N}}} \underset{\text{x-ray ionization cross section}}{\underset{\uparrow}{\sigma(\nu)}}\,\mathrm{d}\nu$$

- corresponding heating rate as function of hydrogen column density



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further heating processes

- turbulent heating

$$n\Gamma_{\rm turbulence} = \frac{1/2 n m_{\rm H} v^2}{\ell/v}$$

- ambipolar diffusion heating

$$n\Gamma_{\rm ad} = n_{\rm e} n_{\rm n} m < \sigma v > v_{\rm d}^2$$

- gravitational heating (PdV heating due to gravitational contraction, free-fall solution)

$$n\Gamma_{\rm gravity} = \frac{5}{2} kTv \left| \frac{{\rm d}n}{{\rm d}r} \right| = \frac{15}{4} kT \frac{n}{\tau_{\rm ff}}$$

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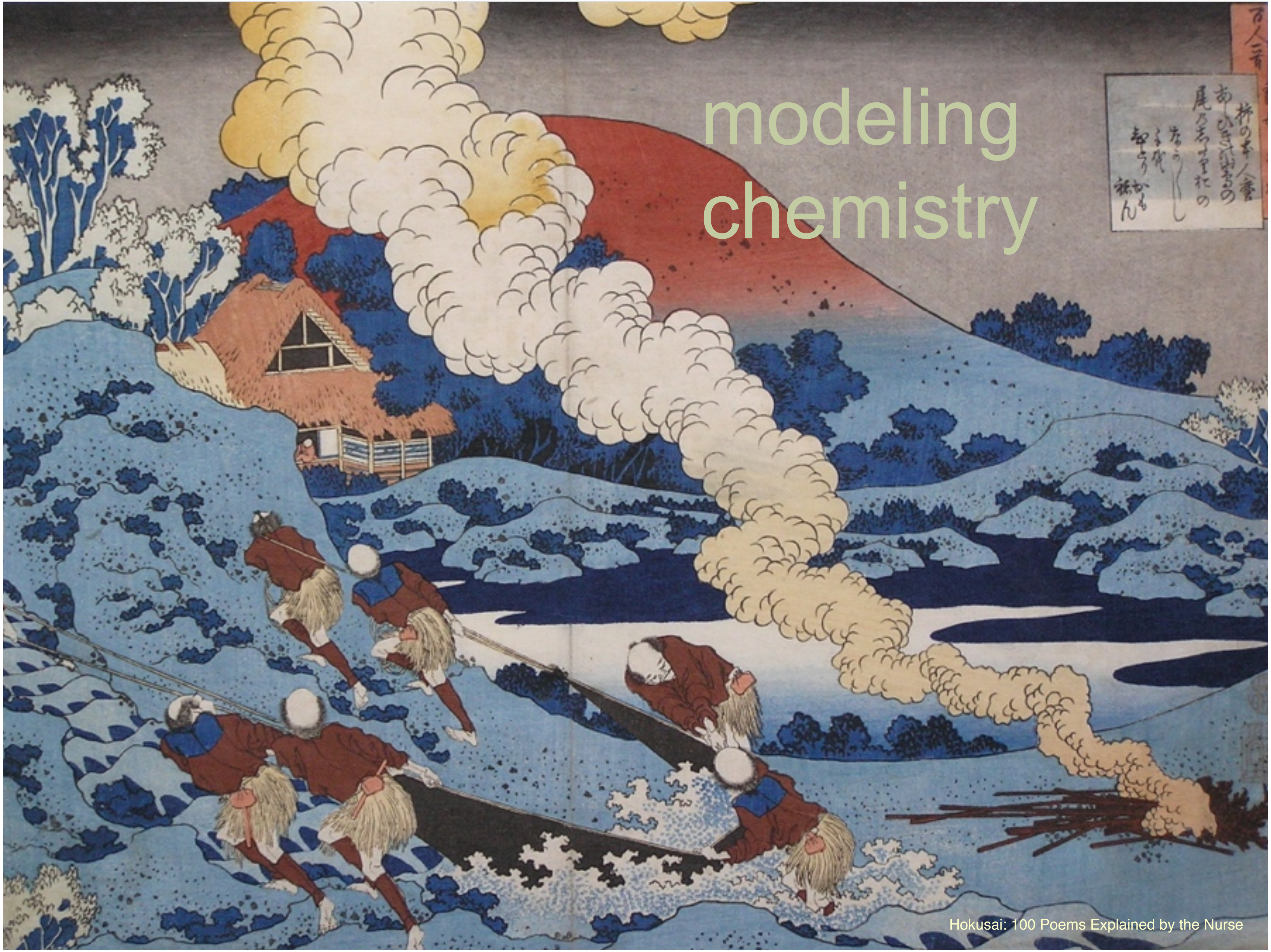
Hiroshige - Evening Shower at Atake and the Great Bridge

end

modeling chemistry



Hokusai: 100 Poems Explained by the Nurse

chemical reactions

gas-phase chemical reactions

reaction categories

- bond-forming reactions (link atoms together into more complex configurations)
- bond-destroying reactions (fragment species into smaller entities), e.g. photodissociation, dissociative recombination, collisional dissociation, etc.
- bond-rearranging processes (transfer parts of one reactant to another one), e.g. ion-molecule exchange reactions, charge-transfer reactions, neutral-neutral reactions, etc.

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gas-phase chemical reactions

