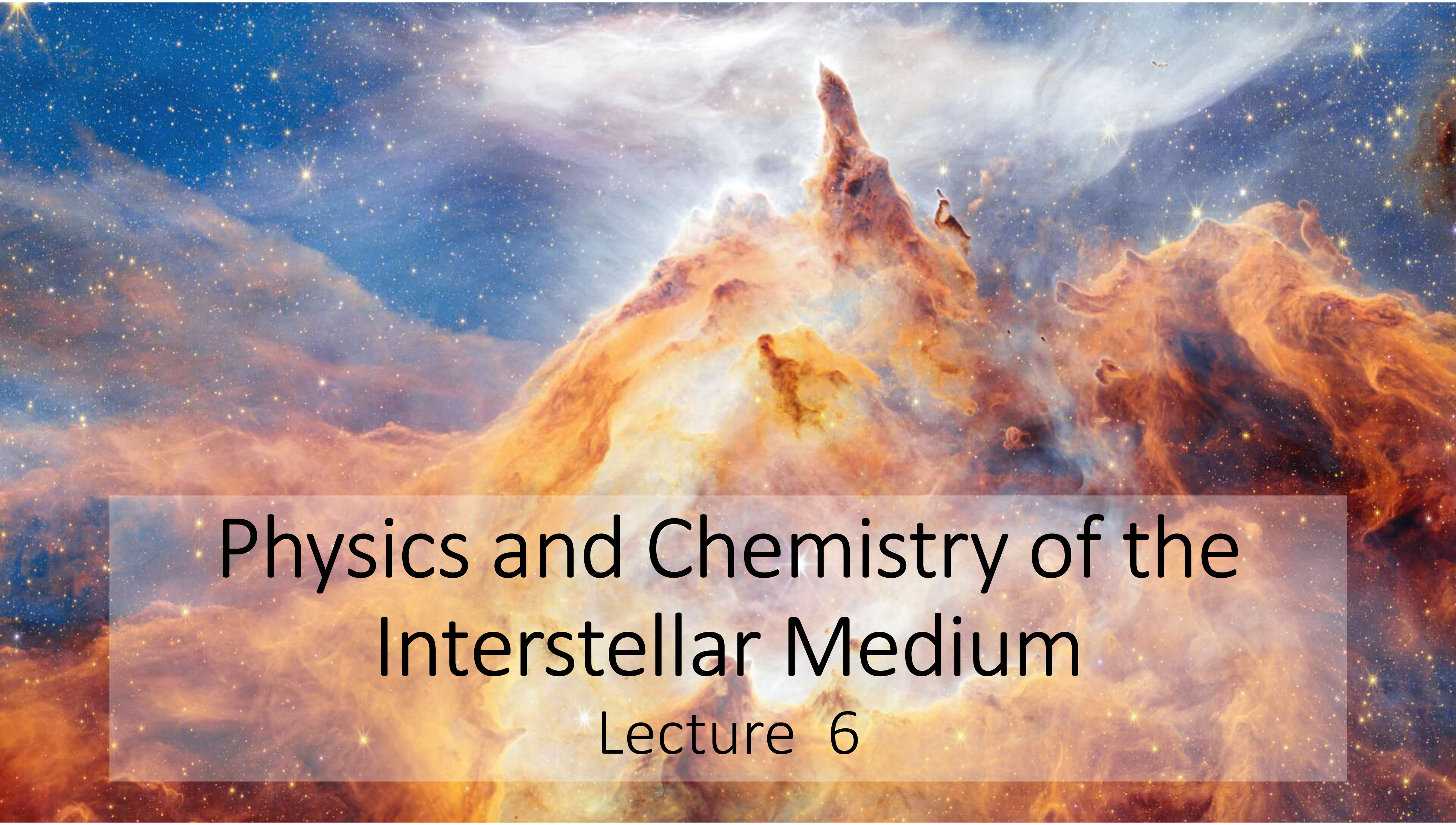


Physics and Chemistry of the Interstellar Medium

Lecture 6

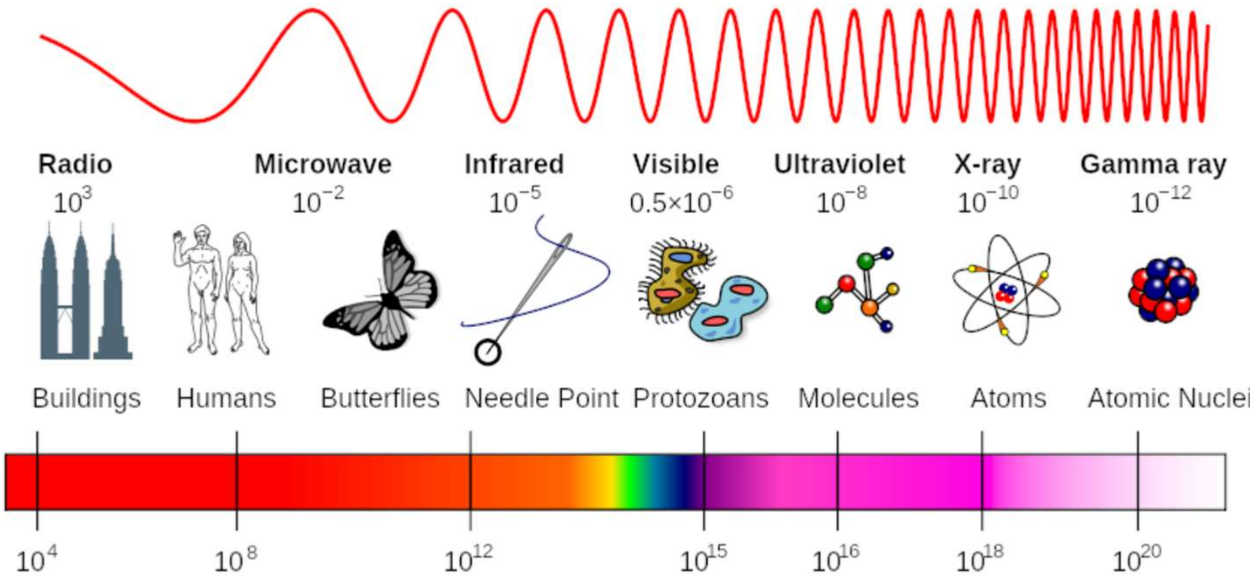
Radiation

Lecture V

3.1. Dirac perturbation theory

3.2. Discrete systems

- The hydrogen atom
- Fine structure
- Hyperfine structure
- Multiple electrons
- Molecules



Molecules

Combination of multiple atoms with their interaction

- Additional terms in Hamiltonian

$$\hat{H}_{at} = \sum_n \frac{\vec{p}_n^2}{2m_n} + \sum_e \frac{\vec{p}_e^2}{2m_e} - \sum_{i=n}\sum_{j=e} \frac{Z_i e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|} + \frac{1}{2}\sum_{i=e}\sum_{j=e\neq i} \frac{e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|} + \frac{1}{2}\sum_{i=n}\sum_{j=n\neq i} \frac{Z_i Z_j e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|}$$

  - Coulomb interaction between electrons and nuclei of different atoms, between electrons of different nuclei, between nuclei

- Total Hamiltonian expanded in series in terms of $\kappa = \sqrt[4]{\frac{m_e}{m_n}}$

- Behavior of different terms: (electron/nucleus mass ratio)

- $\kappa^0 \rightarrow$ electronic states/transitions
  - Equivalent to behavior in atoms

- $\kappa^2 \rightarrow$ vibrational states/transitions
  - Described by excursion from rest position ξ

Molecules

H_2

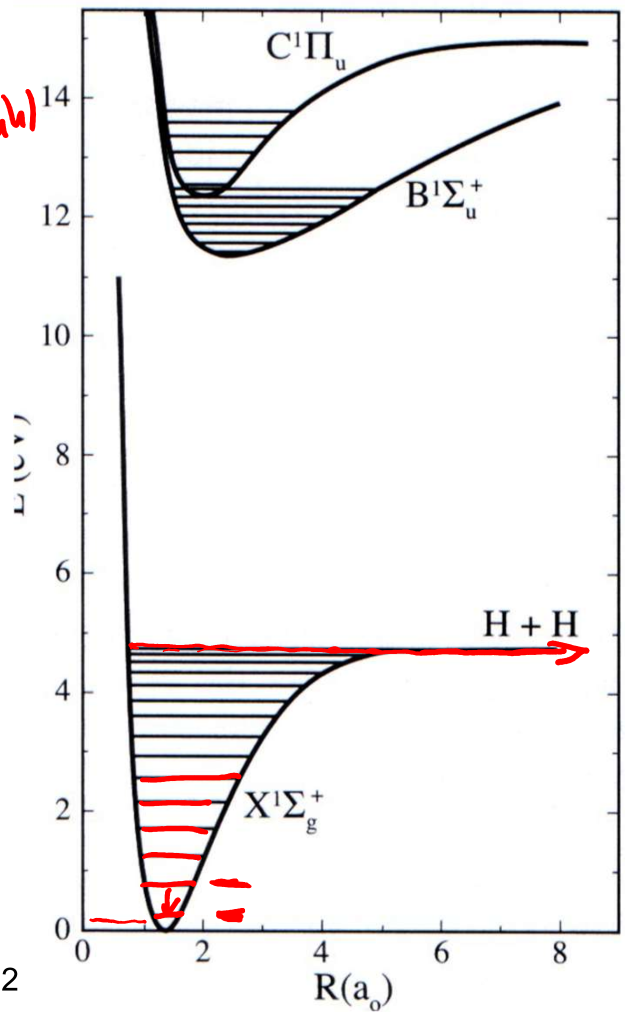
Series expansion of eigenvalues

- Behavior of different terms:
  - $\kappa^0 \rightarrow$ electronic states/transitions (at UV/optical)
  - $\kappa^2 \rightarrow$ vibrational states/transitions
    - Described by excursion from rest position ξ
    - $E_{n,v} = T_{kin,vib} + \frac{1}{2}(\xi - \bar{\xi})^2 \frac{\partial^2 E_n(\xi)}{\partial \xi^2}$
    - = harmonic oscillator in potential given by electronic state
  - Energies in NIR (2.1µm for H_2, 4.6µm for CO)

