

# ISM

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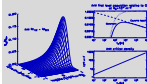
<http://www.das.uchile.cl/~simon>

- I Introduction: Observations of the ISM
- II Microscopic Processes.
- III Astrophysics of Gaseous Nebulae.
- IV Interstellar Dust.
- V Dynamics of the ISM.
- VI Selectec topics: protoplanetary disks, planetary nebulae, SNRs.



# Part II

## Microscopic Processes



### Thermal Equilibrium of the ISM

Cooling of the ISM: detailed balance, critical density

Ionic & atomic cooling of the ISM

Molecular excitation & molecular structure

Atomic/molecular coupling with radiation

Heating of the ISM

### Molecule formation

Grain catalysis

Ion-molecule chemistry

Observational validation

Chemical fractionation

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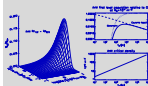
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# Thermal Equilibrium of the ISM

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$$\underbrace{n \frac{d}{dt} \left( \frac{3}{2} kT \right)}_{\text{variation of internal E.}} - \underbrace{kT \frac{dn}{dt}}_{\text{power}} = \underbrace{\frac{\text{cooling rate}}{\Gamma} - \frac{\text{heating}}{\Lambda}}_{\text{J s}^{-1} \text{ cm}^{-3}}$$

In steady state,  $dn/dt = dT/dt = 0$ , so the temperature  $T$  is determined by  $\Lambda(T) = \Gamma(T)$ .

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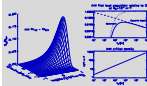
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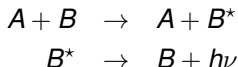
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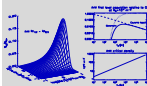
# Cooling of the ISM

Radiative cooling (ref. Dyson & Williams, Chap. 3, Spitzer, Chap. 4 & 6, Osterbrock, Chap. 3).



Requisites for a mechanism of radiative cooling

- frequent encounters, i.e.  $A$  &  $B$  abundant
- $E(B^*) - E(B) \lesssim kT$ .
- large rate of  $B$  excitations: high 'collision strength'
- time scale for radiative decay of  $B^*$  less than  $\tau_{\text{col}}$
- large escape probability of the output  $h\nu$ .



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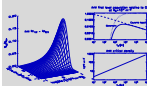
## Detailed balance: abundance of excited species

In steady state, the density  $n_j$  of species  $B^*$  in level  $j$  is determined by an equation of detailed balance, which models systems with a finite number of microscopic states:

$$\sum_k \left( \left\{ \begin{matrix} n_e \\ n_{\text{H}_2} \\ n_{\text{H}_I} \end{matrix} \right\} n_j \gamma_{jk} + n_j B_{jk} J_\nu \right) + \sum_{k < j} (A_{jk} n_j) \\ = \sum_k \left( n_k \left\{ \begin{matrix} n_e \\ n_{\text{H}_2} \\ n_{\text{H}_I} \end{matrix} \right\} \gamma_{kj} + B_{kj} J_\nu n_k \right) + \sum_{k > j} (n_k A_{kj}),$$

which we may also write using a simplified notation:

$$\sum_{i \neq j} n_j C_{ji} + n_j B_{ji} U_{\nu_{ji}} + \sum_{i < j} n_j A_{ji} = \sum_{i \neq j} n_i C_{ij} + n_i B_{ji} U_{\nu_{ij}} + \sum_{i > j} n_i A_{ij}.$$



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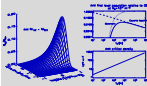
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## Detailed balance: rate of collisional excitation

For any collision partner (i.e. either  $n_{\text{H}_2}$  or  $n_{\text{H}_\text{I}}$ ), the specific rate of collisional excitations is

$$\gamma_{jk} = \langle u \sigma_{jk}(u) \rangle = \frac{4}{\sqrt{\pi}} \left( \frac{m_r}{2kT} \right)^{3/2} \int_0^\infty du u^3 \sigma_{jk}(u) \exp \left( -\frac{m_r}{2kT} u^2 \right).$$

the specific rate (i.e. per pair of particles, in units of  $\text{m}^3 \text{s}^{-1}$ ) of collisional de-excitations  $\gamma_{kj}$  must be related to  $\gamma_{jk}$ : in thermodynamic equilibrium any microscopic process must be balanced by its inverse (*principle of detailed balance*, otherwise the distribution functions would depend on  $t$  and there would be no equilibrium).



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In **LTE** the rate of collisional excitations  $j \rightarrow k$  with relative velocity  $\vec{u} \in [\vec{u}, \vec{u} + d\vec{u}]$  must equal the rate of de-excitations  $k \rightarrow j$  in the corresponding velocity range  $\vec{v}$ ,

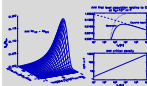
$$n_j^{\text{LTE}} \frac{n_e}{n_{\text{H}_2}} \sigma_{jk}(u) f(u) u d\vec{u} = n_k^{\text{LTE}} \frac{n_e}{n_{\text{H}_1}} \sigma_{kj}(v) f(v) v d\vec{v},$$

with  $f(u) = \left(\frac{1}{\pi} \frac{m}{2kT}\right)^{3/2} \exp\left(-\frac{m}{2kT} u^2\right)$ ,  
and  $\frac{1}{2} m_r v^2 = \frac{1}{2} m_r u^2 - E_{jk}$ <sup>1</sup>,

$$\xrightarrow{\text{tarea}} g_j u^2 \sigma_{jk}(u) = g_k v^2 \sigma_{kj}(v), \text{ or}$$

$$C_{kj} = C_{jk} \frac{g_j}{g_k} e^{E_{jk}/kT}.$$

<sup>1</sup>note threshold excitation energy



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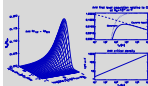


# Critical density

The *critical density* is defined as the density at which the rate of collisional de-excitations is equal to the rate of radiative de-excitations:

$$\sum_{k < j} C_{kj} = \sum_{k < j} A_{jk}.$$

A good cooling mechanism is therefore one that involves abundant species, an effective collision strength  $\gtrsim 1$ , a critical density  $n_{\text{crit}} \gg n_e$ , and optically thin transport of the output  $h\nu_{jk}$ .



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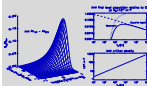
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# Ionic & atomic cooling of the ISM

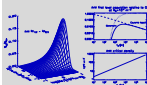
For ionic collisions, the cross-section of collisional excitation highlights the Coulomb cross-section.

$$\sigma_{jk}(E) = \frac{\pi a_o^2 \Omega_{jk}(E)}{E/E_o},$$

where  $E_o$  is 1 Rydberg,  $a_o$  is the Bohr radius, and  $\Omega_{jk}(E)$  (of order 1), is the *collision strength* as a function of kinetic energy  $E$ . Finally the rate of excitations  $j \rightarrow k$  (with units of  $s^{-1}$ ) is (tarea),

$$C_{jk} = \left\{ \begin{array}{c} n_e \\ n_{H_2} \\ n_{H_I} \end{array} \right\} \sqrt{\frac{2\pi}{kT}} \left( \frac{h}{2\pi} \right)^2 \frac{1}{m_r^{3/2}} \frac{\Gamma_{jk}}{g_j} e^{-E_{jk}/kT},$$

where  $\Gamma_{jk}$ , the *effective collision strength*, is the Maxwellian average of  $\Omega(E)$ .



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## Fine structure cooling in the IR

In LS coupling energy levels are ordered according to the Hund rules (Shu I Chap. 27):

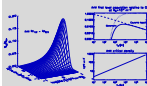
- Higher S  $\rightarrow$  lower energy
- Higher L  $\rightarrow$  lower energy
- Higher J  $\rightarrow$  higher energy if less than half-filled, lower energy if more than half-filled

Spectroscopic notation in spin-orbit coupling (ver Shu I,27):

$2S+1L_J$ , with degeneracy  $(2J+1)$

### Examples:

- [Ar VI]  $4.52\mu\text{m}$ ,  $^2P_{\frac{1}{2}} \leftarrow ^2P_{\frac{3}{2}}$ ,  $Z=18$
- [Al VI]  $3.65\mu\text{m}$ ,  $^3P_2 \leftarrow ^3P_1$ ,  $Z=13$



