

Interstellar Medium 2020

Lecture 7: Molecules and molecular clouds



Paul van der Werf

Course Contents

1. Introduction and ecology of the interstellar medium
2. Physical conditions and radiative processes
3. The atomic interstellar medium
4. Ionization and recombination
5. HII regions
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7. Molecules and their excitation
8. Thermal balance
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11. Shocks, supernova remnants and the 3-phase ISM
12. Extragalactic ISM and outlook

Today's Lecture

Molecules and their excitation

1. Molecular structure and molecular spectra
2. The H_2 problem
3. Molecules as probes

Corresponding textbook material: Draine Ch. 5 and 31

Molecular spectra

Born-Oppenheimer approximation:

we can, to good approximation, consider the nuclei fixed and the electrons moving in the resulting potential.

Based on this we can derive that three types of transitions occur:

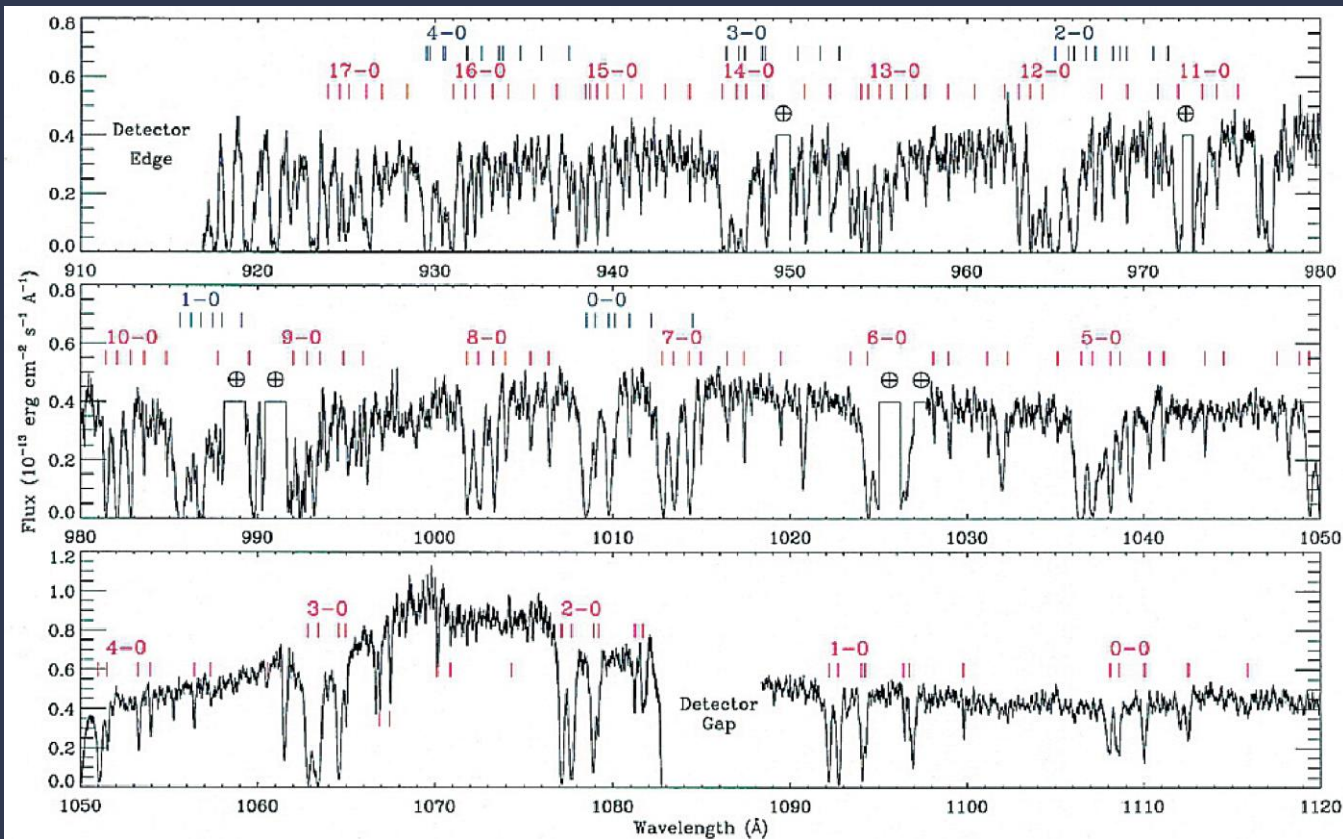
1. Electronic transitions (mostly optical/UV)
2. Vibrational transitions (mostly near/mid-IR)
3. Rotational transitions (mostly far-IR/mm/radio)

Electronic transitions

Reconfiguration of electron cloud

- As for atoms/ions, but with non-spherical potential
- High excitation energies ($E/k \sim 50000$ K), so not collisionally excited
- UV absorption lines

H₂ UV absorption lines



FUSE spectrum
towards a bright UV
source, showing H₂
absorption lines
(Shull *et al.*, 2000)

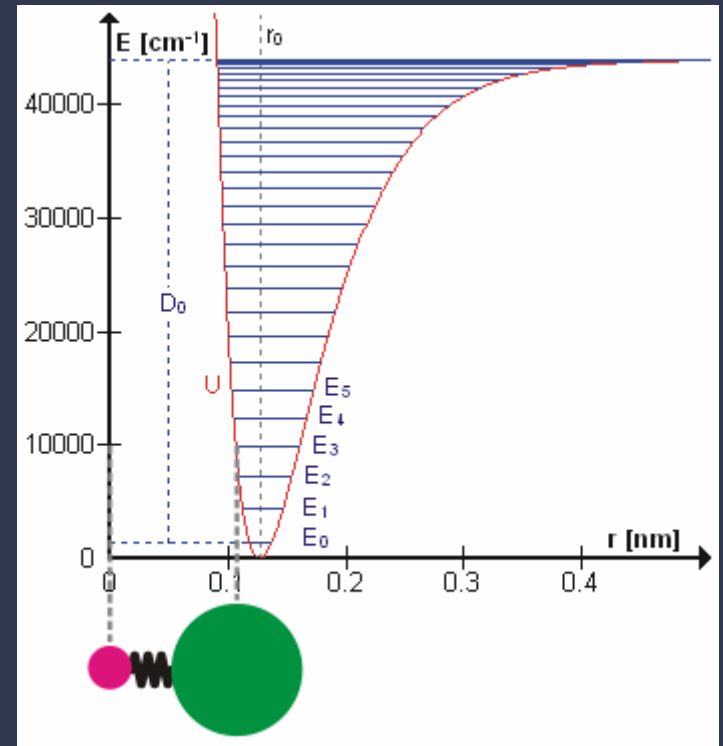
- blue tick marks: H₂ Werner band
- red tick marks: H₂ Lyman band

Vibrational energy levels

Spring analogy, with spring constant determined by the mode of vibration and the nature of the chemical bond.

Quantum harmonic oscillator:

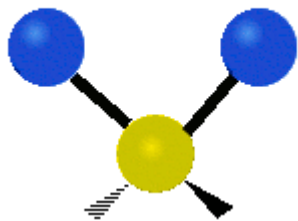
$$E_v = h\nu_0 \left(v + \frac{1}{2} \right) \quad v = 0, 1, 2, \dots$$



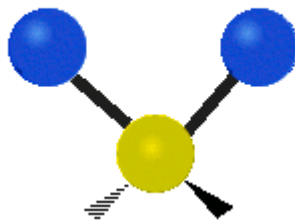
(from wikipedia)

- Excitation energies $E/k \sim 1000 \text{ K}$, so usually not collisionally excited
- IR absorption bands
- Fluorescent emission

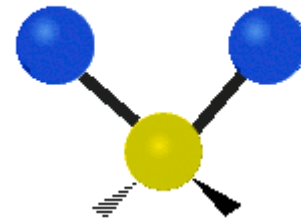
Vibrational modes in polyatomic molecules