vib. Qzahl

v

$v = 1 \rightarrow 0$ S(1) 2,12 µm

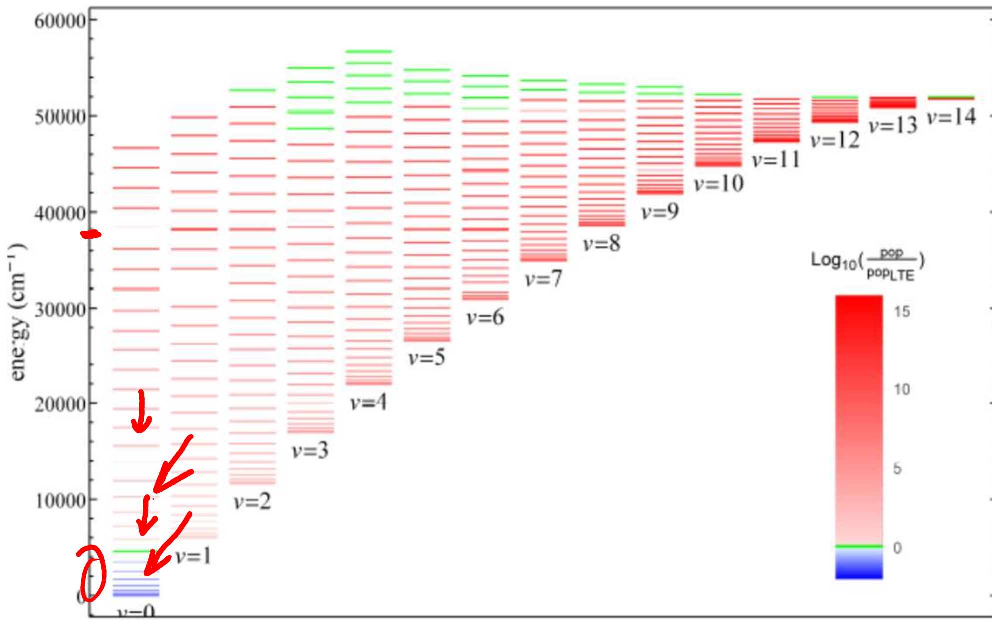


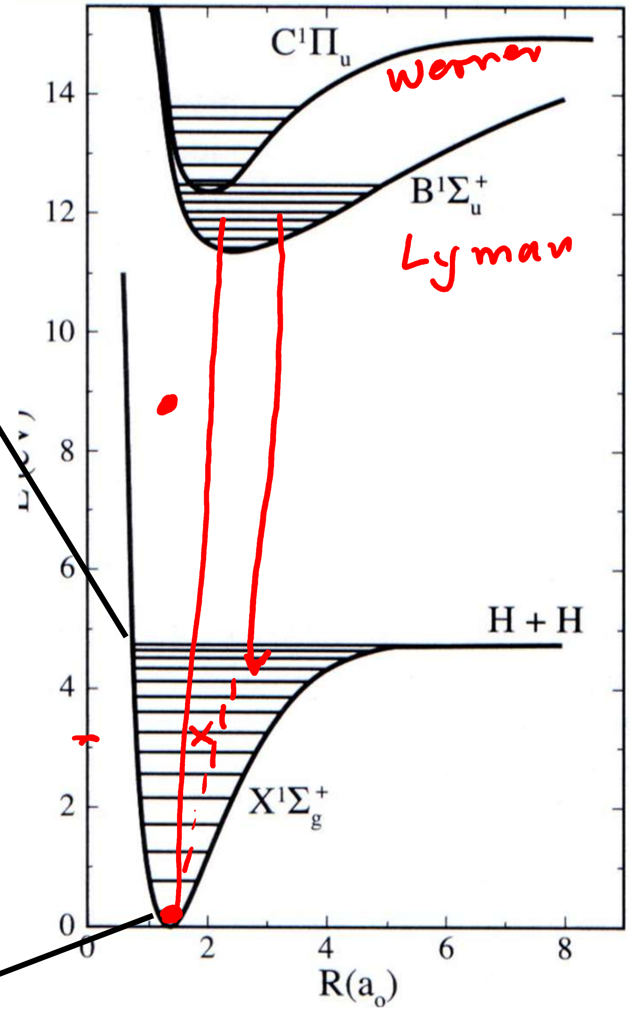
Vibrational levels of H_2

Molecules

Series expansion of eigenvalues

- Behavior of different terms:
  - $\kappa^4 \rightarrow$ rotational states/transitions
    - Energies in FIR/radio
    - Ro-vib structure





Molecules

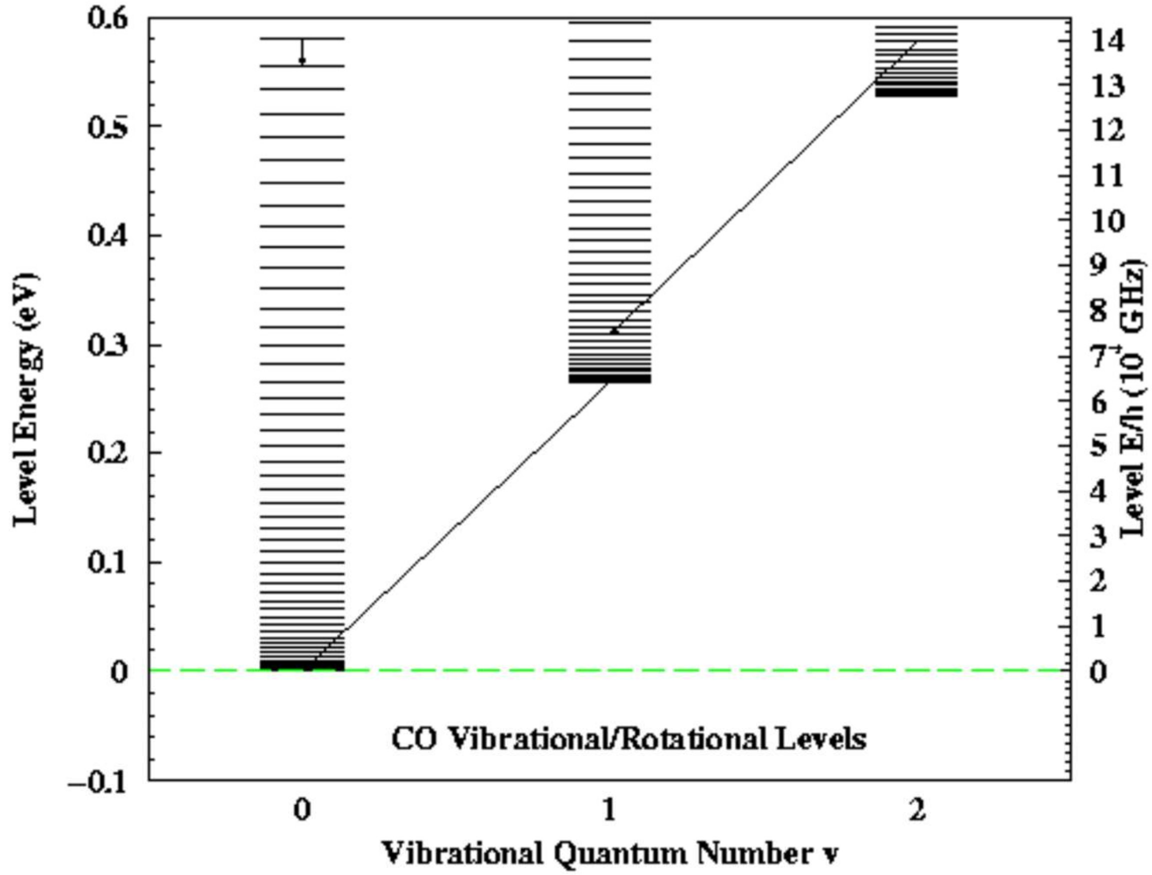
Series expansion of eigenvalues

- Behavior of different terms:
- $\kappa^0 \rightarrow$ electronic states/transitions
- $\kappa^2 \rightarrow$ vibrational states/transitions
- $\kappa^4 \rightarrow$ rotational states/transitions
- Energies scale:

$$E_n : E_{n,v} : E_{n,v,j} = 1 : \kappa^2 : \kappa^4$$

  - Electron/nucleus mass ratio guarantees separation in electromagnetic spectrum

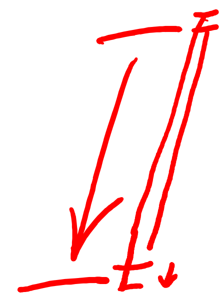
optical/UV – NIR – FIR/radio



Additional transition

(known from atomic transitions)

- Fine-structure splitting
- Hyperfine structure splitting
- x axis given by symmetry of molecules here
  - FS and HFS depend on total combination of L, S, I
- Chemical bonding tries to saturate subshells, so that $L = 0, S = 0$
  - Fine structure rare in molecules, only for radicals
- Hund rules apply for open shells



Molecules

Nuclear spin

- Special case for systems with identical atoms and odd number of nucleons:
  - e.g. H_2, H_2O, H_2O^+, …
  - 2nd Pauli principle also holds for nucleons
    - Anti-symmetry of spin configuration against proton exchange
    - Not all values of J allowed
  - 2 configurations:
    - **Para**: $I_1 \uparrow\downarrow I_2 \rightarrow I = 0$ $\quad$ $o : p \rightarrow 3 : 1$
      - J must be even
    - **Ortho**: $I_1 \uparrow\uparrow I_2 \rightarrow I = 1$
      - J must be odd
  - Separate transition ladders
  - There are almost no interactions changing the nuclear spin

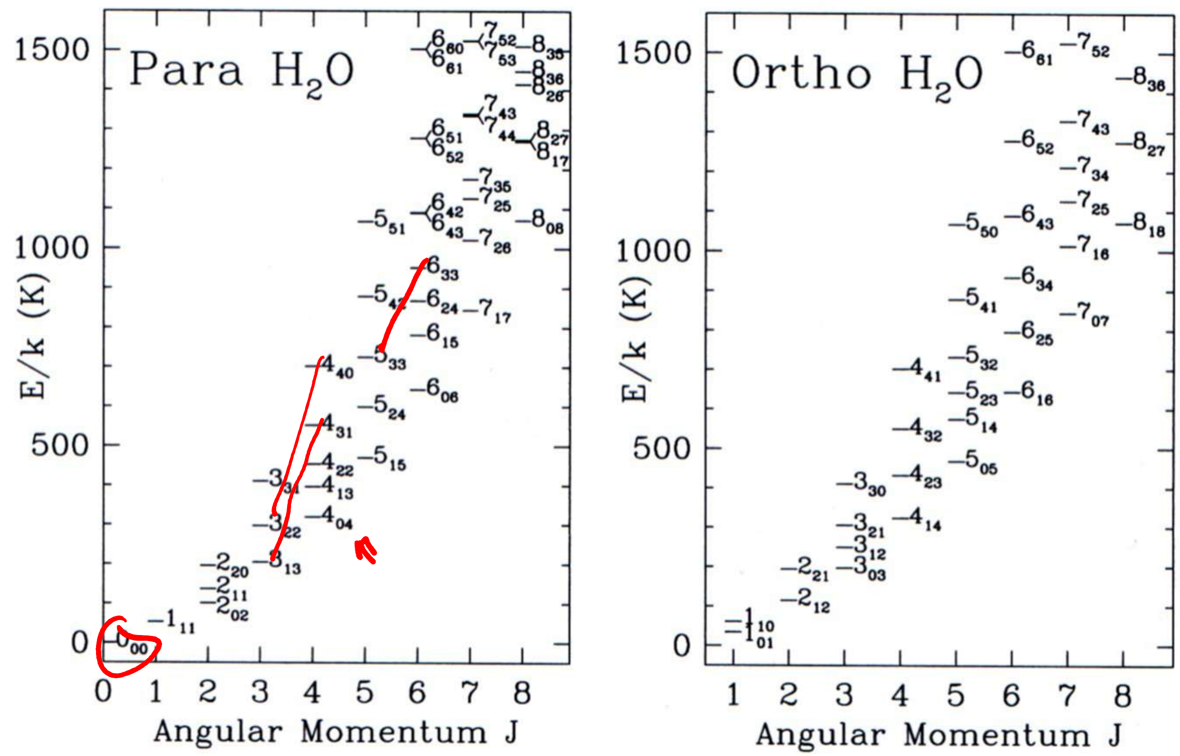
asym. Kreisel

Nuclear spin

K_a, K_c

J_{K_a, K_c}

- 2 configurations:
  - Para- and ortho- species are basically separate species
  - Relative abundance governed by (spin-)temperature at formation