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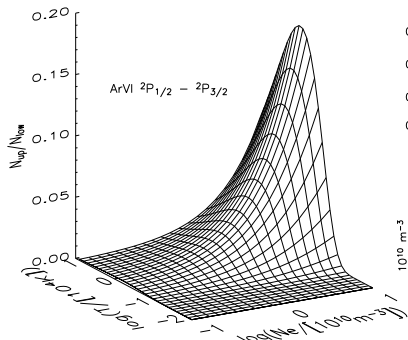
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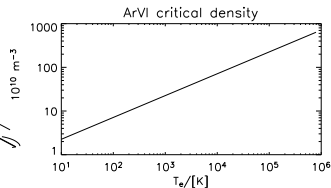
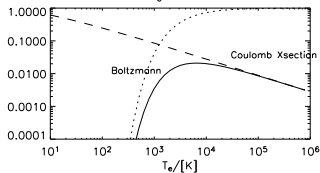
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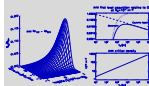
# Ar VI $2P_{1/2} - 2P_{3/2}$ population



Ar VI first level population relative to GS  
at  $N_e = 10^{10} \text{ m}^{-3}$



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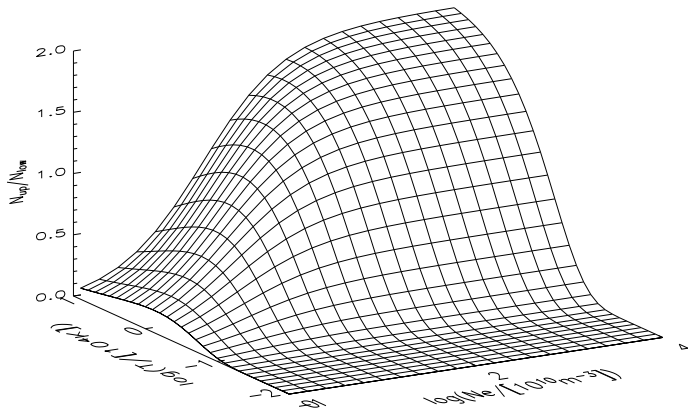
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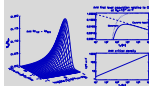
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# Ar VI $2P_{3/2}$ population



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## Cooling of H II regions

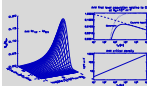
For gas in a steady state, where every ionization event is balanced by a recombination event (case of a nebula photoionised by OB stars), the cooling mechanisms are:

- 1 Recombination radiation (postponed to chapter on photoionised nebulae)
- 2 Continuum emission (free-free, bound-free):  
 $A + B \rightarrow A + B + h\nu$  (postponed to chapter on photoionised nebulae)
- 3 Collisionally excited line emission:

$$\Lambda_{CE} = \sum_X \sum_i n(X, i) \sum_{j < i} A_{i,j} (E_i - E_j)$$

e.g.

- [O II]  $\lambda\lambda 3726, 3729$   $^4S_{3/2} \leftarrow ^2D_{3/2, 5/2}$ .
- [O III]  $\lambda\lambda 4959, 5007$   $^3P_{2,1} \leftarrow ^1D_2$ .



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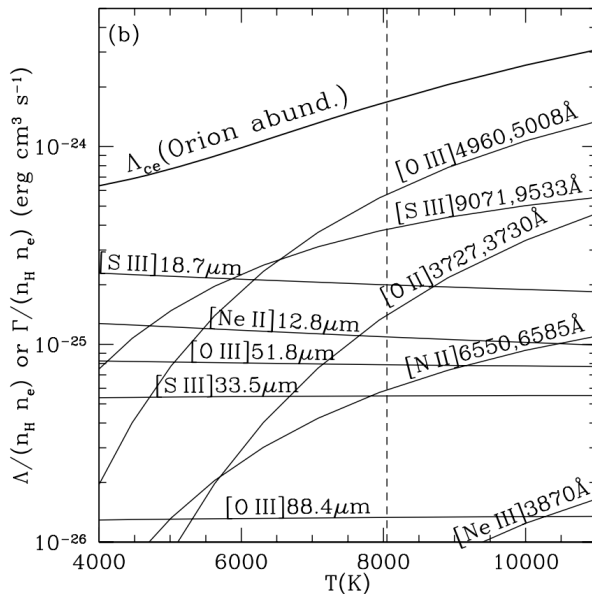
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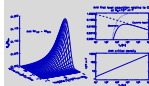
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# Cooling of H II regions: collisionally excited line radiation



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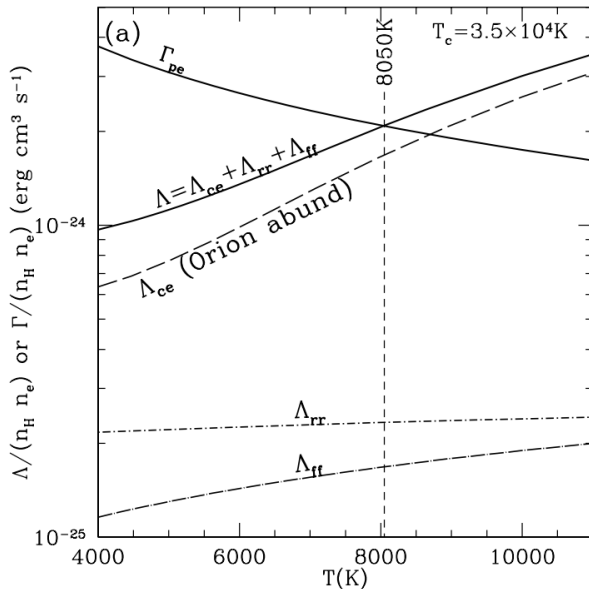
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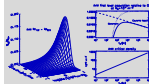


# Cooling of H II regions: collisionally excited line radiation

$$Z \sim Z_{\odot}$$



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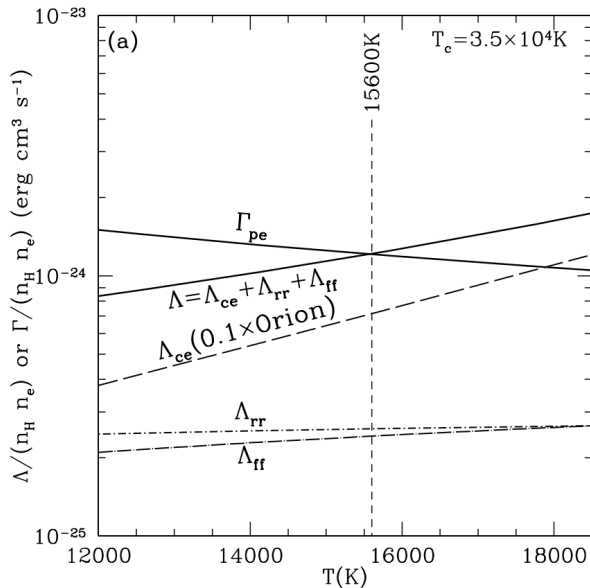
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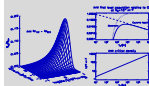
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# Cooling of H II regions: collisionally excited line radiation

$$z \sim 0.1 z_{\odot}$$



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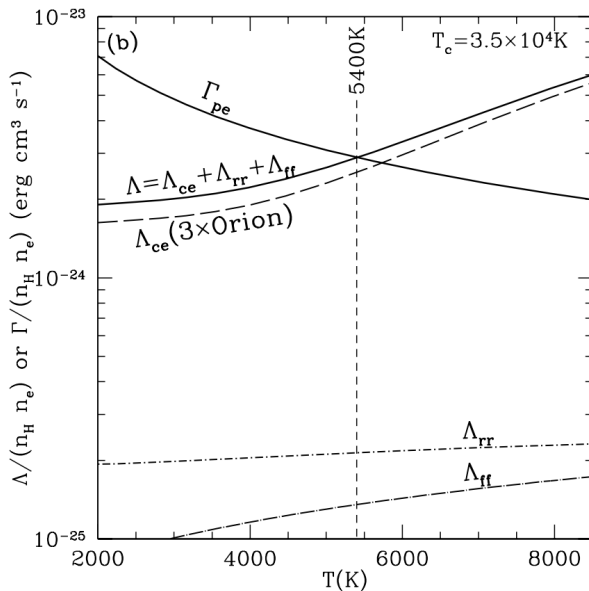
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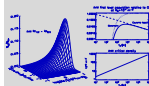
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# Cooling of H II regions: collisionally excited line radiation

$$z \sim 3z_{\odot}$$



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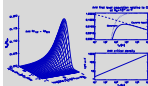
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# Cooling of the neutral ISM

Occurs through excitation of low-lying electronic states, fine structure levels dominate.