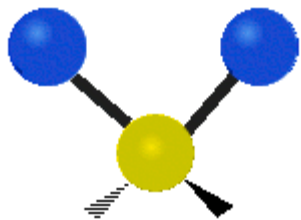
symmetric stretch



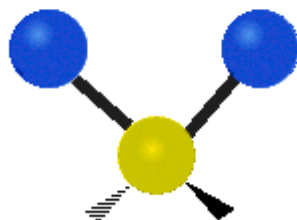
asymmetric stretch



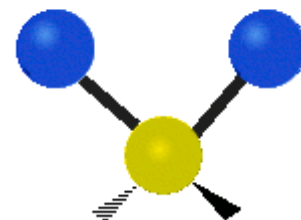
bending



rocking



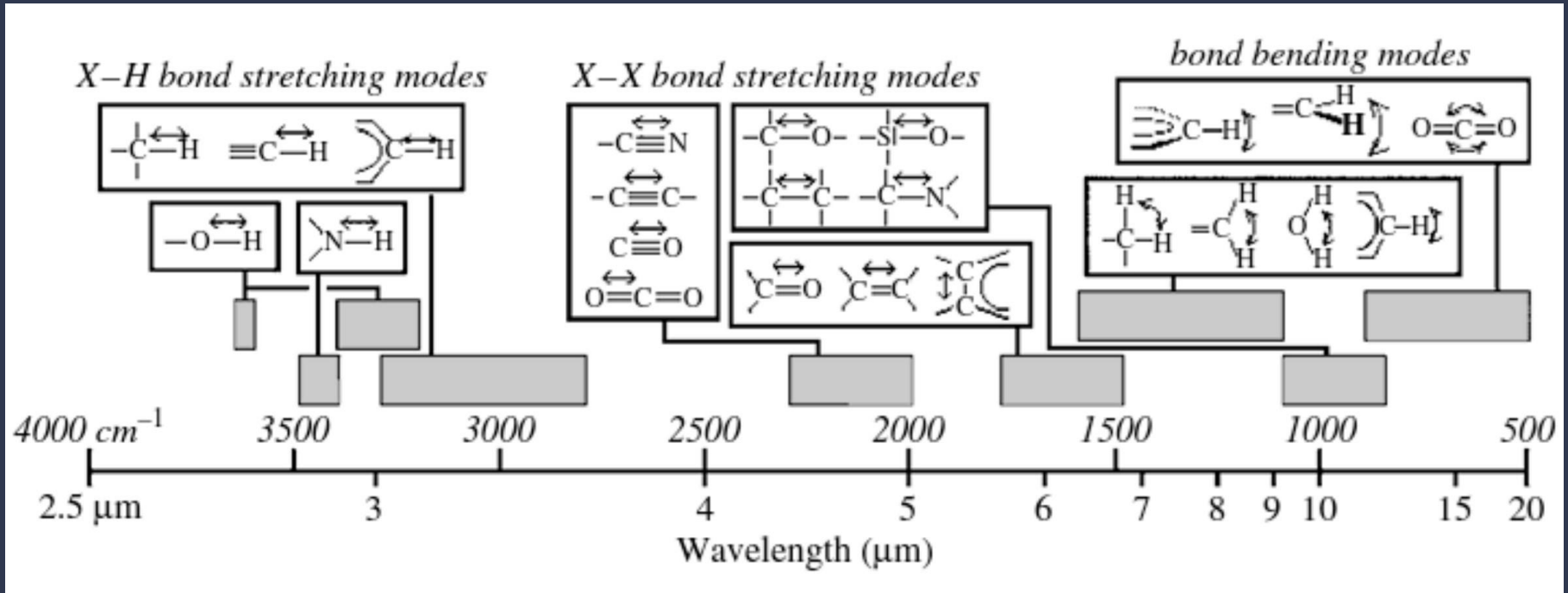
wagging



twisting

(from wikipedia)

Characteristic vibrational band frequencies



(credit Jonathan Williams)

Rotational levels of linear molecules

Simple treatment for end-over-end rotation

- valid for e.g., H_2 , HD, CO, CS, HF, CO^+ , CH^+ , SiO, ...
- and also: HCN, HNC, HCO^+ , N_2H^+ , ...
- but not for instance: OH, OH^+ , O_2 , N_2 , CO_2 , ...

Classical rigid rotor: $E_{\text{rot}}(J) = \frac{J^2}{2I}$ where $I = m_r r_n^2$

J : angular momentum

I : moment of inertia

r_n : internuclear distance

m_r : reduced mass

$$\frac{1}{m_r} = \frac{1}{m_1} + \frac{1}{m_2}$$

Rotational levels of linear molecules

Quantum rigid rotor: $E_{\text{rot}}(J) = \frac{\hbar^2}{2m_r r_n^2} J(J+1)$ $J = 0, 1, 2, \dots$

Define the **rotational constant** $B_v = \frac{\hbar^2}{2m_r r_n^2}$

(NB: why the dependence on vibrational quantum number v ?),

Then we can write $E_{\text{rot}}(J) = B_v J(J+1)$

and inserting numbers: $\frac{E_{\text{rot}}(J)}{k} = 24 \text{ K} \frac{m_{\text{H}}}{m_r} \left(\frac{0.1 \text{ nm}}{r_n} \right)^2 J(J+1)$

so:

- lines in mm/submm/far-IR
- typical molecular cloud temperatures (so expect collisional excitation)

Rotational lines of H₂ and CO

$$\frac{E_{\text{rot}}(J)}{k} = 24 \text{ K} \frac{m_{\text{H}}}{m_r} \left(\frac{0.1 \text{ nm}}{r_n} \right)^2 J(J+1)$$

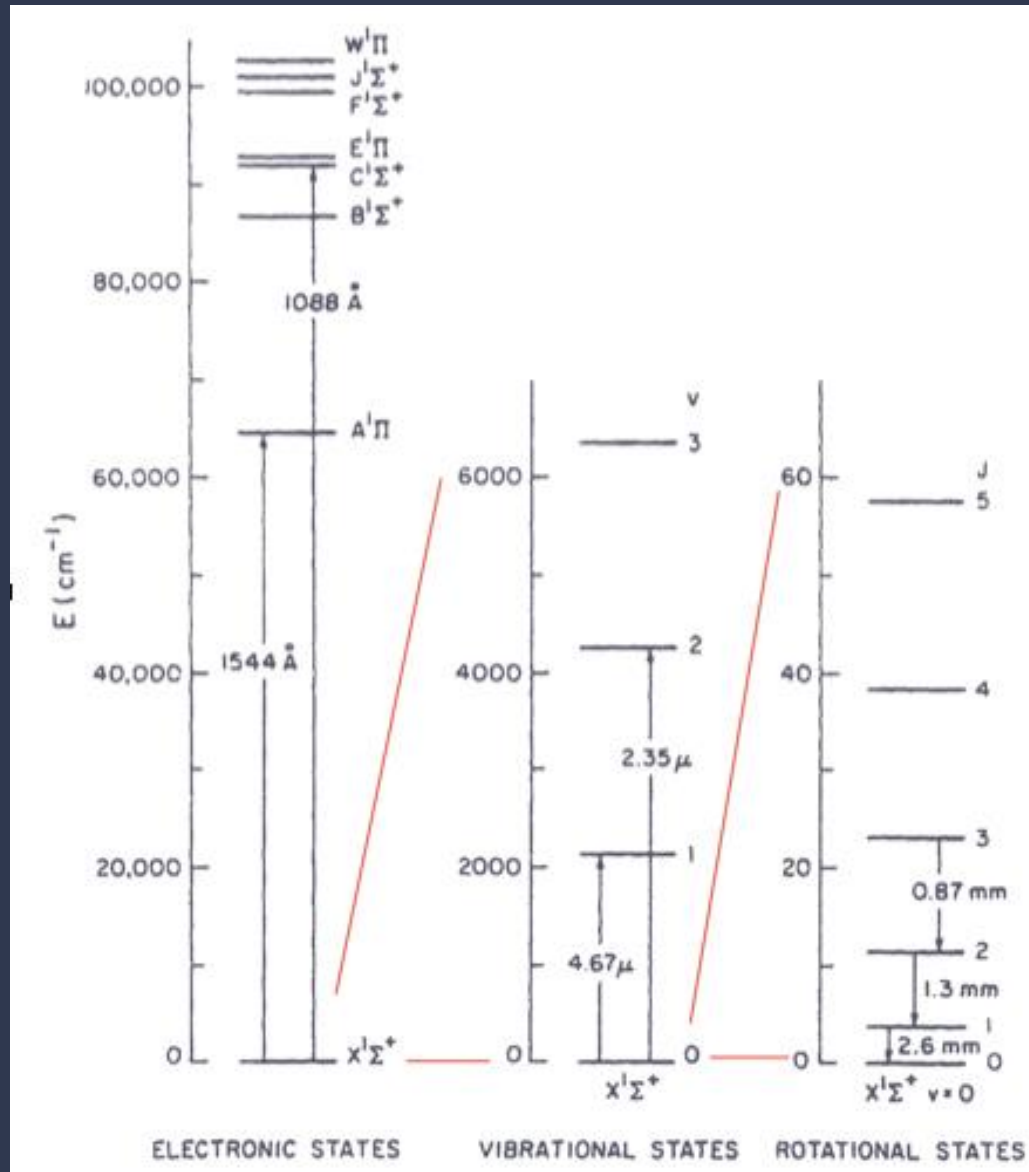
For simple molecules: r_n roughly constant
 m_r varies

