





### Rate Equations

Ionization structure of gas in PN or AGN dominated by rate equations:

Atoms can be ionized and can recombine  $\implies$  number density,  $n$ , of ions can change with time:

$$\frac{dn_Z(z)}{dt} = n_Z(z-1)\lambda(z-1, z) - n_Z(z)\lambda(z, z+1) + \lambda(z, z-1) + n_Z(z+1)\lambda(z+1, z) \quad (10.1)$$

where

$n_Z(z)$ : number density of species  $Z$  in ionization stage  $z$ .

$\lambda(z, z+1)$ : transition rate from stage  $z$  to  $z+1$

In equilibrium:  $dn_Z/dt = 0$  and thus

$$\frac{n_Z(z+1)}{n_Z(z)} = \frac{\lambda(z, z+1)}{\lambda(z+1, z)} \quad (10.2)$$

In Eq. (10.1) only adjacent ionization stages are connected, calculation gets (much) more complicated if also  $z, z+2$ , etc. are connected.

Processes entering  $\lambda$ :

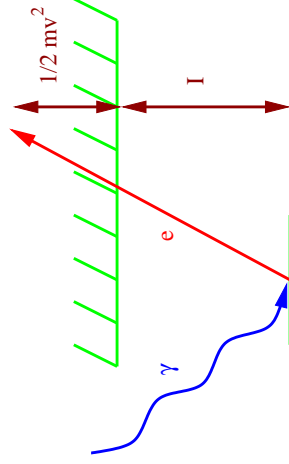
- Photoionization
- Collisional Ionization
- Radiative Recombination
- Dielectronic Recombination

Ionization Equilibrium

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### Photoionization, I



Photoionization: ionization of an ion by a photon.

Reaction equation:



Photon needs energy  $h\nu >$  ionization energy  $I =: h\nu_{\text{thresh}}$ , remaining energy,  $h\nu - I$ , goes into kinetic energy of electron.

Photoionization rate:

$$\gamma_\gamma(z, z+1) =: \Gamma_{Z,z} = \int_{\nu_{\text{thresh}}}^{\infty} \frac{F_\nu}{h\nu} \sigma_{\text{bf}}(\nu) d\nu \quad (10.3)$$

where  $\sigma_{\text{bf}}$ : photoionization cross-section ("bf": bound-free).

$F_\nu$ : number of photons passing through in the frequency interval  $\nu, \nu + d\nu$  per  $\text{cm}^2$  and per second.

Ionization Equilibrium

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### Photoionization, II

Behavior of  $\sigma_{\text{bf}}$  can be found using semi-classical approximations similar to those for the line emissivity.

For Hydrogen, for absorption from the  $n^{\text{th}}$  level, Menzel & Pekeris (1935) found:

$$\sigma_{\text{bf}} = \left( \frac{64\pi^4 m_e e^{10}}{3\sqrt{3} ch^6} \right) \frac{1}{n^5 \nu^3} g_{\text{bf}}(n, \nu) \propto \frac{1}{\nu^3} \quad (10.4)$$

where  $g_{\text{bf}}$  is tabulated, e.g., by Karzas & Latter.

- Useful fitting formulae for all elements and ions of astrophysical interest have been published by Verner & Yakovlev (1995, A&A Suppl. 109, 125).
- Detailed computations have been performed by the opacity project (TOP, Seaton et al.) and by the Iron project (Butler et al).

See

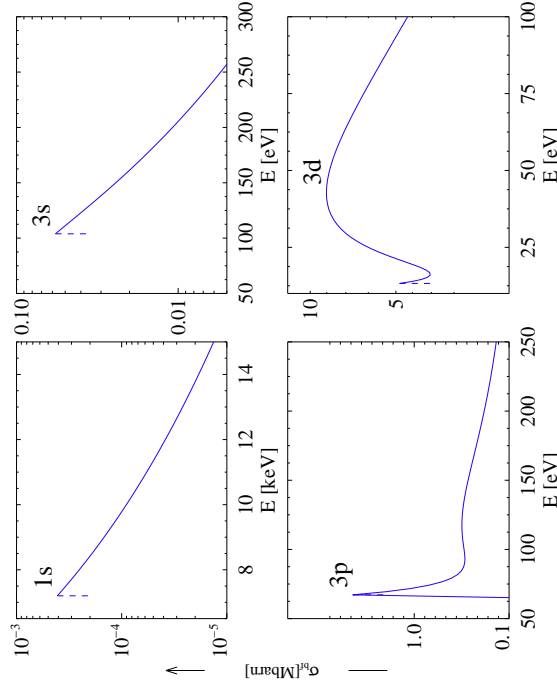
<http://www.usm.uni-muenchen.de/people/ip/iron-project.html>  
and <http://vizier.u-strasbg.fr/topbase/home.html>

Ionization Equilibrium

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### Photoionization, III



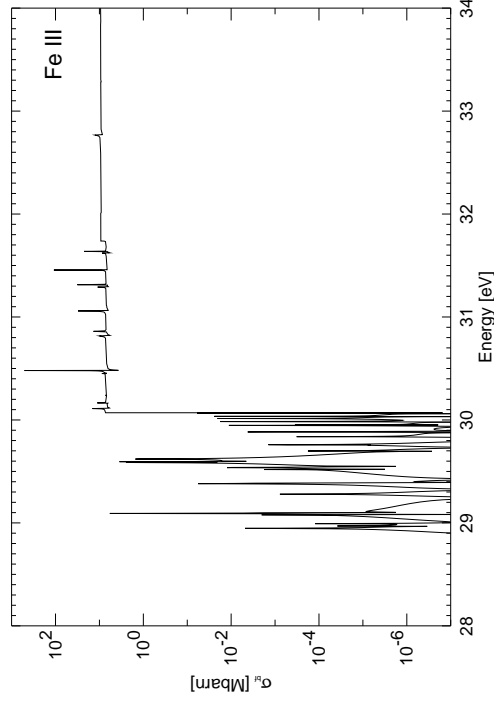
Fe subshell cross sections according to Verner et al.

Ionization Equilibrium

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## Photoionization, IV

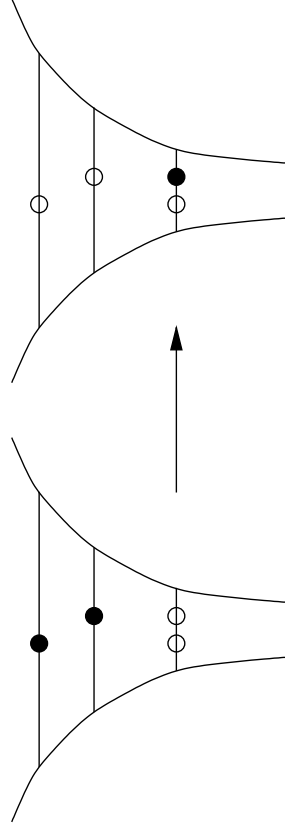


TOP cross-section for Fe III

Ionization Equilibrium



## Photoionization, V

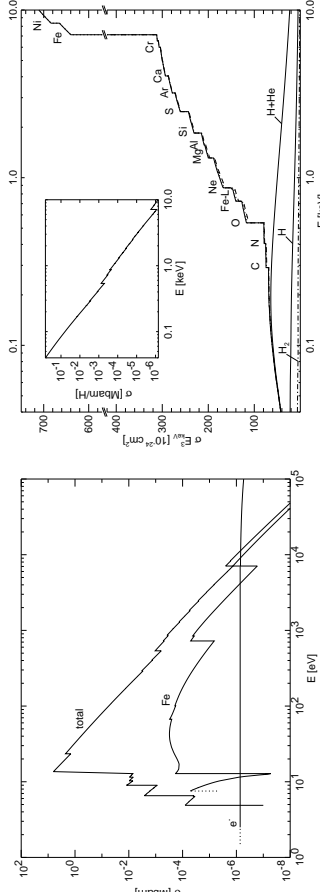


Resonances close to threshold on previous slide:  $\sigma_{\text{bf}}$  influenced by autoionization resonances.