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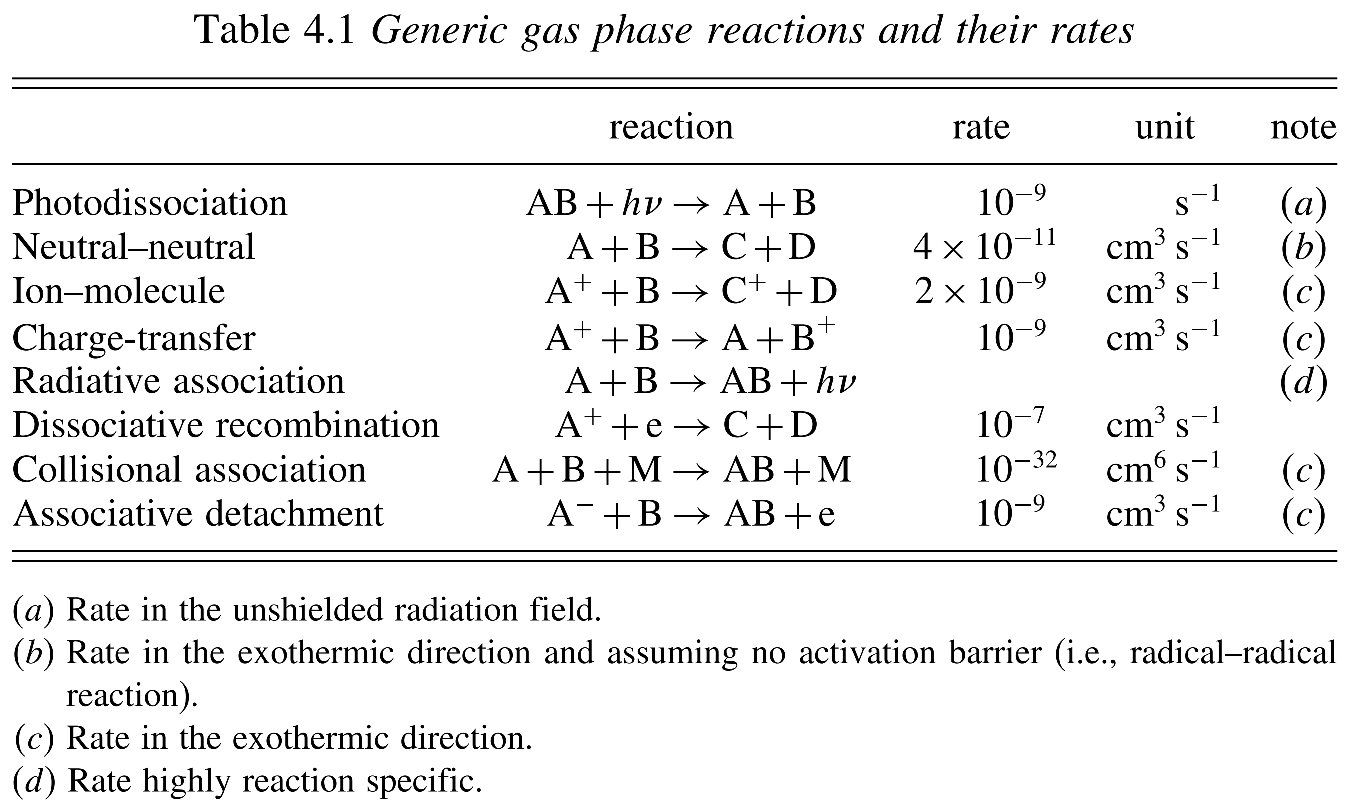

Table 4.1 *Generic gas phase reactions and their rates*

	reaction	rate	unit	note
Photodissociation	$AB + h\nu \rightarrow A + B$	10^{-9}	s^{-1}	(*a*)
Neutral–neutral	$A + B \rightarrow C + D$	4×10^{-11}	$cm^3\ s^{-1}$	(*b*)
Ion–molecule	$A^+ + B \rightarrow C^+ + D$	2×10^{-9}	$cm^3\ s^{-1}$	(*c*)
Charge-transfer	$A^+ + B \rightarrow A + B^+$	10^{-9}	$cm^3\ s^{-1}$	(*c*)
Radiative association	$A + B \rightarrow AB + h\nu$			(*d*)
Dissociative recombination	$A^+ + e \rightarrow C + D$	10^{-7}	$cm^3\ s^{-1}$	
Collisional association	$A + B + M \rightarrow AB + M$	10^{-32}	$cm^6\ s^{-1}$	(*c*)
Associative detachment	$A^- + B \rightarrow AB + e$	10^{-9}	$cm^3\ s^{-1}$	(*c*)

(*a*) Rate in the unshielded radiation field.
(*b*) Rate in the exothermic direction and assuming no activation barrier (i.e., radical–radical reaction).
(*c*) Rate in the exothermic direction.
(*d*) Rate highly reaction specific.

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gas-phase chemical reactions

reaction rates

- the corresponding rates are

$$\frac{\mathrm{d}n(\mathrm{A})}{\mathrm{d}t} = -k\,n(\mathrm{A}) = -\frac{\mathrm{d}n(\mathrm{C})}{\mathrm{d}t}$$

one reactant

$$\frac{\mathrm{d}n(\mathrm{A})}{\mathrm{d}t} = -k\,n(\mathrm{A})\,n(\mathrm{B}) = -\frac{\mathrm{d}n(\mathrm{C})}{\mathrm{d}t}$$

two reaction partners

$$\frac{\mathrm{d}n(\mathrm{A})}{\mathrm{d}t} = -k\,n(\mathrm{A})\,n(\mathrm{B})\,n(\mathrm{M}) = -\frac{\mathrm{d}n(\mathrm{AB})}{\mathrm{d}t}$$

three reaction partners

- so, modeling chemistry is all about finding the right reaction coefficients ***k***
- in the above the photodissociation or ionization belongs to the first category (radiation is a ‘background’ field)

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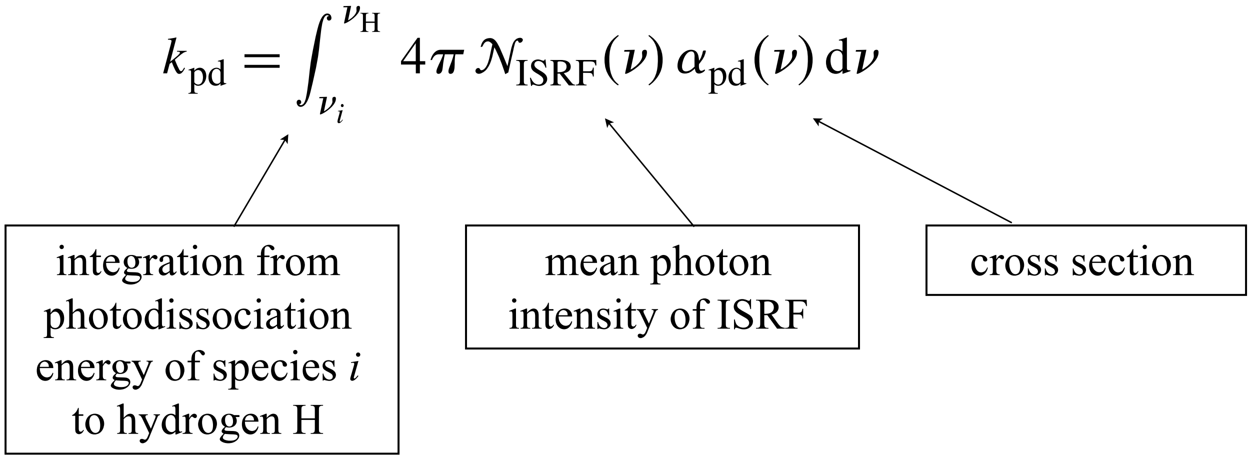
photochemistry