- for H₂ : $m_r = m_{\text{H}} / 2$ $\rightarrow \Delta E (J=1-0) = 170 \text{ K}$
- for CO : $m_r = 6.9 m_{\text{H}}$ $\rightarrow \Delta E (J=1-0) = 5.5 \text{ K}$

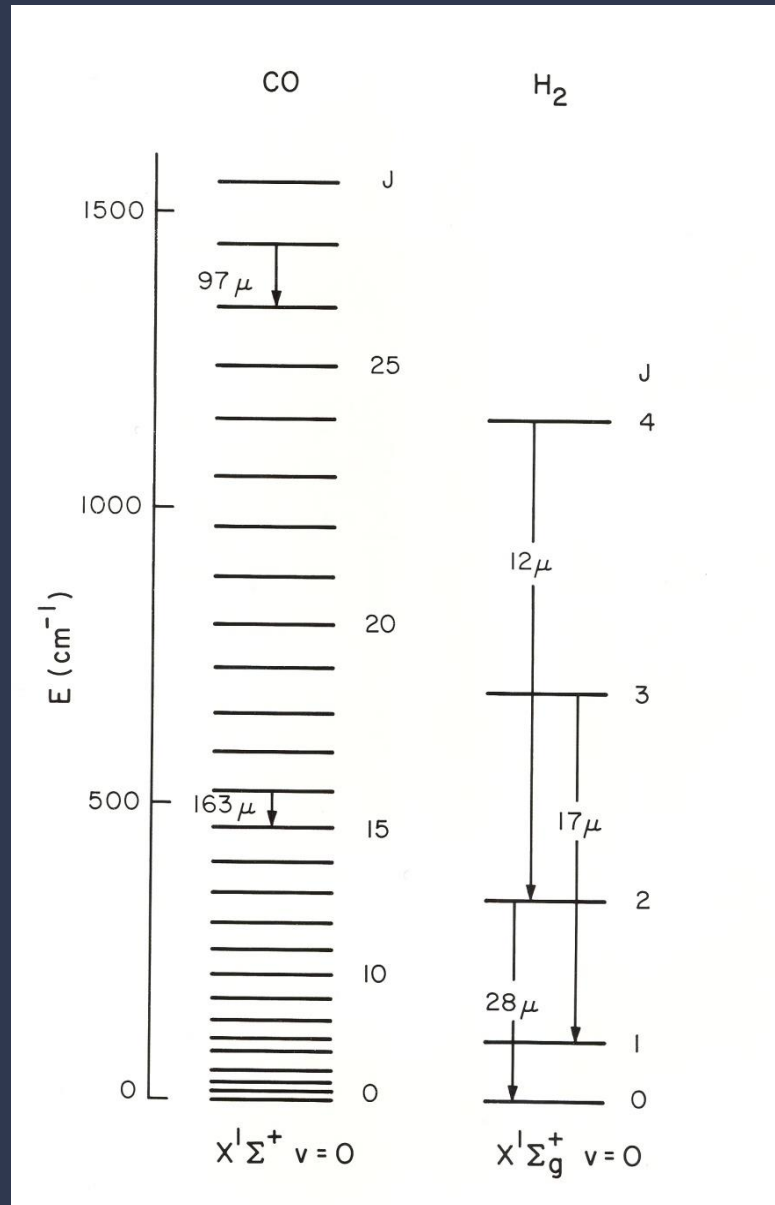
So:

- energy spacing is smaller for heavier molecules
- CO lines are good probes of cold molecular gas, but H₂ lines are not