Ionization Equilibrium



## Photoionization, VI



$\sigma_{\text{bf}}$  per H-atom for material of solar composition from the optical to the X-ray regime.

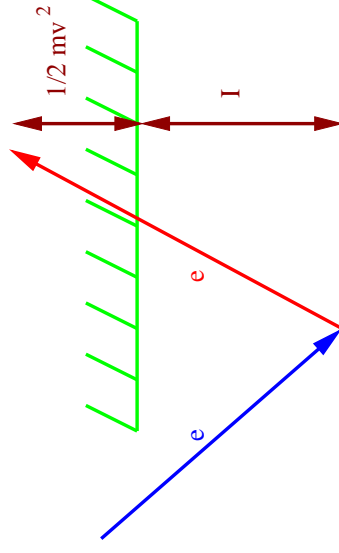
Note strong  $E^{-3}$  dependency above the absorption edges.

In the X-rays, most of the absorption is *not* from hydrogen, although absorbing columns are still given in terms of an equivalent hydrogen column,  $N_{\text{H}}$ .

Ionization Equilibrium



## Collisional Ionization, I



Reaction equation:



Collisional ionization rate depends on electron velocity distribution:

$$\gamma_{\text{coll.}}(z, z+1) = n_e C_Z(z, T_e) = \int_{v_{\text{thresh}}}^{\infty} \sigma_i(v) f(v) v^3 v =: \langle v \sigma_i \rangle \quad (10.5)$$

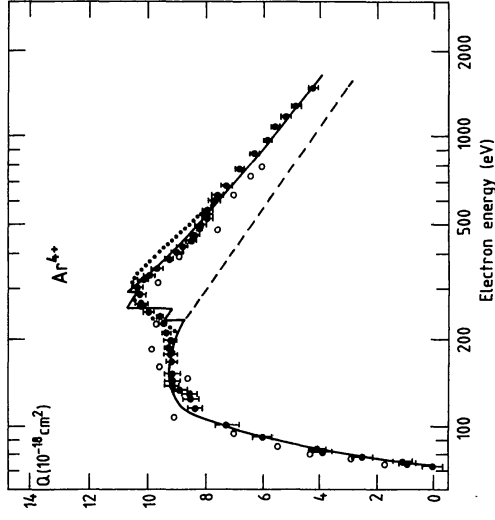
where  $\sigma_i$ : collisional ionization cross-section,

and  $C_Z$ : collisional ionization rate coefficient (units  $\text{cm}^3 \text{s}^{-1}$ ).

Ionization Equilibrium



### Collisional Ionization, II



$C_Z$  is usually given in tabulated form or by using approximate fits.

Typical fitting formula:

$$C_Z(z, T) = A_z T^{1/2} \frac{\exp(-I/kT)}{1 + a_z(T/I_z)} \quad (10.6)$$

where  $T_Z = I/kT$ .

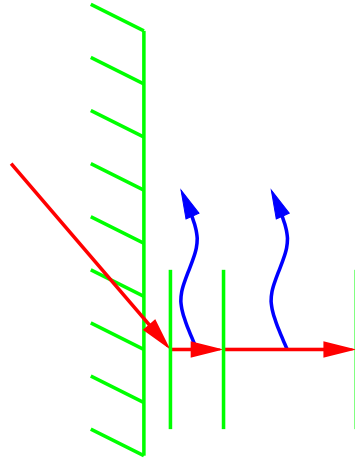
See, e.g., Arnaud & Rothenflug, 1985, A&A Suppl. 60, 425, Shull & van Steenburg, 1982, ApJ Suppl. 48, 95.

$\sigma_i(v)$  for Ar III (Arnaud & Rothenflug, Fig. 8)



### Radiative Recombination, I

**Radiative Recombination:**  
Capture of an electron into the excited state of an ion with subsequent radiative cascade to ground state.



Reaction equation:

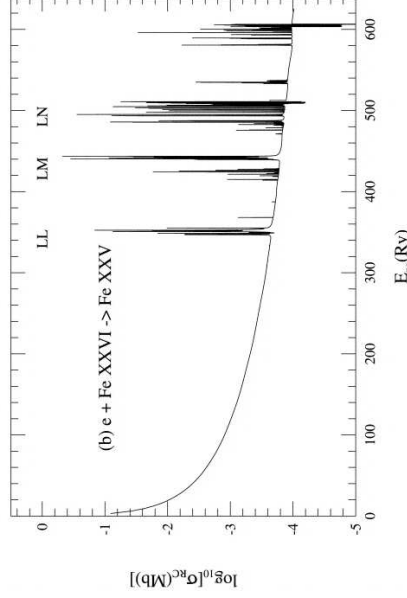


Recombination rate:

$$\lambda_{fb} = n_e \alpha_{Z,z}(T) = n_e \int_0^\infty \sigma_{fb} v f(v) d^3v =: n_e \langle \sigma_{fb} v \rangle \quad (10.7)$$



### Radiative Recombination, II



The recombination cross-section,  $\sigma_{fb}$ , can be obtained from the photoabsorption cross-section,  $\sigma_{bf}$  using the Milne relation,

$$\sigma_{fb}(v) = \frac{g_{z,n}}{g_{z+1,1}} \frac{h^2 v^2}{m_e^2 c^2 v^2} \sigma_{bf}(v) \quad (10.8)$$

Nahar et al., 2001, ApJ Suppl. 133, 255

The cross-section for recombination,  $\sigma_b$ , can be easily computed using the principle of detailed balance that we used, e.g., in the derivation of the self-absorption spectrum for demagnetizing and synchrotron radiation. The derivation given below follows Osterbrock, Astrophysics of Galactic Nebulae and Active Galactic Nuclei.

The microphysical processes that are balanced here are photoionization by photons in the energy range from  $h\nu$  to  $h(\nu + d\nu)$ , with (spontaneous or induced) recombinations from electrons in the velocity range from  $v$  to  $v + dv$ . Thus,  $v$  and  $\nu$  are related by

$$\frac{1}{2} n_e v^2 + h\nu_{\text{recomb}} = h\nu \quad (10.9)$$

$$m_e v dv = h d\nu \quad (10.10)$$

In thermodynamical equilibrium, the rate of induced recombinations is  $\exp(-h\nu/kT_e)$  times the rate of induced ionizations, such that

$$n_e n_{Z,z+1} \sigma_b(v) f(v) dv = (1 - \exp(-h\nu/kT_e)) n_{Z,z} \frac{4\pi B_{\nu}(T_e)}{h\nu} \sigma_{bf}(v) dv \quad (10.11)$$

Because we are in thermodynamical equilibrium, the radiation field is a Planckian,  $B_\nu$ , and the electron distribution,  $f(v)$ , is given by the Maxwell-Boltzmann distribution,

$$f(v) = \frac{4}{\sqrt{\pi}} \left( \frac{m_e}{2kT_e} \right)^{3/2} v^2 e^{-m_e v^2 / 2kT_e} \quad (10.12)$$

As is shown in many introductory books to astrophysics, in thermodynamical equilibrium the ionization structure is given by the Saha equation,

$$\frac{n_{Z,z+1} n_e}{n_{Z,z}} = \frac{2g_{z+1}}{g_z} \left( \frac{2\pi m_e kT_e}{h^2} \right)^2 e^{-h\nu_{\text{recomb}}/kT_e} \quad (10.13)$$

where the  $g_i$  are the statistical weights of the two ionization stages.