- photodissociation rate

$$\boxed{\mathrm{AB} + h\nu \rightarrow \mathrm{A} + \mathrm{B}}$$



$$k_{\mathrm{pd}} = \int_{\nu_i}^{\nu_{\mathrm{H}}} 4\pi\, \mathcal{N}_{\mathrm{ISRF}}(\nu)\, \alpha_{\mathrm{pd}}(\nu)\, \mathrm{d}\nu$$

integration from photodissociation energy of species *i* to hydrogen H

mean photon intensity of ISRF

cross section

- parametrization

$$\boxed{k_{\mathrm{pd}} = a \exp[-bA_v]}$$

Table 4.2 *Some important photo reactions and their rates*[a]

Reaction			*a*	*b*
CH	→	C + H	2.7 (−10)	1.3
CH_2	→	CH + H	5.0 (−11)	1.7
CH	→	C + H	2.7 (−10)	1.3
O_2	→	O + O	3.3 (−10)	1.4
OH	→	O + H	7.6 (−10)	2.0
CO	→	C + O	1.7 (−10)	3.2[b]
H_2O	→	OH + H	5.1 (−10)	1.8
CH	→	$CH^+ + e$	3.2 (−10)	3.0
CH_2	→	$CH_2^+ + e$	1.0 (−9)	2.3
CH^+	→	$C^+ + H$	1.8 (−10)	2.8
CH_2^+	→	$CH^+ + H$	1.7 (−9)	1.7
CH_3^+	→	$CH_2^+ + H$	1.0 (−9)	1.7
CH_3^+	→	$CH^+ + H_2$	1.0 (−9)	1.7

[a] Rates are $k_{\mathrm{pd}} = a \exp[-bA_v]$.

[b] Self-shielding can be important for CO dissociation.

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neutral-neutral reactions

$$\boxed{\mathrm{A}+\mathrm{B} \rightleftharpoons \mathrm{C}+\mathrm{D}+\Delta E,}$$

- neutral-neutral reactions often involve a enthalpy difference

$$\Delta H(\mathrm{reaction}) = H(\mathrm{products}) - H(\mathrm{reactants})$$

- which leads to a energy barrier $\Delta E = -\Delta H$

- typical rate coefficients have the form

$$\boxed{k = \alpha\,(T/300)^{\beta} \exp[-\gamma/kT]}$$

Table 4.4 *Neutral–neutral reactions* [a]

reaction	α	β	γ
$H_2+O \rightarrow OH+H$	9.0(−12)	1.0	4.5(3)
$H+OH \rightarrow O+H_2$	4.2(−12)	1.0	3.5(3)
$H_2+OH \rightarrow H_2O+H$	3.6(−11)		2.1(3)
$H+H_2O \rightarrow OH+H_2$	1.5(−10)		1.0(4)
$H+O_2 \rightarrow OH+O$	3.7(−10)		8.5(3)
$OH+O \rightarrow O_2+H$	4.0(−10)		6.0(2)
$H_2+C \rightarrow CH+H$	1.2(−9)	0.5	1.4(4)
$H+CH \rightarrow C+H_2$	1.2(−9)	0.5	2.2(3)
$C^+ +H_2 \rightarrow CH^+ +H$	9.4(−12)	1.25	4.7(3)

[a] Reaction rates of the form $k = \alpha\,(T/300)^{\beta} \exp[-\gamma/kT]$.

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ion-molecule reactions

- ion-molecule reactions occur usually rapidly because the have a strong polarization-induced interaction potential which helps to overcome activation barrier
- reactions are typically very fast
- even small amounts of ionization can drive very rich chemistry
- rate coefficients are typically constants that correspond to effective geometric cross sections

$$\boxed{k = \alpha}$$

$$\boxed{A^+ + B \rightarrow C^+ + D}$$

Table 4.7 *Ion–molecule reactions*

reaction	α
$H_2^+ + H_2 \rightarrow H_3^+ + H$	2.1 (–9)
$H_3^+ + O \rightarrow OH^+ + H_2$	8.0 (–10)
$H_3^+ + CO \rightarrow HCO^+ + H_2$	1.7 (–9)
$H_3^+ + H_2O \rightarrow H_3O^+ + H_2$	5.9 (–9)
$OH^+ + H_2 \rightarrow H_2O^+ + H$	1.1 (–9)
$H_2O^+ + H_2 \rightarrow H_3O^+ + H$	6.1 (–10)
$C^+ + OH \rightarrow CO^+ + H$	7.7 (–10)
$C^+ + H_2O \rightarrow HCO^+ + H$	2.7 (–9)
$CO^+ + H_2 \rightarrow HCO^+ + H$	2.0 (–9)
$He^+ + CO \rightarrow C^+ + O + He$	1.6 (–9)
$He^+ + O_2 \rightarrow O^+ + O + He$	1.0 (–9)
$He^+ + H_2O \rightarrow OH^+ + H + He$	3.7 (–10)
$He^+ + H_2O \rightarrow H_2O^+ + He$	7.0 (–11)
$He^+ + OH \rightarrow O^+ + H + He$	1.1 (–9)

[a] Reaction rates are of the form $k = \alpha$.

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further reactions

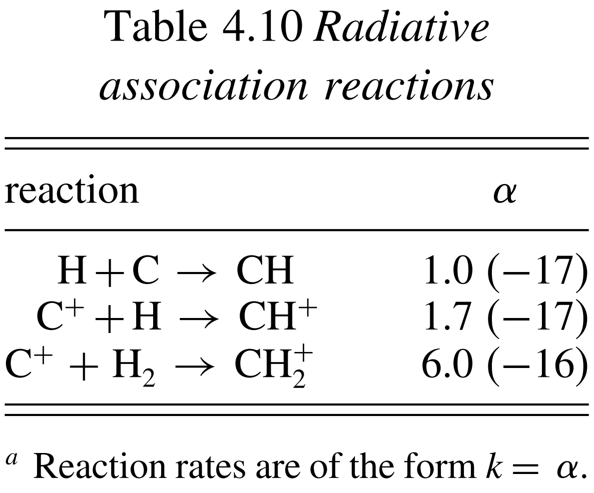

Table 4.10 *Radiative association reactions*

reaction	α
$H + C \rightarrow CH$	1.0 (−17)
$C^+ + H \rightarrow CH^+$	1.7 (−17)
$C^+ + H_2 \rightarrow CH_2^+$	6.0 (−16)

[a] Reaction rates are of the form $k = \alpha$.