Examples: Table 3.1 in Dyson & Williams complemented by the list of lines in <http://www.pa.uky.edu/~peter/atomic/>

Transition	collision partner	$\Delta E/k$
[C I] $\lambda 157.7 \mu\text{m}$ $^2\text{P}_{1/2} \leftarrow ^2\text{P}_{3/2}$	H,e,H <sub>2</sub>	92 K
[Si II] $\lambda 34.8 \mu\text{m}$ $^2\text{P}_{1/2} \leftarrow ^2\text{P}_{3/2}$	e	92 K
[O I] $\lambda 63.2 \mu\text{m}$ $^3\text{P}_1 \leftarrow ^3\text{P}_2$	H,e	228 K
[O I] $\lambda 145.5 \mu\text{m}$ $^3\text{P}_0 \leftarrow ^3\text{P}_2$	H,e	326 K



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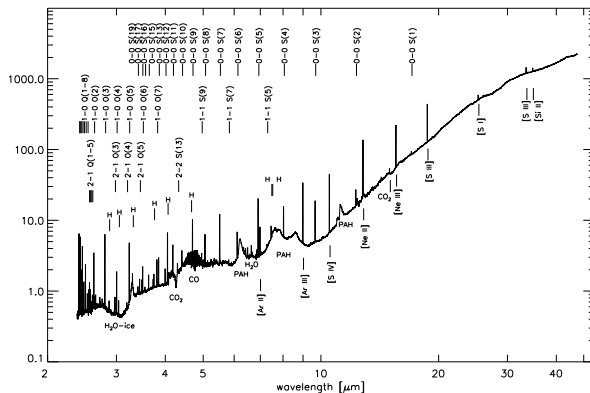
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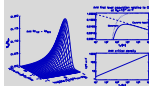
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# Molecular excitation - CO & H<sub>2</sub>

*ISO* observations (Van Dishoeck, 2004, ARA&A, 42, 119) suggest that the contribution from H<sub>2</sub> cooling is more important than estimates based on *IRAS* data: H<sub>2</sub> is among the brightest emission lines in molecular clouds exposed to UV radiation, as for instance in Orion KL (note prominent dust continuum):



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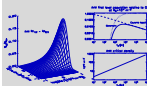
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## fluorescent $\text{H}_2$ : not a gas coolant

The rotational excitation of the ground vibrational state of  $\text{H}_2$  is usually collisional (i.e. thermal), while higher vibrational states are excited by fluorescence (hence not a cooling process).

$\Rightarrow$  near-IR rovib  $\text{H}_2$  is usually fluorescent, so not a coolant (except some of the lower-level rovib lines, in shocked regions).



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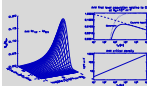
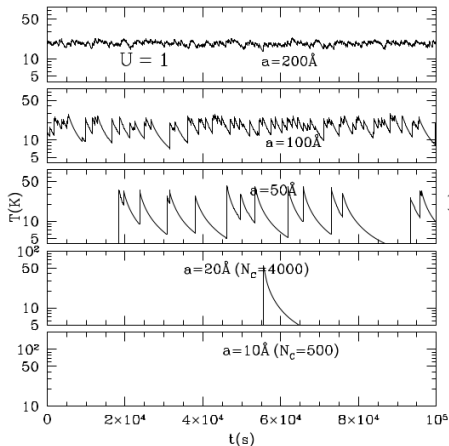
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## Dust continuum: not a gas coolant

The most luminous spectral component in the molecular ISM is the mid-IR to far-IR continuum, due to dust. Dust is responsible for transporting the UV radiation of the exciting stars, but is not always coupled to the molecular gas. Collisions are efficient dust heating sources in the denser media only, such as dense SNRs or dense circumstellar disks.



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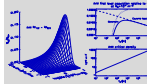
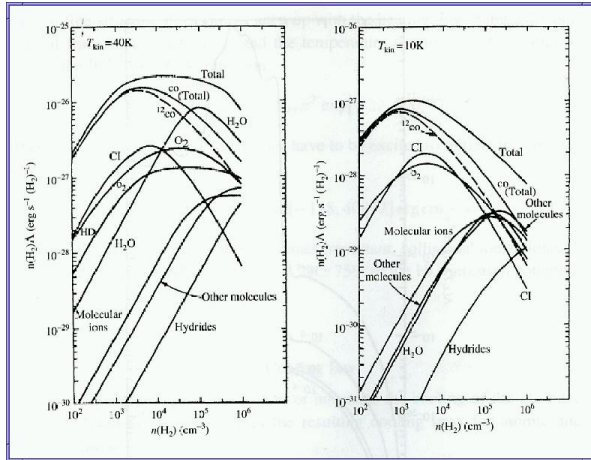
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# CO rotational-line cooling

The main cooling agents for cold molecular clouds are low-level rotational transitions of CO in the sub-mm. (Figure 2.11 from Tielens 2005).



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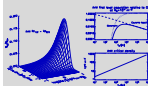
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## Summary: diatomic molecules

In the Born-Oppenheimer approximation the Hamiltonian for a diatomic molecule AB separates,  $H = H_{AB} + H_{el}$ , where  $H_{AB}$  represents the kinetic energy of the nuclei, and  $H_{el}$  all the rest. It is also customary to factorize  $\phi = \phi_{el}\phi_{AB}$  and obtain <sup>2</sup>:

$$H_{el}\phi_{el} = E_{el}(R) \phi_{el},$$

$$H_{AB}\phi_{AB} + E_{el}(R) \phi_{AB} = E \phi_{AB},$$

and using the centre of mass coordinates,

$$\phi_{AB} = \phi_{trans}(\vec{X}_{CM})\phi_{intern}(\vec{R}),$$

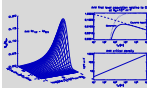
$$-\frac{\hbar^2}{2M}\nabla_{CM}^2\phi_{trans} = E_{trans} \phi_{trans}$$

$$-\frac{\hbar^2}{2\mu}\nabla_{\vec{R}}^2\phi_{intern} + E_{el}(R) \phi_{intern} = E_{intern} \phi_{intern},$$

with  $E = E_{intern} + E_{trans}$ .

---

<sup>2</sup>provided additional approximations according to Messiah, Vol. 2, XVIII.64 (p791), but exactly according to Shu I, 28. Probably valid only for processes slower than a rotation period.



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The Laplacian in spherical coordinates,

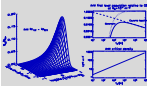
$$\nabla_{\vec{R}}^2 = \frac{1}{R^2} \left[ \frac{\partial}{\partial R} \left( R^2 \frac{\partial}{\partial R} \right) - \frac{L^2}{\hbar^2} \right],$$

inspires the decomposition of the wave function for the internal degrees of freedom in spherical harmonics,

$$\phi_{\text{intern}}(\vec{R}) = \frac{1}{R} Z_{\text{vib}}(R) Y_{Jm}(\theta, \varphi),$$

The 1-D equation for  $Z_{\text{vib}}(R)$  is a function of  $E_{\text{el}}(R)$ , the energy eigenvalue of the electronic wave function:

$$-\frac{\hbar^2}{2\mu} \frac{d^2 Z_{\text{vib}}}{dR^2} + E_{\text{el}}(R) Z_{\text{vib}} = \left[ E_{\text{intern}} - \frac{J(J+1)\hbar^2}{2\mu R^2} \right] Z_{\text{vib}}.$$



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In the harmonic approximation we expand the 1-D equation for  $Z_{\text{vib}}$  about  $R_o$ , the AB separation in the fundamental state, highlighting the natural frequency  $\mu\omega_o \equiv E''_{\text{el}}(R_o)$  :

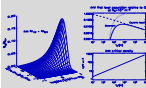
$$-\frac{\hbar^2}{2\mu} \frac{d^2 Z_{\text{vib}}}{dx^2} + \frac{\mu}{2} \omega_o^2 x^2 Z_{\text{vib}} = E_{\text{vib}} Z_{\text{vib}},$$

$$x \equiv R - R_o, \quad \text{and}$$

$$E_{\text{intern}} = E_{\text{el}}(R_o) + E_{\text{vib}} + E_{\text{rot}},$$

$$E_{\text{rot}} = J(J+1) \frac{\hbar}{2\mu R_o^2} \equiv J(J+1)B, \quad B: \text{rotational constant},$$

$$E_{\text{vib}} = \left(v + \frac{1}{2}\right) \hbar \omega_o.$$



#### Thermal Equilibrium of the ISM

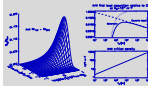
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The quantum numbers that determine the nuclear state of the molecule are  $J, m, v$ . Note the rigid body assumption:  $\phi_{\text{el}}$  is independent of  $J$ , which is the fundamental hypothesis implicit in the decomposition  $\phi = \phi_{\text{el}}\phi_{\text{AB}}$ . The quantum numbers that characterise the electronic state of the molecule are  $\Lambda$ , and  $S$ , where  $\Lambda$  corresponds to the projection of  $L_{\text{tot}}$  along the internuclear axis<sup>3</sup>, and  $S$  is the total spin.

