

Hydrogen

As an example of absorption and emission by
atoms/molecules

QM versus classical physics

- ❑ Action, [energy] · [time] or [momentum] · [distance], is quantized in unit of \hbar
- ❑ Heisenberg's uncertainty principle
- ❑ Pauli exclusion principle

A photon with ν has momentum $p = h\nu/c$

De Broglie wavelength $\lambda = \frac{h}{p} = \frac{h}{m_e v}$

OK only if an orbit of circumferences = $n \lambda$ (standing waves), so

$$2\pi a_n = n \lambda = \frac{nh}{m_e v} \rightarrow a_n = n \lambda = \frac{n\hbar}{m_e v}$$

Orbital angular momentum, $L = m_e a_n v = n\hbar$

Balance of Coulomb force and centrifugal force, $\frac{e^2}{a_n^2} = \frac{m_e v^2}{a_n}$

$$a_n = \frac{n^2 \hbar^2}{m_e e^2} = 0.53 n^2 [\text{\AA}] \propto n^2 \quad \text{(Bohr radius)}$$

$$\nu = R_\infty \left(1 + \frac{m_e}{M}\right)^{-1} [1/n_1^2 - 1/n_2^2] = 3.28805 \times 10^{15} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] [\text{Hz}]$$

Lowest state of H, $p^2 r^2 \approx \langle \Delta p^2 \rangle \langle \Delta r^2 \rangle \approx \hbar^2$

Virial theorem, $2E_K + E_p = 0$

Lowest (ground state) energy

$$\varepsilon_1 = -\frac{1}{2}E_p = -\frac{1}{2} \frac{Ze^2}{r} = -\frac{1}{2} \frac{p^2}{\mu} \approx -\frac{1}{2\mu} \frac{\hbar^2}{r^2}$$

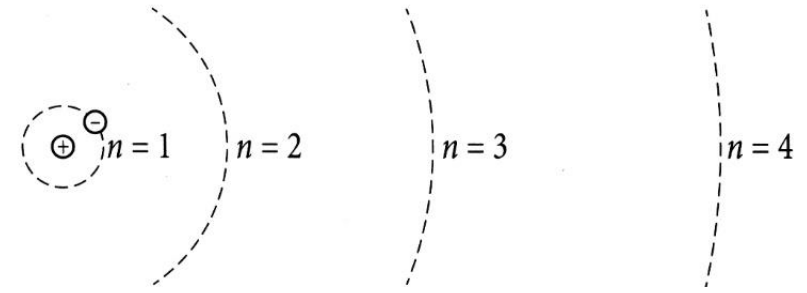
μ : reduced mass

$$\frac{Ze^2}{r} = \frac{\hbar^2}{\mu r^2} \Rightarrow r = \frac{\hbar^2}{\mu Ze^2} \quad (\text{Bohr's radius})$$

$$\varepsilon_1 = -\frac{1}{2} \frac{Ze^2 \mu Ze^2}{\hbar^2} = -\frac{1}{2} \frac{Z^2 \mu e^4}{\hbar^2}$$

For H, $Z = 1$, $\varepsilon_1 = -13.6 \text{ eV}$, $r \approx 5.3 \times 10^{-9} \text{ [cm]}$

Electron Orbitals



$$n = 1, 2, 3, 4, \dots,$$

K, L, M, N, ...

Principal quantum number \leftrightarrow Energy

$$\ell = 0, 1, 2, \dots, n - 1,$$

s, p, d, f, g, h, i, ...

e.g., Iron ($Z = 26$) K-alpha at 6.4 keV in X rays

Orbital quantum number \leftrightarrow Ang. Momentum

sharp, principal, diffuse, fundamental, ...

$$m_z = 0, \pm 1, \pm 2, \dots, \pm \ell,$$

Magnetic quantum number \leftrightarrow AM Direction

□ An *s* state has no angular momentum; a *p* state $AM = \sqrt{2} \hbar$.

□ In H, $n = 1, \ell = 0$

□ n, ℓ, m_z in unit of \hbar

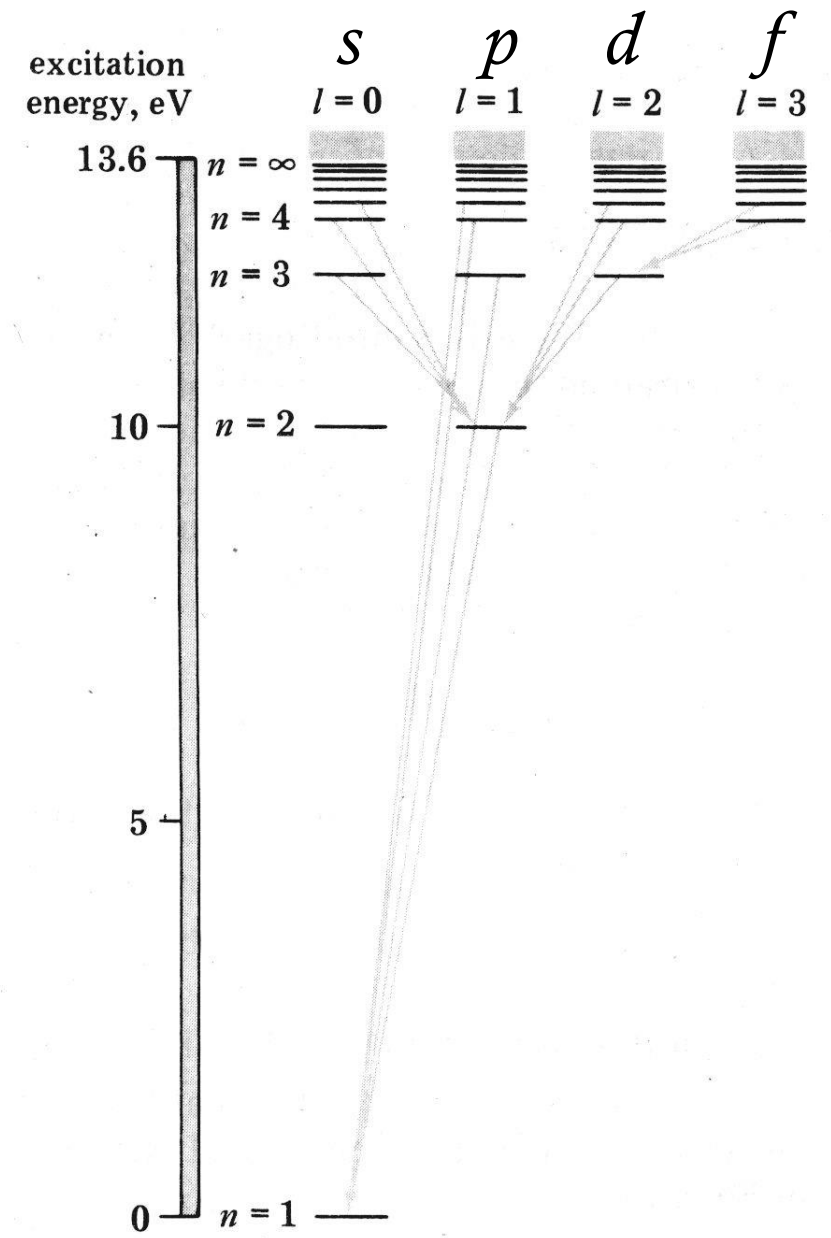
TABLE 6.2 THE SYMBOLIC DESIGNATION OF ATOMIC STATES IN HYDROGEN

	$l = 0$	$l = 1$	$l = 2$	$l = 3$	$l = 4$	$l = 5$
$n = 1$	1s					
$n = 2$	2s	2p				
$n = 3$	3s	3p	3d			
$n = 4$	4s	4p	4d	4f		
$n = 5$	5s	5p	5d	5f	5g	
$n = 6$	6s	6p	6d	6f	6g	6h

Selection Rules

For an allowed transition

- Δn no restriction
- $\Delta \ell = \pm 1$
- $\Delta m = 0, \pm 1$



An electron has a spin of $1/2$. Projection onto the z -axis can have only $-\hbar/2$ or $+\hbar/2$, not distinguishable (degenerate) if there is no external field. Each electron has orbital angular momentum $\ell\hbar$, and spin angular momentum $\hbar/2$.

A subshell, i.e., a given pair of quantum numbers $n \ell$ has $2(2\ell + 1)$ electronic wave functions.

For multi-electron atoms, Pauli exclusion principle forbids 2 electrons sharing the same wave function.

An s subshell has at most 2 electrons; a p subshell at most 6, and a d subshell up to 10.

Exercise

Atomic carbon has 6 electrons. What is its ground state configuration?

A: 2 in 1s, 2 in 2s, and 2 in 2p; $1s^2 2s^2 2p^2$

In general,

Total angular momentum (added in the vector sense) $\mathcal{L}\hbar$,

Total spin angular momentum $S\hbar$, L-S coupling (spin-orbit interaction; fine structure)

Each (\mathcal{L}, S) , called a **term**, is designated by $^{2S+1}\mathcal{L}^p$, where $\mathcal{L} = S, P, D, F, \dots$, for orbital momentum $\mathcal{L} = 0, 1, 2, 3 \dots$ and p = “blank” (for even parity; whether the wave function changes sign through origin) or “o” (for odd parity)

Total electronic angular momentum, $J\hbar$

Transitions connecting two terms are called **multiplets**. Terms with two/three possible J values, are called **doublets, triplets**, etc.

A term, with \vec{L} and \vec{S} vectors (may point to different directions) has a multiplicity of $g = (2S + 1)(2L + 1)$. Including spin-orbit coupling, each state is split into sub-states, each with J , with a degeneracy $g = (2J + 1)$.

□ For H, $n_{\text{lower}} = 1$ (Lyman, 1906), 2 (Balmer, 1885),
 3 (Paschen, 1908), 4 (Brackett, 1922),
 5 (Pfund, 1924), 6 (Humphreys, 1953)

□ α : $\Delta n = 1$; β : $\Delta n = 2$; ...