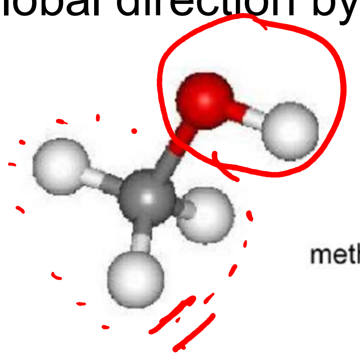


Molecules

Methanol

Nuclear spin

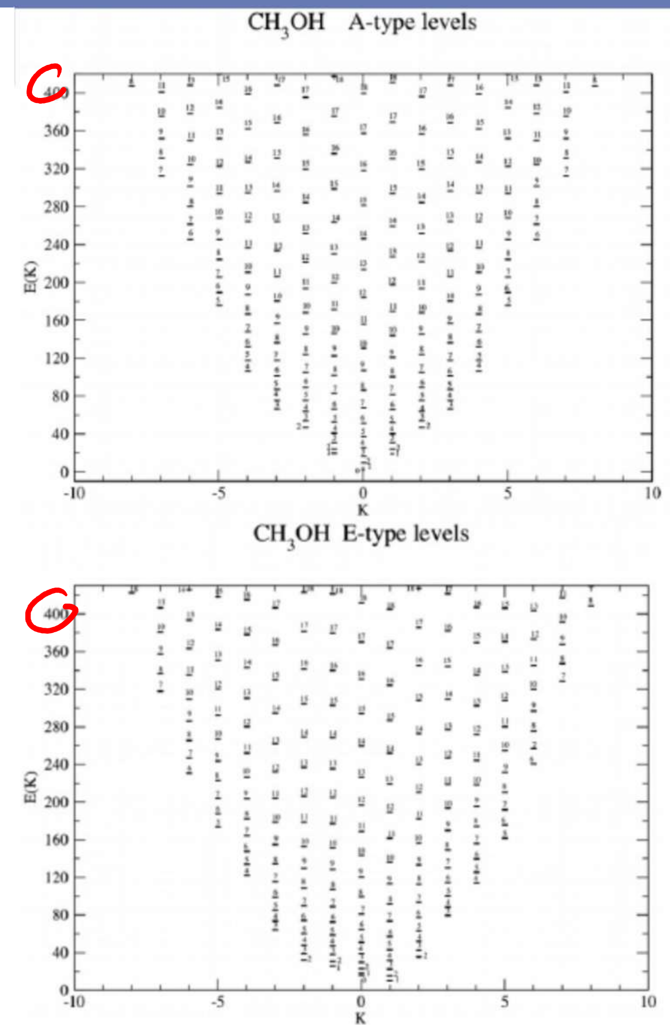
- 2 configurations:
  - Equivalent case for methyl-group in many molecules: 3 protons
  - Global direction by molecule axis



methanol

CH_3 - Gruppe
Methyl

Maser
6.7 GHz
12.2 GHz



- A-symmetry: $I = 3/2$
- E-symmetry: $I = 1/2$

Molecules

Spectroscopic notation

- **Based on projection onto main symmetry axis of molecule**
  - *Without main symmetry axis → no good quantum numbers anymore*
- **Full notation:**

$n^{2S+1}\Lambda^{\pm}_{g/u}$ or or $n^{2S+1}\Lambda^{\pm}_{\Omega}$

homo-nuclear molecules (H_2, O_2, …) all other molecules

$\Lambda = 0 : \Sigma$
$1 : \Pi$
$2 : \Delta$
$3 : \Phi$

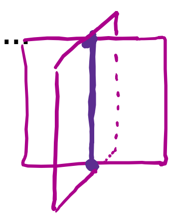
- – n = main quantum number
  - Encoded in letters: X = ground state,
    A,B,C, … = numbered states with same multiplicity as X
    a,b,c, … = numbered states with different multiplicity as X
    - a - impossible
    - A – hardly used, rather X
  - Often omitted in notation
- S = total electron spin
  - Determined multiplicity of state: $2S+1$
  - Σ = projection of spin onto main axis: $\Sigma = -S, -S+1, \ldots, S$

Spectroscopic notation

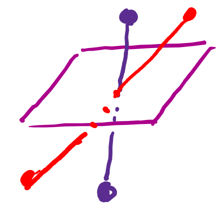
- Full notation:

$$\boldsymbol{n^{2S+1}\,\Lambda^{\pm}_{g/u}} \qquad \text{or} \qquad \boldsymbol{n^{2S+1}\,\Lambda^{\pm}_{\Omega}}$$

  - Λ = projection of orbital momentum onto main axis
    - Encoded in greek capital letters: $\Sigma\,(\Lambda = 0), \Pi(\Lambda = 1), \Delta(\Lambda = 2), \Phi, (\Lambda = 3)$ ..



  - $\pm$ = symmetry/anti-symmetry w.r.t. mirroring on planes containing molecule axis (only used for states)
  - g/u = symmetry/anti-symmetry w.r.t. mirroring on central plane (gerade/ungerade)



  - Ω = projection of total electronic angular momentum onto main axis $\Omega = |\Lambda + \Sigma|$

- Examples:
  - Ground state of H_2: $X^1\Sigma_g^+$ $\Lambda = 0$ (most symmetric configuration)
  - Ground state of CO: $X^1\Sigma^+$
  - Ground state of OH: $X^2\Pi^+_{3/2}$ (non-zero electronic orbital momentum: → FS electronic configuration of $1\sigma^2\ 2\sigma^2\ 3\sigma^2\ 1\pi^3$ OH Λ split of ground state: $X^2\Pi^+_{1/2}, \Delta\,\mathrm{E}$ = 1.61 GHz) $\Lambda = 1$ $S = 1/2$

Molecules

Spectroscopic notation

- Auxiliary quantum numbers explicitly given for more complex configurations:
  - *F* = total angular momentum including nuclear spin
  - *L* = total orbital momentum of electrons
    - Encoded in capital letters: S, P, D, F, …
  - *N* = total orbital momentum (without electron spin)
    - Includes rotation of the molecule
  - *K* = projection of N onto molecule axis
  - *O* or *J* = molecular rotational momentum
- Usually, the Hund rules also apply to the energy levels in molecules

Molecules

Spectroscopic notation

- **Transitions**:
  - Letter for electronic transition: B – X
  - Number for vibrational level: 5 – 0
  - Coding for rotational transition based on ΔJ combined with lower level number:

$B^1X_u^+ \leftrightarrow X^1\Sigma_g^+$

Designation	$(J_u - J_\ell)$	Note
$O(J_\ell)$	-2	Electric quadrupole transition
$P(J_\ell)$	-1	Electric dipole transition
$Q(J_\ell)$	0	Electric dipole or electric quadrupole; $Q(0)$ is forbidden
$R(J_\ell)$	$+1$	Electric dipole transition
$S(J_\ell)$	$+2$	Electric quadrupole transition

- Example:
  - Ortho-H_2 ro-vib transition in electr. ground state X:

v=1, J=3 → v=0, J=1: **1-0 S(1)** = 2.122μm

$(v=1, J=3) \to (v=0, J=1)$

$(1,3) - (0,1)$

Molecules

CO: tracer for H_2

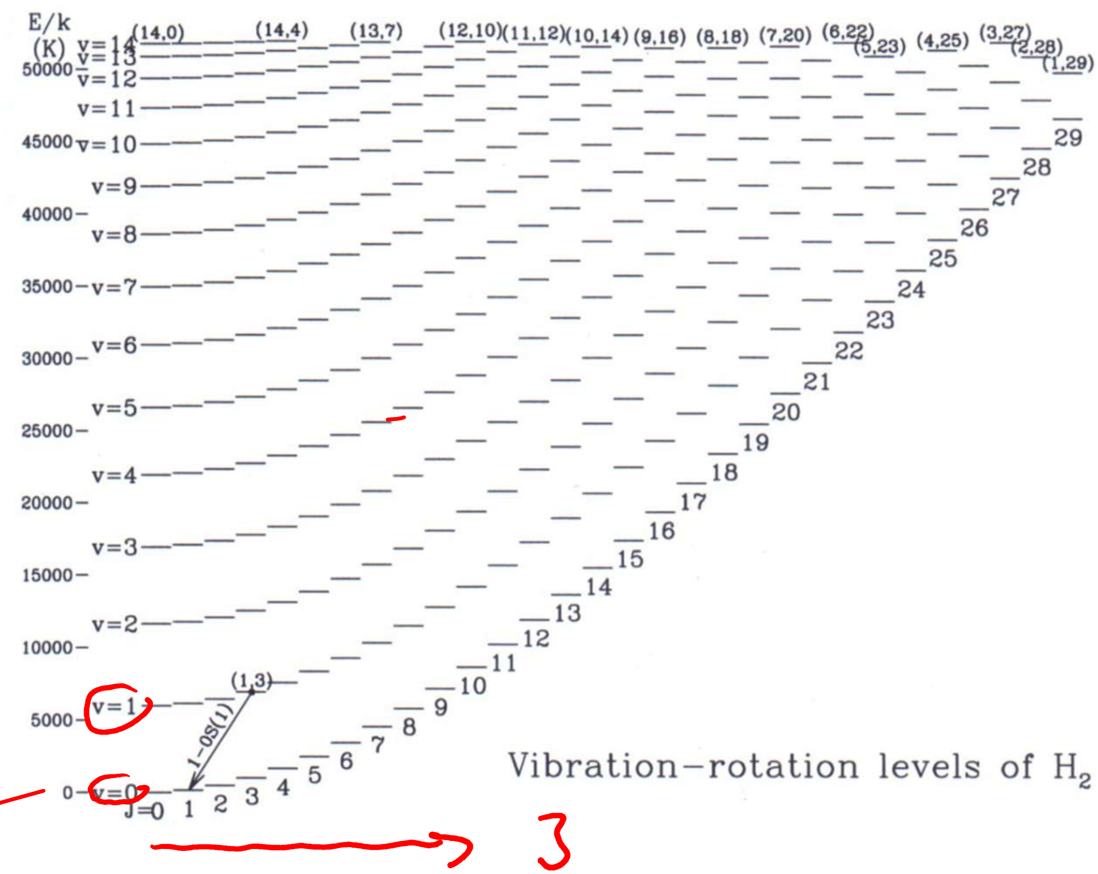
Spectroscopic notation

- Example:
  - H_2 ro-vib transition in electr. ground state
    X: v=1, J=3 → v=0, J=1: 1-0 S(1)
  - **Remember**: due to ortho/para-types only

    $\Delta J = 0, \pm 2$

    possible

E

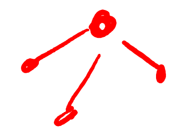


Vibration−rotation levels of H_2

Molecules

Rotational transitions

- **Classical approach**
  - $E_{rot} = \frac{1}{2\theta} \vec{J}^2$
  - θ = moment of inertia
  - $\vec{J}$ = molecular rotational momentum
- **Quantum-mechanics**
  - $E_{rot} = \frac{\hbar^2}{2\theta} J(J+1)$
  - For good quantum numbers J



- **Problem**:
  - In general Θ is a **tensor**! → 3 components in its main axis system $\theta_1, \theta_2, \theta_3$
    - $\theta_1 = \theta_2 = \theta_3$ = spherical gyro CH_4, SF_6
    - $\theta_1 = \theta_2 \neq \theta_3$ = symmetric gyro NH_3
    - $\theta_1 \neq \theta_2 \neq \theta_3$ = asymmetric gyro H_2O

Molecules

Rotational transitions

- **Symmetric gyro**
  - Clear main axis: good rotational quantum numbers can be defined
  - 2 moments: $\vec{J}$ = total angular momentum,
    $\vec{K}$ = projection of $\vec{J}$ onto symmetry axis with θ_3
    $\rightarrow$ $\vec{J}^2 - \vec{K}^2$ = angular momentum in the direction of θ_1, θ_2

$$E_{rot} = \frac{\hbar^2}{2\Theta_3}\vec{K}^2 + \frac{\hbar^2}{2\Theta_1}\left(\vec{J}^2 - \vec{K}^2\right) = A\vec{K}^2 + B\left(\vec{J}^2 - \vec{K}^2\right) = B\vec{J}^2 + (A-B)\vec{K}^2$$

- Quantum-mechanically:

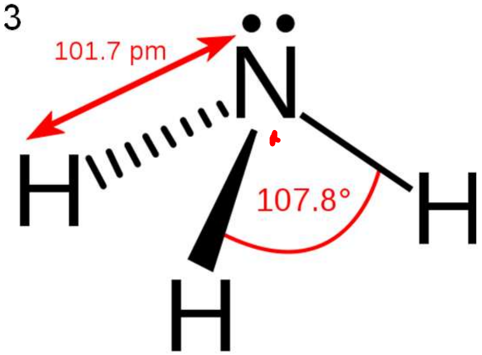
$$E_{rot} = BJ(J+1) + (A-B)k^2$$

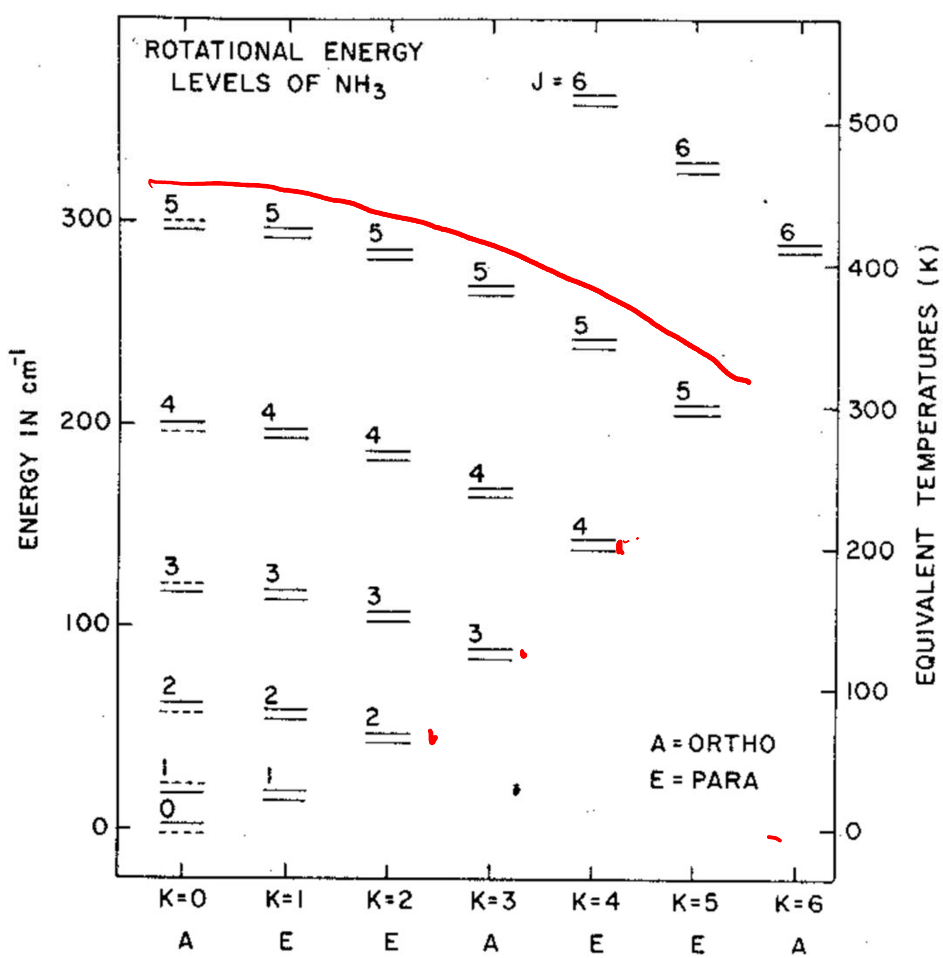
  - $E_{rot} = B\,J(J+1) + (A-B)K^2$
  - Momenta quantized with $K = -J, \dots, 0, \dots, J$

Molecules

Rotational transitions

- **Symmetric gyro**
  - $E_{rot} = B\,J(J+1) + (A-B)K^2$
- Example: NH_3



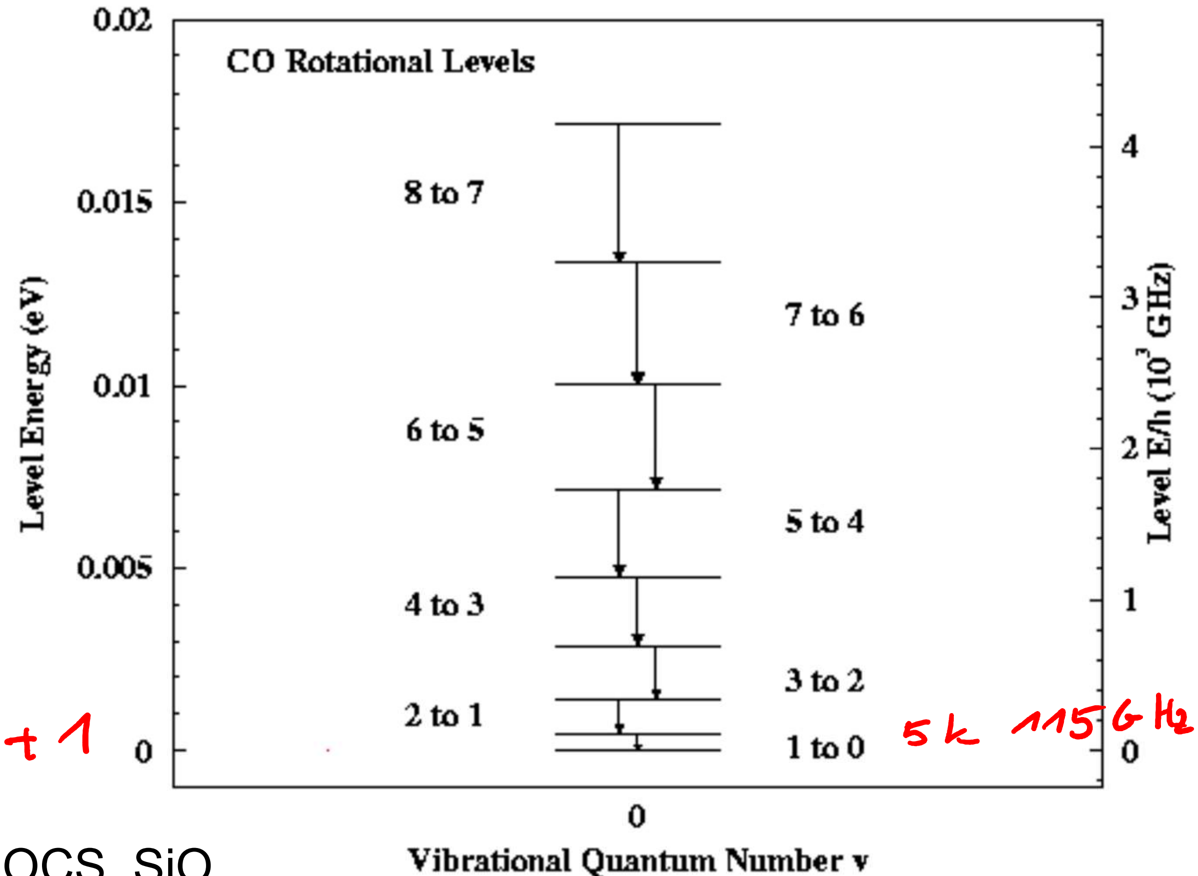


  - $\theta_3 > \theta_1, \theta_2 \rightarrow A < B$
  - Diagram is falling with K
  - Additional split by inversion transitions (23GHz)

Rotational transitions

- *Symmetric gyro*
  - $E_{rot} = B\,J(J+1) + (A-B)K^2$

- **Special case: Spherical gyro**
  - $A = B$
  - $E_{rot} = B\,J(J+1)$
  - Degeneracy with respect to $K = -J, \dots, 0, \dots, J$
  - Gives statistical weights $g_J = 2J + 1$
  - Most important: CO
    CH^+, CS, CN, HCN, HCO^+, HNC, OCS, SiO, …



Transition Strengths

Remember: Dirac perturbation theory

- Transition from state $|a\rangle$ to state $|a'\rangle$ determined by Fermi's Golden rule:

$$W_{a,a'} = \frac{2\pi}{\hbar} \left|\langle a'|\hat{H}_i|a\rangle\right|^2 \delta\left(E_{a'} - E_a\right)$$

- So far discussed for discrete systems:
  - Energy conservation term $\delta\left(E_{a'} - E_a\right)$
  - Determines line frequencies

- Open:
  - Transition strength = Harmonic variation of $\left|d_{a,a'}\right|, \left|M_{a,a'}\right|, \left|Q_{a,a'}\right|$
  - Determines line intensities

Discrete systems:

Transition strength:

- Compute for different orders of $\vec{E}$ field interaction → **selection rules**

Elektrische Dipol-Ü.

- **“Allowed transitions”**: first order interaction

= dipole transition $\langle d_{a,a'} \rangle = \left\langle a'_{at} \left| e\dot{\vec{r}} \right| a_{at} \right\rangle$

- Einstein coefficient: $A_{a,a'} \propto \left| \langle d_{a,a'} \rangle \right|^2$

- $\left| \langle d_{a,a'} \rangle \right|^2 > 0$ If

1) parity must chang
2) $\Delta L = 0, \pm 1$ außer $L=0 \not\to L=0$
3) $\Delta J = 0, \pm 1$ except for $J=0 \not\to J=0$
4) single Electron must change $\Delta l = \pm 1$
5) $\Delta S = 0$ (no spin flip!)

$\to A \sim 10^8\ s^{-1}$

Discrete Systems

Selection rules:

- Example NII (or CI)

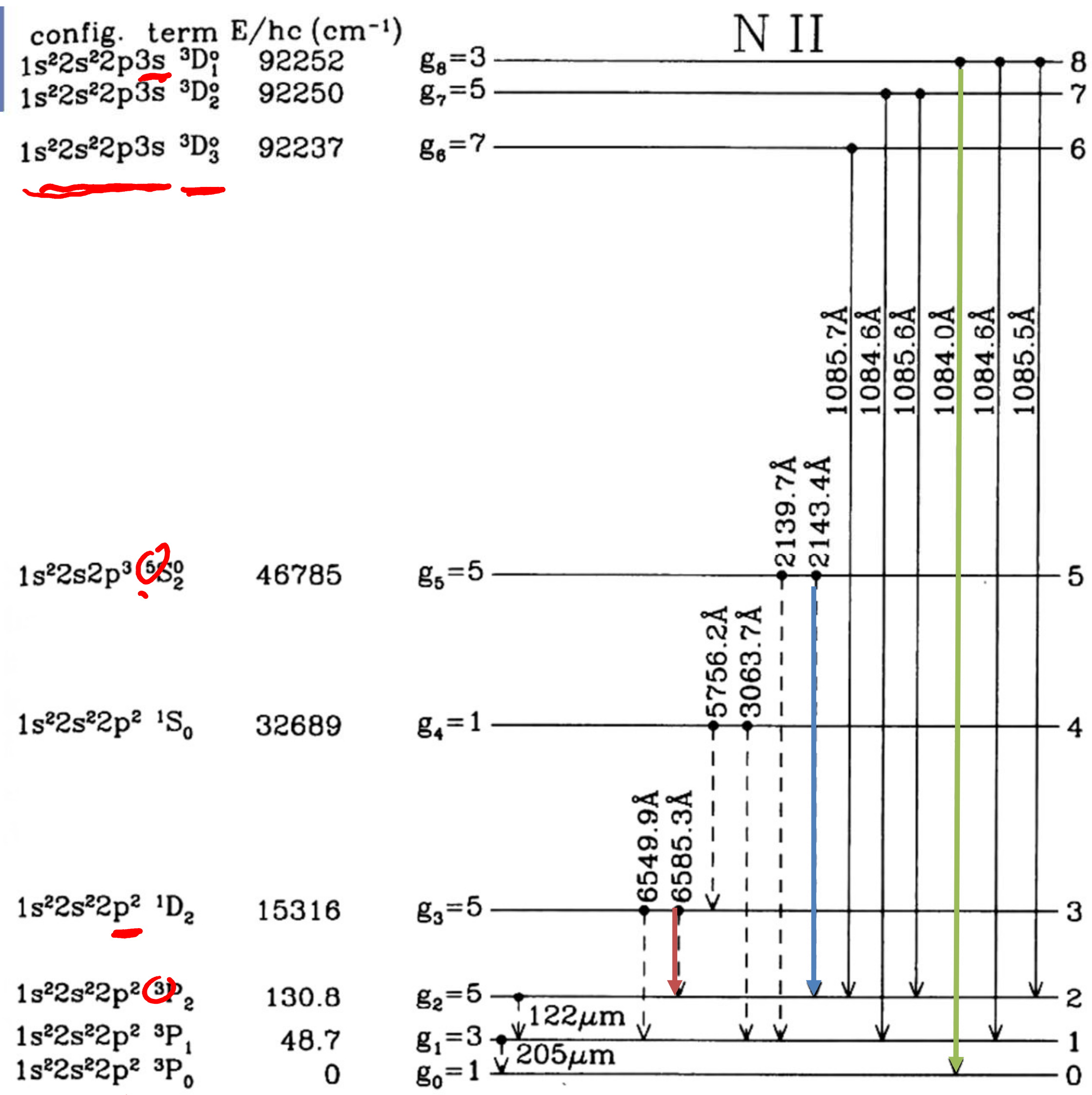
$^3D^o_1 \to {}^3P_0$

$\Delta S = 0$
$\Delta S = \pm 1$
$\Delta l = \pm 1$

Allowed
(if depopulation by allowed transitions works, forbidden transitions can be ignored)

Forbidden by $\Delta S = 0$

Forbidden by $\Delta l = \pm 1$



Discrete Systems

Selection rules:

- **“Allowed transitions”:**
  - Example: NII or CI: 1s^2 2s^2 2p 3s $^3D_3^0$- 1s^2 2s^2 2p^2 $^3P_2$
  - Notation: without brackets – Example: **CI 3255 Å**
  - Typical Einstein coefficient: $A \cong 10^8 s^{-1}$

- **“Spin-forbidden transitions”:**
  - Electric dipole
  - But requires spin flip: $\Delta S \neq 0$
  - Example NII or CI: 1s^2 2s^2 2p^3 $^5S_2^0$ - 1s^2 2s^2 2p^2 $^3P_2$
  - Notation: single bracket - Example: **CI] 6429 Å**
  - Typical Einstein coefficient: $A \triangleq 10^2 s^{-1}$ (<< than allowed transitions)

Discrete Systems

Selection rules:

- **"Forbidden transitions":** $|M_{a,a'}|, |Q_{a,a'}|$
  - Higher order interaction terms:
  - Example: NII or CI: $1s^2\ 2s^2\ 2p^2\ {}^1D_2$ - $1s^2\ 2s^2\ 2p^2\ {}^2P_2$

    = magnetic dipole transition

  - Notation: square brackets - Example: **[CI] 9826 Å**
  - Typical Einstein coefficient: $A \approx 10^{-2}\,s^{-1}$
  - No clear hierarchy for magnetic dipole and electric quadrupole transitions
  - Less constraints on change of quantum numbers.