$$\boxed{k = \alpha}$$

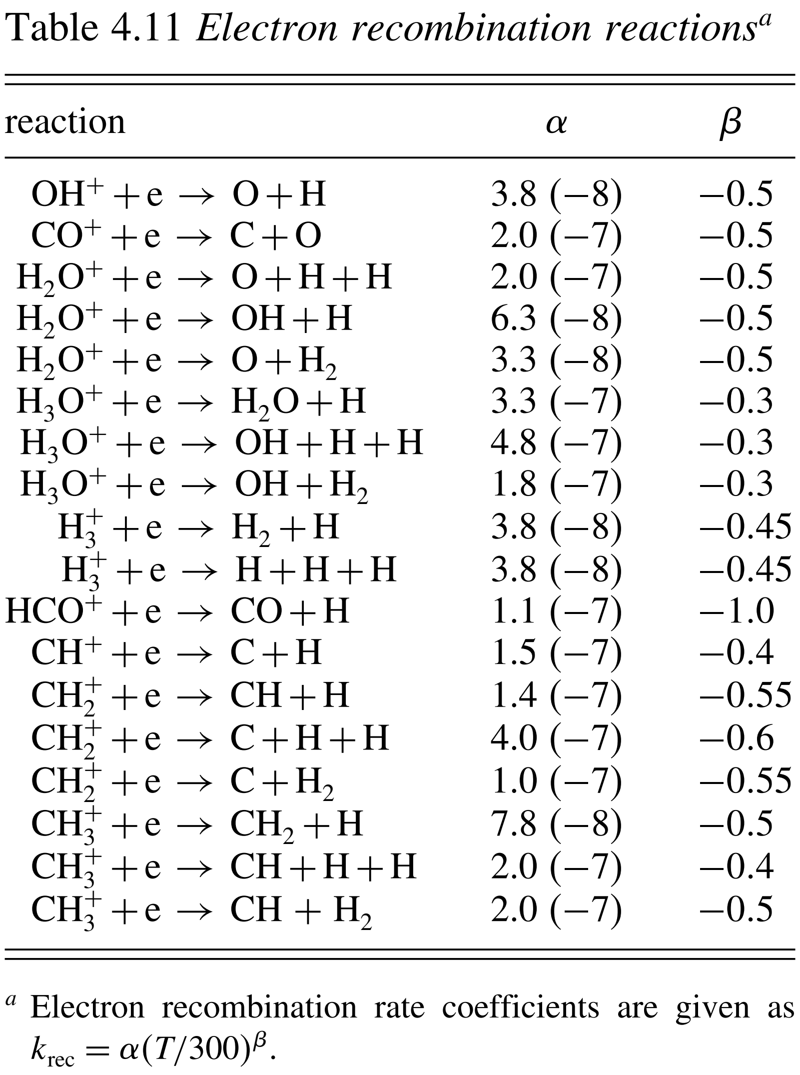

Table 4.11 *Electron recombination reactions*[a]

reaction	α	β
$OH^+ + e \rightarrow O + H$	3.8 (−8)	−0.5
$CO^+ + e \rightarrow C + O$	2.0 (−7)	−0.5
$H_2O^+ + e \rightarrow O + H + H$	2.0 (−7)	−0.5
$H_2O^+ + e \rightarrow OH + H$	6.3 (−8)	−0.5
$H_2O^+ + e \rightarrow O + H_2$	3.3 (−8)	−0.5
$H_3O^+ + e \rightarrow H_2O + H$	3.3 (−7)	−0.3
$H_3O^+ + e \rightarrow OH + H + H$	4.8 (−7)	−0.3
$H_3O^+ + e \rightarrow OH + H_2$	1.8 (−7)	−0.3
$H_3^+ + e \rightarrow H_2 + H$	3.8 (−8)	−0.45
$H_3^+ + e \rightarrow H + H + H$	3.8 (−8)	−0.45
$HCO^+ + e \rightarrow CO + H$	1.1 (−7)	−1.0
$CH^+ + e \rightarrow C + H$	1.5 (−7)	−0.4
$CH_2^+ + e \rightarrow CH + H$	1.4 (−7)	−0.55
$CH_2^+ + e \rightarrow C + H + H$	4.0 (−7)	−0.6
$CH_2^+ + e \rightarrow C + H_2$	1.0 (−7)	−0.55
$CH_3^+ + e \rightarrow CH_2 + H$	7.8 (−8)	−0.5
$CH_3^+ + e \rightarrow CH + H + H$	2.0 (−7)	−0.4
$CH_3^+ + e \rightarrow CH + H_2$	2.0 (−7)	−0.5

[a] Electron recombination rate coefficients are given as $k_{\rm rec} = \alpha (T/300)^{\beta}$.

$$\boxed{k_{\rm rec} = \alpha (T/300)^{\beta}}$$

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chemical reaction network

$$\frac{\mathrm{d}n(i)}{\mathrm{d}t} = -n(i)\sum_j n(j)k_{ij} + \sum_{j,k} n(j)n(k)k_{jk} + \sum_j n(j)k_j - n(i)\sum_j k_j$$

change of species *i* with time

sum of all bimolecular reactions destroying species *i*

sum of all bimolecular reactions forming species *i*

sum of all unimolecular reactions forming / destroying species *i*

e.g. photodissociation, photoionization, CR-ionization

Master equation describing summing over all gain and loss reactions

this network includes only unimolecular und bimolecular reactions (no triple reactions)

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chemical reaction network

$$\frac{\mathrm{d}n(i)}{\mathrm{d}t} = -n(i)\sum_{j} n(j)k_{ij} + \sum_{j,k} n(j)n(k)k_{jk} + \sum_{j} n(j)k_{j} - n(i)\sum_{j} k_{j}$$