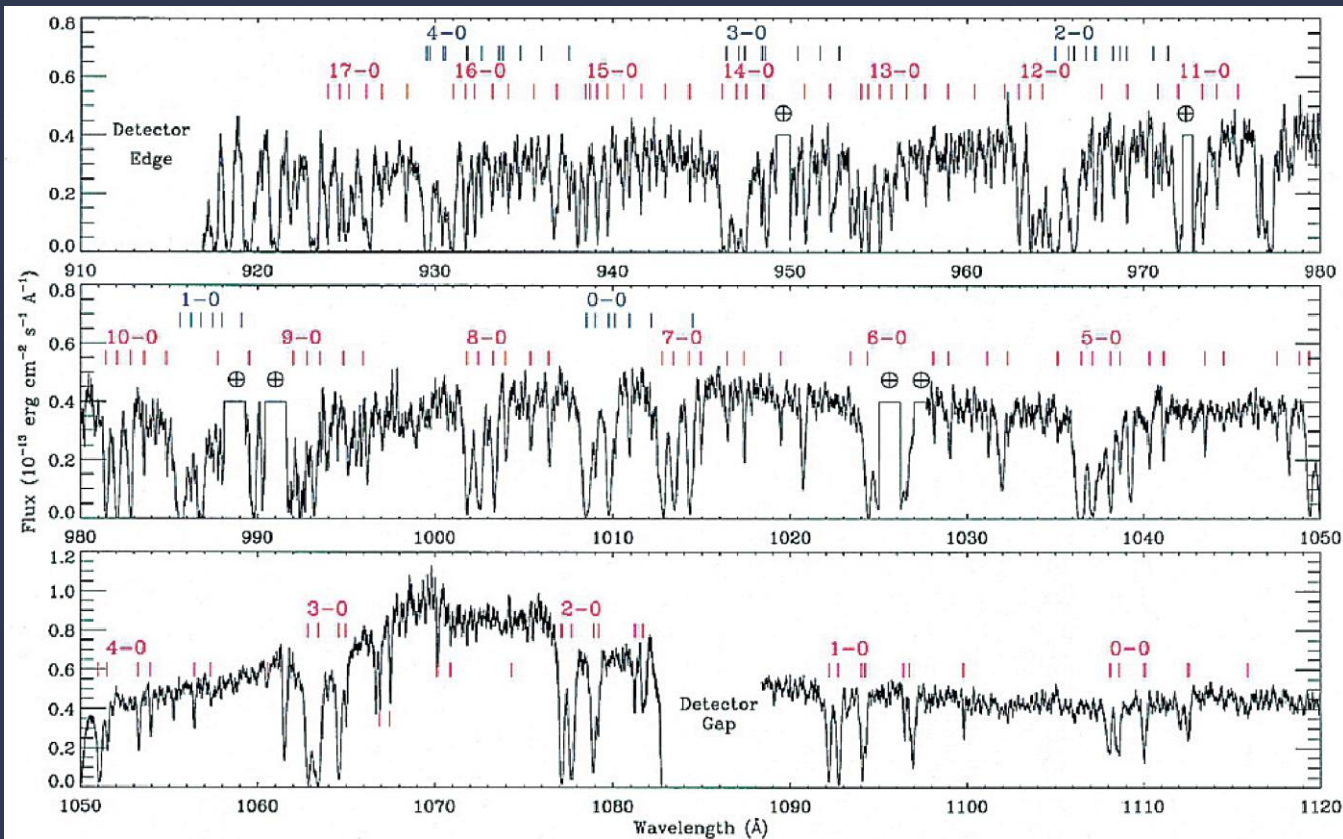
Energy levels of CO



Rotational line spectra: CO vs H₂



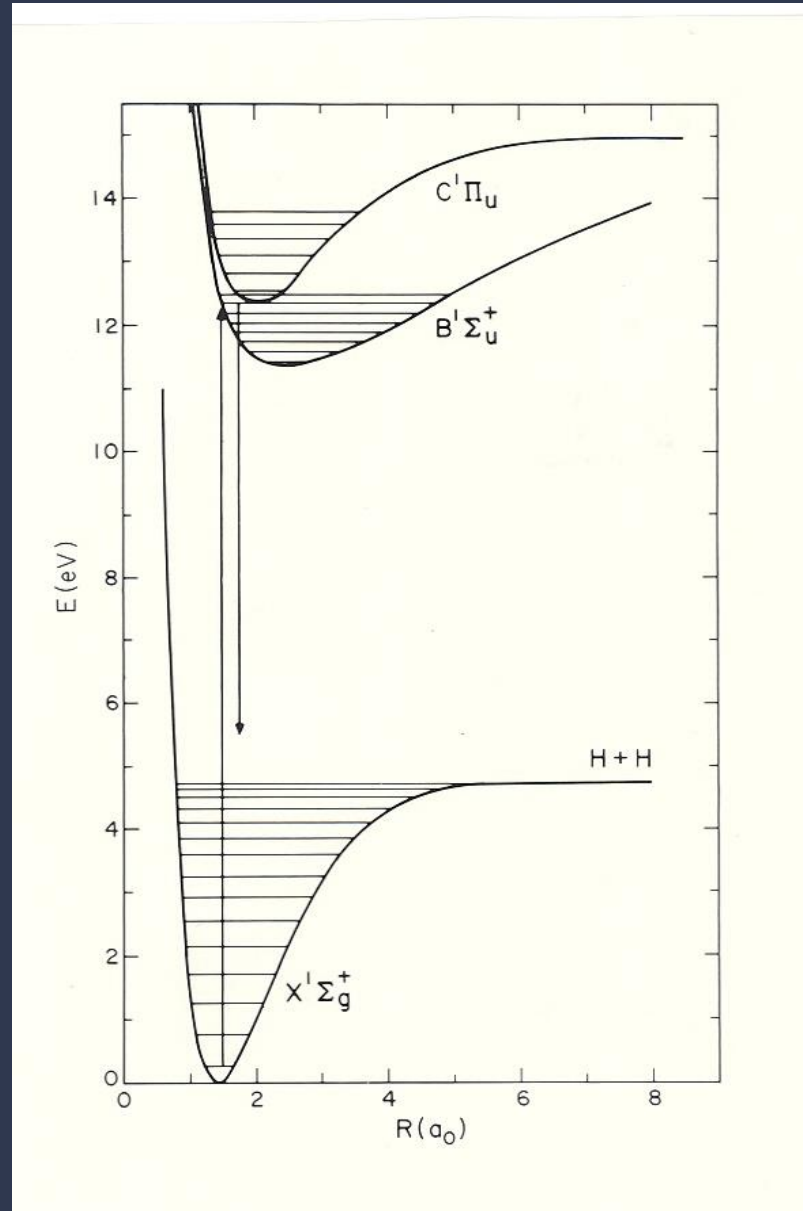
H₂ UV absorption lines



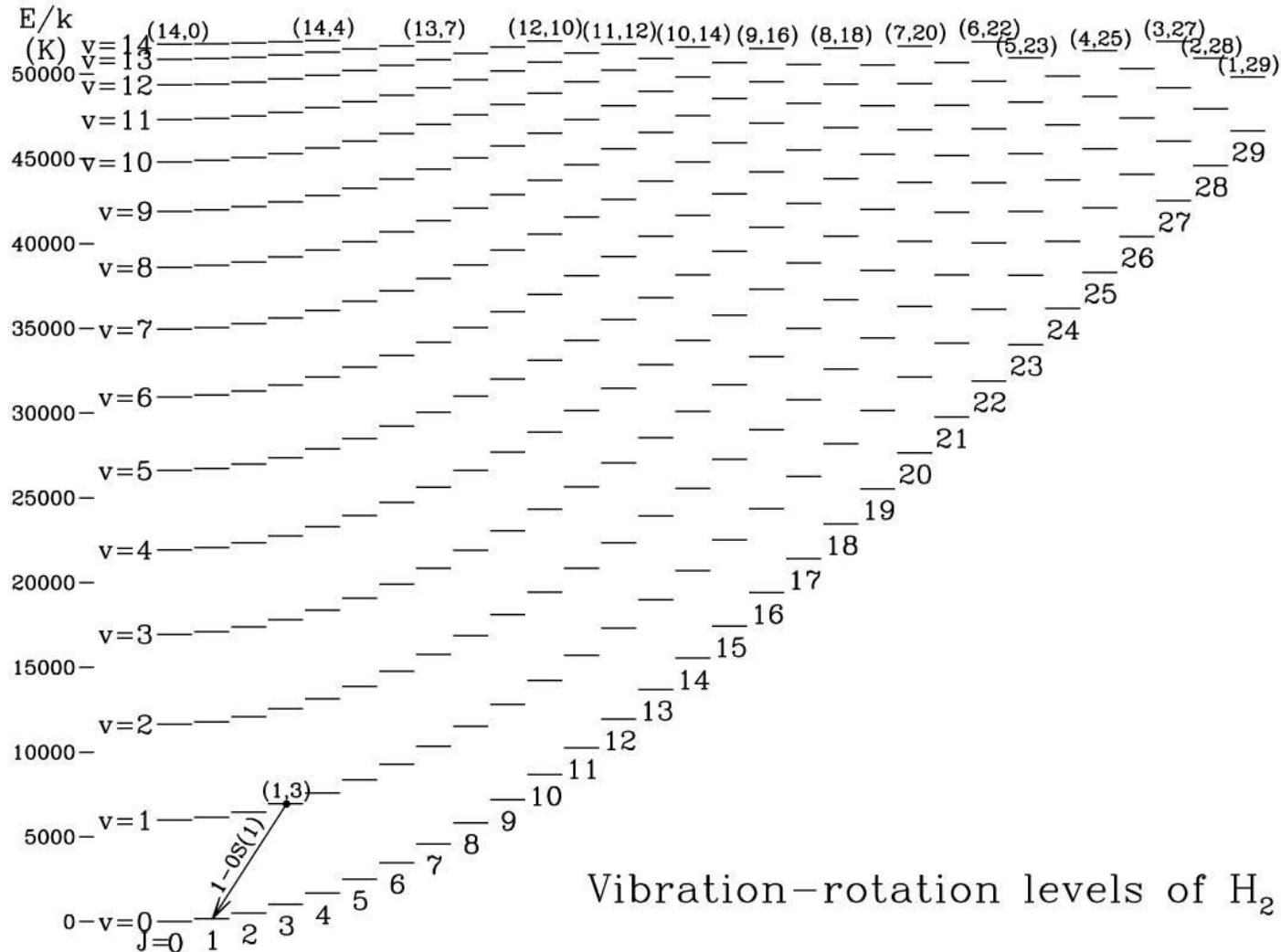
FUSE spectrum
towards a bright UV
source, showing H₂
absorption lines
(Shull *et al.*, 2000)