Discrete Systems

Selection rules:

- **Hierarchy of transition strengths:**
  - Allowed transitions: 1
  - Semi-forbidden transitions: 10^{-6}
  - Forbidden transitions: 10^{-10}

- **Forbidden lines irrelevant in the lab, but important in space**
  - Every species has levels that have only forbidden radiative transitions
    - In the lab they are depopulated by collisions
    - No collisions in > 10^{10}s in space

Discrete Systems

Selection rules:

Table 13. Selection rules for atomic spectra (cf. PAULI, 1925; LAPORTE, 1924; SHORTLEY, 1940)

	Electric dipole (allowed)	Magnetic dipole (forbidden)	Electric quadrupole (forbidden)
(1)	$\Delta J = 0, \pm 1$ $(0 \nleftrightarrow 0)$	$\Delta J = 0, \pm 1$ $(0 \nleftrightarrow 0)$	$\Delta J = 0, \pm 1, \pm 2$ $(0 \nleftrightarrow 0, \frac{1}{2} \nleftrightarrow \frac{1}{2}, 0 \nleftrightarrow 1)$
(2)	$\Delta M = 0, \pm 1$	$\Delta M = 0, \pm 1$	$\Delta M = 0, \pm 1, \pm 2$
(3)	Parity change	No parity change	No parity change
(4)	One electron jump $\Delta l = \pm 1$ For $L-S$ coupling	No electron jump $\Delta l = 0$ $\Delta n = 0$	One or no electron jump $\Delta l = 0, \pm 2$
(5)	$\Delta S = 0$	$\Delta S = 0$	$\Delta S = 0$
(6)	$\Delta L = 0, \pm 1$ $(0 \nleftrightarrow 0)$	$\Delta L = 0$	$\Delta L = 0, \pm 1, \pm 2$ $(0 \nleftrightarrow 0, 0 \nleftrightarrow 1)$

Molecules

Selection rules for molecules:

- Same principle, more quantum numbers to be considered:

Table 18. Selection rules for diatomic molecular spectra[1]

Coupling	Electric dipole (allowed)	Magnetic dipole (forbidden)	Electric quadrupole (forbidden)
(1) General	$\Delta J=0, \pm 1$ $(0 \not\leftrightarrow 0)$	$\Delta J=0, \pm 1$ $(0 \not\leftrightarrow 0)$	$\Delta J=0, \pm 1, \pm 2$ $(0 \not\leftrightarrow 0, 0 \not\leftrightarrow 1, \frac{1}{2} \not\leftrightarrow \frac{1}{2})$
(2) General	$(+ \leftrightarrow -, + \not\leftrightarrow +, - \not\leftrightarrow -)$	$(+ \leftrightarrow +, - \leftrightarrow -, + \not\leftrightarrow -)$	$(+ \leftrightarrow +, - \leftrightarrow -, + \not\leftrightarrow -$
(3) General	$(s \not\leftrightarrow a, s \leftrightarrow s, a \leftrightarrow a)$	$(s \leftrightarrow s, a \leftrightarrow a, s \not\leftrightarrow a)$	$(s \leftrightarrow s, a \leftrightarrow a, s \not\leftrightarrow a)$
(4) General	$(g \leftrightarrow u, g \not\leftrightarrow g, u \not\leftrightarrow u)$	$(g \leftrightarrow g, u \leftrightarrow u, g \not\leftrightarrow u)$	$(g \leftrightarrow g, u \leftrightarrow u, g \not\leftrightarrow u)$
(5) (a) and (b)	$\Delta S=0$	$\Delta S=0$	$\Delta S=0$
(6) (a)	$\Delta \Lambda=0, \pm 1$	$\Delta \Lambda=0$ if $\Delta \Sigma=\pm 1$; $\Delta \Lambda=\pm 1$ if $\Delta \Sigma=0$	$\Delta \Lambda=0, \pm 1, \pm 2$
(b)	$\Delta \Lambda=0, \pm 1$	$\Delta \Lambda=0, \pm 1$	$\Delta \Lambda=0, \pm 1, \pm 2$
(7) (a)	$\Delta \Sigma=0$	see (6) (a)	$\Delta \Sigma=0$
(8) (a)	$\Delta \Omega=0, \pm 1$	$\Delta \Omega=\pm 1$	$\Delta \Omega=0, \pm 1, \pm 2$
(9) (a)	$\Delta J \neq 0$ for $\Omega=0 \leftrightarrow \Omega=0$	—	$\Delta J \neq 1$ for $\Omega=0 \leftrightarrow \Omega=0$
(10) (b)	$\Delta K=0, \pm 1$	$\Delta K=0, \pm 1$	$\Delta K=0, \pm 1, \pm 2$
(11) (b)	$\Delta K \neq 0$ for $\Sigma \leftrightarrow \Sigma$ transitions	$\Delta K=0$ for $\Sigma \leftrightarrow \Sigma$ transitions	$\Delta K=0, \pm 1, \pm 2$ for $\Sigma \leftrightarrow \Sigma$ transitions
(12) (b)	$\Sigma^{+} \not\leftrightarrow \Sigma^{-}$	$\Sigma^{+} \not\leftrightarrow \Sigma^{-}$	$\Sigma^{+} \not\leftrightarrow \Sigma^{-}$

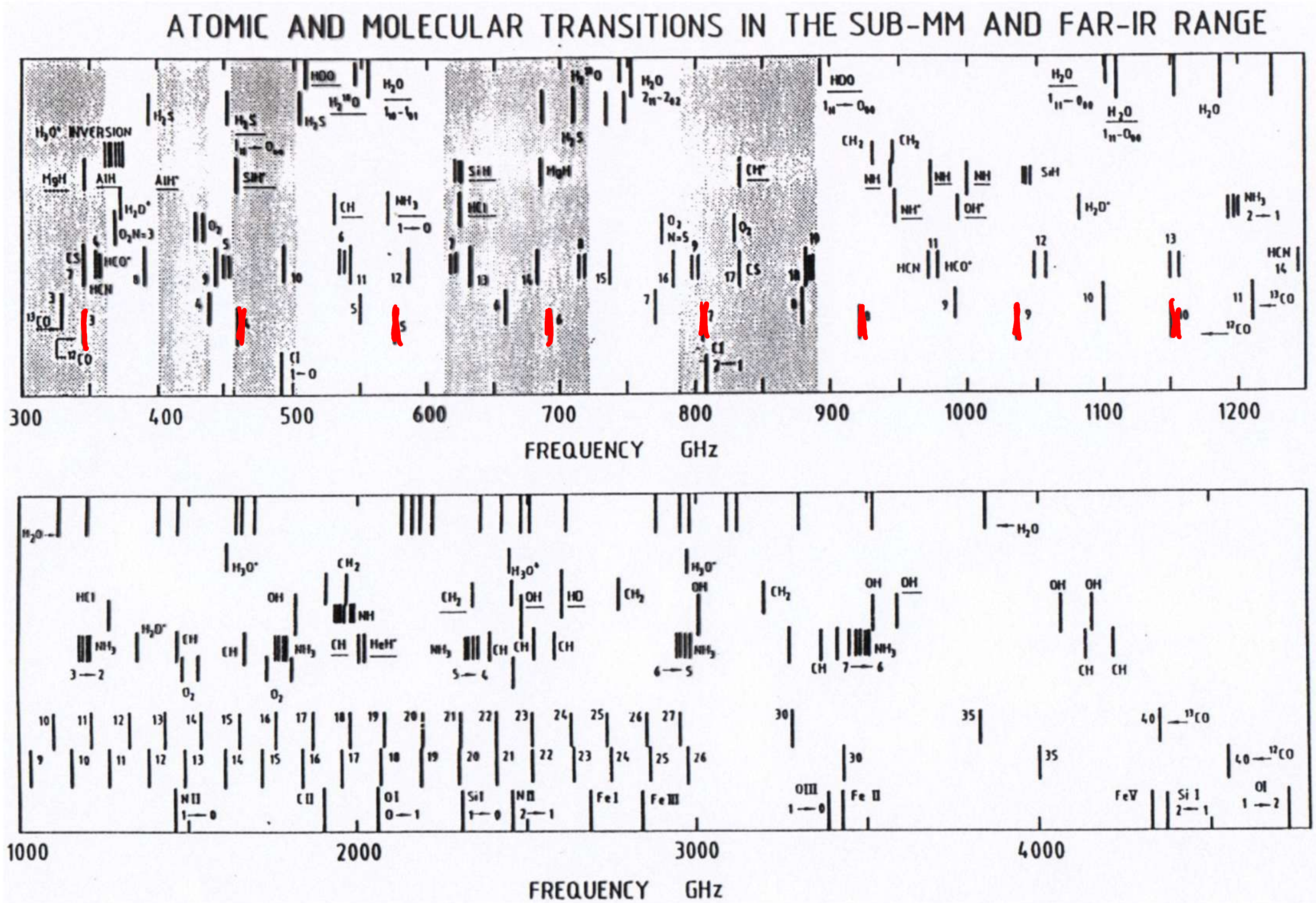
Selection rules:

Resulting transitions

$\Delta E = E_J - E_{J-1}$

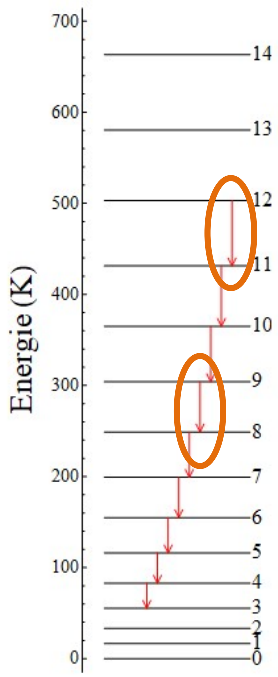
$B(J(J+1) - (J-1)J)$

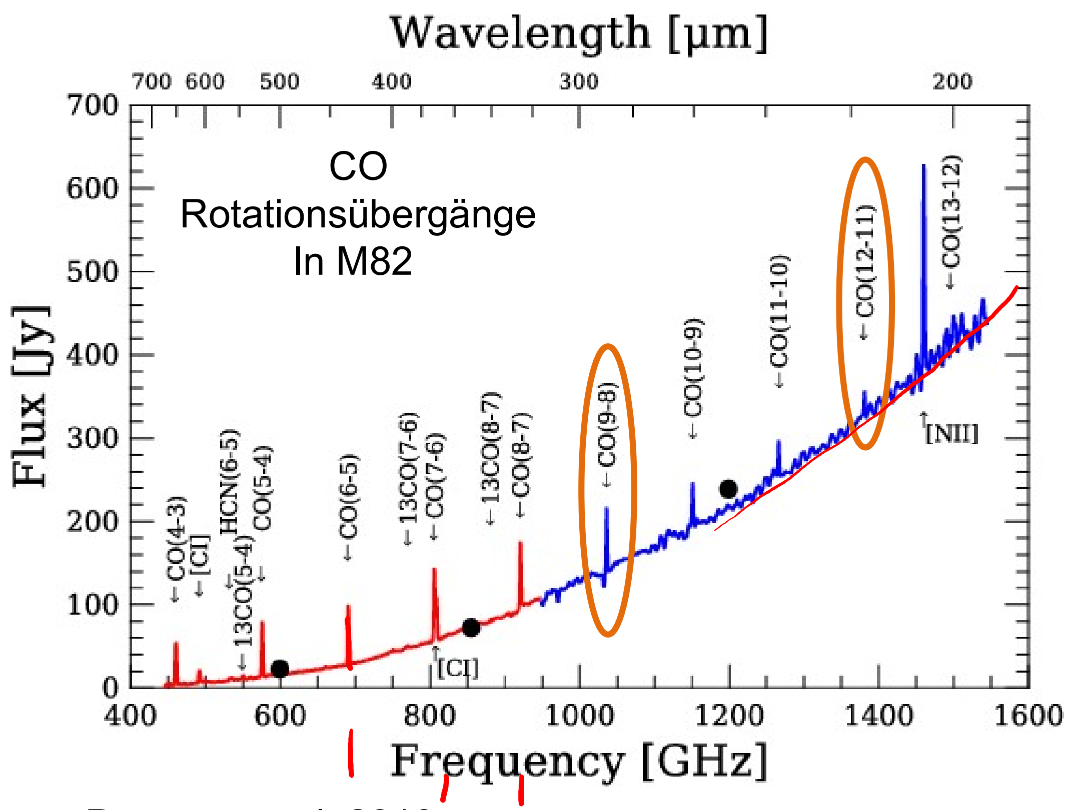
$= \underline{2 \cdot B \cdot J}$



Selection rules:

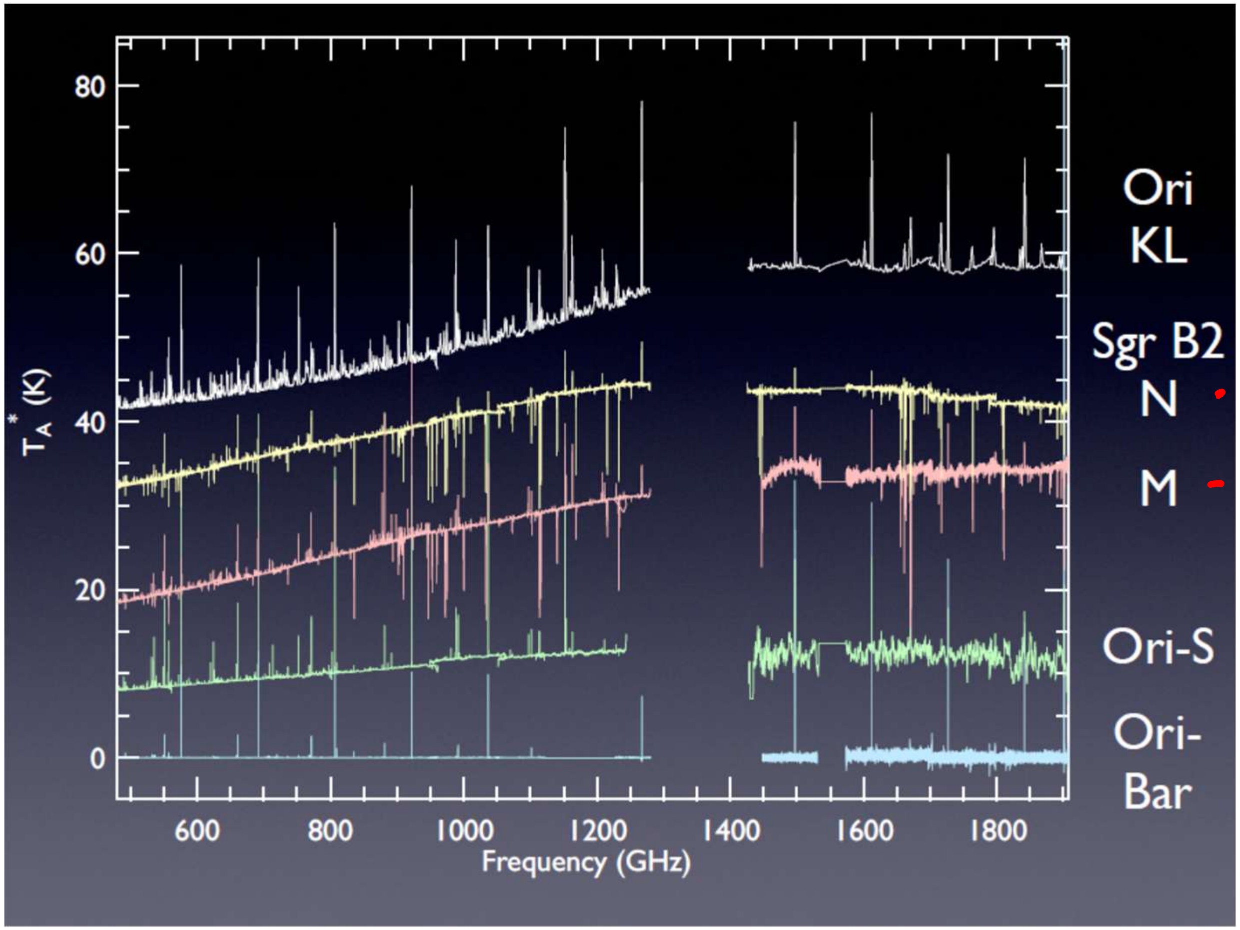
- Simple spectra





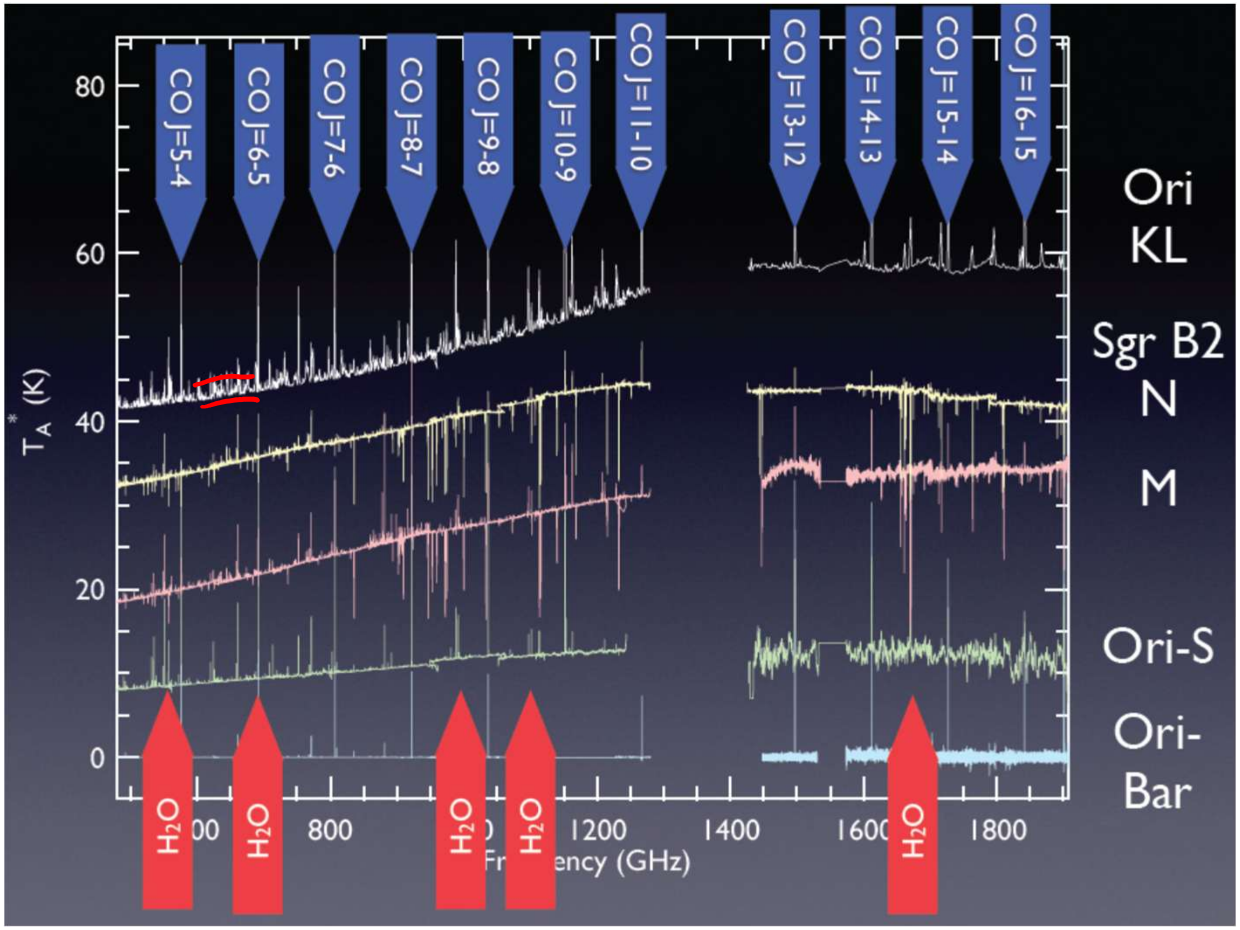
Panuzzo et al. 2010

Selection rules:



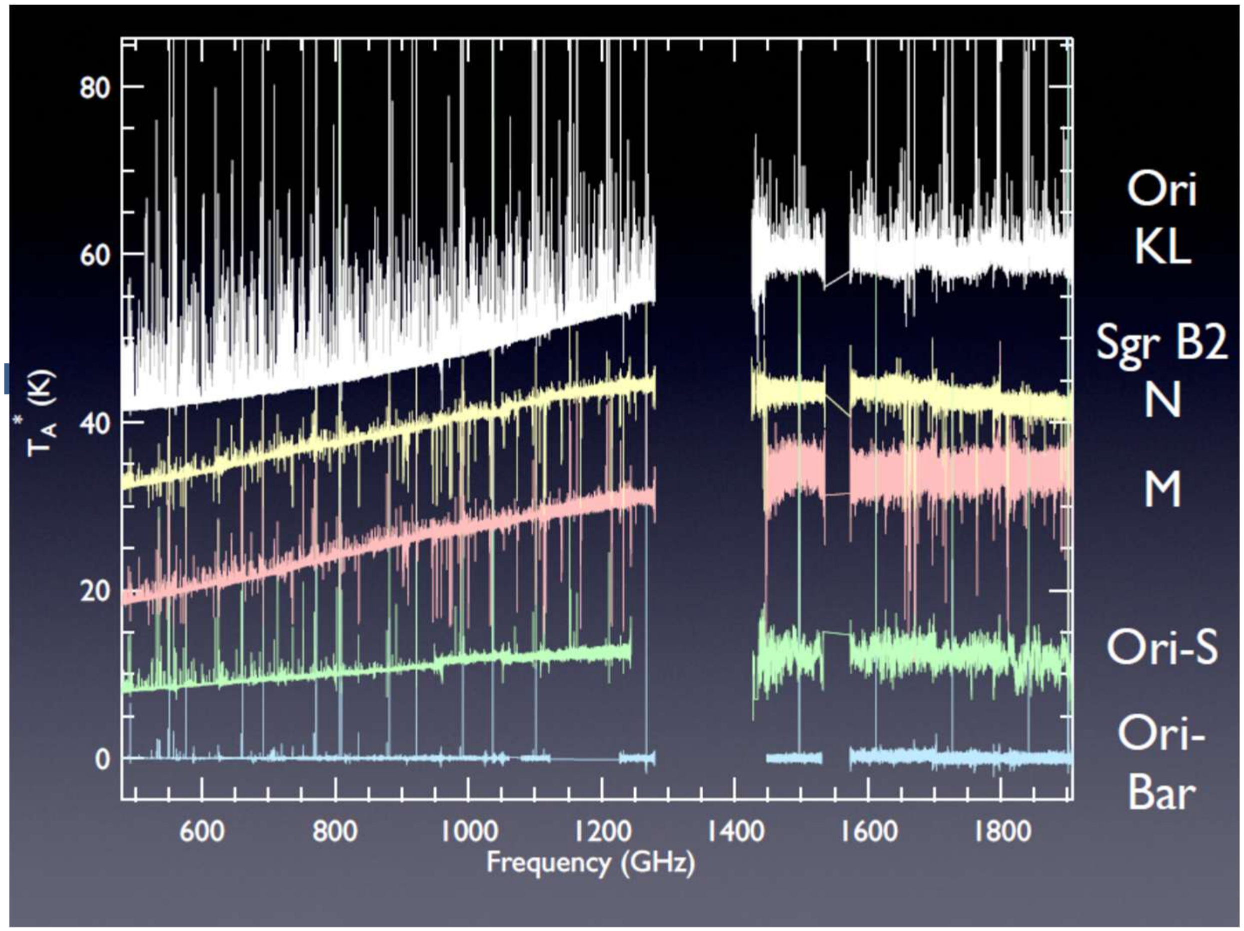
Source: E. Bergin (Univ. of Michigan)