change of species i with time

sum of all bimolecular reactions destroying species i

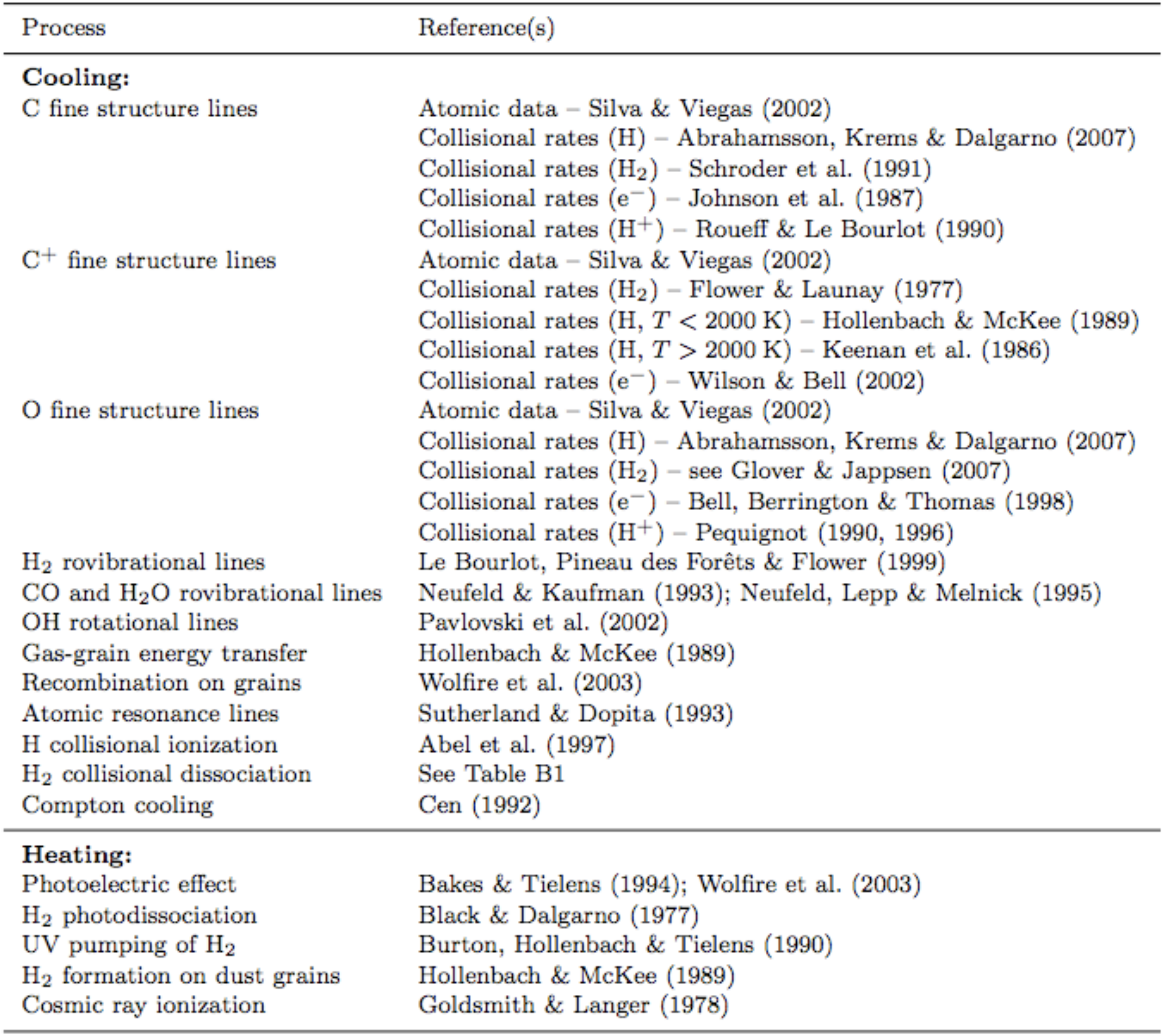
sum of all bimolecular reactions forming species i

sum of all unimolecular reactions forming / destroying species i

e.g. photodissociation, photoionization, CR-ionization

vector $\boldsymbol{n}(t)$ contains the abundances of all species

in steady state $\sum_i \frac{dn(i)}{dt} = 0$



Process	Reference(s)
Cooling:	
C fine structure lines	Atomic data – Silva & Viegas (2002)
	Collisional rates (H) – Abrahamsson, Krems & Dalgarno (2007)
	Collisional rates (H_2) – Schroder et al. (1991)
	Collisional rates (e^-) – Johnson et al. (1987)
	Collisional rates (H^+) – Roueff & Le Bourlot (1990)
C^+ fine structure lines	Atomic data – Silva & Viegas (2002)
	Collisional rates (H_2) – Flower & Launay (1977)
	Collisional rates (H, $T < 2000$ K) – Hollenbach & McKee (1989)
	Collisional rates (H, $T > 2000$ K) – Keenan et al. (1986)
	Collisional rates (e^-) – Wilson & Bell (2002)
O fine structure lines	Atomic data – Silva & Viegas (2002)
	Collisional rates (H) – Abrahamsson, Krems & Dalgarno (2007)
	Collisional rates (H_2) – see Glover & Jappsen (2007)
	Collisional rates (e^-) – Bell, Berrington & Thomas (1998)
	Collisional rates (H^+) – Pequignot (1990, 1996)
H_2 rovibrational lines	Le Bourlot, Pineau des Forêts & Flower (1999)
CO and H_2O rovibrational lines	Neufeld & Kaufman (1993); Neufeld, Lepp & Melnick (1995)
OH rotational lines	Pavlovski et al. (2002)
Gas-grain energy transfer	Hollenbach & McKee (1989)
Recombination on grains	Wolfire et al. (2003)
Atomic resonance lines	Sutherland & Dopita (1993)
H collisional ionization	Abel et al. (1997)
H_2 collisional dissociation	See Table B1
Compton cooling	Cen (1992)
Heating:	
Photoelectric effect	Bakes & Tielens (1994); Wolfire et al. (2003)
H_2 photodissociation	Black & Dalgarno (1977)
UV pumping of H_2	Burton, Hollenbach & Tielens (1990)
H_2 formation on dust grains	Hollenbach & McKee (1989)
Cosmic ray ionization	Goldsmith & Langer (1978)

(Glover, Federrath, Mac Low, Klessen, 2010, MNRS, 404, 2)

No.	Reaction	Rate coefficient ($\mathrm{cm^3\,s^{-1}}$)
1	$\mathrm{H + e^- \rightarrow H^- + \gamma}$	$k_1 = \mathrm{dex}[-17.845 + 0.762 \log T + 0.1523 (\log T)^2 - 0.03274(\log T)^3]$ $= \mathrm{dex}[-16.420 + 0.1998(\log T)^2 - 5.447 \times 10^{-3}(\log T)^4 + 4.0415 \times 10^{-5}(\log T)^6]$
2	$\mathrm{H^- + H \rightarrow H_2 + e^-}$	$k_2 = 1.5 \times 10^{-9}$ $= 4.0 \times 10^{-9} T^{-0.17}$
3	$\mathrm{H + H^+ \rightarrow H_2^+ + \gamma}$	$k_3 = \mathrm{dex}[-19.38 - 1.523 \log T + 1.118(\log T)^2 - 0.1269(\log T)^3]$
4	$\mathrm{H + H_2^+ \rightarrow H_2 + H^+}$	$k_4 = 6.4 \times 10^{-10}$
5	$\mathrm{H^- + H^+ \rightarrow H + H}$	$k_5 = 2.4 \times 10^{-6}\, T^{-1/2}\, (1.0 + T/20\,000)$
6	$\mathrm{H_2^+ + e^- \rightarrow H + H}$	$k_6 = 1.0 \times 10^{-8}$ $= 1.32 \times 10^{-6} T^{-0.76}$
7	$\mathrm{H_2 + H^+ \rightarrow H_2^+ + H}$	$k_7 = [-3.323\,2183 \times 10^{-7} + 3.373\,5382 \times 10^{-7} \ln T - 1.449\,1368 \times 10^{-7}(\ln T)^2 + 3.417\,2805 \times 10^{-8}(\ln T)^3 - 4.781\,3720 \times 10^{-9}(\ln T)^4 + 3.973\,1542 \times 10^{-10}(\ln T)^5 - 1.817\,1411 \times 10^{-11}(\ln T)^6 + 3.531\,1932 \times 10^{-13}(\ln T)^7] \times \exp\left(\frac{-21\,237.15}{T}\right)$
8	$\mathrm{H_2 + e^- \rightarrow H + H + e^-}$	$k_8 = 3.73 \times 10^{-9} T^{0.1121} \exp\left(\frac{-99\,430}{T}\right)$
9	$\mathrm{H_2 + H \rightarrow H + H + H}$	$k_{9,1} = 6.67 \times 10^{-12} T^{1/2} \exp\left[-(1 + \frac{63\,590}{T})\right]$ $k_{9,\mathrm{h}} = 3.52 \times 10^{-9} \exp\left(-\frac{43\,900}{T}\right)$ $n_{\mathrm{cr,H}} = \mathrm{dex}\left[3.0 - 0.416 \log\left(\frac{T}{10\,000}\right) - 0.327 \left\{\log\left(\frac{T}{10\,000}\right)\right\}^2\right]$