Inserting everything gives the Milne relation

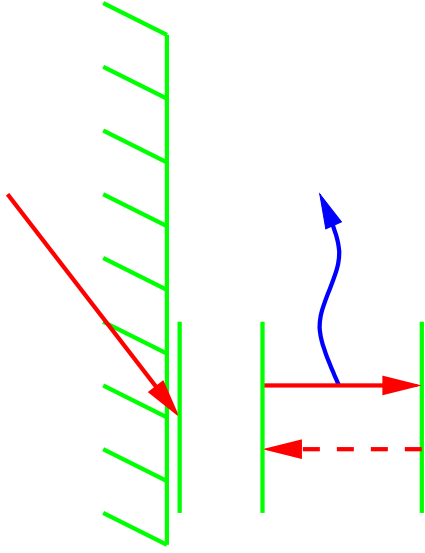
$$\sigma_b(v) = \frac{g_{z,n}}{g_{z+1,1}} \frac{h^2 v^2}{m_e^2 c^2} \sigma_{bf}(v) \quad (10.8)$$

for the recombination cross section  $\sigma_b$  into the  $n$ th level of the ion  $(Z, z)$ . Here, we've explicitly written down the statistical weight of this level as  $g_{z,n}$  and assumed that the recombining ion,  $(Z, z+1)$  is in its ground state ( $v = 1$ ).

An alternative derivation using quantum mechanics uses symmetry arguments for the relevant matrix elements  $\langle z | H | z+1 \rangle$ .



## Dielectronic Recombination



**Dielectronic Recombination:**  
Capture of electron into excited Rydberg state, followed by radiative stabilization.

Reaction equation:



Since two electrons excited  $\implies$  dielectronic recombination leads to emission of satellite lines, important, e.g., in solar corona.

Ionization Equilibrium

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## Photoionization

Assume: cloud irradiated by photons

Goal: only source for ionization: photoionization

Equilibrium: number ionizations = number of recombinations

$$\int_{\nu_{\text{ion}}}^{\infty} \sigma_{\text{bi}}(\nu) \frac{F_{\nu}}{h\nu} n(X^r) d\nu = \alpha(T) n_e n(X^{r+1}) \quad (10.14)$$

where

- $\sigma_{\text{bi}}(\nu)$ : photoionization cross section ( $\text{cm}^2$ ;  $\propto E^{-3}$ )
- $\alpha(T_e)$ : Recombination coefficient ( $\text{cm}^3 \text{s}^{-1}$ )
- $n_i$ : particle density ( $\text{cm}^{-3}$ )
- $F_{\nu}$ : local photon flux ( $\text{erg cm}^{-2} \text{s}^{-1} \text{keV}^{-1}$ ),  $F_{\nu} = L_{\nu} / (4\pi D^2)$

Since  $a(\nu)$  is a quickly decreasing function:

$$\frac{n(X^{r+1})}{n(X^r)} \sim \frac{\sigma_{\text{bi}}(\nu_{\text{ion}})}{\alpha(T)} \frac{L}{4\pi D^2 n_e} \frac{1}{h\nu_{\text{ion}}} \quad (10.15)$$

i.e., ionization equilibrium mainly depends on the ionization parameter

$$U = \frac{L / (4\pi D^2) h\nu_{\text{ion}}}{n_e} \frac{1}{c} = \frac{\# \text{ ionizing photons/cm}^3}{\# \text{ electrons/cm}^3} \quad (10.16)$$

Warning: there are many other definitions for the ionization parameter!

Photoionization Equilibrium

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## Photoionization

In reality, most physical processes presented in this lecture need to be considered:

**Ionization:**

- Photoionization
- collisional Ionization
- Auger-Ionization

**Recombination:**

- radiative recombination
- dielectric recombination

**Continuum Processes:**

- Bremsstrahlung
- Compton-Scattering

*Real life:* Solution of RT problem using advanced radiation codes such as Cloudy or XSTAR (it is *not* worthwhile to develop your own code...).

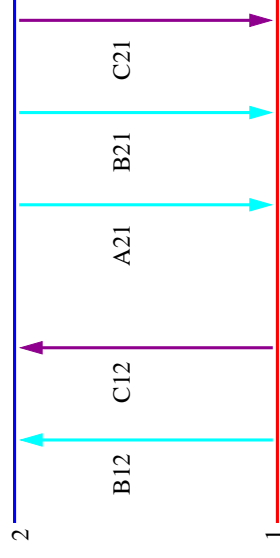
Photoionization Equilibrium

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## Line Diagnostics

Before performing a detailed spectral analysis: get rough overview on physical properties of gas: Density, Temperature, Mass. For this, full blown photoionization computations are not necessary  $\implies$  Line diagnostics



Makes use of excitation mechanisms for line emission:

- Collisional Excitation,  $C_{12}$
- Radiative Deexcitation,  $A_{21}$
- Collisional Deexcitation,  $C_{21}$

$B_{21}$  and  $B_{12}$  can generally be ignored

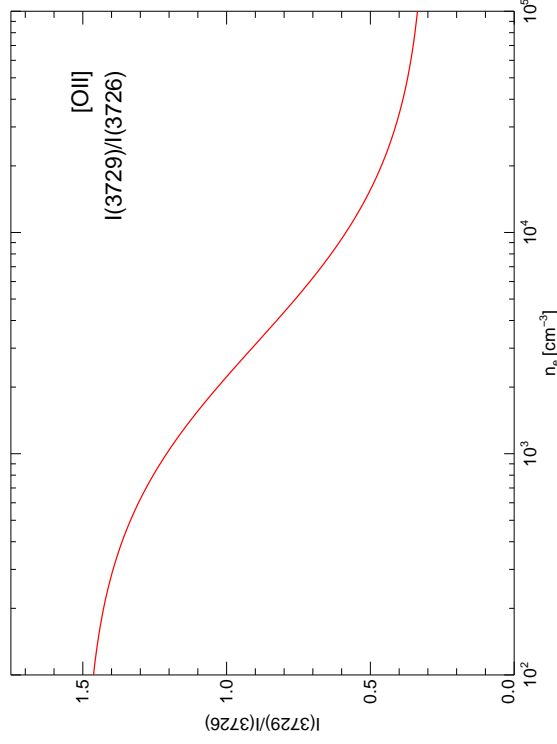
Line Diagnostics

1





## Line Diagnostics: Density, III

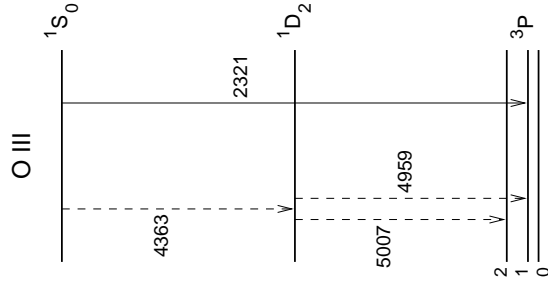


Line Diagnostics

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## Line Diagnostics: Temperature, I



To determine temperature use two levels with different excitation energy and make use of the different excitation probabilities for collisional excitation into the different levels.