- blue tick marks: H₂ Werner band
- red tick marks: H₂ Lyman band

H₂ electronic and vibrational energy levels



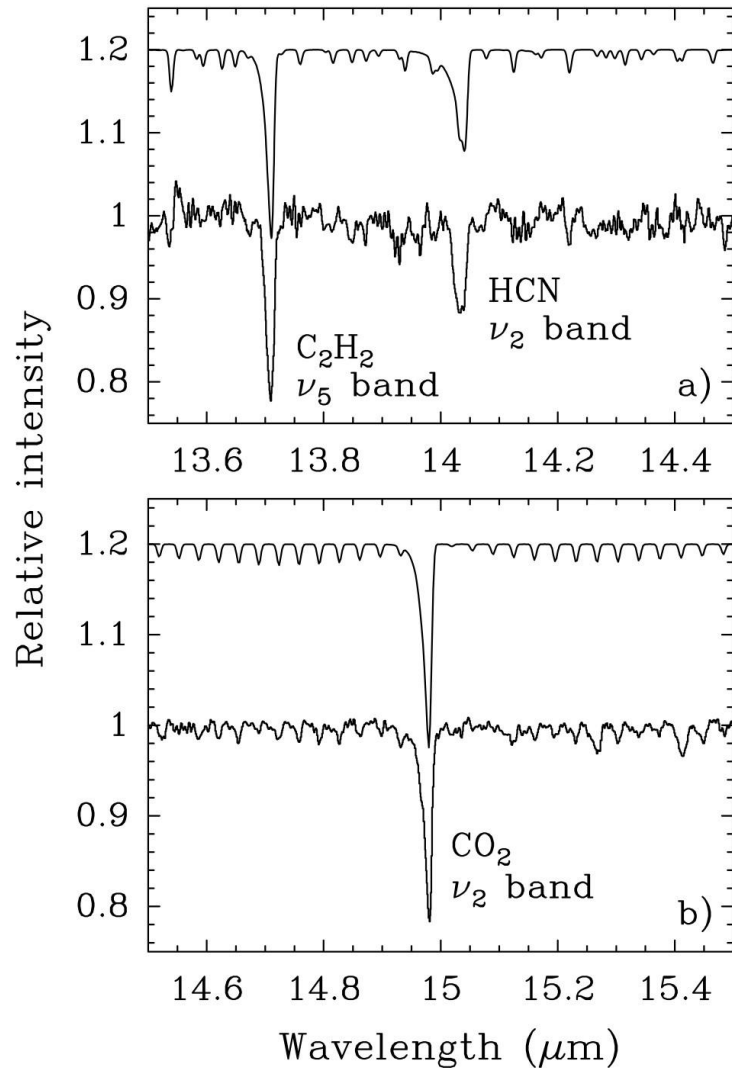
H₂ rovibrational energy levels



Note: for H₂
 $\Delta J = \pm 2$

Vibration-rotation levels of H₂

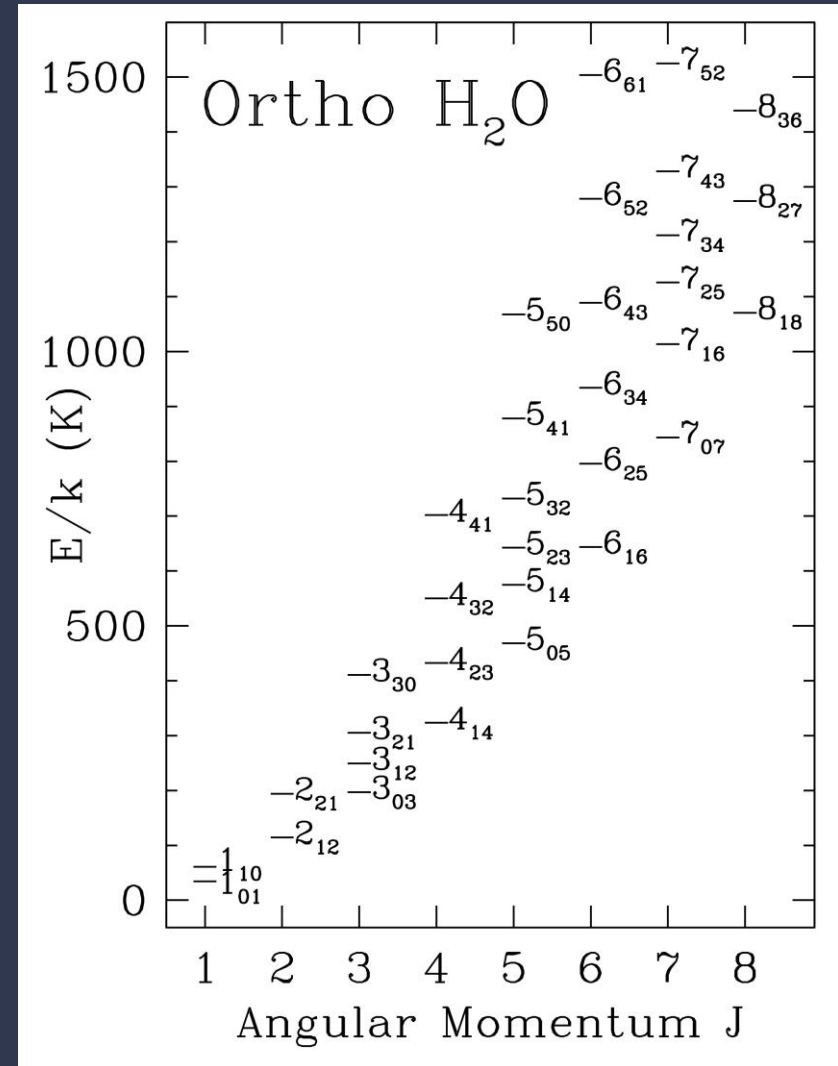
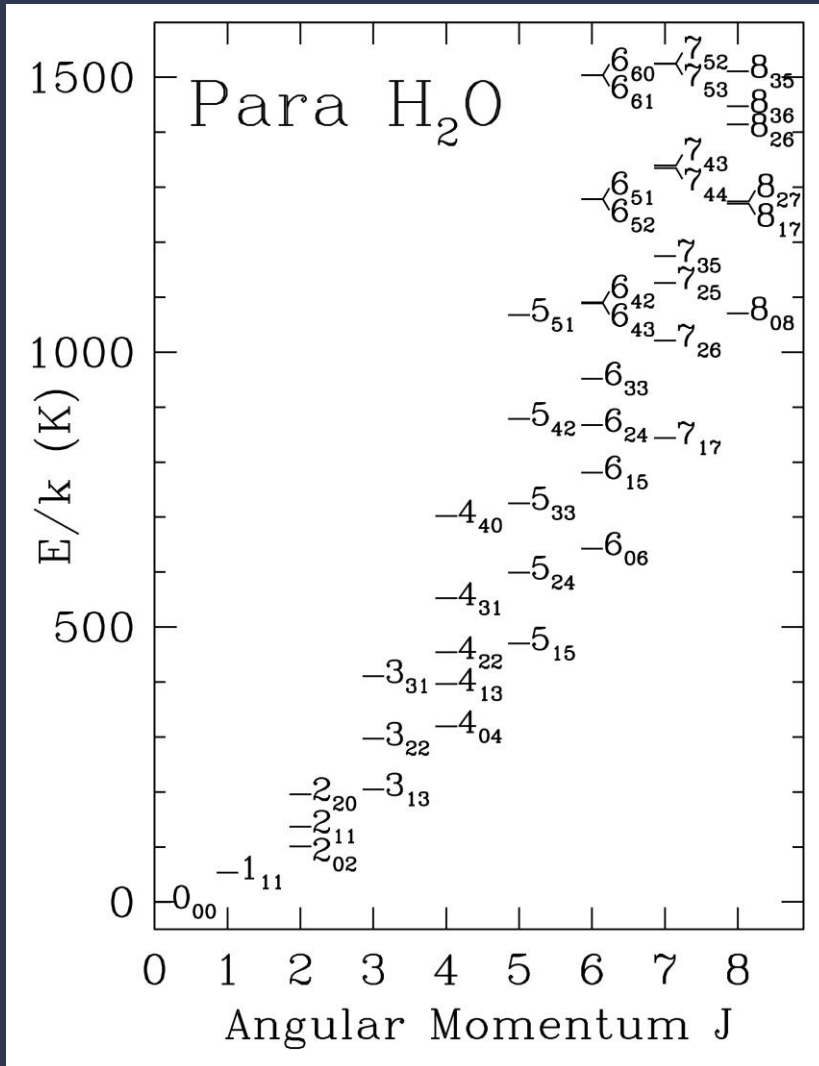
Vibrational absorption bands



Vibrational absorption bands of C_2H_2 (acetylene), HCN and CO_2 in Orion (data below model)