(Glover, Federrath, Mac Low, Klessen, 2010, MNRS, 404, 2)

No.	Reaction	Rate coefficient ($cm^3\ s^{-1}$)
36	$CH + H_2 \rightarrow CH_2 + H$	$k_{36} = 5.46 \times 10^{-10} \exp\left(-\frac{1943}{T}\right)$
37	$CH + C \rightarrow C_2 + H$	$k_{37} = 6.59 \times 10^{-11}$
38	$CH + O \rightarrow CO + H$	$k_{38} = 6.6 \times 10^{-11}$
		$= 1.02 \times 10^{-10} \exp\left(-\frac{914}{T}\right)$
39	$CH_2 + H \rightarrow CH + H_2$	$k_{39} = 6.64 \times 10^{-11}$
40	$CH_2 + O \rightarrow CO + H + H$	$k_{40} = 1.33 \times 10^{-10}$
41	$CH_2 + O \rightarrow CO + H_2$	$k_{41} = 8.0 \times 10^{-11}$
42	$C_2 + O \rightarrow CO + C$	$k_{42} = 5.0 \times 10^{-11} \left(\frac{T}{300}\right)^{0.5}$
		$= 5.0 \times 10^{-11} \left(\frac{T}{300}\right)^{0.757}$
43	$O + H_2 \rightarrow OH + H$	$k_{43} = 3.14 \times 10^{-13} \left(\frac{T}{300}\right)^{2.7} \exp\left(-\frac{3150}{T}\right)$
44	$OH + H \rightarrow O + H_2$	$k_{44} = 6.99 \times 10^{-14} \left(\frac{T}{300}\right)^{2.8} \exp\left(-\frac{1950}{T}\right)$
45	$OH + H_2 \rightarrow H_2O + H$	$k_{45} = 2.05 \times 10^{-12} \left(\frac{T}{300}\right)^{1.52} \exp\left(-\frac{1736}{T}\right)$
46	$OH + C \rightarrow CO + H$	$k_{46} = 1.0 \times 10^{-10}$
47	$OH + O \rightarrow O_2 + H$	$k_{47} = 3.50 \times 10^{-11}$
		$= 1.77 \times 10^{-11} \exp\left(\frac{178}{T}\right)$
48	$OH + OH \rightarrow H_2O + H$	$k_{48} = 1.65 \times 10^{-12} \left(\frac{T}{300}\right)^{1.14} \exp\left(-\frac{50}{T}\right)$
49	$H_2O + H \rightarrow H_2 + OH$	$k_{49} = 1.59 \times 10^{-11} \left(\frac{T}{300}\right)^{1.2} \exp\left(-\frac{9610}{T}\right)$
50	$O_2 + H \rightarrow OH + O$	$k_{50} = 2.61 \times 10^{-10} \exp\left(-\frac{8156}{T}\right)$
51	$O_2 + H_2 \rightarrow OH + OH$	$k_{51} = 3.16 \times 10^{-10} \exp\left(-\frac{21\,890}{T}\right)$
52	$O_2 + C \rightarrow CO + O$	$k_{52} = 4.7 \times 10^{-11} \left(\frac{T}{300}\right)^{-0.34}$
		$= 2.48 \times 10^{-12} \left(\frac{T}{300}\right)^{1.54} \exp\left(\frac{613}{T}\right)$
53	$CO + H \rightarrow C + OH$	$k_{53} = 1.1 \times 10^{-10} \left(\frac{T}{300}\right)^{0.5} \exp\left(-\frac{77\,700}{T}\right)$
54	$H_2^+ + H_2 \rightarrow H_3^+ + H$	$k_{54} = 2.24 \times 10^{-9} \left(\frac{T}{300}\right)^{0.042} \exp\left(-\frac{T}{46\,600}\right)$
55	$H_3^+ + H \rightarrow H_2^+ + H_2$	$k_{55} = 7.7 \times 10^{-9} \exp\left(-\frac{17\,560}{T}\right)$

(Glover, Federrath, Mac Low, Klessen, 2010, MNRS, 404, 2)