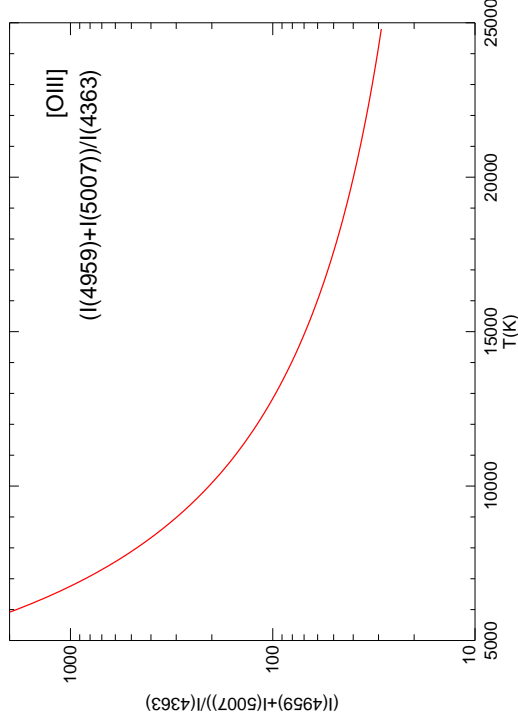
For  $T \sim 10000$  K, use mainly O III and N II

Line Diagnostics

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## Line Diagnostics: Temperature, II



Line Diagnostics

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## Line Diagnostics: Mass

Mass determination: Determine number of emitting atoms from line strength.

Hydrogen:  $H\beta$  (less influenced by radiative transfer effects)

$$j_{H\beta} = n_e n_p \alpha_{H\beta} \frac{h\nu_{H\beta}}{4\pi} = \frac{n_e^{\text{eff}} h\nu_{H\beta}}{4\pi} = 1.24 \times 10^{-25} \text{ erg s}^{-1} \text{ cm}^{-3} \text{ sr}^{-1} \frac{n_e^2}{4\pi} \quad (10.32)$$

where  $\alpha_{H\beta}^{\text{eff}}$ : effective recombination coefficient for  $n = 4 \rightarrow n = 2$  transition (weakly temperature dependent).

Total emissivity

$$L_{H\beta} = \iiint j_{H\beta} d\Omega dV \quad (10.33)$$

$$= \frac{4\pi n_e^2}{3} \cdot 1.24 \times 10^{-25} r^3 f \text{ erg s}^{-1} \propto \int n_e^2 dV \quad (10.34)$$

where  $\int n_e^2 dV$ : emission measure, and  $f$ : filling factor.

Line Diagnostics

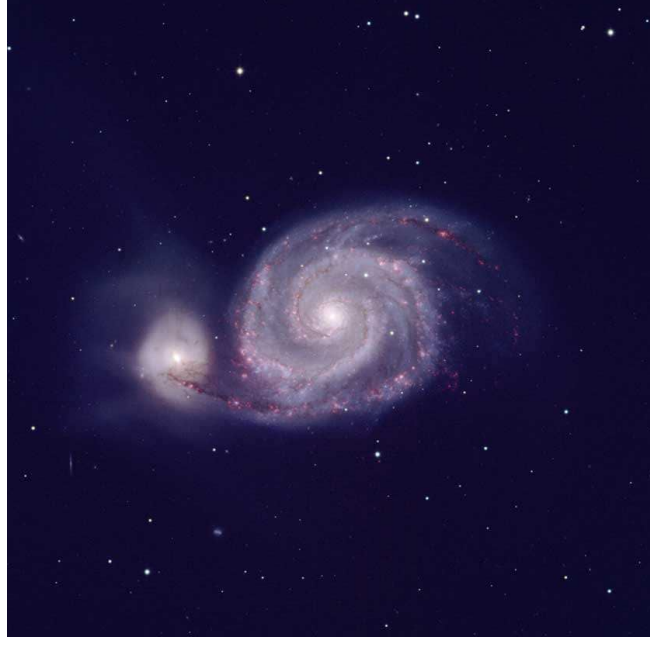
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11-1

## Molecules and Molecular Spectra



M51, NOAO, T. Rector



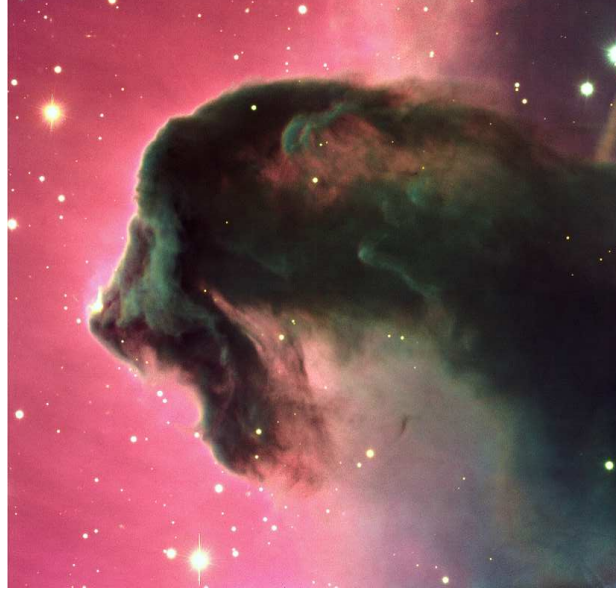
11-2

### Introduction

1. Observational Examples
2. History
3. Molecular Spectroscopy
4. H<sub>2</sub> and CO
5. Molecular Clouds
6. Dust and Molecule Formation
7. Starformation

#### Literature:

Rohlfs & Wilson: Tools of Radio Astronomy, Springer  
Cowley: An Introduction to Cosmochemistry, CUP



The Horsehead Nebula  
(VLT KUEYEN + FORS 2)

ESO PR Photo 02a/02 (25 January 2002)

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**Molecules: History**

- Secchi, 1878: First notice of molecular features in stellar spectra (class III and IV; no explanation)  
Today known as TiO, C<sub>2</sub>, and CN bands
- 1930s: Molecular lines in spectra of planetary atmospheres and comets as well as low temperature stars
- 1941: Interstellar absorption lines due to CN, CH, and CH<sup>+</sup> in optical spectrum of ζ Oph
- Weinreb et al, 1963: Radio absorption lines at  $\lambda = 18$  cm from OH towards SNR Cas A (not associated with Cas A, but with foreground clouds).  
Discovery of masers (=non-LTE!)
- Cheung et al., 1968: First multi-atom molecules: NH<sub>3</sub> and H<sub>2</sub>O ( $\lambda = 1.35$  cm).
- Snyder et al., 1969: Formaldehyde (H<sub>2</sub>CO).
- Today: ~130 different molecules known

Molecules: History

1

**Molecular Hamiltonian, I**

Simplest case: diatomic molecule

Hamiltonian: due to motion of nuclei and electrons.

Assume molecular size  $a$  ( $\sim 1$  Å).

Heisenberg:

$$\Delta p \Delta q \geq \hbar \quad (11.1)$$

 $\implies$  typical energy spacing

$$\Delta E \sim \frac{\Delta p^2}{2m} \sim \frac{\hbar^2}{2ma} \quad (11.2)$$

since  $\Delta q \sim a$ .For electrons:  $\Delta E \sim 1$  eV ( $\hat{=} 10^4$  K),for nuclei:  $\Delta E \sim 0.001$  eV ( $\hat{=} 10$  K) $\implies$  To first order, can ignore kinetic energy of nucleiIn other words: electrons move much faster than nuclei  $\implies$  can assume quasi-stationarity.QM: Computation in "Born-Oppenheimer approximation", i.e., factorize wave-function  $\Psi = \Psi_e \Psi_{\text{nuc}}$  and compute  $\Psi_e$  using the assumption that the nuclei are fixed.