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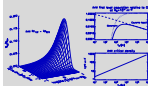
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<sup>3</sup>the only component of  $\vec{L}$  that is conserved in diatomic molecules



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## Interaction with electromagnetic radiation

The coupling term between charged particles and the electromagnetic field,  $\vec{p}_i \cdot \vec{A}(\vec{k} \cdot \vec{x} - wt)^4$ , can be expressed through an expansion in  $\vec{k} \cdot \vec{x}$  as  $H_{\text{int}} = H_{\text{d}} + H_{\text{M}} + H_{\text{Q}}$  (see Shu I,24), for which

$$H_{\text{d}} = -\vec{E} \cdot \vec{d} \text{ (zeroth order)}$$

where, for a molecule,  $\vec{d} = \vec{d}_{\text{el}} + \vec{d}_{\text{nuc}}$ .

$$H_{\text{M}} = -\vec{B} \cdot \vec{M} \text{ (first order)}$$

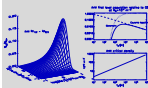
where the magnetic dipole moment  $\vec{M} \propto \vec{L}$ , and

$$H_{\text{Q}} = -\frac{e}{6} \vec{\nabla} \vec{E} : (3\vec{x}\vec{x} - |\vec{x}|^2 \mathbb{I}) \text{ (also order one).}$$

In general  $H_{\text{M}} > H_{\text{Q}}$ .

---

<sup>4</sup>when substituting  $\vec{p} \rightarrow \vec{p} - \frac{q}{c} \vec{A}$ , and neglecting terms in  $A^2$  (OK for the ISM) see Shu I, 21



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# Bound-bound transition probabilities and cross-sections

In time-dependent perturbation theory, the rate of radiative excitations  $i \rightarrow f$  is:

$$\frac{dP_{if}}{dt} \propto \Re(\omega_{if}) |\langle \phi_f | H_{\text{int}}(\omega) | \phi_i \rangle|^2.$$

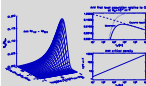
In a cubic box where the occupation number of state  $\vec{n}$  is  $\Re$ , the density of states is  $d^3\vec{n} = V d^3\omega / (2\pi c)^3$ , with a volume  $V \rightarrow \infty$ . The absorption cross-section  $\sigma_{if}$  derives from  $P_{if} = N_f / N_i \propto \#$  of absorbed photons <sup>5</sup>:

$$P_{if} = \int d^3\vec{n} \frac{\Re(\vec{n})}{V} c t \sigma_{if} \Rightarrow \frac{dP_{if}}{dt} = \int_0^\infty \sigma_{if} c \Re(\omega) \frac{4\pi\omega^2}{(2\pi)^3 c^2} d\omega$$

Identifying (see Shu I, 22, 23), we obtain

$$\sigma_{if} \propto |\langle \phi_f | H_{\text{int}}(\omega) | \phi_i \rangle|^2 \delta(\omega - \omega_{if}).$$

<sup>5</sup>note *optically thin* case:  $dN_f = -\Gamma N_f dt + \frac{dP_{if}}{dt} N_i dt$ .



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## Oscillator strength

For the electric dipole Hamiltonian, one gets

$$\sigma_{if} = \frac{4\pi^2}{3\hbar c} \left| \langle \phi_f | \vec{d} | \phi_i \rangle \right|^2 \delta(\omega - \omega_{if}),$$

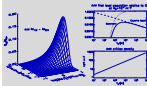
which is usually expressed in terms of the oscillator strength  $f_{if}$ ,

$$\sigma_{if} = \frac{\pi e^2}{m_e c} f_{if} \delta(\nu - \nu_{if}), \quad \text{con} \quad f_{if} \equiv \frac{4\pi m_e}{3e^2 \hbar} \nu_{if} \left| \langle \phi_f | \vec{d} | \phi_i \rangle \right|^2.$$

For a single electron with position  $\vec{x}$ ,

$$f_{if} = \frac{2m_e(\omega_{if} \langle f | \vec{x} | i \rangle)^2}{3\hbar \omega_{if}},$$

which is roughly the ratio between the vibrational potential energy of the electron and that of the radiated photon.



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## Relationship with Einstein coefficients

The equation of detailed balance,

$$n_i B_{if} J_{\nu if} = n_f A_{fi} + n_f B_{fi} J_{\nu fi},$$

and the LTE relationships,

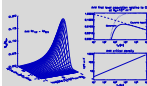
$$\frac{n_f}{n_i} = \frac{g_f}{g_i} \exp\left(-\frac{h\nu_{if}}{kT}\right), \quad \text{and} \quad J_\nu = B_\nu(T), \quad \text{lead to}$$

$$A_{fi} = \frac{g_i}{g_f} (2h\nu^3 / c^2) B_{if}, \quad B_{fi} = \frac{c^2}{2h\nu^3} A_{fi} = (g_i / g_f) B_{if},$$

where the rate of stimulated excitations is related to the oscillator strength<sup>6</sup> :

$$B_{if} = \frac{4\pi^2}{h\nu} \frac{e^2}{m_e c} f_{if}.$$

<sup>6</sup>using the requirement  $n_i B_{if} J_{\nu if} = \int d\nu \int d\Omega \sigma_{if} n_i \frac{J_\nu}{h\nu} = \int d\nu 4\pi \sigma_{if} n_i \frac{J_\nu}{h\nu}$



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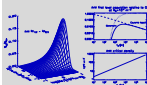
- Electric dipole

- atoms:  $\Delta l = 1$ ,  $\Delta m = 0$ .
- molecules:
  - vibrational-rotational transitions, or rovibrational,  $\Delta J = \pm 1$ ,  $\Delta m = 0, \pm 1$ , allowed when  $\Lambda \neq 0$ ,  $\Delta J = 0$ <sup>7</sup>.
  - electronic transitions,  $\Delta \Lambda = 0, \pm 1$ ,  $\Delta S = 0$
  - electronic-vibrational-rotational transitions (i.e. *vibronic* transitions):  $\Delta J = 0, \pm 1$ ,  $\Delta m = 0, \pm 1$  and  $\Delta J \neq 0$  si  $\Lambda = \Delta \Lambda = 0$  and if  $J = 0$ .

$$\Delta J = \begin{cases} +1 \rightarrow \text{R branch} \\ 0 \rightarrow \text{Q branch} \\ -1 \rightarrow \text{P branch} \end{cases}$$

- magnetic dipole, atoms:  $\Delta l = 0$ ,  $\Delta m = 0, \pm 1$ .
- electric quadrupole, atoms:  $\Delta l = 0, \pm 2$ ,  $\Delta m = 0, \pm 1, \pm 2$ , rotational transitions in molecules  $\Delta J = 0, \pm 1, \pm 2$ .

<sup>7</sup>Lambda doubling, two states  $\pm \Lambda$  for each  $J$ . Example: hyperfine structure of the OH  $\Lambda$  doublet at  $\sim 1.7$  GHz.



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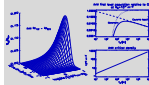
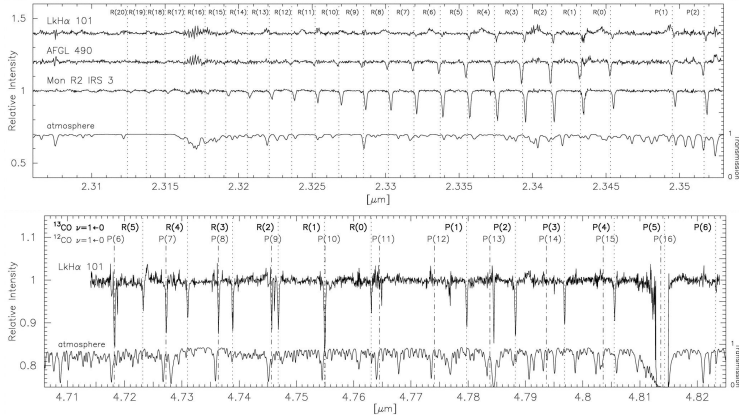
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# Selection rules – CO<sup>8</sup>

ISM



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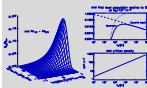
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## Selection rules – H<sub>2</sub>

In the case of H<sub>2</sub> we have  $\vec{d} = 0$ . Moreover the fundamental state is  $\vec{L} = 0$ , and  $\vec{S} = 0$ , so that  $\vec{M} = 0$  and all low-energy transitions for H<sub>2</sub> are quadrupolar.

Note that the antisymmetry of the nuclear wave function implies that the state  $J = 1$  ( $J$  odd) is triplet (**Ortho** H<sub>2</sub>,  $I = S_{\text{nuclear}} = 1$ ), while  $J = 0$  ( $J$  even) is singlet (**Para** H<sub>2</sub>,  $I = 0$ ).