□ Balmer alpha, or $H\alpha$, $H(3p) \rightarrow H(2s)$, $\lambda 656.28$ nm

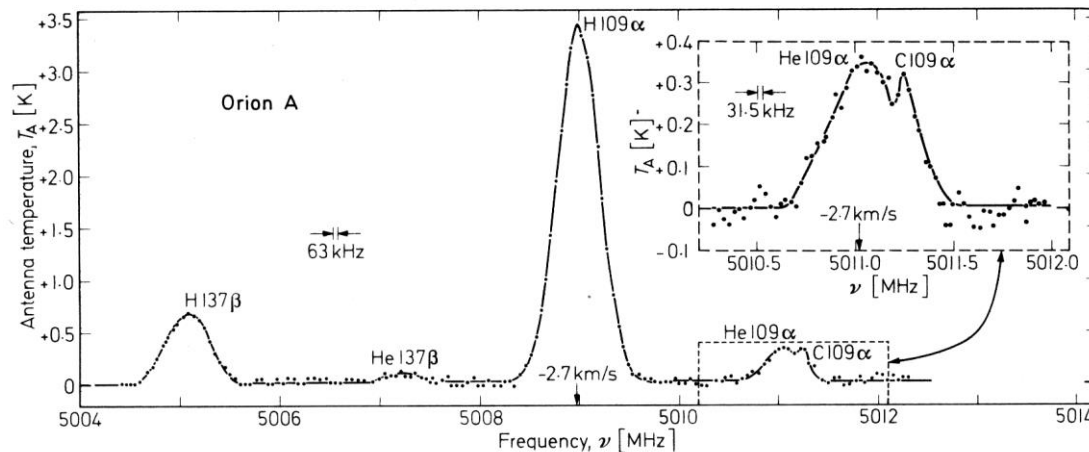


Fig. 12. Broadband spectrogram of the 109α region of the spectrum of the Orion Nebula. The frequency resolution is 63 kHz for the broadband spectrogram and 31.5 kHz for the narrow band spectrum centered on the He 109α line. (After CHURCHWELL and MEZGER, 1970, by permission of Gordon & Breach Science Publishers)

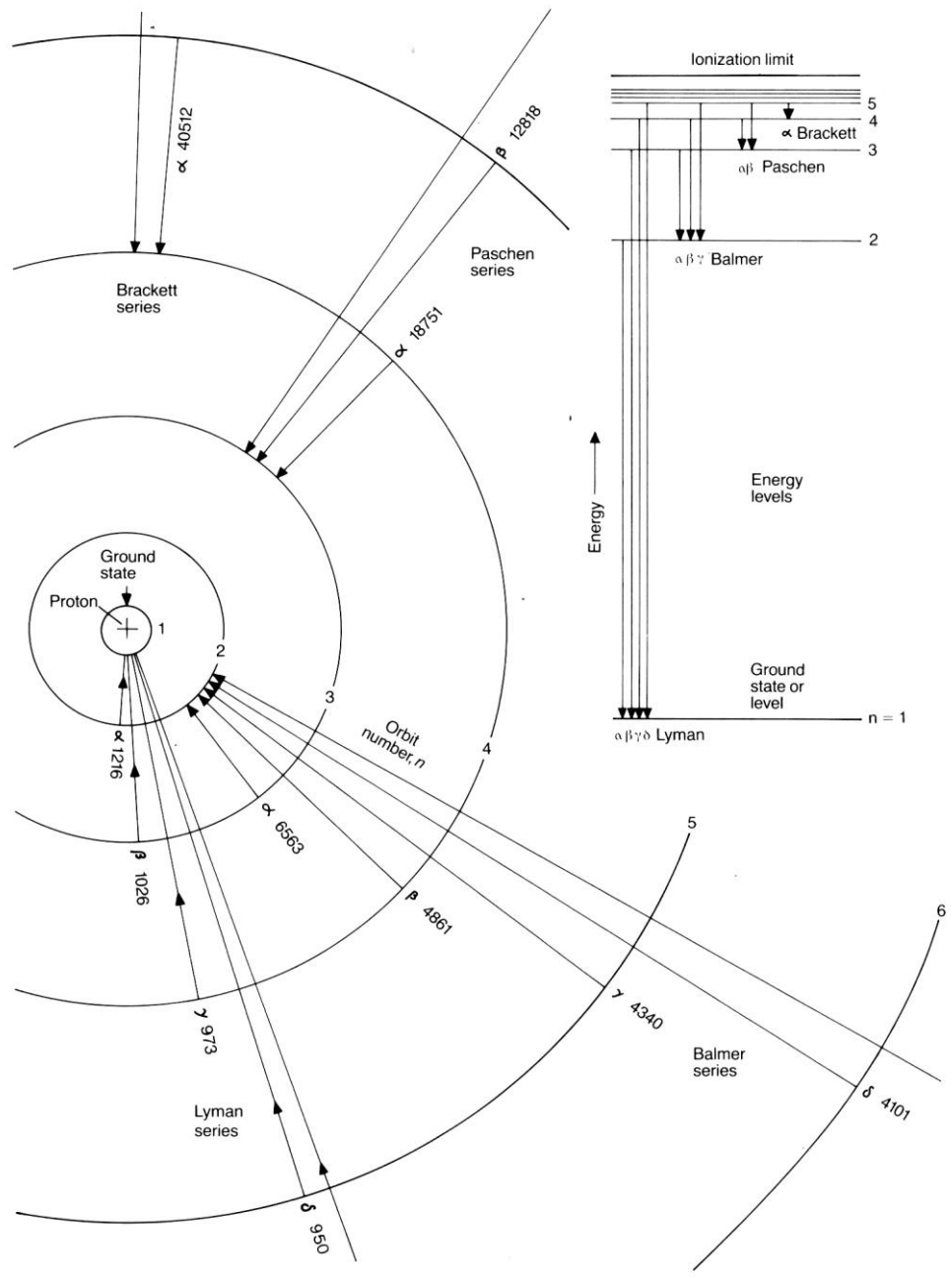
$H109\alpha$

Table 11. The wavelengths in Å of the $m \rightarrow n$ transitions of hydrogen for $n=1$ to 6, $m=2$ to 21, and $m=\infty$, and for the $n=4$ Pickering series for ionized helium (HeII)¹. Here the wavelengths are in Å where $1 \text{ Å} = 10^{-8} \text{ cm}$

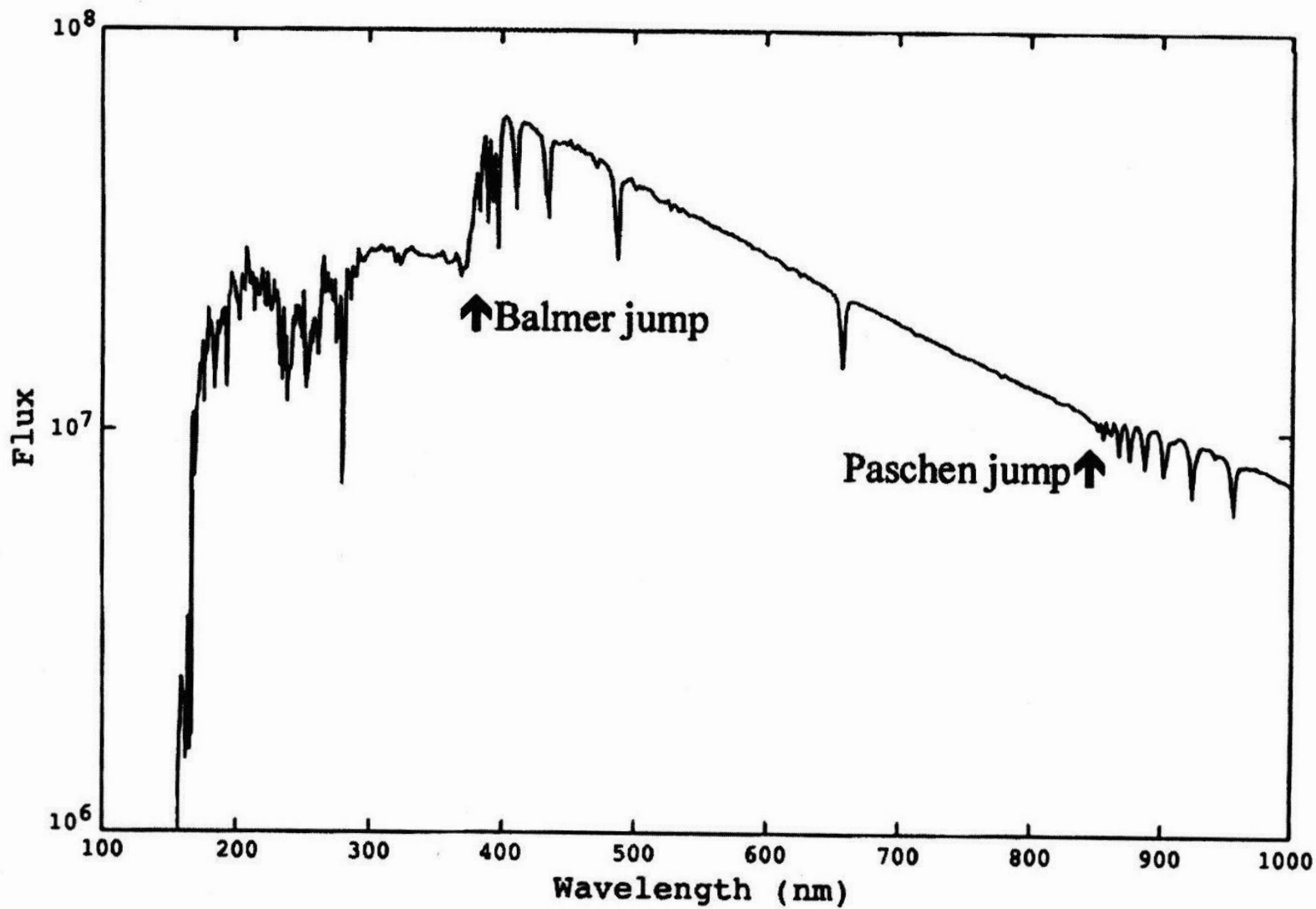
Series m	Lyman ($n=1$)	Balmer ($n=2$)	Paschen ($n=3$)	Brackett ($n=4$)	Pfund ($n=5$)	Humphreys ($n=6$)	Pickering (He ⁺ , $n=4$)
2	1,215.67						
3	1,025.72	6,562.80					
4	972.537	4,861.32	18,751.0				
5	949.743	4,340.46	12,818.1	40,512.0			10,123.64
6	937.803	4,101.73	10,938.1	26,252.0	74,578		6,560.10
7	930.748	3,970.07	10,049.4	21,655.0	46,525	123,680	5,411.52
8	926.226	3,889.05	9,545.98	19,445.6	37,395	75,005	4,859.32
9	923.150	3,835.38	9,229.02	18,174.1	32,961	59,066	4,541.59
10	920.963	3,797.90	9,014.91	17,362.1	30,384	51,273	4,338.67
11	919.352	3,770.63	8,862.79	16,806.5	28,722	46,712	4,199.83
12	918.129	3,750.15	8,750.47	16,407.2	27,575	43,753	4,100.04
13	917.181	3,734.37	8,665.02	16,109.3	26,744	41,697	4,025.60
14	916.429	3,721.94	8,598.39	15,880.5	26,119	40,198	3,968.43
15	915.824	3,711.97	8,545.39	15,700.7	25,636	39,065	3,923.48
16	915.329	3,703.85	8,502.49	15,556.5	25,254	38,184	3,887.44
17	914.919	3,697.15	8,467.26	15,438.9	24,946	37,484	3,858.07
18	914.576	3,691.55	8,437.96	15,341.8	24,693	36,916	3,833.80
19	914.286	3,686.83	8,413.32	15,260.6	24,483	36,449	3,813.50
20	914.039	3,682.81	8,392.40	15,191.8	24,307	36,060	3,796.33
21	913.826	3,679.35					3,781.68
∞	911.5	3,646.0	8,203.6	14,584	22,788	32,814	3,644.67

Continuum

¹ Data from WIESE, SMITH, and GLENNON (1966).