Molecular Spectroscopy

1

**Molecular Hamiltonian, II**

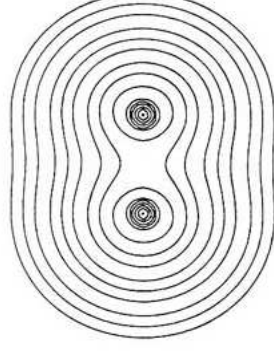
Transitions in molecule due to three different categories:

1. electronic transitions between different levels  
typical energies:  $\sim$  eV  
 $\implies$  visual or UV
2. vibrational transitions due to oscillation of nuclei  
typical energies: 0.1 to 0.01 eV  
 $\implies$  infrared
3. rotational transitions due to rotation of nuclei around common  
typical energies:  $10^{-3}$  eV  
 $\implies$  cm and mm wavebands

Will now look at these in (some) detail.

Molecular Spectroscopy

2

**Electronic States, I****O<sub>2</sub>**

Basic building-block: electronic states.

Generally, in molecules, distinction between "state", "level", and "term" from atomic spectra is *not* made!

Diatomic molecules: classify electron angular momentum along internuclear axis.

In this case, wavefunction has  $\varphi$ -symmetry $\implies \Psi \propto \exp(im\varphi)$ ,  $\Psi$  for other two coordinates depend on  $m^2$  only  $\implies$  electronic states independent of sign of  $m$ . Therefore use

$$\lambda = |m|, \quad \lambda = 0, 1, 2, \dots \quad (11.3)$$

to describe wave functions.

Electronic states with  $\lambda = 0, 1, 2, 3, \dots$  are called  $\sigma, \pi, \delta, \phi$ .

Molecular Spectroscopy

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**Electronic States, II**

State of molecule: sum of orbital angular momenta,  $L$ . Projection of  $L$  onto axis gives  $M_L$ , characterized by quantum number  $\Lambda$ .

$\Lambda = 0, 1, 2, 3, \dots$  are called  $\Sigma, \Pi, \Delta, \Phi, \dots$ ,

Finally, multiplicity: Total electronic angular momentum (quantum number  $S$ ).

Write as in atoms,  $2^{S+1}\Lambda$ , such as  $2^2\Sigma, 4\Pi$ , etc.

Sometimes, the sum of  $\Lambda$  and  $\Sigma$  is appended to the term symbol:

For example, for  $4\Pi$ :

$\Lambda = 1$  and

$\Sigma = -3/2, -1/2, 1/2, 3/2$ ,

such that

$$4\Pi_{5/2}, 4\Pi_{3/2}, 4\Pi_{1/2}, 4\Pi_{-1/2}$$

Individual states are sorted in a strange way.  $X$  is ground state (sometimes addl.  $g$  appended), higher states are  $A, B, C$ , other terms  $a, b, \dots$  (e.g., ground state of CN is  $X^2\Pi$ , ground state of  $H_2$  is  $X^1\Sigma_g$ ).

Molecular Spectroscopy

**Electronic States, III**

Energy of electronic state: In molecular spectroscopy, use wavenumber  $\tilde{\nu}$  instead of Energy:

$$E = h\nu = \frac{hc}{\lambda} = hc\tilde{\nu} \quad (11.4)$$

The energy expressed in terms of wavenumber is called a term value (not to be confused with "terms" of atomic physics!)

The electronic term value is given by

$$T_e = T_0 + A \cdot \Lambda \cdot \Sigma \quad (11.5)$$

where  $\Sigma$  is the projection of  $S$  on the internuclear axis, and  $A, T_0$  are constants.

$\implies$  Spin has large influence on energy!

Typical energies are on the order of several eV.

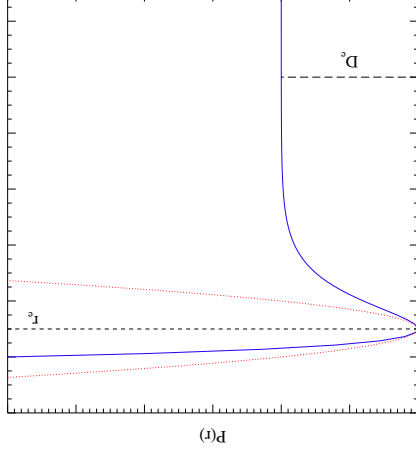
The sign of  $A$  determines the order of energies:

$A > 0 \implies$  Regular multiplet

$A < 0 \implies$  Inverted multiplet

append  $x$  or  $z$  to designation of state

Molecular Spectroscopy

**Vibrations**

The internuclear potential  $P(r)$  is similar to the Morse potential,

$$P(r) = D_e \left( 1 - e^{-a(r-r_e)} \right)^2 \quad (11.6)$$

$$\sim a^2 D_e (r - r_e)^2$$

where  $D_e$  is the potential energy at large distances (=dissociation energy), and  $r_e$  is the minimum of the potential energy (distance of nuclei).

The Schrödinger equation gives the vibrational energies

$$E(v) = h\nu_{\text{osc}}(v + 1/2) \quad \text{with} \quad \nu_{\text{osc}} = \frac{a}{2\pi} \sqrt{\frac{2D_e}{m}} \quad (11.7)$$

where  $v = 0, 1, 2, \dots$  is called the vibrational quantum number.

Molecular Spectroscopy

**Rotational Spectra, I**

Kinetic energy of rotation:

$$H_{\text{rot}} = \frac{1}{2} \Theta \omega^2 = \frac{J^2}{2\Theta} \quad (11.8)$$

where  $J$  is angular momentum and where  $\Theta$  is the moment of inertia.

For a diatomic molecule with nuclei  $A$  and  $B$ ,

$$\Theta = m_A r_A^2 + m_B r_B^2 =: m r_e^2 \quad (11.9)$$

where

$$r_e = r_A - r_B \quad (11.10)$$

and where the reduced mass is

$$m = \frac{m_A m_B}{m_A + m_B} \quad (11.11)$$

Finally, the angular momentum is

$$J = \Theta \omega \quad (11.12)$$

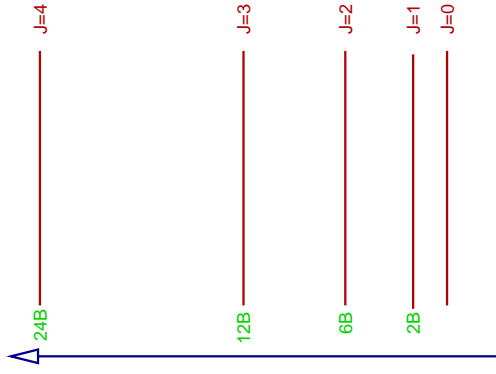
Normally, the moment of inertia is a tensor

$\implies$  use value appropriate for direction of  $\omega \dots$

Molecular Spectroscopy



## Rotational Spectra, II



Solution of the Schrödinger equation for the angular momentum gives

$$E_{\text{rot}}(J) = \frac{\hbar^2}{2I} J(J+1) \quad (11.13)$$

where  $J$  is quantum number of angular momentum, and where

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

Or in units of wave-number:

$$\begin{aligned} F(J) &= \frac{E_{\text{rot}}}{hc} \\ &= \frac{h}{8\pi^2 I c} J(J+1) \\ &= B \cdot J(J+1) \end{aligned} \quad (11.14)$$

Molecular Spectroscopy

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## Rotational Spectra, III

Actual molecules have centrifugal stretching due to rotation.