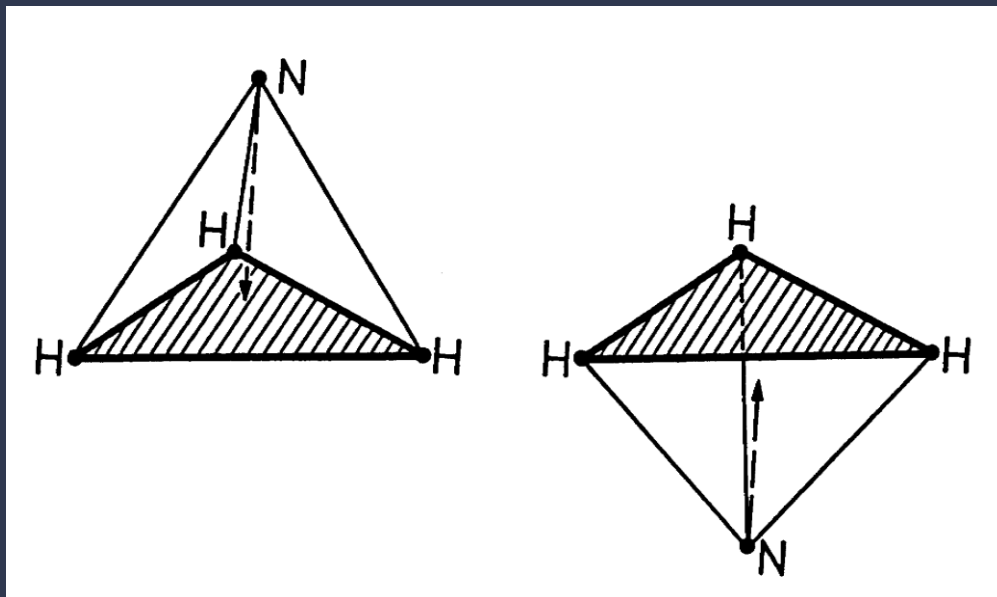
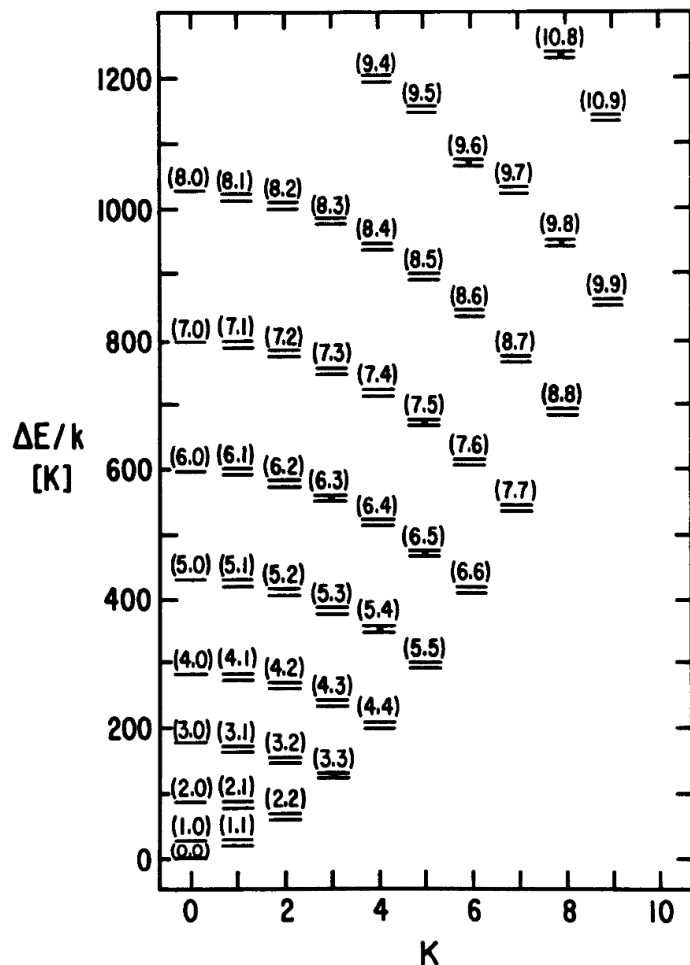
(Boonman *et al.*, 2003)

Rotational energy levels of H₂O



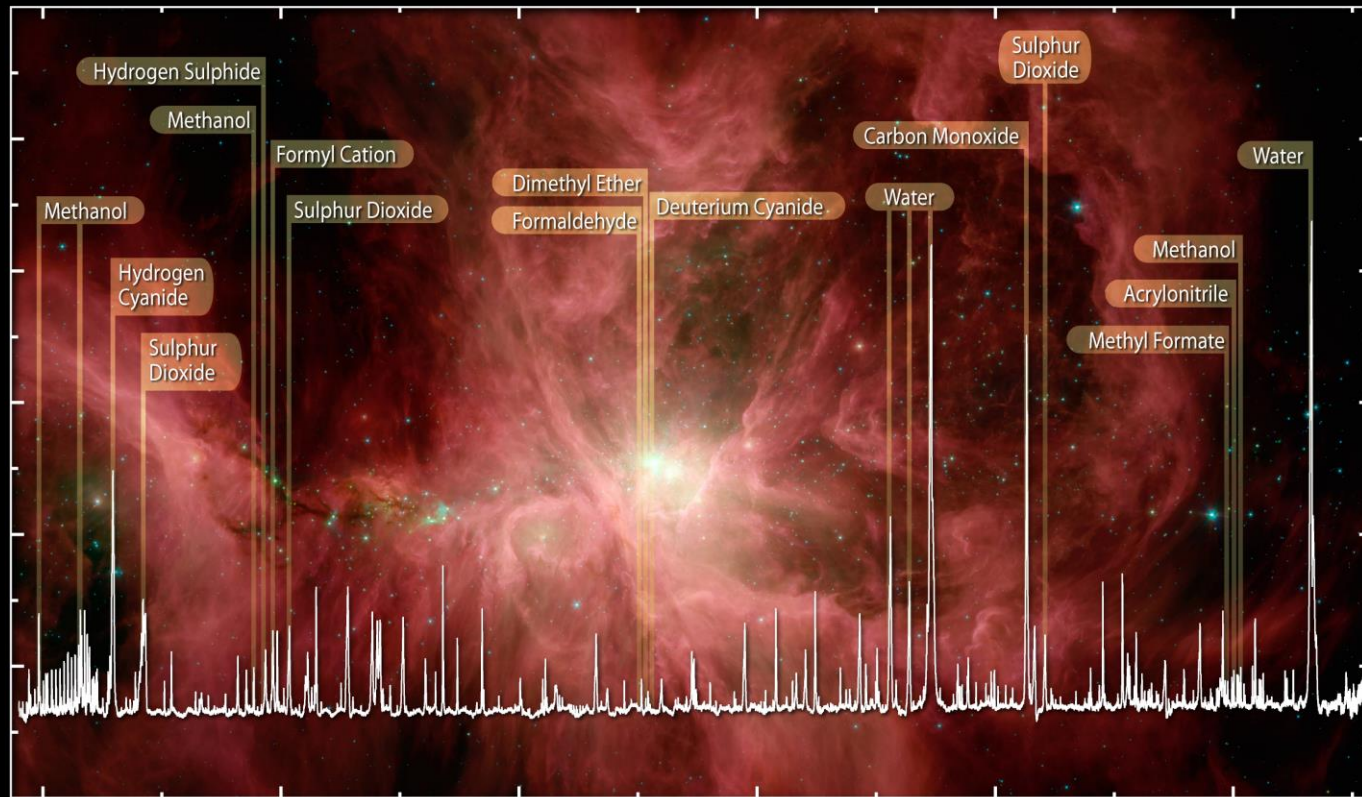
(Draine, Fig. 5.5)

Energy levels of NH_3



Note inversion doubling of all rotational transitions

Partial spectrum of the Orion star forming region



HIFI Spectrum of Water and
Organics in the Orion Nebula

© ESA, HEXOS and the HIFI consortium
E. Bergin

Today's Lecture

Molecules and their excitation

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3. Molecules as probes

Rotational transitions for linear molecules

Start with **heteronuclear molecules** (CO, CS, HD, SiO, HCN, HCO⁺,...)

Since the charge distribution is asymmetric, these have a **permanent electric dipole moment μ** [Debye].