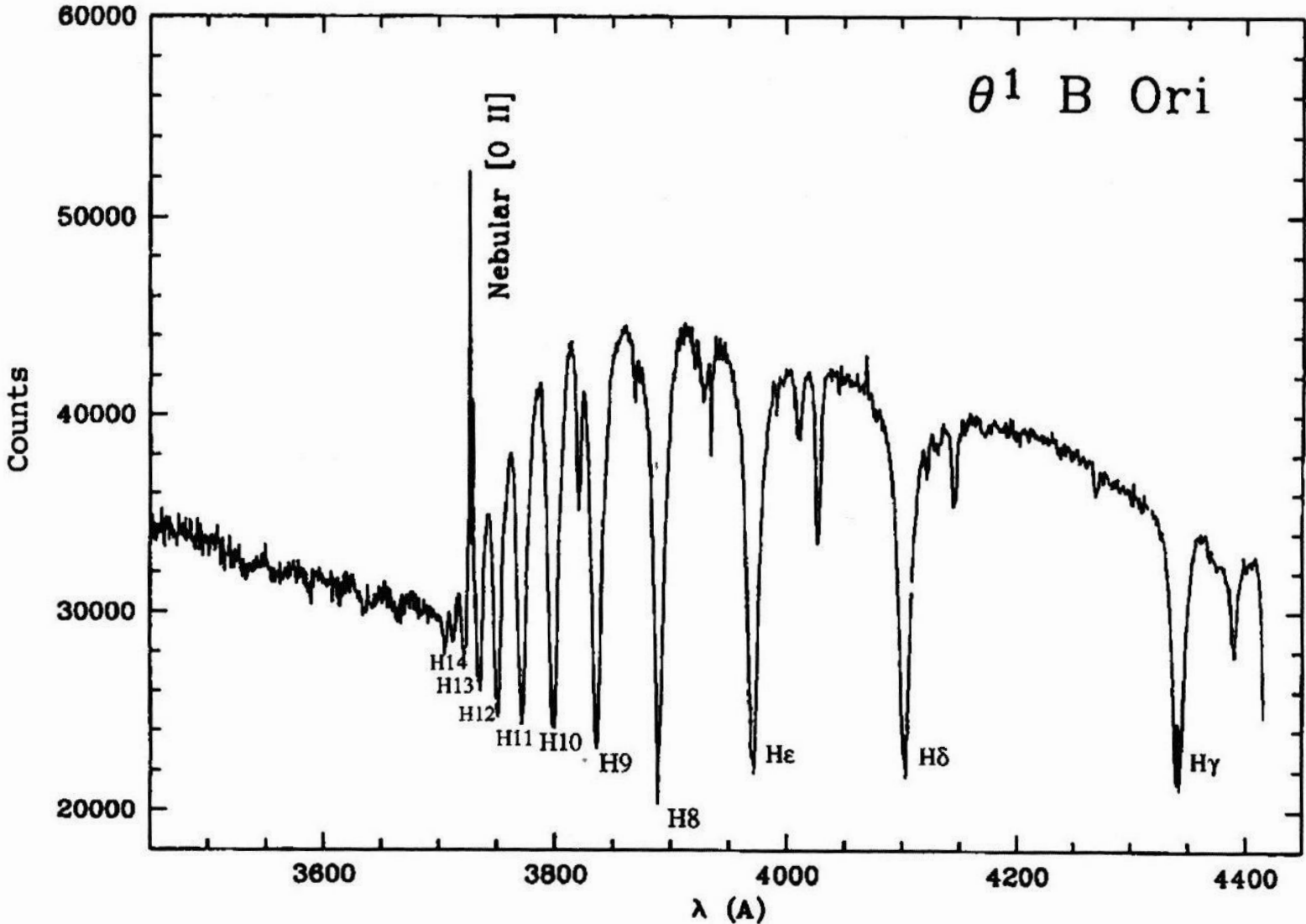


Model spectrum of an A5 star



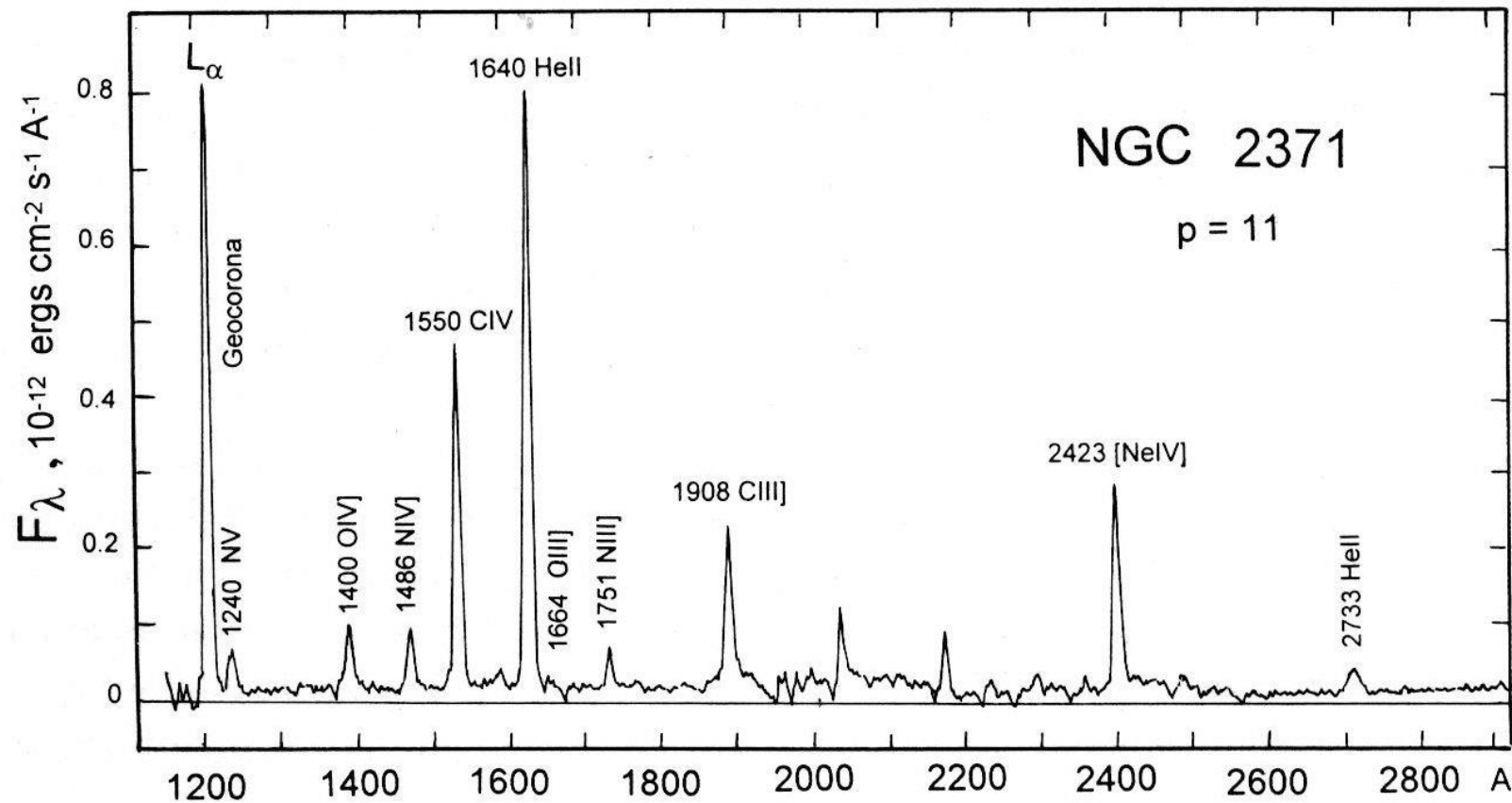
Tennyson

Balmer absorption series up to H14 of a B-type star

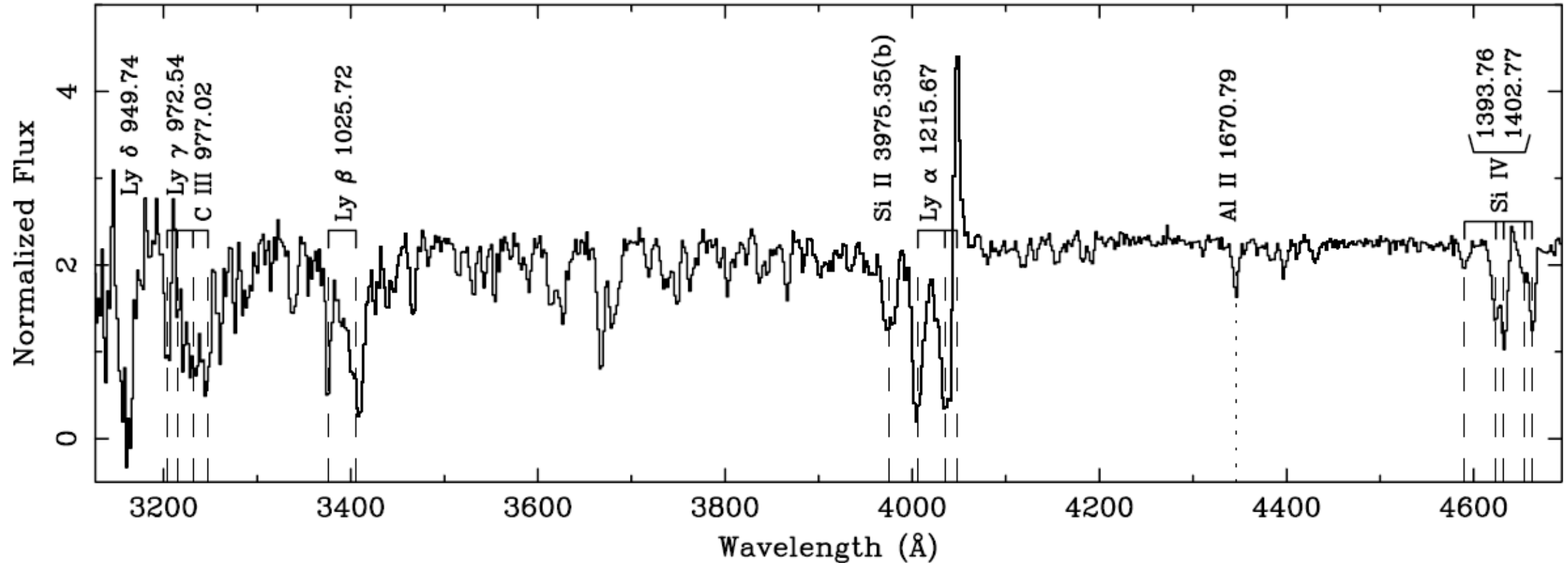


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The IUE spectrum of a planetary nebula. Note Ly-alpha at 121.5 nm, and also the high excitation lines of 1550 C IV and 1640 He II, the forbidden line 2423 [Ne IV], and semi-forbidden line 1908 C III].