In H<sub>2</sub> the exclusion principle<sup>9</sup> forbids  $\Delta J = 1$ , unless the transition involves a change in spin state. The spin transitions can only occur through the exchange of protons in collisions. Radiative transitions between spin states can occur, but at a rate corresponding to the quadrupolar transitions in the Hamiltonian of the deviations to the Born-Oppenheimer approximations.



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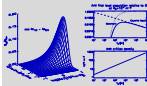
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<sup>9</sup>the requirement that the wave function be antisymmetric



In the ISM, **Ortho** and **Para**  $\text{H}_2$  are effectively different molecules. The distinction extends to all molecules that contain  $\text{H}_2$  radicals.

Rovibrational transitions between an upper level <sup>1</sup> and a lower level <sup>2</sup> are written  $(\nu_1 - \nu_2)O(J_2)$ , when  $J_2 - J_1 = -2$ ,  $(\nu_1 - \nu_2)Q(J_2)$  when  $J_2 - J_1 = 0$ ,  $(\nu_1 - \nu_2)S(J_2)$  when  $J_2 - J_1 = +2$ .

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# H<sub>2</sub> energy levels

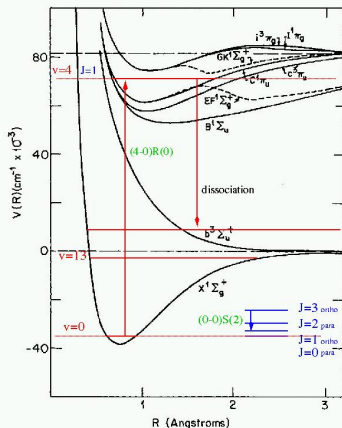
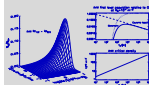


Figure 1 Total energy as a function of internuclear separation for low-lying states of H<sub>2</sub>. Horizontal dashed lines denote total energy of two H atoms at infinite separation (both atoms in ground state; one atom in ground state and the other in the first excited states).

$$\Lambda = 0, 1, 2, \dots$$

$\Leftrightarrow \Sigma, \Pi, \Delta$   
levels in  $E_{el}(R)$ :  
 $X, B, C, D$ .

The energy separation between levels  $B$  and  $C$  with respect to  $X$  are  $\sim 11$  eV and 14 eV.



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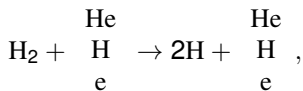
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## Dissociation of H<sub>2</sub>

The collisional dissociation of H<sub>2</sub>,

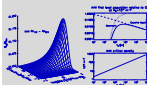


requires temperatures of order the binding energy of H<sub>2</sub>,  
 $4.48 \text{ eV}/k = 52000 \text{ K}^{10}$ .

But an H<sub>2</sub> cloud is more likely to be photo-dissociated before it reaches 50 000 K. The dissociation continuum of H<sub>2</sub> (i.e. free states of H+H) starts 14.7 eV above the fundamental level of H<sub>2</sub> (i.e. X<sup>1</sup>Σ, para-H<sub>2</sub>), while the ionization continuum (the ejection of one electron) starts at 15.4 eV. Both continua, ionising and dissociating, lie above 13.6 eV. In the context of a molecular cloud surrounded by H I, the H<sub>2</sub> dissociating radiation is completely absorbed by the Lyman continuum of H I.

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<sup>10</sup>the law of mass-action does not change this result because the number of continuum states accessible to both products and reactants is similar, in contrast with ionisation, which is described by the Saha equation



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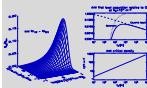
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# Dissociation of H<sub>2</sub>

The likeliest mechanism for H<sub>2</sub> dissociation is absorption to the rovibrational bands of excited electronic states (e.g. B or C), and

- 1 subsequent de-excitation to dissociated levels of lower energy (e.g. b<sup>3</sup>Σ), or
- 2 decay to the vibrational continuum of electronic state X (with  $v \geq 14$ ), or
- 3 decay to excited levels of the fundamental state and subsequent absorption to the dissociating continuum (one order of magnitude slower than mechanisms 1) and 2) , Stecher & Williams 1967, ApJ 149, L29)



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## IR emission from H<sub>2</sub>

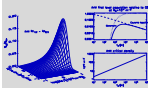
Since the rate of radiative transitions within the ground state electronic level of H<sub>2</sub> is quadrupolar, the distribution of ro-vibrational population is dominated by collisions between H<sub>2</sub> molecules.

If  $kT \gg \Delta E_{\text{FIR}}$ , the typical energy difference between rotational levels of ground state H<sub>2</sub>, the occupation numbers of the ro-vibrational levels in the ground state electronic state follow LTE:

$$N(v, J) \propto \omega(J) \exp(-B(J(J+1))/kT),$$

in which  $\omega(J) = 3 \times (2J+1)$  for ortho-H<sub>2</sub>, and  $\omega(J) = 1 \times (2J+1)$  for para-H<sub>2</sub>. This situation (i.e. hot molecular gas) is typical of shocks in the ISM.

In the presence of an intense UV field the IR emission of H<sub>2</sub> is fluorescent (Black & Van Dishoeck, 1987, ApJ, 322, 412). Fluorescence dominates if  $kT \ll \Delta E_{\text{FIR}}$ . The absorption of one UV photon excites H<sub>2</sub> to an electronic state, leading to photodissociation (with a 15% probability), and to an IR cascade in all other cases.



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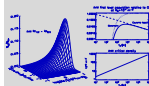
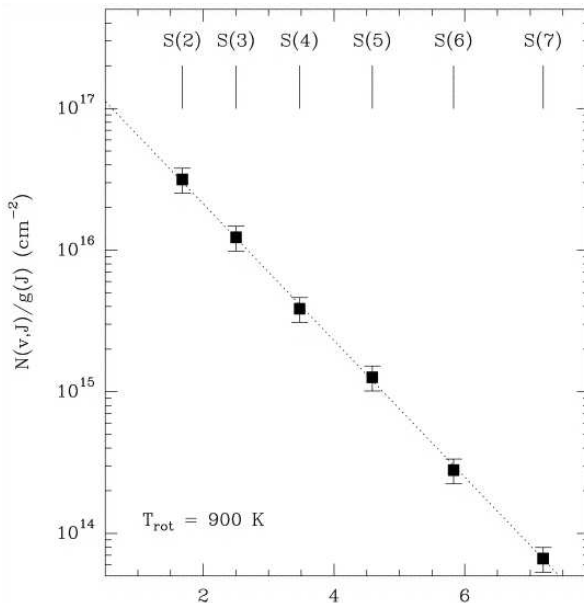
Ion-molecule chemistry

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## IR emission from H<sub>2</sub>

Example excitation diagram for the Helix nebula.



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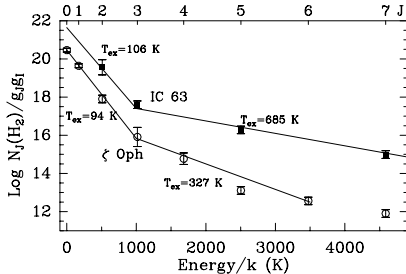
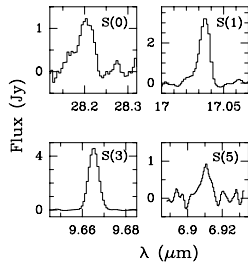
Grain catalysis

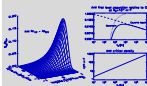
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# IR emission from $\text{H}_2$ , $\zeta$ Oph





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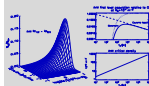
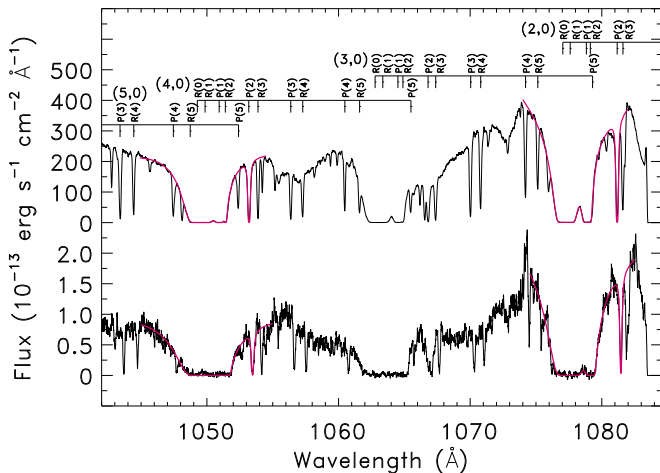
Ion-molecule chemistry

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## Heating of the neutral ISM

H<sub>2</sub> is an important source of UV opacity, as shown in the *FUSE* spectra of HD210839 and HD154368 (Rachford et al., 2002, ApJ, 577, 221).