To first order, gives energy correction, therefore for rotational terms in general:

$$F(J) = BJ(J+1) - D[J(J+1)]^2 \quad (11.15)$$

with some constant  $D \ll B$ .

Order of magnitude of  $B$ : Typical separation of nuclei in molecule  $a \sim 1\text{Å} \sim 10^{-8}\text{ cm}$ . For CO, reduced mass is about 10 amu, or  $1.6 \times 10^{-23}\text{ g}$ . Therefore

$$I \approx 1.6 \times 10^{-23} \cdot 10^{-16} = 1.6 \times 10^{-39}\text{ g cm}^2 \quad \text{such that } B = 1.75\text{ cm}^{-1}$$

Therefore, the wavenumber of a transition between  $J = 1$  and  $J = 0$  is

$$\tilde{\nu}_{J=1 \rightarrow J=0} = 3B - 1B = 2B = 3.5\text{ cm}^{-1}$$

corresponding to  $\lambda = 3\text{ mm}$ , or  $\nu = 100\text{ GHz}$ .

Molecular Spectroscopy

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## Reality

In reality, rotators vibrate  $\implies$  rotations and vibrations are coupled  $\implies$  All constants are not constants...

Rotations:

$$F(J) = J(J+1)B_v - (J(J+1))^2 D_v \quad (11.16)$$

where

$$B_v = B - \alpha_e(v+1/2) \quad (11.17)$$

with some correcting constant  $\alpha_e$ . In principle similar equation for  $D_v$ , with constant  $\beta_e$ , but usually setting  $D_v = D$  is sufficient.

Vibrations:

$$G(v) = \omega_e(v+1/2) - \omega_e x_e(v+1/2)^2 + \omega_e y_e(v+1/2)^3 + \dots \quad (11.18)$$

where  $\omega_e, \omega_e x_e, \omega_e y_e$ , etc. are constants.

Typically, all constants ( $\alpha_e, D_v, \omega_e, \dots$ ) are tabulated (determined from experiments)

Molecular Spectroscopy

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Table 11.1. Selected Constants for Diatomic Molecules. (Units are  $\text{cm}^{-1}$  except as indicated.)

State	$T_e$	$\omega_e$	$\omega_e x_e$	$B_e$	$D_e$	$r_e(\text{Å})$
$C^{12}2\Sigma^+$	10089.8	2443.77	69.524	31.362 <sub>5</sub>	1.664 <sub>4</sub>	2.23
$B^{12}2\Sigma^+$	91700.0	1358.09	20.888	20.15 <sub>4</sub>	1.184 <sub>5</sub>	1.29
$X^{12}1\Sigma^+$	0.0	4401.21 <sub>5</sub>	121.33 <sub>6</sub>	60.853 <sub>6</sub>	3.062 <sub>5</sub>	4.71
$D^{12}1\Sigma^+$	20022.50	1788.22	16.440	1.752 <sub>7</sub>	0.01608	6.7 <sub>2</sub>
$C^{12}2\Sigma^+$	13312.1	1961.8	1.87			1.23
$A^{11}\Sigma^+$	8391.00	1608.35	12.07 <sub>8</sub>	0.016 <sub>3</sub>	6.44	1.32
$B^{11}\Sigma^+$	6434.2 <sub>7</sub>	1470.4 <sub>5</sub>	11.1 <sub>9</sub>	1.485 <sub>2</sub>	0.016 <sub>34</sub>	6.22
$D^{11}\Sigma^+$	716.2 <sub>4</sub>	1641.35	11.67	1.632 <sub>4</sub>	0.01661	6.44
$X^{11}\Sigma^+$	0.0	1854.71	13.34 <sub>6</sub>	1.819 <sub>8</sub>	0.017 <sub>6</sub>	6.92
$D^{12}1\Sigma^+$	5486.3	1004.7 <sub>1</sub>	8.7 <sub>8</sub>	1.162	0.013	7.150
$A^{11}\Sigma^+$	9245.28	1812.5 <sub>6</sub>	12.60 <sub>5</sub>	1.7151	0.01708	5.93
$B^{12}\Sigma^+$	25752.0	2163.9	20.2	1.973	0.023	6.61
$X^{12}\Sigma^+$	0.0	2068.59	13.087	1.899 <sub>7</sub>	0.0173 <sub>6</sub>	6.40
$D^{12}1\Sigma^+$	1109 <sub>2</sub>					
$A^{12}\Sigma^+$	55825.4 <sub>6</sub>	1228.60	10.468	1.3446	0.018 <sub>9</sub>	6.41
$B^{12}\Sigma^+$	48686.70	1743.4 <sub>1</sub>	14.3 <sub>6</sub>	1.69124	0.01904	6.36
$X^{12}\Sigma^+$	0.0	2169.814	13.2883	1.9313	0.0175	6.121
$D^{12}1\Sigma^+$	4392					
$A^{11}\Sigma^+$	3737.76 <sub>1</sub>	848.81 <sub>5</sub>	18.910 <sub>8</sub>	0.7242	19.38	0.96966
$X^{11}1\Sigma^+$	0.0					
$C^{12}1\Sigma^+$	19617.0	838.26	4.76	0.48989	0.00306	6.7
$B^{11}\Sigma^+$	1947.12	1633.5	875.	5.	[0.50617]	[1.67]
$D^{11}\Sigma^+$	16293.5	1631.5 <sub>1</sub>				
$A^{11}\Sigma^+$	1431.0	1431.0	3.942	0.51337	0.0029 <sub>1</sub>	6.1
$B^{11}\Sigma^+$	11322.0 <sub>5</sub>	[911.20]	(3.7 <sub>2</sub> )	0.50739	0.00315	6.92
$A^{11}\Sigma^+$	1431.0	867.78	3.942	0.50739	0.00315	6.92
$D^{12}\Sigma^+$	12025.	924 <sub>2</sub>	5.1			
$E^{11}\Sigma^+$	14089.91					
$D^{12}\Sigma^+$	1014.6	(4.6)	0.54922	0.00337	[6.0]	1.60
$D^{12}\Sigma^+$	2215.6					
$D^{12}\Sigma^+$	197.5					
$X^{12}\Sigma^+$	96.4					
$X^{12}\Sigma^+$	0.0					

Corney, Tab. 11.1



### Selection Rules

Total energy of a molecular level of a diatomic molecule:

$$T(v, J) = T_e + G(v) + F(J) \quad (11.19)$$

Compute line wavenumbers from differences of levels obeying selection rules.

Most important for spectroscopy: rotational-vibrational transitions.

For these the following selection rules apply:

- Selection rule for  $J$ :  
 $\Delta J = 0, \pm 1$  and  $J = 0 \not\rightarrow J = 0$ .
- Selection rule for  $v$ :  
 $\Delta v \neq 0$  (only true for pure harmonic oscillator)

Also need finite dipole moment for these dipole-transitions to be possible

Note: homonuclear molecules have no dipole moment  $\Rightarrow$  only quadrupole lines possible ( $\Delta J = \pm 2$ ).

Most common:

$J' = J'' + 1$ : R-Branch

$J' = J''$  : Q-Branch

$J' = J'' - 1$ : P-Branch

Note:  $J = 0 \not\rightarrow J = 0$  means that there is no Q-branch for most ground states.