Lyman and other absorption lines of a Wolf-Rayet shell nebula GRB 021004, showing doublets due to Doppler effect in the shell



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Mirabal+03

Brackett-alpha of the protostars Orion-BN object

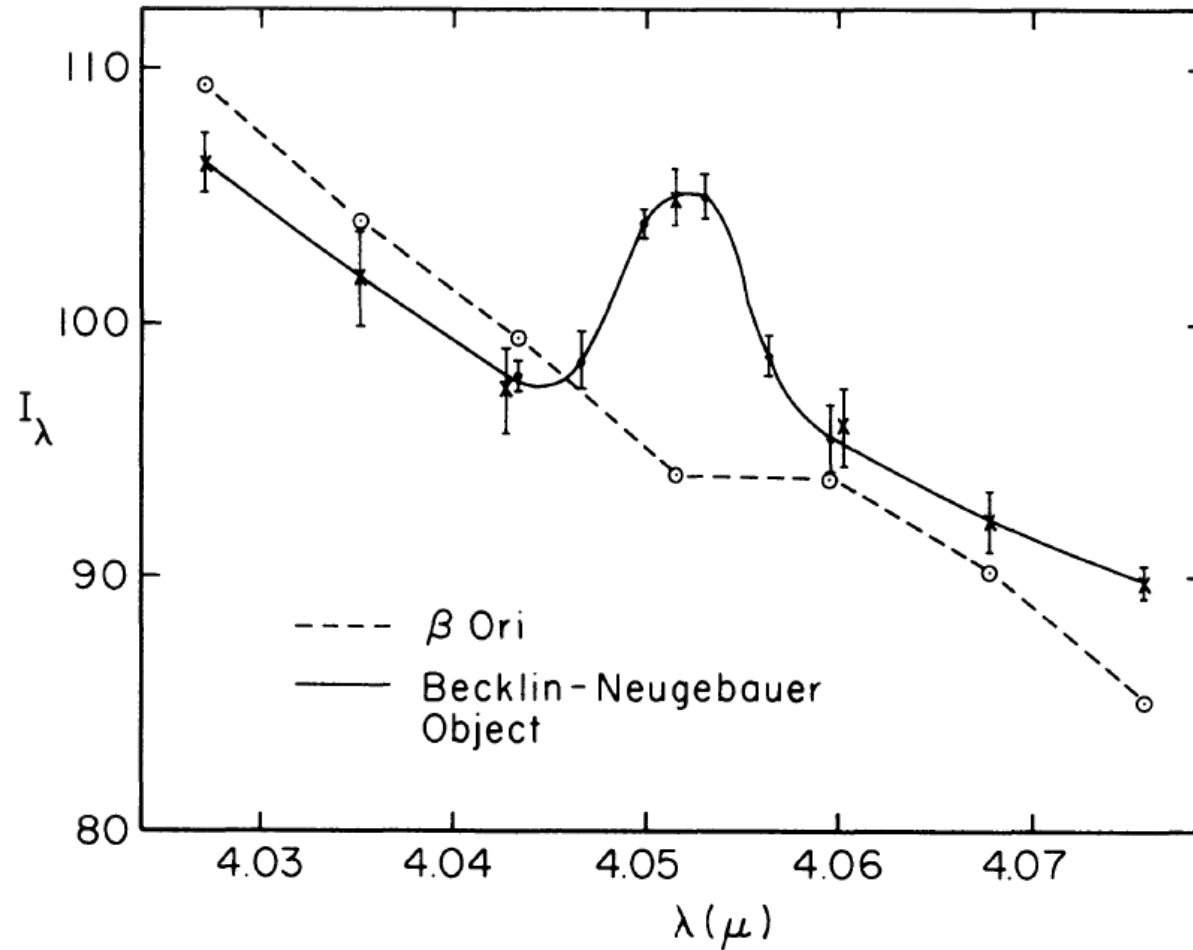


FIG. 1.—Spectra of the BN object and β Ori. The two independent sets of data for the BN object are indicated by dots and \times 's.

Grasdalen 1976

NIR spectrum of the Seyfert galaxy Mrk 231 , showing Paschen-alpha and Brackett-gamma lines.

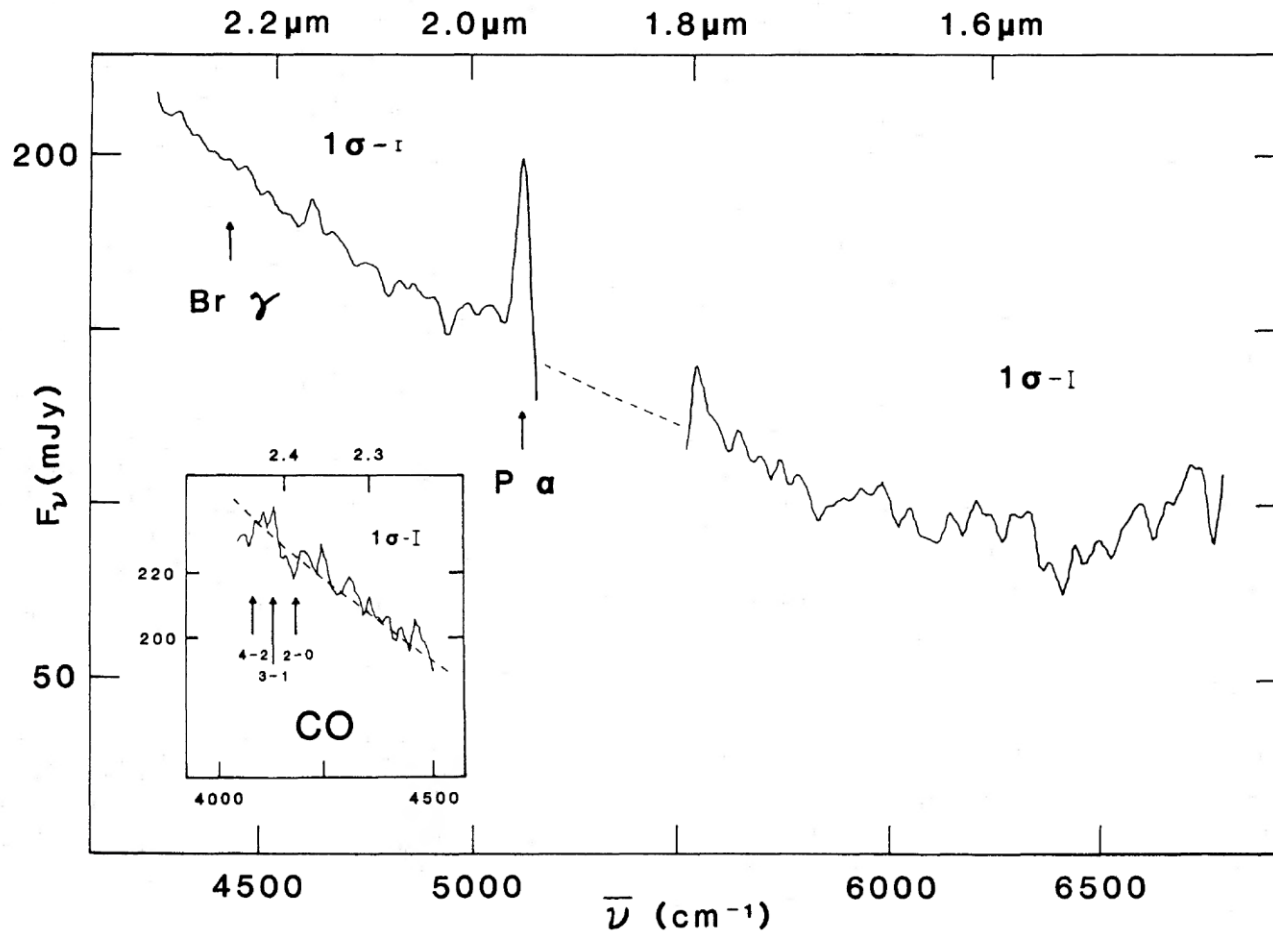


FIG. 1.—The near-infrared spectrum of Mrk 231. These data have been smoothed to a resolution of 54 cm^{-1} . The dashed line represents the portion of the spectrum in which atmospheric transmission drops below 50% and has therefore been omitted. The weak emission feature at 4620 cm^{-1} is the result of insufficient correction for the $\text{Br}\gamma$ absorption line in the A type calibration star GC 18704. (*inset*) The $4000\text{--}4400 \text{ cm}^{-1}$ region of the spectrum at the original 16 cm^{-1} resolution. The expected locations of the first overtone CO bands have been marked.

For higher energy states, $p_n r_n = n\hbar$

$$\mathcal{E}_n = -\frac{p_n^2}{2\mu} \approx -\frac{n^2 \hbar^2}{2\mu r_n^2} = -\frac{Z^2 \mu e^4}{2n^2 \hbar^2}$$

For the n -th radial state, the phase space volume is

$(4\pi p_n^2 \Delta p_n)(4\pi r_n^2 \Delta r_n)$, # of possible states with principle quantum number n

$$= \frac{\text{Total phase space volume}}{\text{volume of unit cell}} = \frac{16\pi^2 n^2 \hbar^3}{\hbar^3} \propto n^2$$

Electron spin parallel or anti-parallel to that of the nucleus, so the n -th state has $2n^2$ different substates, all having the same energy.