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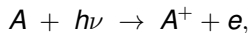
Ion-molecule chemistry

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# Heating mechanisms

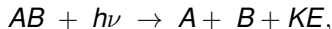
## ① Photoionisation:



in the case of the neutral ISM, photoionisation heating is dominated by  $C^+$ , with an ionization potential of 11.3 eV. The average kinetic energy of the ejected electron is

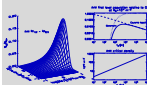
$$\frac{3}{2}kT_i = \frac{\int_{\nu_i}^{\infty} (J(\nu)/h\nu)\alpha_i(\nu)h(\nu - \nu_i)d\nu}{\int_{\nu_i}^{\infty} (J(\nu)/h\nu)\alpha_i(\nu)d\nu}.$$

## ② Photodissociation:



dominated by  $H_2$  photodissociation.

## ③ collisional de-excitation (in particular for $H_2$ , when $n(H_2) > 10^4 \text{ cm}^{-3}$ ).



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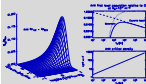
#### 4 photoelectric effect on dust grains.

The grain heating efficiency,  $\epsilon_{\text{grain}}$ , defined as the ratio between output gas heating and input UV radiation (Tielens Chap. 3.3.1), is

$$\epsilon_{\text{grain}} = Y \times \frac{h\nu - W - \phi}{h\nu},$$

where the electron escape probability  $Y$  is the ratio between the  $e^- - e^-$  mean free path  $l_e \approx 10 \text{ \AA}$ , and the absorption depth of UV radiation,  $l_a \approx 100 \text{ \AA}$ :  $Y \approx l_e/l_a$ .  $W$  is the work function of the grain and  $\phi = Z \times e^2/a$  is the surface potential for a grain of size  $a$ . The ionization potential of a grain is thus  $I = W + \phi$ .

The heating efficiency is larger for smaller grains, since  $l_a \approx l_e$ . The ejection of photoelectrons from grains is the dominant heating source in the neutral ISM exposed to FUV radiation, as in the case of PDRs. Photoionisation is dominant in the case of the ionised gas.



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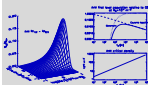


- The total photoelectric heating rate from grains per unit volume,  $n\Gamma_{\text{grain}}$ , can be written:

$$n\Gamma_{\text{grain}} = \int_{a_{\min}}^{a_{\max}} n(a) da \sum_i \int_{\nu_i}^{\nu_H} \frac{J_{\nu}}{h\nu} \alpha_{\text{grain},i}(\nu) E_{\text{kin}}(a, i) d\nu,$$

where  $a$  is grain diameter, and  $i$  runs over grain ionisation stage, and  $h\nu_H = 13.6$  eV.

- in addition to photo-electric heating, grains can also heat the gas through inelastic collisions if the solid state temperature is larger than the gas temperature.



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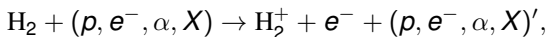
Grain catalysis

Ion-molecule chemistry

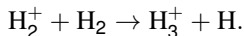
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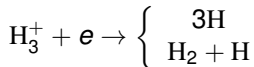
- 5 heating from cosmic rays:  
Important for molecular phase. Cosmic rays, as well as X-rays, ionise  $\text{H}_2$  (IP=15.4 eV):



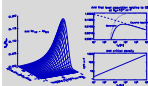
followed by the formation of  $\text{H}_3^+$ :



An important mechanism for the destruction of  $\text{H}_3^+$  is its dissociative recombination,



Since both the formation and the destruction of  $\text{H}_3^+$  are exothermic (the energy released into the ISM in the process is 11 eV), the  $\text{H}_3^+$  cycle is a heating source of the ISM.



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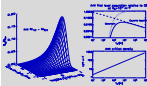
## 6 Turbulent heating.

Important in molecular clouds at  $\sim 10$  K, without UV field. In a turbulent flow the kinetic energy density will trickle down a hierarchy of scales, until it is dissipated by diffusion at the smallest scale fixed by viscosity. The timescale for downwards energy transfer at scale  $l$  can be approximated with the crossing time at the velocity dispersion  $v$ . Thus the rate of heating per unit volume is (Tielens 3.8),

$$n\Gamma_{\text{turbulence}} = \frac{1}{2} \frac{n m_H v^2}{l/v}.$$

The observations of the energy density and velocity dispersion at a given scale  $l$  leads to an estimate of turbulent heating.

The energy densities as a function of scale can be calculated assuming a constant energy transfer rate:  $v^2/(l/v)$  is constant.



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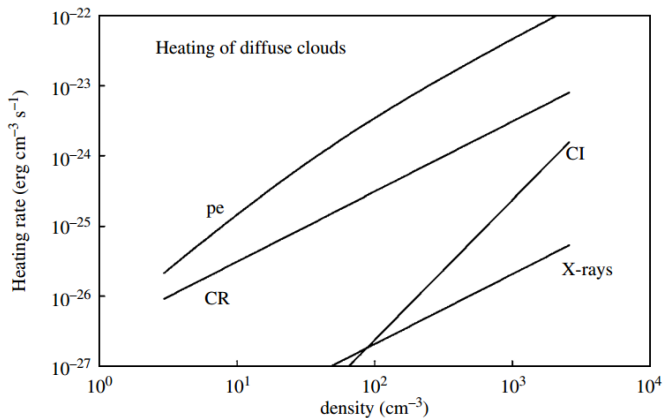
Grain catalysis

Ion-molecule chemistry

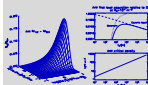
Observational validation

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# Heating mechanisms in neutral diffuse clouds



ISM



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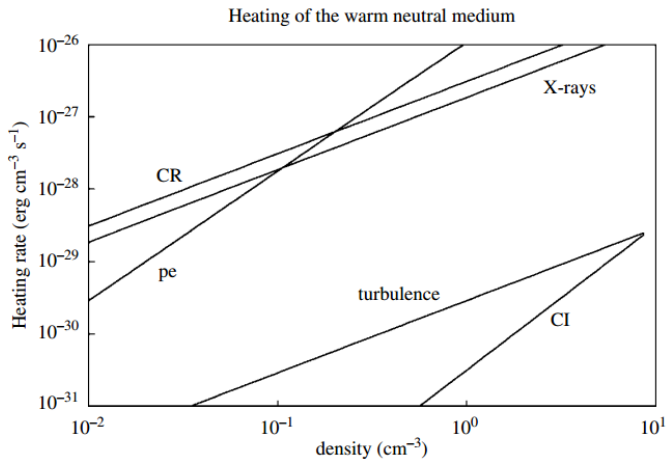
Grain catalysis

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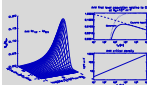
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# Heating mechanisms in WNM



ISM



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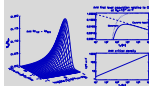
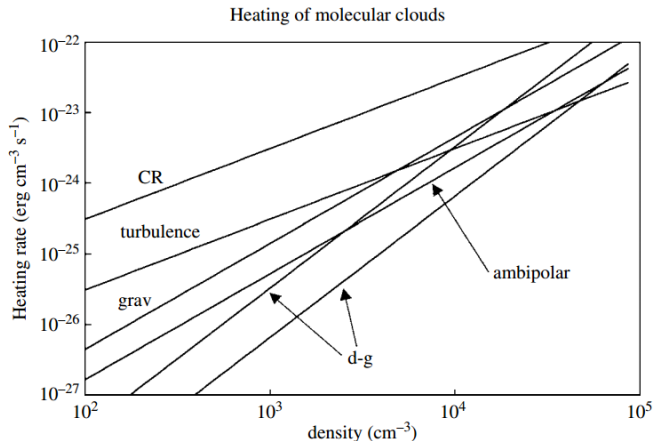
Grain catalysis

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# Heating mechanisms in molecular clouds



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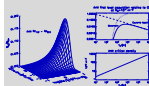
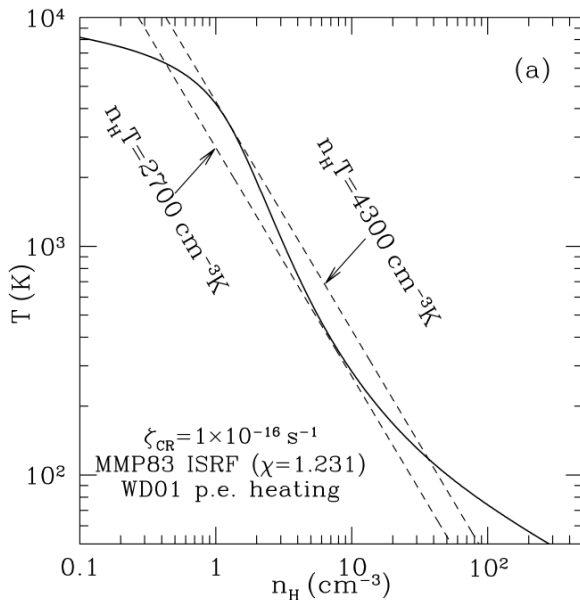
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# Steady state temp. for HI