Molecular Spectroscopy



### Molecular Hydrogen

Because of high abundances: most molecular gas is  $H_2$ .

For review of properties of  $H_2$ , see Shull & Beckwith, 1982, Ann. Rev. Astron. Astrophys. 20, 163

$H_2$  is homonuclear

$\Rightarrow$  no permanent dipole moment

$\Rightarrow$  no rotational dipole transitions.

Only transitions observable are vibrational or electronic.

Vibrational:  $\lambda \sim 6 \mu\text{m}$ , in the infrared.

Problem: Dust extinction in IR is severe

Once H is molecular, it is very difficult to see.

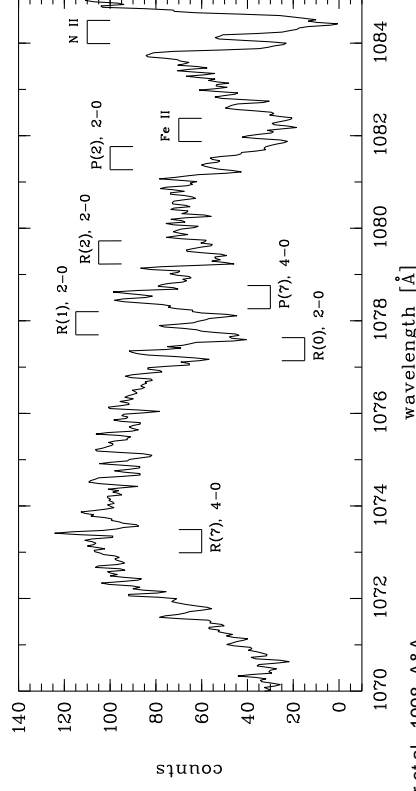
Alternative: Observation of electronic transitions of  $H_2$  in absorption against hot UV-Stars ("Werner-bands").

Note that excitation of transitions requires lots of energy which cannot be produced otherwise.

Molecules: Molecular Hydrogen



### Molecular Hydrogen



Richter et al., 1998, A&A

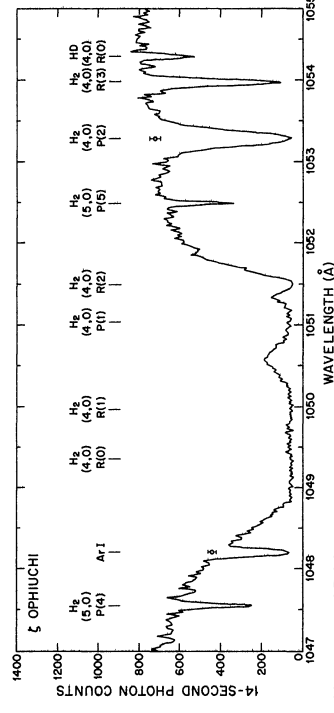
ORFEUS: Discovery of  $H_2$  bands in absorption in direction towards SMC

$\Rightarrow H_2$  also present in diffuse ISM, not only in clouds  
(agrees with Copernicus measurements in Milky Way; Spitzer, 1974).

Molecules: Molecular Hydrogen



### Molecular Hydrogen



Spitzer & Jenkins, 1975, ARAA 13, 133

Observation of  $J = 1 \rightarrow J = 0$  transition can be used to deduce temperature: Boltzmann gives:

$$\frac{N(J)}{N(0)} = (2J + 1) \exp\left(-\frac{85 \text{ K}}{T}\right) \quad (11.20)$$

Typical temperatures for the diffuse medium are between 45 K and 130 K.

For low-density clouds,  $N(1)/N(0)$  might be non-thermal, because molecules have tendency to be in high- $J$  states when relaxing after photon excitation, thermal ratio only good for  $n < 10^{18} \text{ cm}^{-3}$ .

Molecules: Molecular Hydrogen



### Carbon Monoxide

Better than observing H<sub>2</sub> directly is to deduce its presence *indirectly* using other molecules with rotational positions  $\Rightarrow$  use heteronuclear molecules, e.g., CO, CS, HCN.

Candidate Number 1: CO, rotational transitions at 1.3 mm ( $J = 2 \rightarrow J = 1$ ) and 2.6 mm ( $J = 1 \rightarrow J = 0$ ).

Notation: CO(2-1) and CO(1-0)

CO is less abundant than H<sub>2</sub> (see later), but  $A$ -coefficients of lines very large;

$\tau = 1$  reached at CO-column  $\sim 6 \times 10^{15} \text{ cm}^{-2}$ , corresponding to

$$N_{\text{H}} \sim 8 \times 10^{19} \text{ cm}^{-2}$$

$\Rightarrow$  Cannot use "standard" CO to look into thick clouds.

$\Rightarrow$  Use isotope effects!

Molecules: Carbon Monoxide

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### CO: Isotope Effects

CO occurs in several forms:

- <sup>12</sup>C<sup>16</sup>O (= <sup>12</sup>CO)
- <sup>13</sup>C<sup>16</sup>O (= <sup>13</sup>CO)
- <sup>12</sup>C<sup>18</sup>O (= C<sup>18</sup>O)

because of slightly different reduced masses, the wavelength of transitions is slightly different

$\Rightarrow$  can separate emission lines from these species.

Relative abundances:

$$^{12}\text{CO} : ^{13}\text{CO} : \text{C}^{18}\text{O} = 500 : 65 : 1$$

By using <sup>13</sup>CO or C<sup>18</sup>O, we can look deeper into molecular clouds.

Molecules: Carbon Monoxide

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### Column from Lines

To measure mass from emission line, determine the number of emitting atoms,  $N$ .

Observed intensity not trivially  $\propto N$  because of self-absorption.

Excess in line:

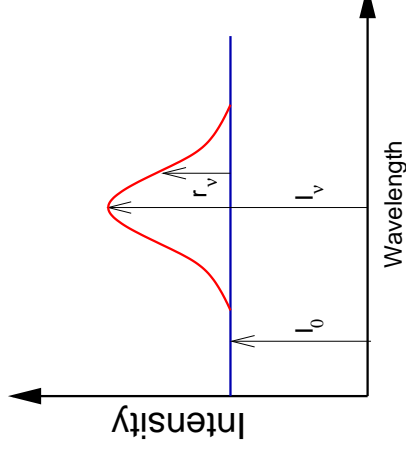
$$r_{\nu} = \frac{I_{\nu} - I_0}{I_0} = \frac{S_{\nu} - I_0}{S_{\nu}} \left( 1 - \exp\left(-\frac{\tau_{\nu}}{\mu}\right) \right) \quad (11.21)$$

where  $\tau$ : optical depth,  $I_0$ : background intens.,  $\mu = \cos \theta$

Inserting  $\tau$  in terms of transition probability  $f_{nm}$  and expanding the exponential gives for the equivalent width

$$W_{\nu} = \int r_{\nu} d\nu \sim \frac{\pi e^2}{mc} T_0 f_{nm} \frac{N_n}{\mu} \quad (11.22)$$

where  $T_0 = (S_{\nu} - I_0)/S_{\nu}$ .



after Cowley, Fig. 14.5

Molecules: Carbon Monoxide

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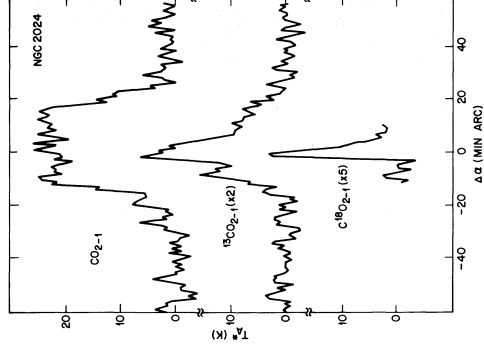


courtesy Matthew T. Russell





### NGC 2024, IV



Right-ascension strip maps over NGC 2024: peak intensities <sup>12</sup>CO, <sup>13</sup>CO, and C<sup>18</sup>O scale as 5:2:1  
 ⇒ cloud is optically thick (lines should scale as the abundances, and they do not!).  
 Last step to get  $N_{CO}$ : use Boltzmann if (and only if) LTE is appropriate...