$n \uparrow\uparrow$, the electron very distant from the nucleus (binding force extremely weak); often ionized then recombined (cascading down)

For H91 α , i.e., $n = 92 \rightarrow 91$

$$\nu(\text{H}91\alpha) = 3.28805 \times 10^{15} \text{ Hz} \left[\frac{1}{91^2} - \frac{1}{92^2} \right]$$

$$\approx 8.5848 \times 10^9 \text{ Hz}$$

This is called a “radio recombination line”.

$$\nu = R_\infty \left(1 + \frac{m_e}{M} \right)^{-1} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] = 3.28805 \times 10^{15} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] [\text{Hz}]$$

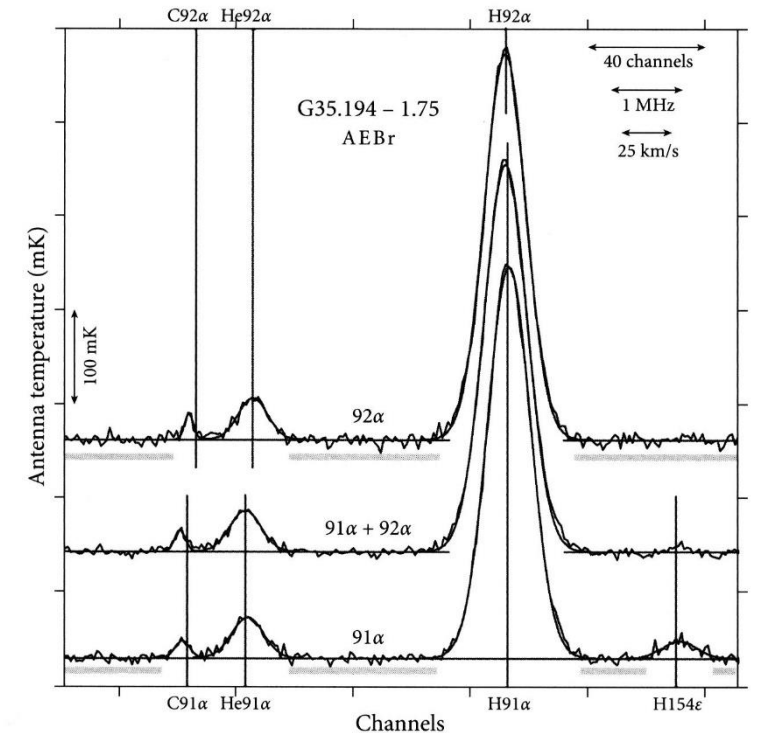


Figure 7.2. Observed recombination-line spectra from the 91 α and 92 α transitions of hydrogen, helium, and carbon observed in an HII region [84].

Considering reduced mass,

$M(\text{He}) \approx 4 M(\text{H})$; $M(\text{C}) \approx 12 M(\text{H})$, so $\nu \nearrow$ a bit

Exercise

What is the highest n level of H atoms expected to find on the surface of the Sun where the gas number density is $\approx 10^{17} \text{ cm}^{-3}$?

A: $n \approx 16$

Tennyson, p.32

$$\mathcal{E}_n = -\frac{Z^2 \mu e^4}{2n^2 \hbar^2}$$

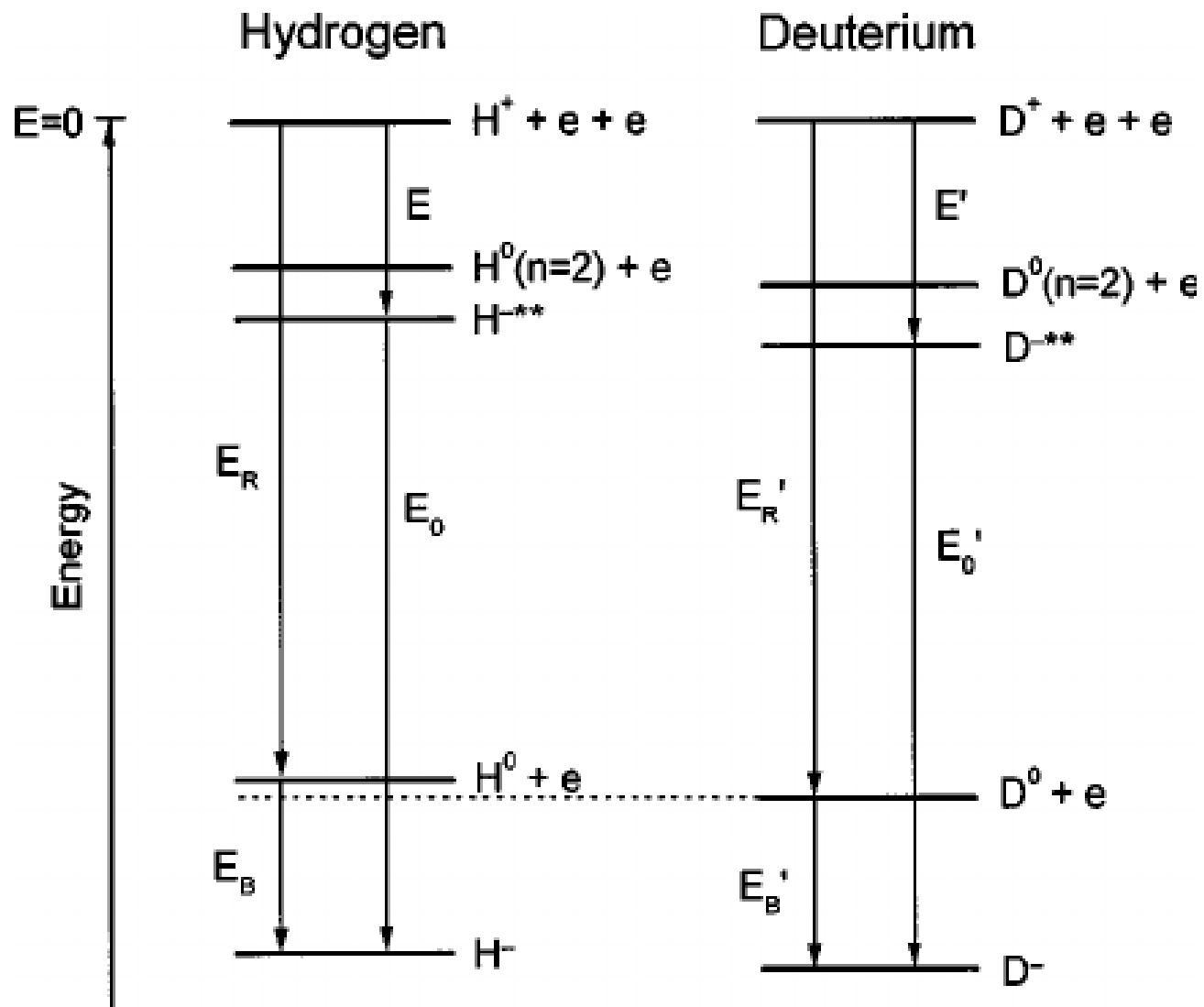
Note that $\mathcal{E}_n \propto \mu$

$$\text{For normal H, } \mu_H = \frac{m_e m_p}{m_e + m_p} = \frac{m_e}{1 + m_e/m_p} \approx m_e (1 - m_e/m_p)$$

$$\text{For deuteron, } \mu_D = \frac{m_e m_D}{m_e + m_D} = \frac{2m_e m_p}{m_e + 2m_p} \approx m_e (1 - m_e/2m_p) > \mu_H$$

So the D lines are shifted 1.5 Å to shorter wavelengths

Note also that $\mathcal{E}_n \propto Z^2$, so for He II ($Z = 2$, with 1 e^-), Z^2 is 4 times larger, and with a different μ .



- For the ground state, the orbital angular momentum is $\ell = 0$. The total spin angular momentum (**hyperfine structure**; interaction with nuclear spin)

$$F = 0 \text{ (spin opposite) or } F = 1 \text{ (spin parallel)}$$

Typically 10^{-6} eV, difficult to observe in optical due to Doppler broadening

Including the nucleus,

$$J = [\text{electronic angular momentum}] / \hbar$$

$$I = [\text{nuclear angular momentum}] / \hbar$$

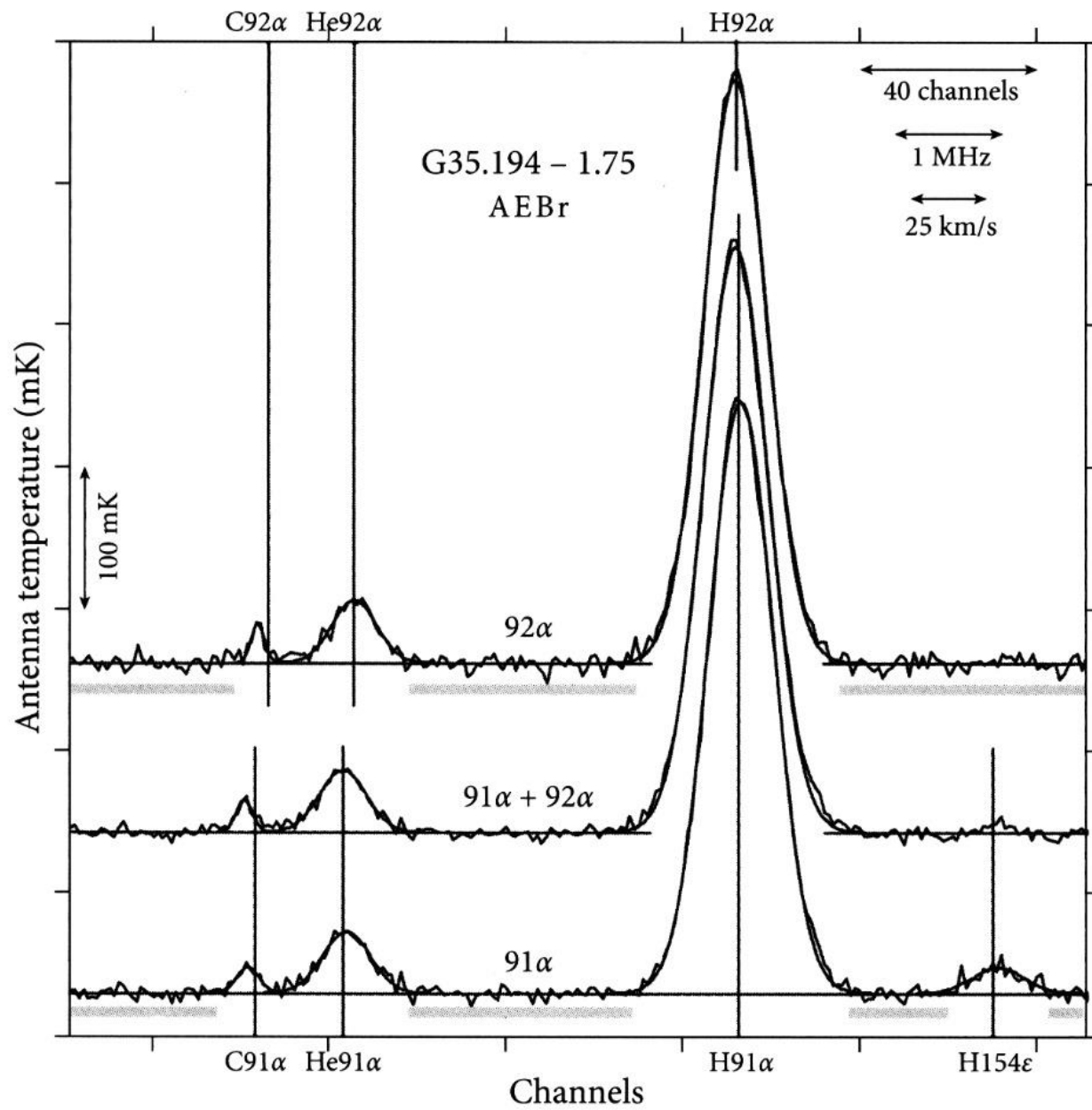
$$F = [\text{total angular momentum}] / \hbar$$

For H, the ground electronic state $1s^2 S_{1/2}$ has $J = 1/2$, and the proton has $I = 1/2$. The state splits into $F = 0$ or $F = 1$, $\Delta E = 6.7 \times 10^{-6}$ eV, $\nu = 1420.4$ MHz, $\lambda \approx 21$ cm.