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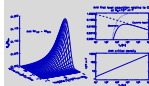
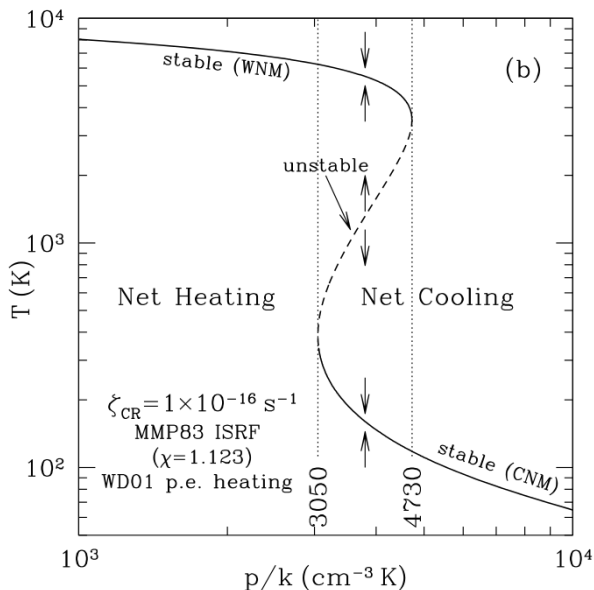
Grain catalysis

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# Two phases for HI



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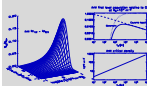
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# Molecule formation

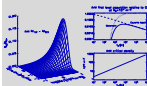
The encounter of two atoms  $A$  and  $B$ , initially unbound, will lead to molecular synthesis if:

- 1 bound states of  $AB$  exist.
- 2 There is a mechanism for molecular stabilization faster than the lifetime of the  $AB^*$  state <sup>11</sup>, of order  $\sim 10^{-13}$  s ( $\approx 1$  vibrational period).

Radiative dissipation of the energy excess of  $AB^*$  is improbable: even for electric dipole decay rates, about  $10^8 \text{ s}^{-1}$  in the UV, only 1 out of  $10^5$  collisions will produce a molecule. The abundance of  $\text{H}_2$  might raise the low probability of condensation via collisions, but the electric dipole transitions of  $\text{H}_2$  are forbidden.  $\text{H}_2$  cannot associate radiatively. The  $\text{H}_2$  half-life in the diffuse interstellar UV radiation field is of  $\sim 300 \text{ yr} \Rightarrow$  some other mechanism must exist for efficient  $\text{H}_2$  formation.

---

<sup>11</sup>the molecule is initially bound at a level with energy equal to that of the colliding pair



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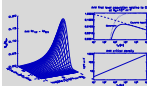
Chemical fractionation

## Grain catalysis of the formation process of $H_2$

The adsorption of hydrogen atoms onto the surface of dust grains allows raising the available timescale for the  $A + B$  encounter, and the grain acts as stabilizing agent by absorbing the excess energy of  $AB^*$ .

Once  $H_2$  is formed, its 4.48 eV of binding energy (the first bound-free transition is at 2500 Å) eject  $H_2$  from the grain surface, and the excess of energy over the grain work function is distributed over the molecular degrees of freedom, leaving the  $H_2$  molecule in an excited state.

IR transitions from the formation pumping of excited levels of  $H_2$  were observed by Burton et al. (2002, MNRAS, 333, 721) in M 17: the line (6-4)O(3) at  $1.73\mu m$  cannot be collisionally excited since its superior level is at  $\Delta E/k \sim 30\,000$  K above ground, yet the intensity of (6-4)O(3) relative to other  $H_2$  lines does not match fluorescent models.



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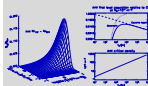
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### Molecule formation

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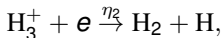
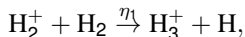
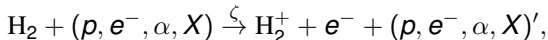
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## Molecule formation - the role of $\text{H}_3^+$

- $\text{H}_3^+$  controls the ionisation stage of the molecular ISM. The  $\text{H}_3^+$  cycle with corresponding rates is:

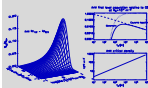


where  $\zeta$  is the ionization rate of  $\text{H}_2$ , in  $\text{s}^{-1}$ . We see that

$$\zeta n_{\text{H}_2} = \eta_1 n_{\text{H}_2} n_{\text{H}_2^+}, \text{ and}$$

$$\eta_2 n_{\text{H}_3^+} n_e = \zeta n_{\text{H}_2}$$

With canonical values for the rates  $\eta_i$ , one gets  $n_{\text{H}_3^+} \gg n_{\text{H}_2^+}$ , and the requisite for neutrality  $n_e \approx n_{\text{H}_3^+}$  allows concluding  $n_e/n_{\text{H}_2} \approx 10^{-8}$ .



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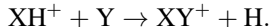
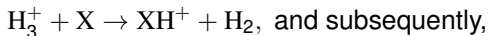
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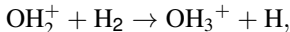
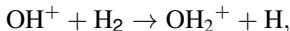
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## Ion-molecule chemistry

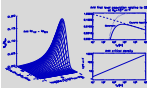
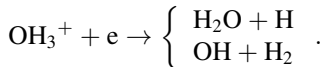
- In ion-molecule chemistry, the standard model for interstellar chemistry,  $\text{H}_3^+$  is cornerstone to all reaction cycles:  
The cycle of an element X (anything short of He,  $\text{O}_2$ ,...) is initiated by  $\text{H}_3^+$  through



Example: production of  $\text{H}_2\text{O}$  and  $\text{OH}$ ,



and finally one dissociative recombination



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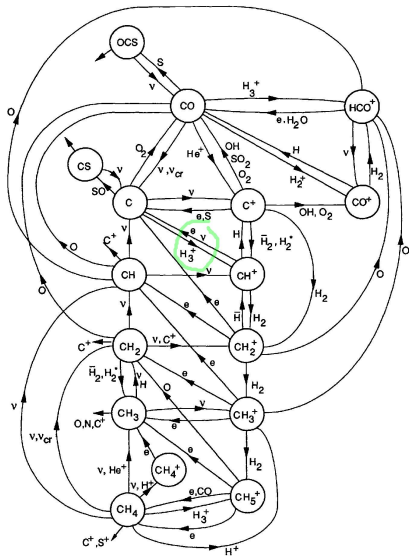
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## ISM

- 



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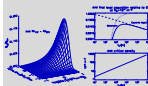
### Heating of the ISM

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Observational validation

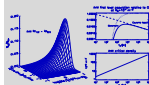
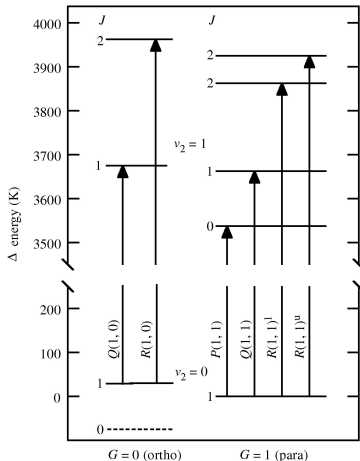
Chemical fractionation



# Molecular formation - validation of the ion-molecule chemical model

$\text{H}_3^+$ , the pillar of chemical cycles in the ISM, was detected by Geballe & Oka (1996, *Nature*, 384, 334; Geballe 2000, *Phil.Trans.R.Soc.Lond.A*, 358, 2503), with an abundance close to that expected from the ionization fraction.

$\text{H}_3^+$  does not have electric dipole moments, and is even worse than  $\text{H}_2$ : it is deprived of excited electronic states (i.e. no UV transitions). It only has two vibration modes. One is symmetrical,  $\nu_1$ , that does not induce electric dipole moment and does not radiate. Only the asymmetrical mode  $\nu_2$  induces an electric dipole.