Selection rules:



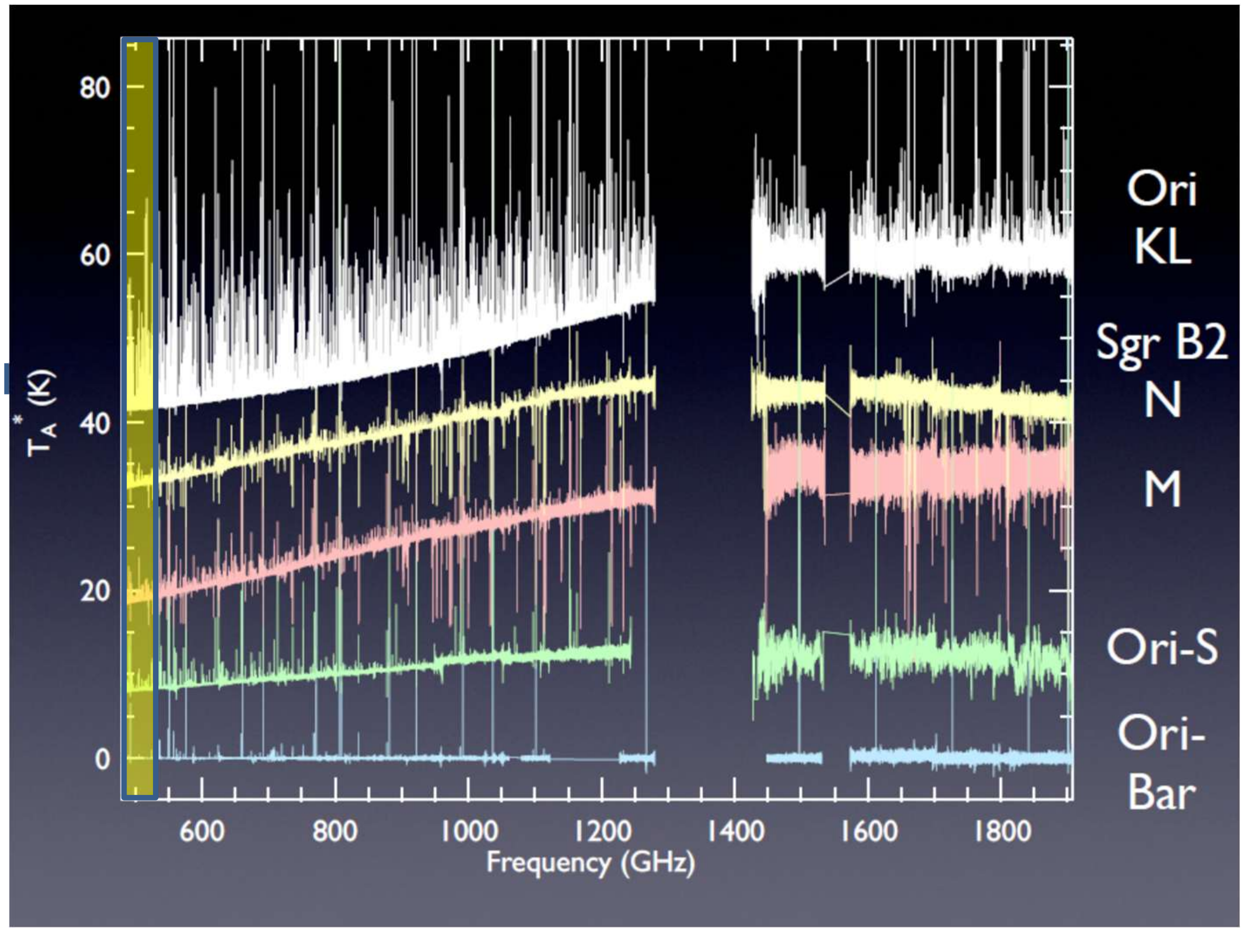
Source: E. Bergin (Univ. of Michigan)

Selection rules:



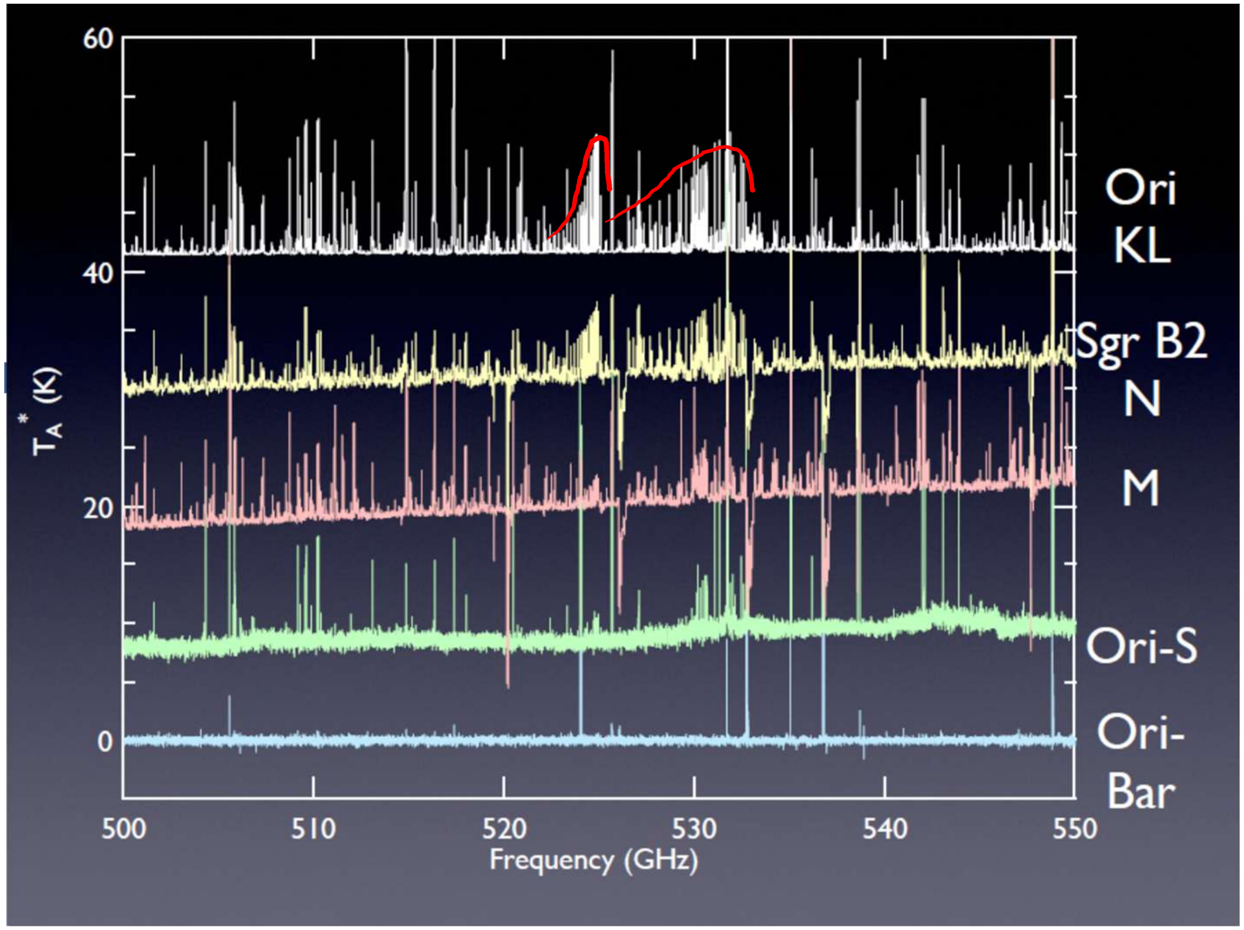
Source: E. Bergin (Univ. of Michigan)

Selection rules:



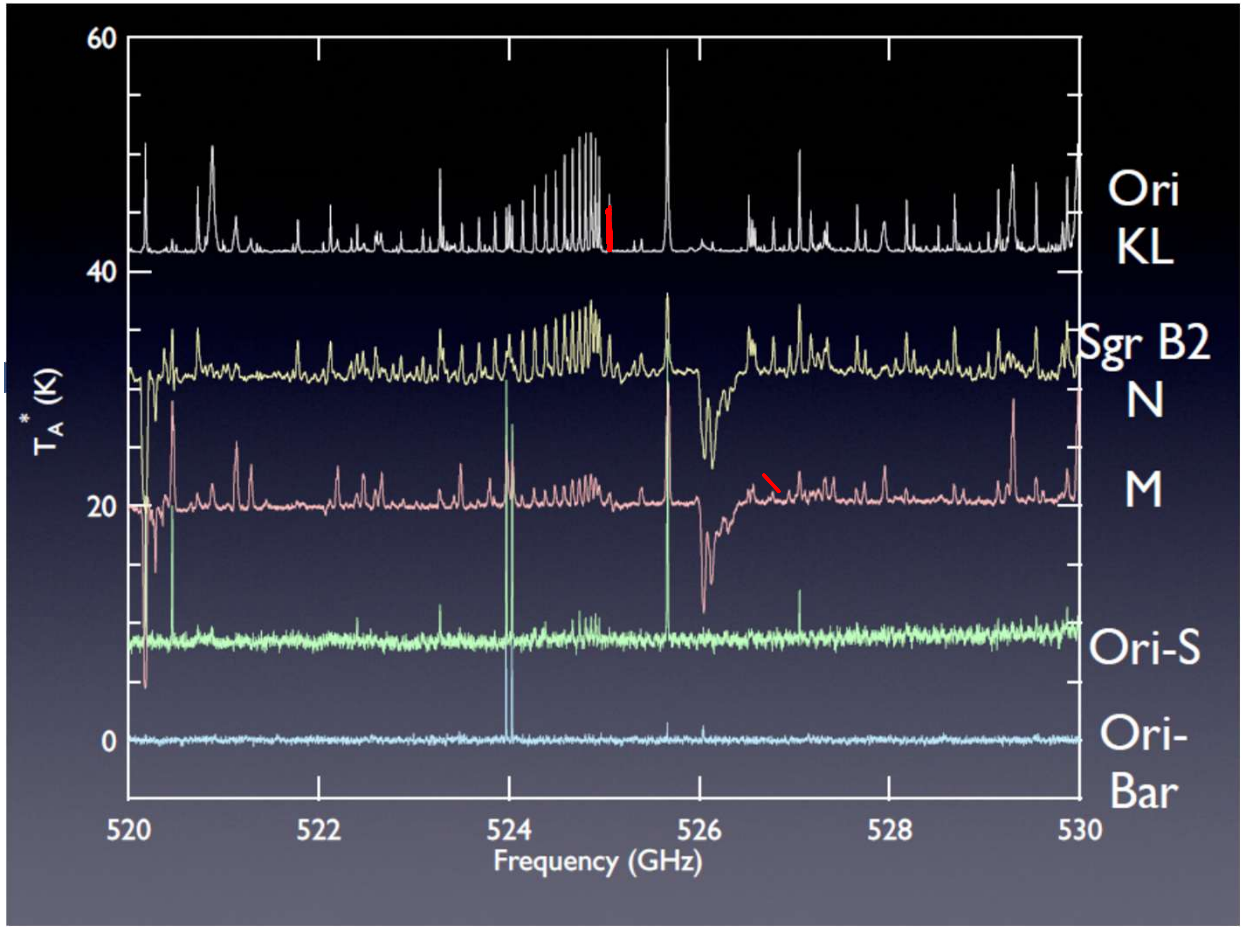
Source: E. Bergin (Univ. of Michigan)