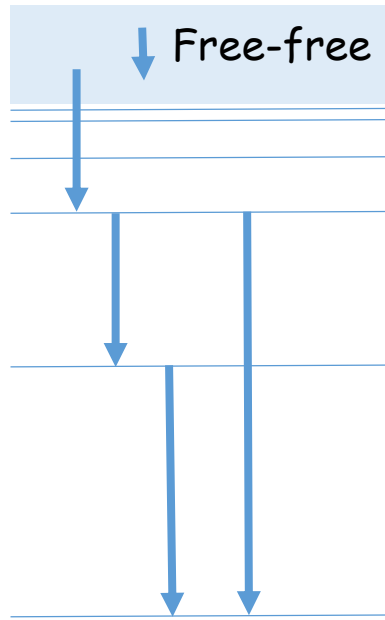
- For $n = 2, \ell = 1$, and with spin, a total angular momentum of $\ell(\ell + 1)\hbar^2 = 2\hbar^2$
3 substates, $\hbar, 0, -\hbar, m = 1, 0, -1$ (magnetic quantum number)
Fine structure, $\Delta\mathcal{E}$ very small, $\sim 10^{-5}$ eV
But with an external \mathbf{B} field \rightarrow **Zeeman splitting**

With a field of $10 \mu\text{G}$, the 21-cm line shifts 10^{-8} , equivalent to an RV of a few km s^{-1} ; very difficult to detect

Detectable by the difference of the two circular polarization signals (more on this when we discuss the magnetic field)

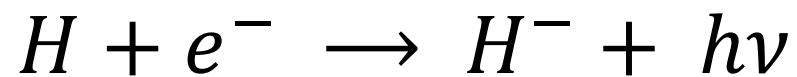


H^+



- ◆ Free-free or free-bound to any level
- ◆ Cascading down \rightarrow emission of photons of different energies

H⁻ (negative H ion)



Ample supplies of free e^{-} from Na, Ca, Mg, ... with low-ionization potentials

He atom similar, with the second e^{-} weakly bounded, shielded by the first e^{-}

$\mathcal{E}_{\text{binding}}(\text{H}^{-}) = 0.75 \text{ eV}$, with only 1 bound state; transitions
→ continuum

Absorption by H⁻ immediately followed by reemission

H⁻ opacity dominates atmospheres cooler than A0 (e.g., Sun)

$T \nearrow$, ionized; $T \searrow$, not much free electrons.

Most of the light we see from the Sun due to H⁻ continuum transitions

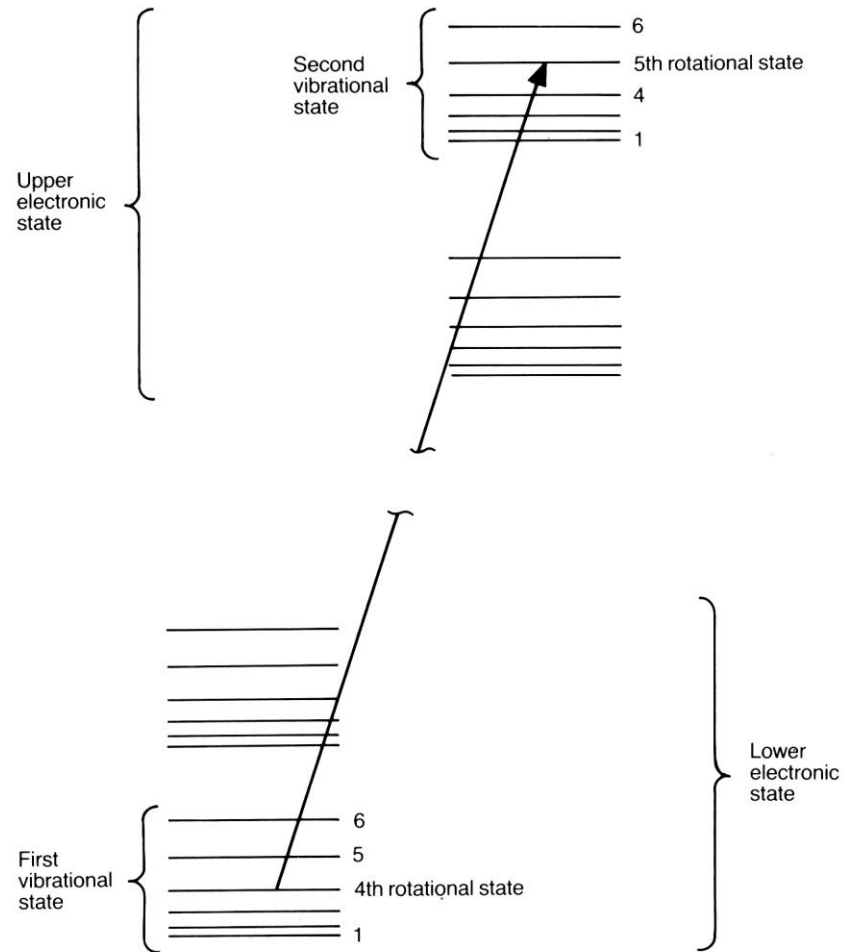
An atom has only electronic transitions.

A molecule can also have electronic transitions, but additionally also vibrational transitions, rotational transitions.

A molecular line is produced by a transition between 2 rotational levels. The set of transitions between 2 rotation-vibration states → a **band**

A band converges with wavelength (toward the red or blue)

The wavelength limit at which the rotational lines pile up is called the **band head**.



Example molecular transitions

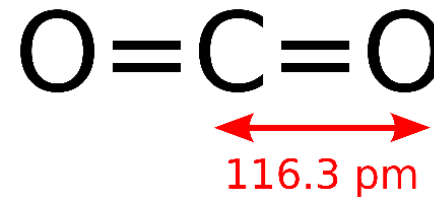
Figure 2.5. Molecular spectra. Two electronic states are shown. Each is divided into vibrational states, of which only the lowest two are drawn. Each of these is split again into rotational states, for which only the lowest six are illustrated. A single molecular absorption line is shown arising from the 4th rotational state of the 1st vibrational state of the lower electronic level, and ending on the 5th rotational state of the 2nd vibrational state of the upper electronic level. The line is a part of *band* of lines created by a set of transitions between the two vibrational states, in which the rotational state number is allowed to change only by plus or minus one. The collection of lines produced between all the vibrational states constitutes a system of bands, all of which replace *one line* in an atomic spectrum. Adapted from *Astrophysics* by L. H. Aller, 2nd edn., Ronald Press Co., New York, 1963.

Dipole radiation is possible only if the molecule has a dipole moment.

H₂, a homonuclear molecule (i.e., consisting of only one type of atoms), has no dipole moment, so can only radiate in less probably transitions, e.g., quadrupole, 10⁻⁹ weaker.

Ortho- spins of protons parallel; para- spins antiparallel

CO₂ has no pure rotation spectrum.



CO has a pure rotation spectrum, astrophysically important in mm to trace molecular gas

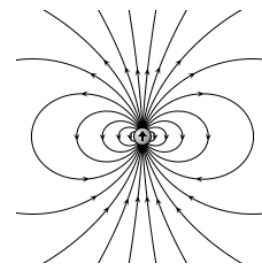


H₂ (dihydrogen, molecular hydrogen)

- Main constituent of cold clouds, not important in stars, except in the coolest substellar objects (brown dwarfs or planetary-mass objects)
- Lacking a permanent electric dipole moment, so cold H₂ very difficult to detect. A rotationally excited molecule would radiate through a relatively slow electric quadrupole transition.
- Only in a heated medium (e.g., a photodissociation PDR region between HII and a molecular cloud) where stellar radiation or stellar wind excites vibrational and electronic states which then decay relatively quickly.

$\mathcal{E}_{\text{dissociation}} = 4.48 \text{ eV}$; H – H bond

https://en.wikipedia.org/wiki/Bond-dissociation_energy



Zero electric
dipole moment

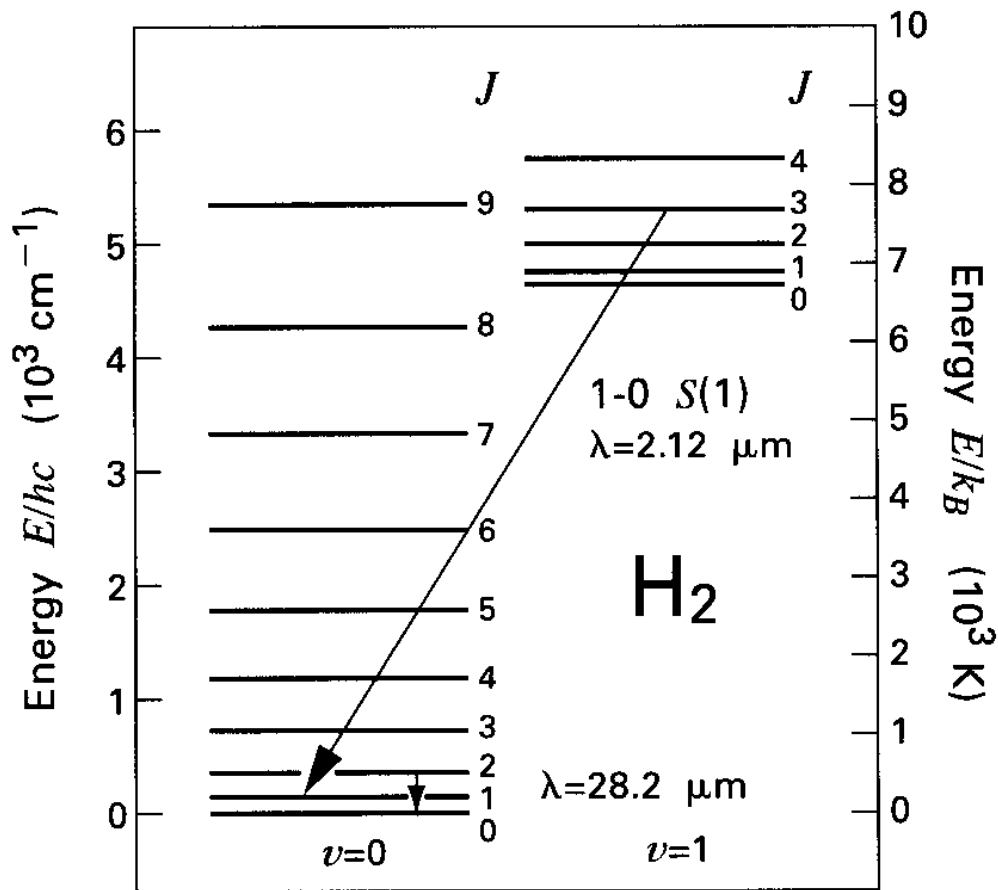


Figure 5.4 Rotational levels of H₂ for the first two vibrational states. Within the $v = 0$ state, the $J = 2 \rightarrow 0$ transition at 28.2 μm is displayed. Also shown is the transition giving the 1-0 S(1) rovibrational line at 2.12 μm . Note that two different energy scales are used.