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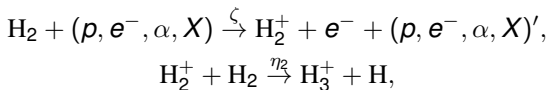
Grain catalysis

Ion-molecule chemistry

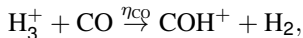
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# The production of $H_3^+$



is balanced by its destruction, mainly through



equating rates, one gets

$$\zeta n_{H_2} = \eta_{CO} n_{H_3^+} n_{CO},$$

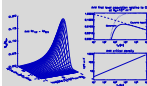
in which  $\eta_{CO} = 1.8 \cdot 10^{-9} \text{ s}^{-1}$ , and

$\zeta = n_{p,X,\alpha,e^-} \eta_1 \approx 3 \cdot 10^{-17} \text{ s}^{-1}$ , gives the product of the cosmic ray density times the ionisation rate of  $H_2$ . In general the relative abundances of CO and  $H_2$  are constant in the diffuse ISM (model: Lee et al., 1996, A&AS, 119, 111, observations: Federman et al. 1980, ApJ 242, 545),  $n_{CO}/n_{H_2} = 1.5 \cdot 10^{-4}$ , so that

$$n_{H_3^+} \approx 10^{-4} \text{ cm}^{-3}, \text{ independent of } n_{H_2}$$

For typical densities  $n_{H_2} \approx 10^4 \text{ cm}^{-3}$ , we have

$$N_{H_3^+} \approx 10^{-9} N_{H_2} \quad !!$$



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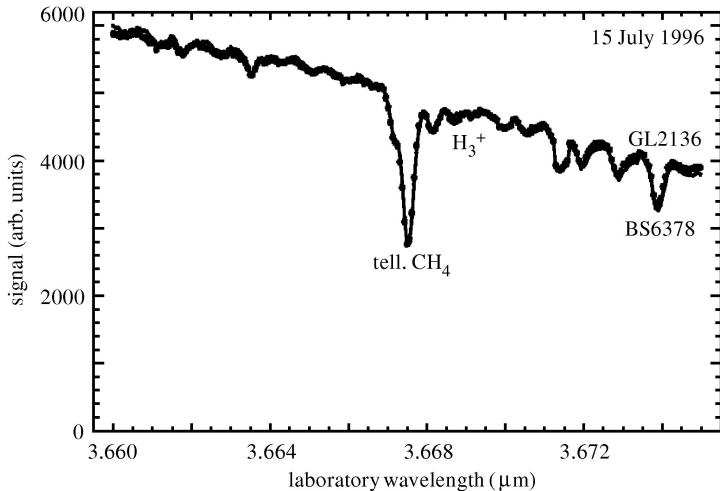
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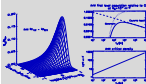
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# Detection of $\text{H}_3^+$ , Oka & Geballe



ISM



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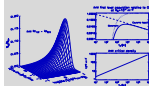
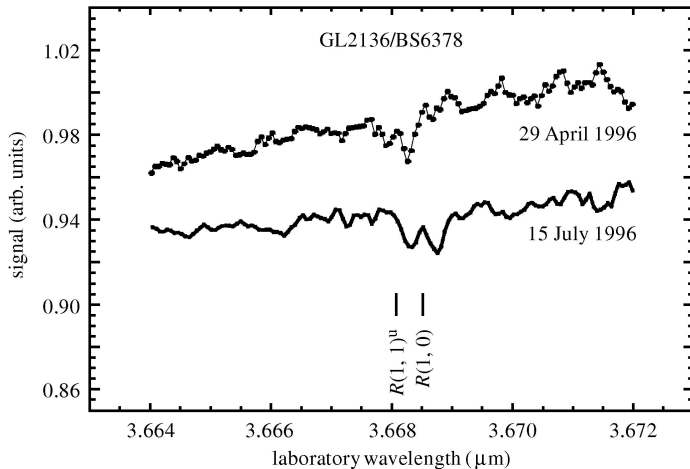
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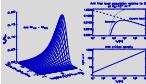
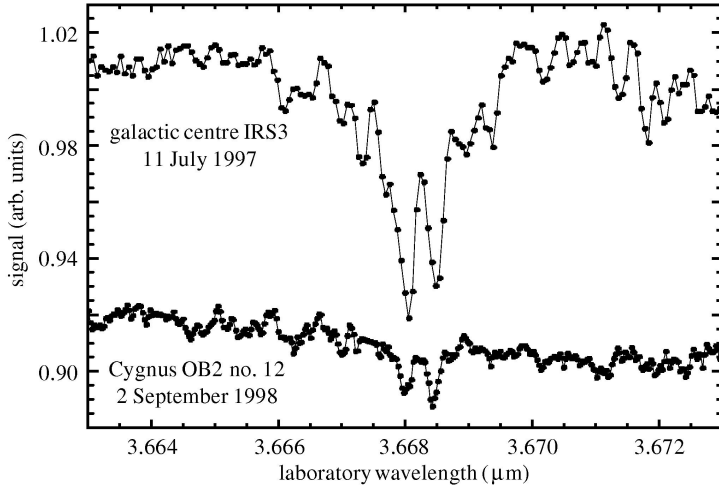
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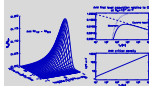
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### Molecule formation

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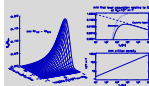
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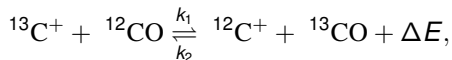
Chemical fractionation

# Chemical fractionation: CO

ISM



The reaction



is slightly exothermic:  $\Delta E/k = 35$  K. Consequently, at low temperatures ( $\lesssim 35$  K), the isotopic ratio  $^{12}\text{C}/^{13}\text{C}$  is different in CO than in the rest of the ISM - there is fractionation in the C isotopes.

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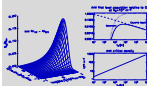
## Chemical fractionation: theory

At constant  $P$  and  $T$ , minimizing the free energy  $G$  gives  $\sum_i \nu_i \mu_i = 0$ , and allows relating the concentration of each species involved in the reaction. For reactions in the gas phase, we can use the chemical potential of ideal gases,  $\mu_i = kT \ln [n_i / \mathcal{Z}_i(T)]$ , with the partition function

$$\mathcal{Z}_i(T) = \frac{h}{\sqrt{2\pi m_i k T}} \sum_a g_i^a e^{-\xi_a/kT},$$

where the energies associated with the internal degrees of freedom are referred to the ground state. We get the law of mass-action (e.g. Shu I, 7),

$$\prod_i n_i^{\nu_i} = \prod_i \mathcal{Z}_i^{\nu_i}.$$



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## Application to CO

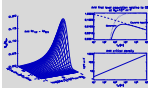
For CO fractionation,

$$\frac{n(^{13}\text{C}^+) n(^{12}\text{CO})}{n(^{12}\text{C}^+) n(^{13}\text{CO})} = e^{-\frac{1}{kT}(\xi(^{12}\text{CO}) - \xi(^{13}\text{CO}))} = \exp\left(-\frac{\Delta E}{kT}\right),$$

where the ground state energy is  $\xi(^{12}\text{CO})$ .

For CO, the rates of reactions in both directions are fast,  $k_1 = k_2 = 2 \cdot 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ , and for cold clouds with  $n(\text{H}_2) \approx 10^4 \text{ cm}^{-3}$  and  $n_{\text{CO}}/n_{\text{H}_2} \approx 10^{-4}$ , the relaxation time is  $\tau_{\text{frac}} \lesssim 1000 \text{ yr}$ . Thus CO is enriched in  $^{13}\text{C}$ , at the expense of the rest of the molecules.

The work function of a dust grain for the adsorption of CO is  $\Delta H \sim 900 \text{ K}$ , and for  $T \lesssim 900 \text{ K}$  the probability of adsorption for grain-CO collisions is 1. Besides the vapor pressure of CO is very high compared to typical ISM pressures (Leger, 1983, A&A, 123, 271). CO is expected to be substantially (of order 50%) condensed onto icy CO mantles on the surface of grains (Whittet et al. 1985, MNRAS, 216, 45).



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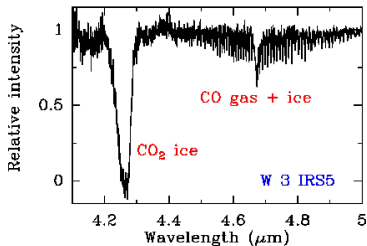
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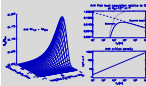
Chemical fractionation



We see that the isotopic ratio  $^{12}\text{C}/^{13}\text{C}$  will be different in the dust than in the gas phase. Additionally the C ratio in any given molecule of the gas phase will depend on the details of the synthesis reactions. The position taken

by CO in relation to  $\text{C}^+$  will determine the C ratio in the product molecule. This result bears on the study of the chemical evolution of galaxies, as well as on studies of molecular cloud structure based on the optically thin isotopes.

Chemical fractionation competes with the process of selective photodissociation.  $^{13}\text{CO}$  is dissociated by interstellar UV radiation, penetrating to deeper lying layers in the clouds than for the main isotope,  $^{12}\text{CO}$ .



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