The Einstein A coefficient for **electric dipole transitions** (rotating dipole with electric dipole moment μ) can be calculated:

$$A_{J,J-1} = \frac{128\pi^3}{3\hbar} \left(\frac{B_v}{hc} \right)^3 \mu^2 \frac{J^4}{J + \frac{1}{2}}$$

with the selection rule **$\Delta J = \pm 1$**

so approximately: $A_{J,J=1} \propto J^3$ and the other A's are zero.

e.g., for CO: $A_{J,J-1} = 1.07 \cdot 10^{-7} \frac{J^4}{J + \frac{1}{2}}$ s⁻¹, so **slow** transitions (nuclear inertia)

How about homonuclear molecules?

Homonuclear molecules (principally H_2) have no permanent dipole moment and hence **no electric dipole transitions**.

Now the strongest transitions are the (much weaker) electric quadrupole transitions with the selection rule $\Delta J = \pm 2$

This results in 2 separate rotational ladders:

- ortho- H_2 (J odd)
- para- H_2 (J even)

Quantum physics also requires (see Draine Sect 5.1.6):

- for para- H_2 : nuclear spins antiparallel ($J_{\text{nuc}} = 0, g_{\text{nuc}} = 1$)
- for ortho- H_2 : nuclear spins parallel ($J_{\text{nuc}} = 1, g_{\text{nuc}} = 3$).

So abundance ratio ortho/para H_2 is expected to be 3.

The H₂ problem

The lowest H₂ transition is the $J = 2-0$ transition at $\lambda = 28 \mu\text{m}$ (from the $J=2$ level which is 511 K above the ground state).

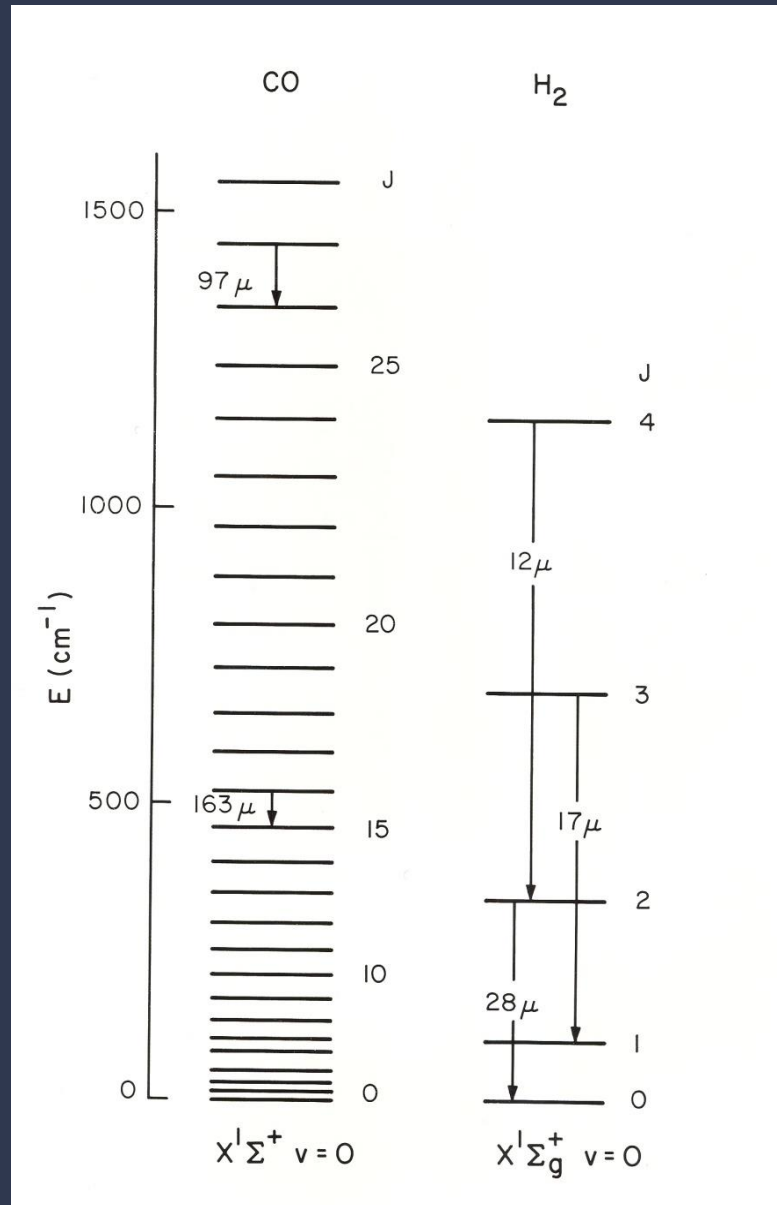
Hence:

- probes only warm H₂ (several 100K)
- can only be observed from space
- very weak line (quadrupole transition)

H₂ emission is very hard to observe directly and is not a tracer of bulk molecular gas.

In contrast: CO $J = 1-0$: $\lambda = 2.6\text{mm}$ (accessible from the ground), $J=1$ level is 5.5 K above ground state: promising probe of cold molecular gas.

Rotational line spectra: CO vs H₂



First detection of H₂ 28 μ m line in the ISM

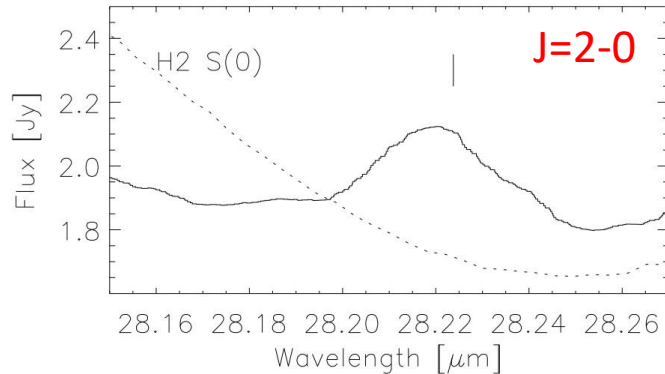


Fig. 3. ISO-SWS spectrum of the H₂ S(0) line (28.21 μm) in the central regions of NGC 6946, with symbols as in Fig. 1.

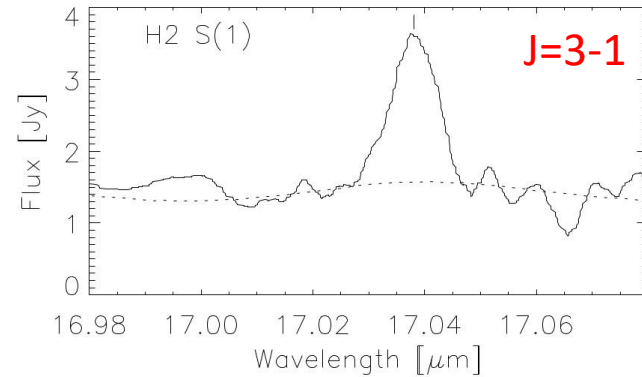


Fig. 1. ISO-SWS spectrum of the H₂ S(1) line (17.03 μm) in the central regions of NGC 6946. The dotted line represents the RSRF of the instrument (see text). The vertical line is the expected wavelength for a heliocentric radial velocity of 48 km s^{-1} .

(Valentijn, Van der Werf, De Graauw & De Jong 1996)

Today's Lecture

Molecules and their excitation

1. Molecular structure and molecular spectra
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Critical densities for rotational lines

Recall $n_{\text{crit}} = \frac{A_{J,J-1}}{k_{J,J-1}}$ and $A_{J,J-1} = \frac{128\pi^3}{3\hbar} \left(\frac{B_v}{hc}\right)^3 \mu^2 \frac{J^4}{J + \frac{1}{2}}$

Since approximately $A_{J,J-1} \propto J^3$, and $k_{J,J-1}$ is a slow function of J , we find that approximately $n_{\text{crit}} \propto J^3$.

We also had approximately $E(J) \propto J^2$ for the level energy.

Implications:

- to excite high- J lines efficiently, we need both high T and high n .
- since high- J line fluxes depend on both T and n , they do not form a clean temperature or density probe.
- using multiple lines, the degeneracy can be broken (in principle)

Tracing densities with molecular lines

Recall $n_{\text{crit}} = \frac{A_{J,J-1}}{k_{J,J-1}}$ and $A_{J,J-1} = \frac{128\pi^3}{3\hbar} \left(\frac{B_v}{hc}\right)^3 \mu^2 \frac{J^4}{J + \frac{1}{2}}$

So: molecules with large μ will have large n_{crit}
molecules with low μ will have low n_{crit} .