CO molecules

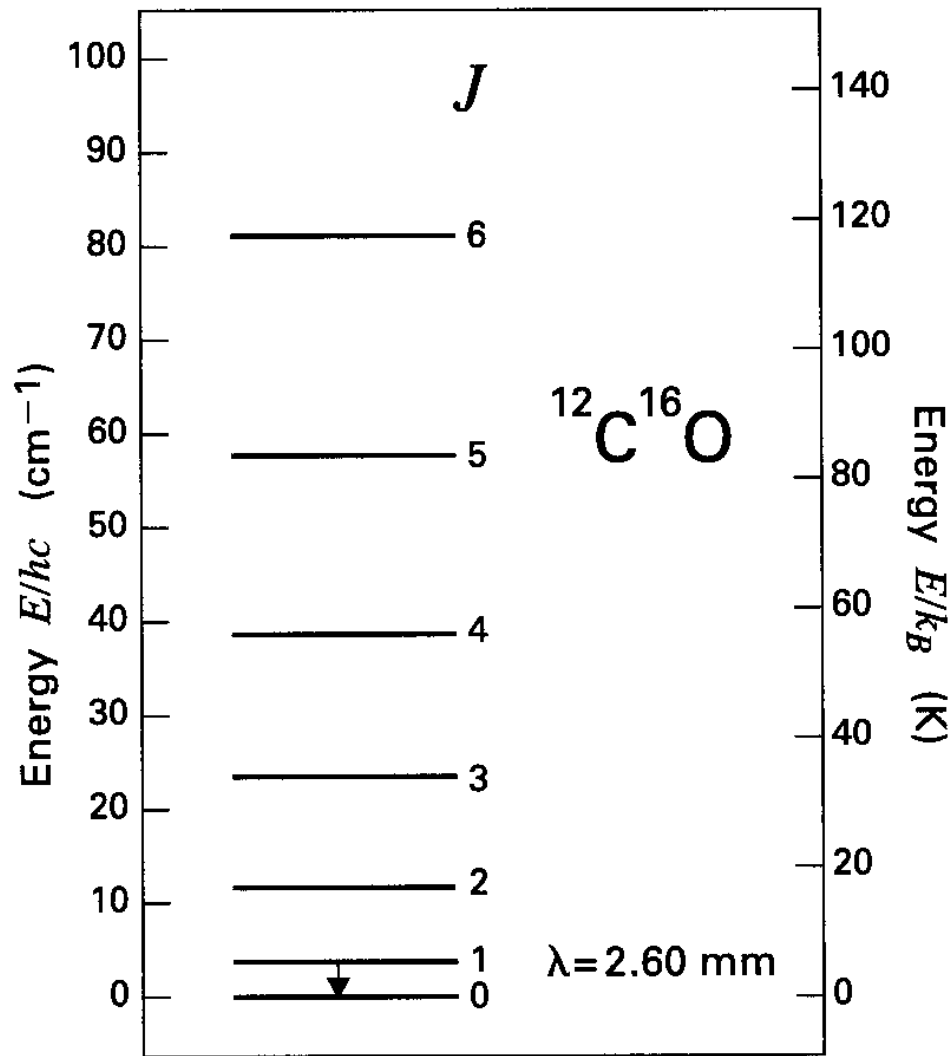
- Simple and most abundant next to H₂
- Strong $\mathcal{E}_{\text{dissociation}} = 11.16 \text{ eV}$; C \equiv O, strongest bond among neutral molecules, self-shielding against stellar UV field
- with a permanent electric dipole moment; radiating strongly at radio frequencies.
- ¹²C¹⁶O easiest to detect; isotopes ¹³C¹⁶O, ¹²C¹⁸O, ¹²C¹⁷O, ¹³C¹⁸O useful as diagnosing tools
- Low critical density for excitation \rightarrow CO used to study large-scale distribution of clouds, as **a tracer** of H₂, $n(\text{CO}) \approx 10^{-4} n(\text{H}_2)$

$$n_{\text{NH}_3}^* \approx 10^3 \text{ cm}^{-3}$$

$$n_{\text{HCN}}^* \approx 10^5 \text{ cm}^{-3} \text{ (for } J = 1 \rightarrow 0 \text{)}$$

- $^{12}\text{C}^{16}\text{O}$ almost always **optically thick**; so its brightness temperature \approx molecular gas kinetic temperature, i.e., little dependence on column density
- Lines from rarer isotopes usually **optically thin**
→ estimate of column density (total mass) of molecular gas
 $N_H = 10^6 N_{^{13}\text{CO}}$

Intensity ratios of optically thin lines from different J levels
→ excitation temperature



$J = 1 - 0$, 2.60 mm = 115 GHz

Only 5 K above the ground level ... can be excited by collisions with ambient molecules or CMB photons

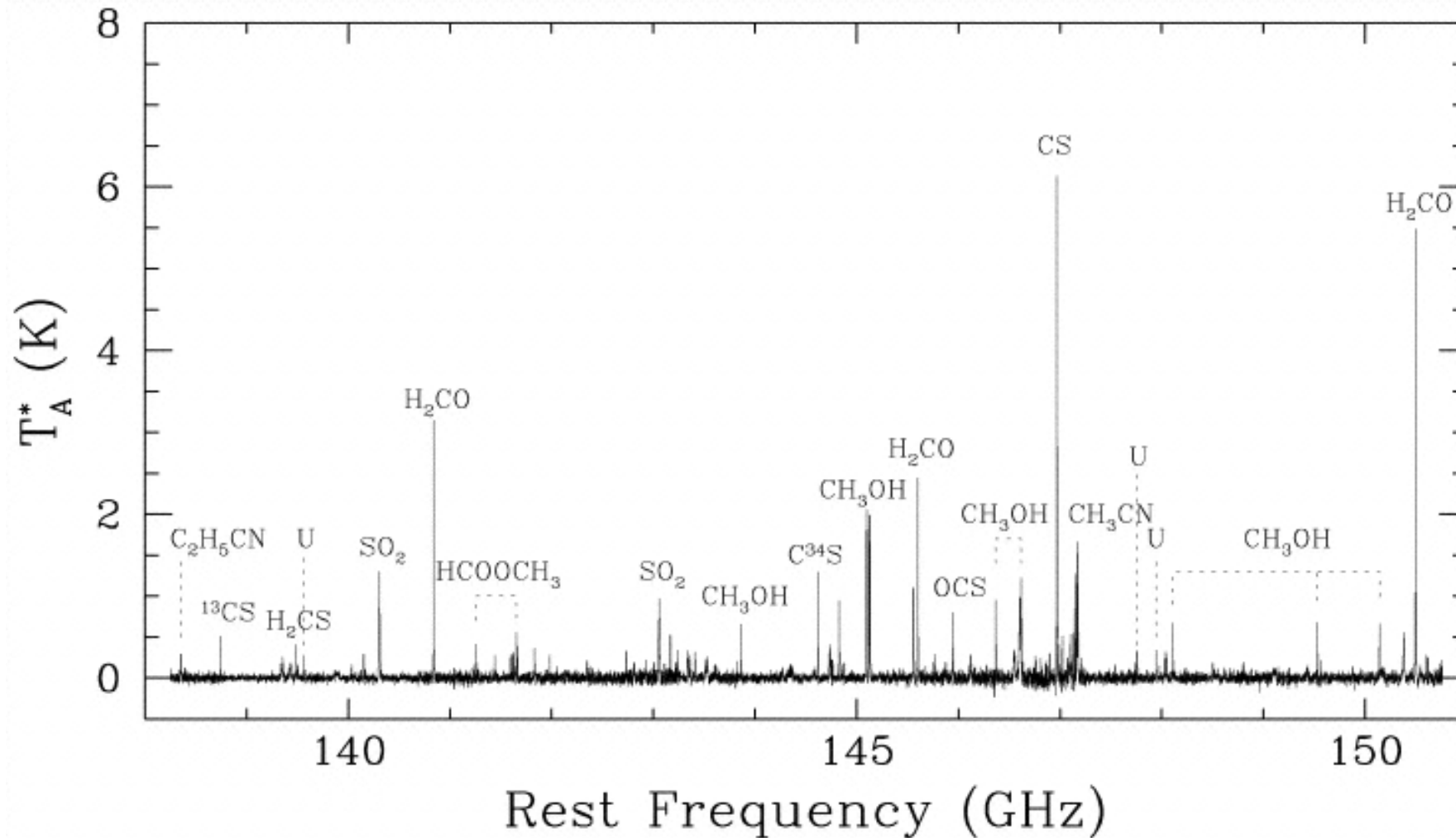
$J = 2 - 1$, 1.30 mm

$J = 3 - 2$, 0.87 mm

$J = 1 - 0$, 2.67 mm for $^{12}\text{C}^{17}\text{O}$
2.72 mm for $^{13}\text{C}^{16}\text{O}$

Figure 5.6 Rotational levels of $^{12}\text{C}^{16}\text{O}$ within the ground ($v = 0$) vibrational state. The astrophysically important $J = 1 \rightarrow 0$ transition at 2.60 mm is shown.