Selection rules:



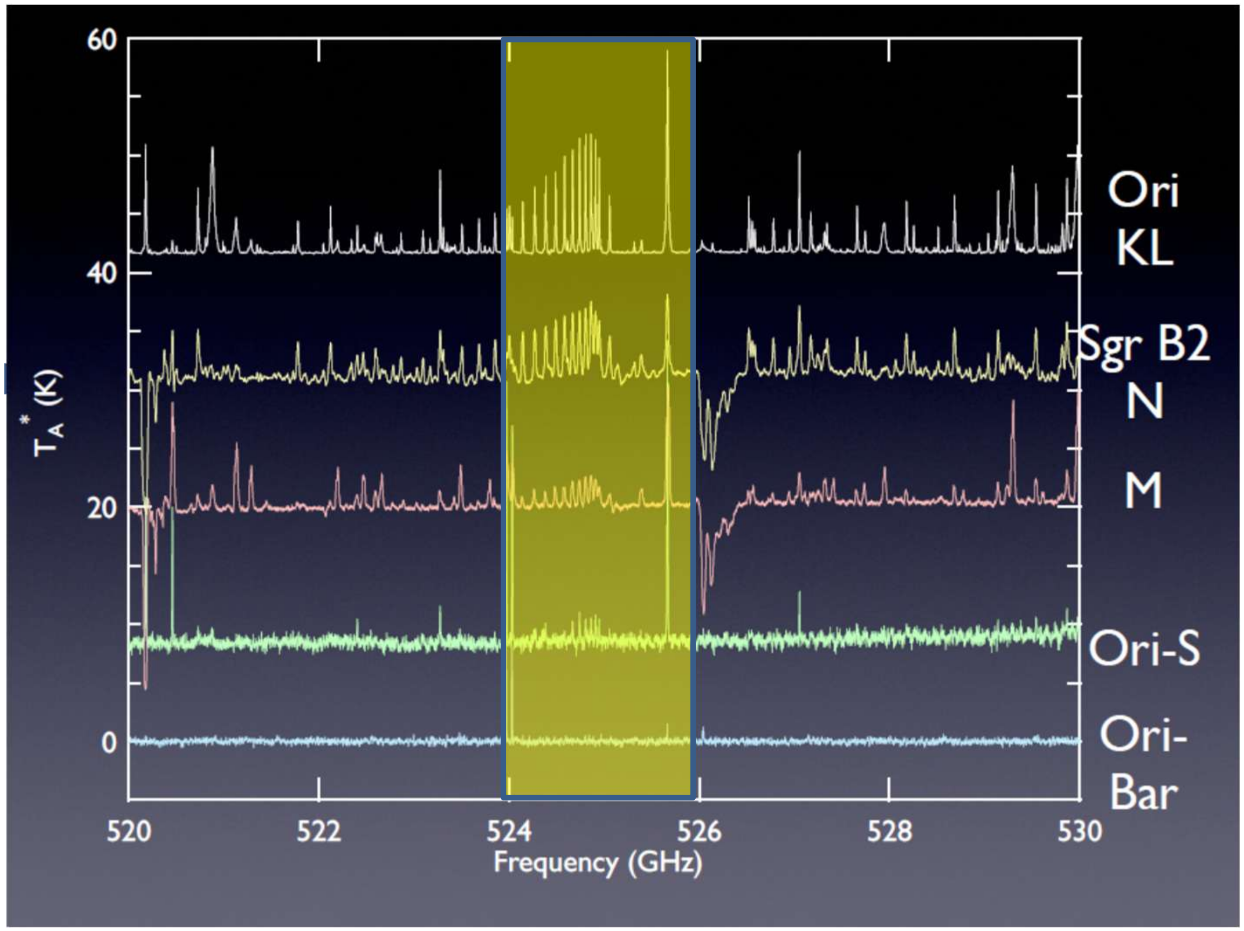
Source: E. Bergin
(Univ. of Michigan)

Selection rules:



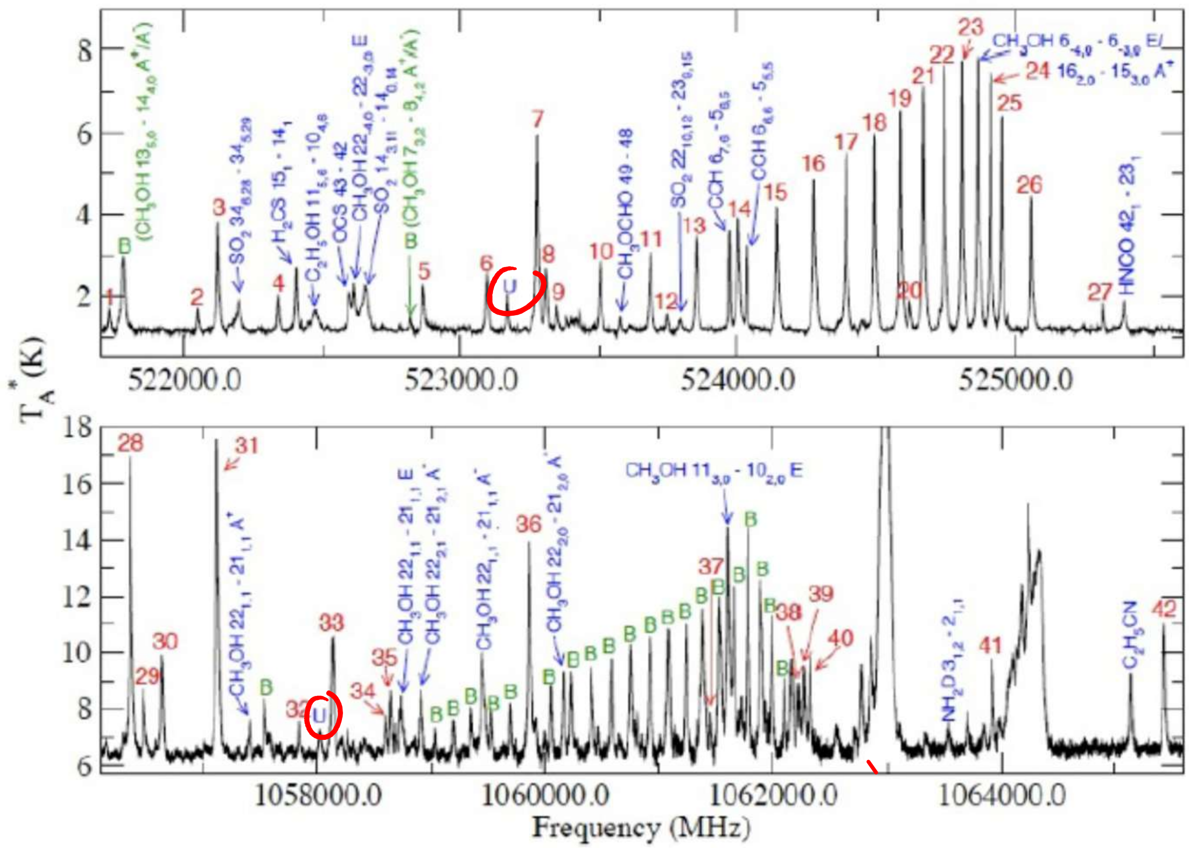
Source: E. Bergin
(Univ. of Michigan)

Selection rules:



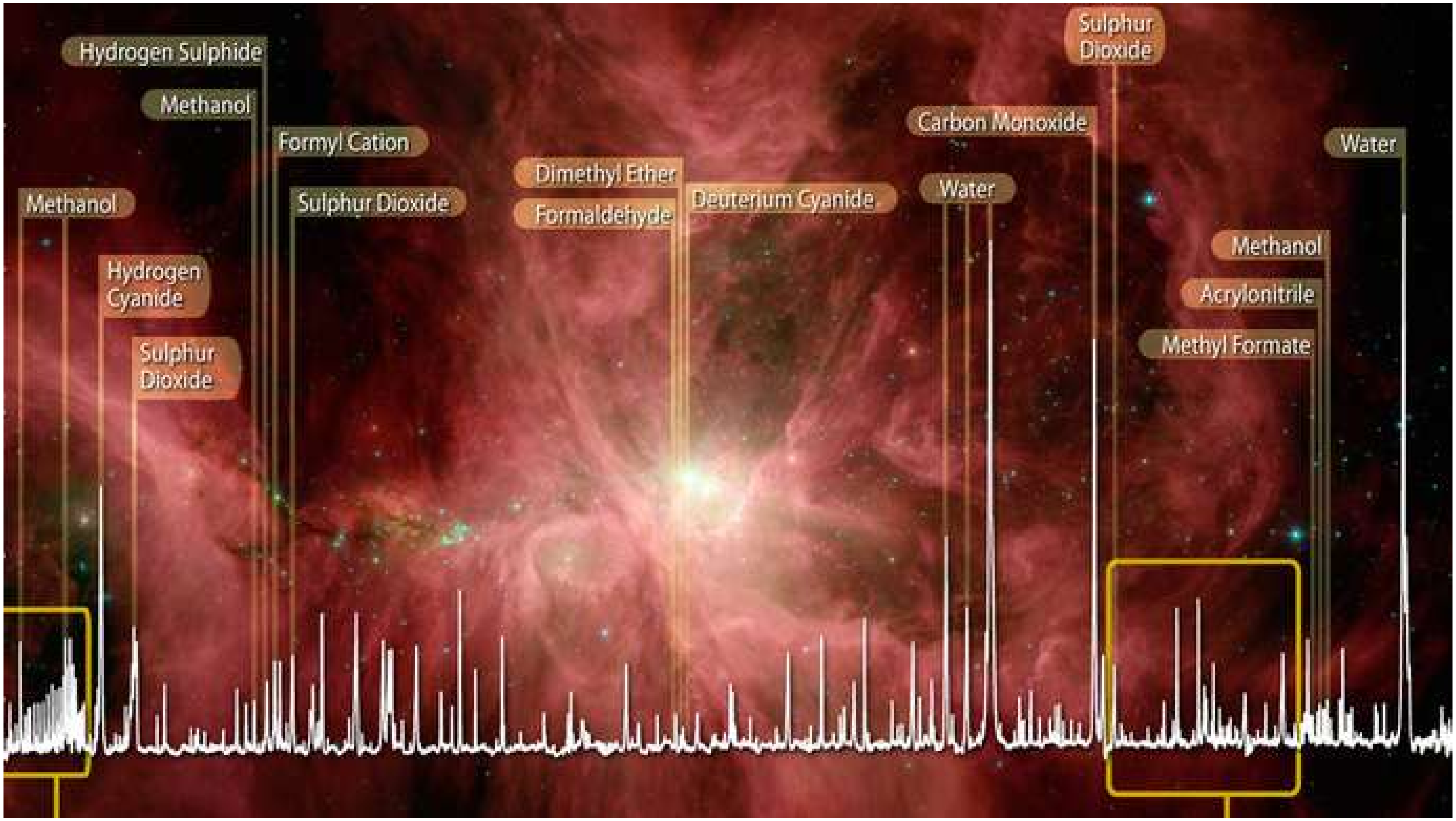
Source: E. Bergin (Univ. of Michigan)

Selection rules:



Wang et al. 2011

Star formation in Orion



Credits: ESA, HEXOS and the HIFI Consortium