(Phillips et al., 1979, Fig. 3b)  
 Intensity is given as antenna temperature,  
 $I = 2kTv^2/c^2$

Molecules: Carbon Monoxide



### From CO to H

Once  $N(CO)$  has been determined: Infer H<sub>2</sub> column using some "standard" ratio. Typical assumptions:

$$\frac{N(^{13}CO)}{N(H_2)} \sim 0.5 \dots 2.0 \times 10^{-6} \quad (11.23)$$

Ratio is determined from UV-data on hydrogen and CO measurements at cloud edges (low  $\tau$ ).

#### Caveats:

- CO usually *not* in LTE for higher  $J$
- $n(H_2)/n(^{12}C), n(^{12}C)/n(^{13}C)$  affected by astration (passage of ISM through stars), ⇒  $n(^{12}C)/n(^{13}C) = 20$  at GC, 90 at large Galactic radii,
- Clumpy clouds? Shadowing? (finite beamsize of telescope...),
- Isotope ratios very different between different cloud complexes
- ...

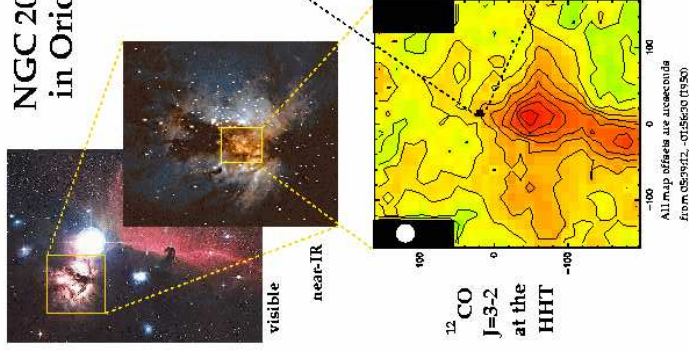
**H<sub>2</sub> mass only determinable to factor of a few!**

Molecules: Carbon Monoxide



For a case study: use NGC 2024 (flame nebula, bright star is Alnitak [ $\zeta$  Ori]; close to horsehead).

### NGC 2024 in Orion



**All Molecules**

List of all observed interstellar and circumstellar molecules

(<http://www.cv.nrao.edu/~awootten/allmols.html>; last updated Nov 2005)

**Molecules with Two Atoms** : AlF, AlCl, C<sub>2</sub>, CH, CH<sup>+</sup>, CN, CO, CO<sup>+</sup>, CP, CS, CSI, HCl, H<sub>2</sub>, KCl, NH, NO, NS, NaCl, OH, PN, SO, SO<sup>+</sup>, SiN, SiO, SiS, HF, SH, FeO(?)

**Molecules with Three Atoms**: C<sub>3</sub>, C<sub>2</sub>H, C<sub>2</sub>O, C<sub>2</sub>S, CH<sub>2</sub>, HCN, HCO, HCO<sup>+</sup>, HCS<sup>+</sup>, HOC<sup>+</sup>, H<sub>2</sub>O, H<sub>2</sub>S, HNC, HNO, MgCN, MgNC, N<sub>2</sub>H<sup>+</sup>, N<sub>2</sub>O, NaCN, OCS, SO<sub>2</sub>, c-SiC<sub>2</sub>, CO<sub>2</sub>, NH<sub>2</sub>, H<sub>3</sub><sup>+</sup>, AINC, SiCN, AINC, SiNC

**Molecules with Four Atoms**: c-C<sub>3</sub>H, l-C<sub>3</sub>H, C<sub>3</sub>N, C<sub>3</sub>O, C<sub>3</sub>S, C<sub>2</sub>H<sub>2</sub>, CH<sub>2</sub>D<sup>+</sup>?, HCCN, HCNH<sup>+</sup>, HNCO, HNCS, HOCO<sup>+</sup>, H<sub>2</sub>CO, H<sub>2</sub>CN, H<sub>2</sub>CS, H<sub>3</sub>O<sup>+</sup>, NH<sub>3</sub>, SiC<sub>3</sub>, C<sub>4</sub>

Molecules: Carbon Monoxide

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**All Molecules**

**Molecules with Five Atoms**: C<sub>5</sub>, C<sub>4</sub>H, C<sub>4</sub>Si, l-C<sub>3</sub>H<sub>2</sub>, c-C<sub>3</sub>H<sub>2</sub>, CH<sub>2</sub>CN, CH<sub>4</sub>, HC<sub>3</sub>N, HC<sub>2</sub>NC, HCOOH, H<sub>2</sub>CHN, H<sub>2</sub>C<sub>2</sub>O, H<sub>2</sub>NCN, HNC<sub>3</sub>, SiH<sub>4</sub>, H<sub>2</sub>COH<sup>+</sup>

**Molecules with Six Atoms**: C<sub>5</sub>H, C<sub>5</sub>O, C<sub>2</sub>H<sub>4</sub>, CH<sub>3</sub>CN, CH<sub>3</sub>NC, CH<sub>3</sub>OH, CH<sub>3</sub>SH, HC<sub>3</sub>NH<sup>+</sup>, HC<sub>2</sub>CHO, HCONH<sub>2</sub>, l-H<sub>2</sub>C<sub>4</sub>, C<sub>5</sub>N, HC<sub>4</sub>N

**Molecules with Seven Atoms**: C<sub>6</sub>H, CH<sub>2</sub>CHCN, CH<sub>3</sub>C<sub>2</sub>H, HC<sub>5</sub>N, HCOCH<sub>3</sub>, NH<sub>2</sub>CH<sub>3</sub>, c-C<sub>2</sub>H<sub>4</sub>O, CH<sub>2</sub>CHOH

**Molecules with Eight Atoms**: CH<sub>3</sub>C<sub>3</sub>N, HCOOCH<sub>3</sub>, CH<sub>3</sub>COOH, C<sub>7</sub>H, H<sub>2</sub>C<sub>6</sub>, CH<sub>2</sub>OHCHO, CH<sub>2</sub>CHCHO

**Molecules with Nine Atoms**: CH<sub>3</sub>C<sub>4</sub>H, CH<sub>3</sub>CH<sub>2</sub>CN, (CH<sub>3</sub>)<sub>2</sub>O, CH<sub>3</sub>CH<sub>2</sub>OH, HC<sub>7</sub>N, C<sub>8</sub>H

**Molecules with Ten or More Atoms**: CH<sub>3</sub>C<sub>5</sub>N?, (CH<sub>3</sub>)<sub>2</sub>CO, NH<sub>2</sub>CH<sub>2</sub>COOH?, CH<sub>3</sub>CH<sub>2</sub>CHO, HC<sub>9</sub>N, CH<sub>3</sub>OC<sub>2</sub>H<sub>5</sub>, HC<sub>11</sub>N,

Molecules: Carbon Monoxide

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