E.g., CO $J=1-0$: $n_{\text{crit}} \sim \text{few } 100 \text{ cm}^{-3}$
but HCN $J=1-0$: $n_{\text{crit}} \sim \text{few } 10^5 \text{ cm}^{-3}$

Generally:

- low CO lines ($J=1-0$, $2-1$) are have low critical densities and good probes of bulk cold molecular gas
- lines of heavier molecules (HCN, CS, HCO^+) probe denser molecular gas
- high lines of any molecule probe warm, dense gas

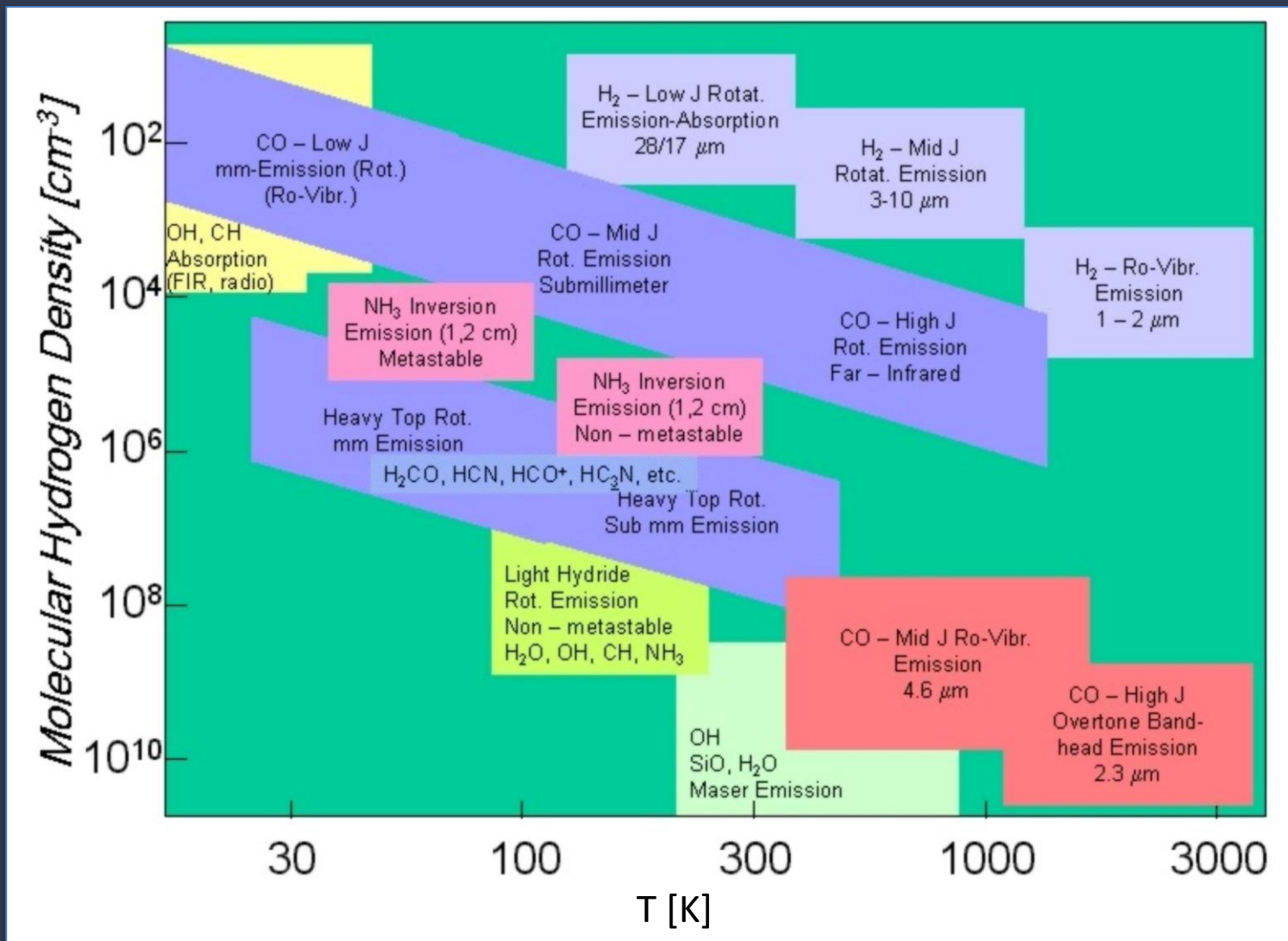
Properties of some important molecules

MOLECULE	LOWEST ROTATIONAL LINE [μm]	ROTATIONAL DIPOLE MOMENT [Debye]	VIBRATIONAL TRANSITIONS [μm]
H ₂	28.1	0	2.3
HD	112.1	5.8×10^{-4}	2.6
OH	119	1.7	2.7
NH	302		3.0
CH	149,562	1.46	3.5
HCl	479	1.11	3.3
CO	2600	0.112	4.8
CS	6110	2	7.8
HCN	3440	3	3.0, 4.9, 14
HCO ⁺	3360	3.3	
NH ₃	524	1.5	2.9, 6.1, 10.5
H ₂ O	538,269	1.85	2.7, 6.3
HDO	590	1.84	3.0, 3.7, 7.1
H ₂ D ⁺	806		
H ₃ O ⁺	760→830	≈1	
O ₂	5350	0	
SiO	6910	3.1	8.1

Critical densities

Species	transition	ν_{ul} [GHz]	E_u [K]	A_{ul} [s ⁻¹]	n_{cr} [cm ⁻³]
CO	1 – 0	115.3	5.5	7.2×10^{-8}	1.1×10^3
	2 – 1	230.8	16.6	6.9×10^{-7}	6.7×10^3
	3 – 2	346.0	33.2	2.5×10^{-6}	2.1×10^4
	4 – 3	461.5	55.4	6.1×10^{-6}	4.4×10^4
	5 – 4	576.9	83.0	1.2×10^{-5}	7.8×10^4
	6 – 5	691.2	116.3	2.1×10^{-5}	1.3×10^5
	7 – 6	806.5	155.0	3.4×10^{-5}	2.0×10^5
CS	1 – 0	49.0	2.4	1.8×10^{-6}	4.6×10^4
	2 – 1	98.0	7.1	1.7×10^{-5}	3.0×10^5
	3 – 2	147.0	14	6.6×10^{-5}	1.3×10^6
	5 – 4	244.9	35	3.1×10^{-4}	8.8×10^6
	7 – 6	342.9	66	1.0×10^{-3}	2.8×10^7
HCO ⁺	10 – 9	489.8	129	2.6×10^{-3}	1.2×10^8
	1 – 0	89.2	4.3	3.0×10^{-5}	1.7×10^5
	3 – 2	267.6	26	1.0×10^{-3}	4.2×10^6
	4 – 3	356.7	43	2.5×10^{-3}	9.7×10^6
HCN	1 – 0	88.6	4.3	2.4×10^{-5}	2.6×10^6
	3 – 2	265.9	26	8.4×10^{-4}	7.8×10^7
	4 – 3	354.5	43	2.1×10^{-3}	1.5×10^8
H ₂ CO	2 ₁₂ – 1 ₁₁	140.8	6.8	5.4×10^{-5}	1.1×10^6
	3 ₁₃ – 2 ₁₂	211.2	17	2.3×10^{-4}	5.6×10^6
	4 ₁₄ – 3 ₁₃	281.5	30	6.0×10^{-4}	9.7×10^6
	5 ₁₅ – 4 ₁₄	351.8	47	1.2×10^{-3}	2.6×10^7
NH ₃	(1,1) inversion	23.7	1.1	1.7×10^{-7}	1.8×10^3
	(2,2) inversion	23.7	42	2.3×10^{-7}	2.1×10^3
H ₂	2-0	1.06E4 ^a	510	2.9×10^{-11}	10
	3-1	1.76E4 ^b	1015	4.8×10^{-10}	300

Molecular lines as probes



(credit: Reinhard Genzel)

Next lecture

Thermal balance

1. What sets the temperature of the ISM?
2. Temperatures of HII regions
3. The origin of the 2-phase ISM
4. Temperatures of molecular clouds