No.	Reaction	Rate coefficient ($cm^3\ s^{-1}$)	Notes
142	$C + e^- \rightarrow C^- + \gamma$	$k_{142} = 2.25 \times 10^{-15}$	
143	$C + H \rightarrow CH + \gamma$	$k_{143} = 1.0 \times 10^{-17}$	
144	$C + H_2 \rightarrow CH_2 + \gamma$	$k_{144} = 1.0 \times 10^{-17}$	
145	$C + C \rightarrow C_2 + \gamma$	$k_{145} = 4.36 \times 10^{-18} \left(\frac{T}{300}\right)^{0.35} \exp\left(-\frac{161.3}{T}\right)$	
146	$C + O \rightarrow CO + \gamma$	$k_{146} = 2.1 \times 10^{-19}$	$T \leq 300\,K$
		$= 3.09 \times 10^{-17} \left(\frac{T}{300}\right)^{0.33} \exp\left(-\frac{1629}{T}\right)$	$T > 300\,K$
147	$C^+ + H \rightarrow CH^+ + \gamma$	$k_{147} = 4.46 \times 10^{-16} T^{-0.5} \exp\left(-\frac{4.93}{T^{2/3}}\right)$	
148	$C^+ + H_2 \rightarrow CH_2^+ + \gamma$	$k_{148} = 4.0 \times 10^{-16} \left(\frac{T}{300}\right)^{-0.2}$	
149	$C^+ + O \rightarrow CO^+ + \gamma$	$k_{149} = 2.5 \times 10^{-18}$	$T \leq 300\,K$
		$= 3.14 \times 10^{-18} \left(\frac{T}{300}\right)^{-0.15} \exp\left(\frac{68}{T}\right)$	$T > 300\,K$
150	$O + e^- \rightarrow O^- + \gamma$	$k_{150} = 1.5 \times 10^{-15}$	
151	$O + H \rightarrow OH + \gamma$	$k_{151} = 9.9 \times 10^{-19} \left(\frac{T}{300}\right)^{-0.38}$	
152	$O + O \rightarrow O_2 + \gamma$	$k_{152} = 4.9 \times 10^{-20} \left(\frac{T}{300}\right)^{1.58}$	
153	$OH + H \rightarrow H_2O + \gamma$	$k_{153} = 5.26 \times 10^{-18} \left(\frac{T}{300}\right)^{-5.22} \exp\left(-\frac{90}{T}\right)$	
154	$H + H + H \rightarrow H_2 + H$	$k_{154} = 1.32 \times 10^{-32} \left(\frac{T}{300}\right)^{-0.38}$	$T \leq 300\,K$
		$= 1.32 \times 10^{-32} \left(\frac{T}{300}\right)^{-1.0}$	$T > 300\,K$
155	$H + H + H_2 \rightarrow H_2 + H_2$	$k_{155} = 2.8 \times 10^{-31}\ T^{-0.6}$	
156	$H + H + He \rightarrow H_2 + He$	$k_{156} = 6.9 \times 10^{-32}\ T^{-0.4}$	
157	$C + C + M \rightarrow C_2 + M$	$k_{157} = 5.99 \times 10^{-33} \left(\frac{T}{5000}\right)^{-1.6}$	$T \leq 5000\,K$
		$= 5.99 \times 10^{-33} \left(\frac{T}{5000}\right)^{-0.64} \exp\left(\frac{5255}{T}\right)$	$T > 5000\,K$
158	$C + O + M \rightarrow CO + M$	$k_{158} = 6.16 \times 10^{-29} \left(\frac{T}{300}\right)^{-3.08}$	$T \leq 2000\,K$
		$= 2.14 \times 10^{-29} \left(\frac{T}{300}\right)^{-3.08} \exp\left(\frac{2114}{T}\right)$	$T > 2000\,K$
159	$C^+ + O + M \rightarrow CO^+ + M$	$k_{159} = 100 \times k_{210}$	
160	$C + O^+ + M \rightarrow CO^+ + M$	$k_{160} = 100 \times k_{210}$	

(Glover, Federrath, Mac Low, Klessen, 2010, MNRS, 404, 2)

Table B2. List of photochemical reactions included in our chemical model.

No.	Reaction	Optically thin rate (s^{-1})	γ
166	$H^- + \gamma \rightarrow H + e^-$	$R_{166} = 7.1 \times 10^{-7}$	0.5
167	$H_2^+ + \gamma \rightarrow H + H^+$	$R_{167} = 1.1 \times 10^{-9}$	1.9
168	$H_2 + \gamma \rightarrow H + H$	$R_{168} = 5.6 \times 10^{-11}$	See Section 2.2
169	$H_3^+ + \gamma \rightarrow H_2 + H^+$	$R_{169} = 4.9 \times 10^{-13}$	1.8
170	$H_3^+ + \gamma \rightarrow H_2^+ + H$	$R_{170} = 4.9 \times 10^{-13}$	2.3
171	$C + \gamma \rightarrow C^+ + e^-$	$R_{171} = 3.1 \times 10^{-10}$	3.0
172	$C^- + \gamma \rightarrow C + e^-$	$R_{172} = 2.4 \times 10^{-7}$	0.9
173	$CH + \gamma \rightarrow C + H$	$R_{173} = 8.7 \times 10^{-10}$	1.2
174	$CH + \gamma \rightarrow CH^+ + e^-$	$R_{174} = 7.7 \times 10^{-10}$	2.8
175	$CH^+ + \gamma \rightarrow C + H^+$	$R_{175} = 2.6 \times 10^{-10}$	2.5
176	$CH_2 + \gamma \rightarrow CH + H$	$R_{176} = 7.1 \times 10^{-10}$	1.7
177	$CH_2 + \gamma \rightarrow CH_2^+ + e^-$	$R_{177} = 5.9 \times 10^{-10}$	2.3
178	$CH_2^+ + \gamma \rightarrow CH^+ + H$	$R_{178} = 4.6 \times 10^{-10}$	1.7
179	$CH_3^+ + \gamma \rightarrow CH_2^+ + H$	$R_{179} = 1.0 \times 10^{-9}$	1.7
180	$CH_3^+ + \gamma \rightarrow CH^+ + H_2$	$R_{180} = 1.0 \times 10^{-9}$	1.7
181	$C_2 + \gamma \rightarrow C + C$	$R_{181} = 1.5 \times 10^{-10}$	2.1
182	$O^- + \gamma \rightarrow O + e^-$	$R_{182} = 2.4 \times 10^{-7}$	0.5
183	$OH + \gamma \rightarrow O + H$	$R_{183} = 3.7 \times 10^{-10}$	1.7
184	$OH + \gamma \rightarrow OH^+ + e^-$	$R_{184} = 1.6 \times 10^{-12}$	3.1

(Glover, Federrath, Mac Low, Klessen, 2010, MNRS, 404, 2)

solving chemical networks

governing equations 1

- the number density n_i of a chemical species i evolves according to

$$\frac{\partial n_i}{\partial t} + \vec{\nabla} \cdot (n_i \vec{v}) - \vec{\nabla} \cdot \left(\mathcal{D} \vec{\nabla} n_i \right) = C(n_i, n_j, T) - D(n_j, T) n_i$$

- three processes are acting to change n_i: advection, diffusion and chemical reactions
- convenient to write the reaction term in two parts, one corresponding to formation (C) and the other to destruction (D)

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governing equations 2

- in astrophysical flows, we generally ignore the diffusion term, as it is much smaller than the advection term
- characteristic diffusion length scale is given by: number density n_i of a chemical species *i* evolves according to

$$L_{\mathrm{diff}} \sim (\mathcal{D}\, t)^{1/2}$$

- the diffusion coefficient $D \sim L_{\mathrm{mfp}}\, v_{\mathrm{th}}$, where L_{mfp} is the particle mean free path and v_{th} is the thermal velocity
- in the diffuse ISM ($n = 1\ \mathrm{cm}^{-3}$, $T = 10^4$ K), we find that $L_{\mathrm{diff}} \sim 10^{11}\, t^{1/2}$ cm

from Simon Glover (Heidelberg)

governing equations 3

- we are therefore left with a set of advection-reaction equations, one for each chemical species

- we generally simplify this set of equations using a technique called operator splitting
- instead of solving the full equations, we treat the advection and reaction portions separately:

$$\frac{\partial n_i}{\partial t} + \vec{\nabla} \cdot (n_i \vec{v}) = 0$$

$$\frac{\mathrm{d}n_i}{\mathrm{d}t} = C(n_i, n_j, T) - D(n_j, T) n_i$$

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operator splitting 1

- operator splitting the advection and reaction steps has a drawback: the introduction of a new source of truncation error

- simplest splitting strategy:
  - Evolve advection eq. from t_0 to t_1
  - Using output from advection step, evolve reaction network from t_0 to t_1
  - Alternatively, we can invert the order of the steps, and solve the reaction substep first, followed by the advection substep

- this scheme is called “first-order splitting”. It introduces a local error of $O(\Delta t)$.

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operator splitting 2

- operator splitting the advection and reaction steps has a drawback: the introduction of a new source of truncation error

- we can do better than this with a scheme known as “Strang splitting”:
  - evolve reaction network from t_0 to $t_0 + \Delta t/2$
  - evolve advection step from t_0 to t_1
  - evolve reaction network from $t_0 + \Delta t/2$ to t_1

- this scheme introduces a local error of $O(\Delta t^2)$.

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operator splitting 3

- note that if the reaction network is stiff, then we always want to evolve it last in our splitting scheme.
- this is to ensure that rapidly reacting species that should be in chemical equilibrium are indeed in equilibrium at the end of every timestep.

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advection

- in general, we can use the same techniques to advect our set of number densities n_i that we use to advect the mass density ρ
- however, since we must conserve the total quantity of each element (hydrogen, helium, carbon etc.), plus the total charge, our number densities must also satisfy a set of $N_{elem} + 1$ constraint equations
- in Eulerian codes, the advection scheme typically does not guarantee that these constraint equations remain satisfied
- we can ensure that the constraint equations are satisfied at the end of every advection step by directly adjusting our number densities ni
- however, this strategy can be highly diffusive
(see e.g. Plewa & Müller, 1999)
- Plewa & Müller suggest that one should instead adjust the fluxes of the various species to ensure local conservation

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consistent multispecies advection (CMA)

- Total flux of element a with mass fraction x_a :

$$F_a = x_a F_\rho$$

- Partial fluxes F_i do not, in general, sum to total flux F_a

$$F_a \neq \sum_i F_i$$

- Hence have to rescale the fluxes by a factor:

$$\phi = \frac{F_a}{\sum_i F_i}$$

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reactions

- A typical chemical reaction network contains processes with a wide range of characteristic timescales
- The resulting rate equations are stiff
- This is a big problem: stiff ODEs can be solved explicitly only if very small timesteps are taken

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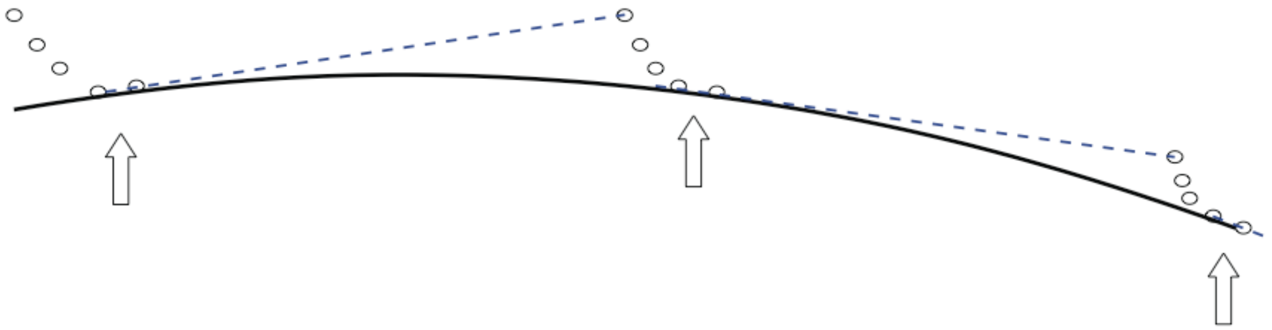
stiffness and stability



From Lee & Gear, 2007, JACM, 201, 258

- Consider a system with a set of fast modes that rapidly reach equilibrium, and a set of slow modes that control the subsequent evolution
- Away from the equilibrium manifold, we get rapid evolution and explicit codes must take small timesteps
- BUT: errors (truncation & roundoff), and advection effects will always displace us from the equilibrium manifold

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stiffness and stability

- We can avoid numerical instability by using an implicit technique
- One of the simplest possible implicit solvers is the 1st order backwards differencing formula (BDF):

$$\frac{n_i(t_1) - n_i(t_0)}{\Delta t} = C(t_1) - D(t_1)n_i(t_1)$$

$$n_i(t_1) = \frac{n_i(t_0) + C(t_1)\Delta t}{1 + D(t_1)}$$

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1st order BDF: pros and cons

- Pros:
  - Simple
  - Fast
  - Solutions are certain to remain ≥ 0

- Cons:
  - Inaccurate
  - No error control

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other solvers

- Higher order BDF (e.g. LSODE, VODE)
- Implicit Runge-Kutta (e.g. SDIRK)
- Rosenbrock (e.g. RODAS)
- For a good overview of different techniques, see Sandu et al. (1997a,b)

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performance

- Implicit solvers typically require some form of Newton iteration
- Solution of a set of N_{sp} coupled equations requires the inversion of a $N_{sp} \times N_{sp}$ matrix
- Computational cost scales as N_{sp}^3
- Values N_{sp} of = 50 - 400 are not uncommon in astrochemistry

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improving performance: exploiting sparseness

- Typically, any given reactant will react with only a small subset of the total number of species
- Hence our $N_{sp} \times N_{sp}$ matrix is <u>sparse</u>
- We can get an easy speedup by using a solver tailored for sparse systems
- Typical speedups of a factor of a few
- See Timmes 1999, Nejad 2005 for examples

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improving performance: dimension reduction

- If our cost is scaling as N_{sp}^3, then we can run faster if we can reduce N_{sp}
- An easy way to do this is by reducing the size of our chemical network
- Analysis of our chemical network can identify reactions and/or reactants that are unimportant and that can safely be omitted
- To perform this analysis, we need to understand the region of n-T-A_V-space in which our models will evolve

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summary

- Three main issues to be aware of: advection, reaction and splitting
- For all but the smallest chemical networks, the reaction substep is the computational bottleneck
- A number of different techniques exist for speeding up the reaction step (such as the quasi-steady state approximation)
- Many of these techniques have yet to be applied to astrophysical flows - there's lots of scope for further work

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a few useful references

General references

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end

Hokusai: 100 Poems Explained by the Nurse