Rotational spectra of molecules toward Orion KL, including “U”nidentified lines



Tennyson
Lee+01

- H atoms, $g_n = 2n^2$ (i.e, for the n-th electronic energy state, there are n^2 orbital angular momentum states; 2 electron spin states)

Two hyperfine energy states, $g_U = 3$, $g_L = 1$

- For linear molecules (e.g., CO) rotation, $g = 2J + 1$, J is the angular momentum quantum number.

Molecules in stars

Stellar matter largely gas or plasma; molecules form primarily below 6000 K, but only OB stars do not contain molecules.

Absorption band spectra, e.g., due to MgH, CaH, FeH, CrH, NaH, OH, SiH, VO, and TiO. Others include CN, CH, MgF, NH, C₂, SrF, zirconium monoxide, YO, ScO, BF, etc.

NH₃ and collision-induced absorption by H₂ in brown dwarfs

CO band heads in the Becklin-Neugebauer (BN) object --- an infrared-emitting, embedded, massive protostar

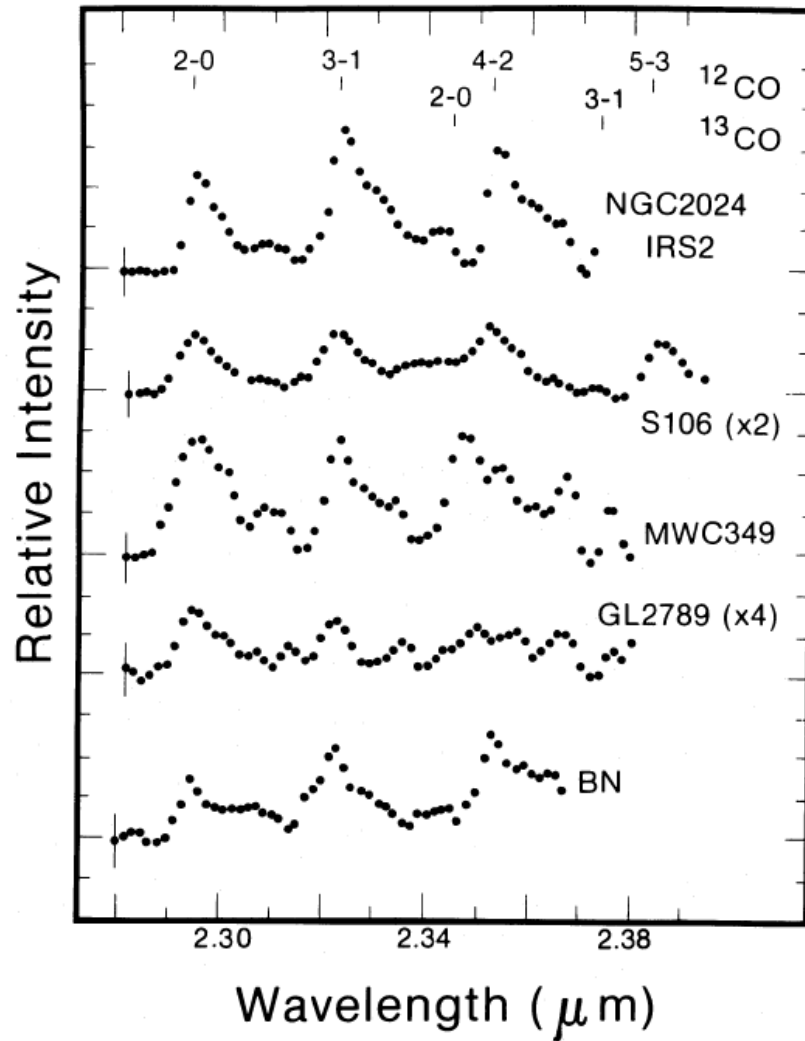


FIG. 2.—Spectra of those sources in which CO band head emission was detected. Linear baselines have been subtracted from each spectrum. The positions of the band heads are indicated at the top of the figure. Vertical scale marks are separated by $2 \times 10^{-17} \text{ W cm}^{-2} \mu\text{m}^{-1}$. Noise levels are indicated on the short wavelength data points.

Gaballe & Persson (1987)

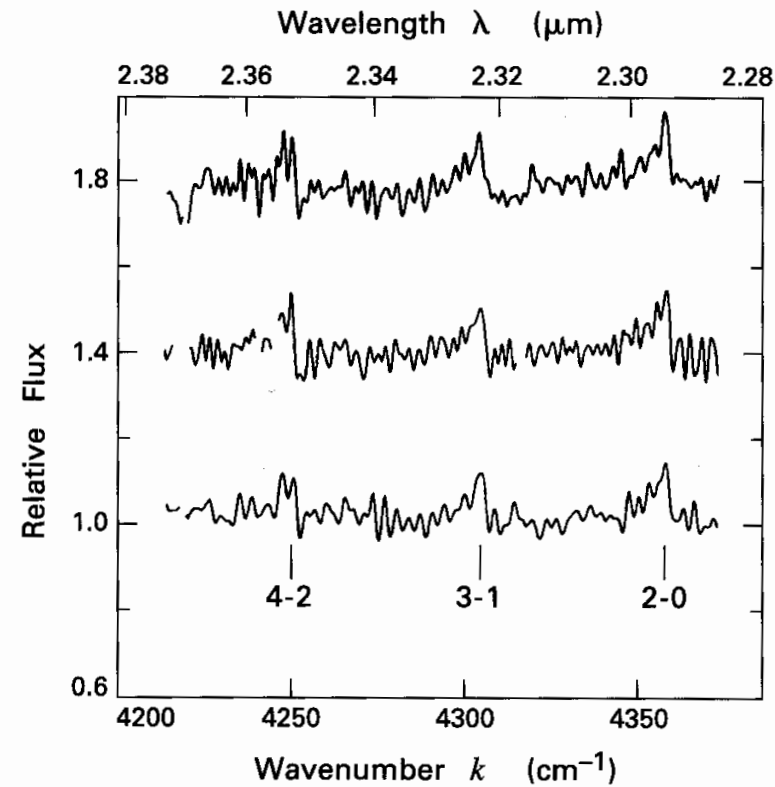
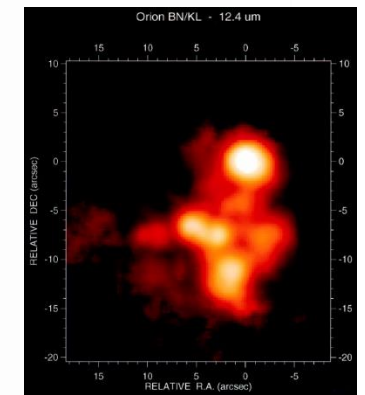
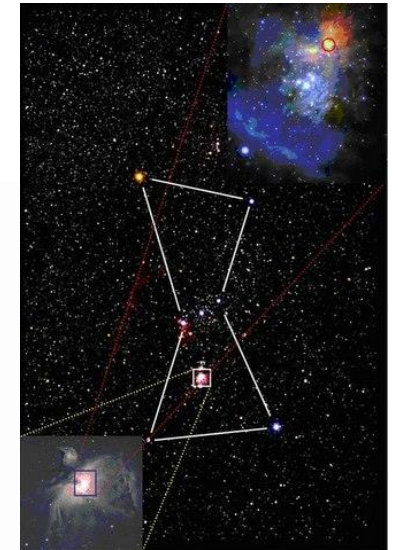


Figure 5.8 Near-infrared spectrum of the BN object in Orion, shown at three different observing times. The relative flux is plotted against the wave number k , defined here as $1/\lambda$.



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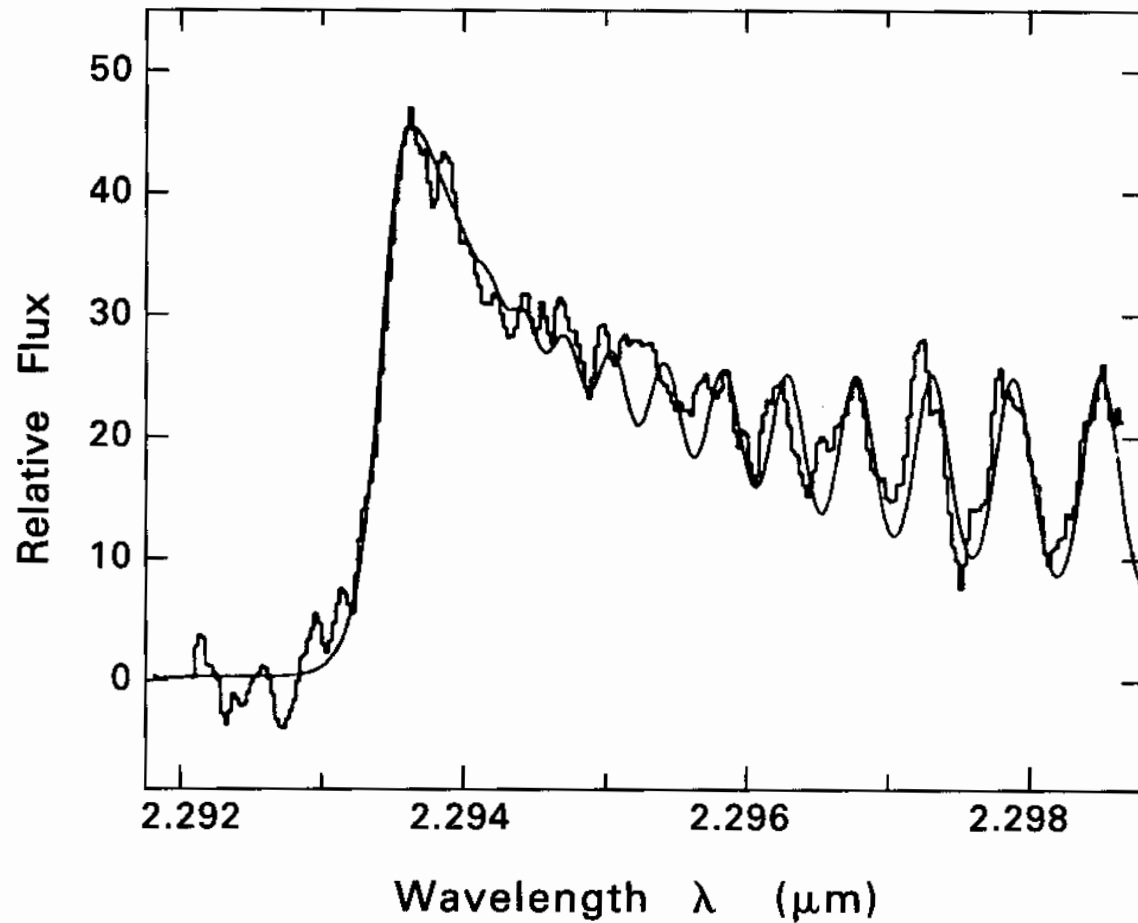
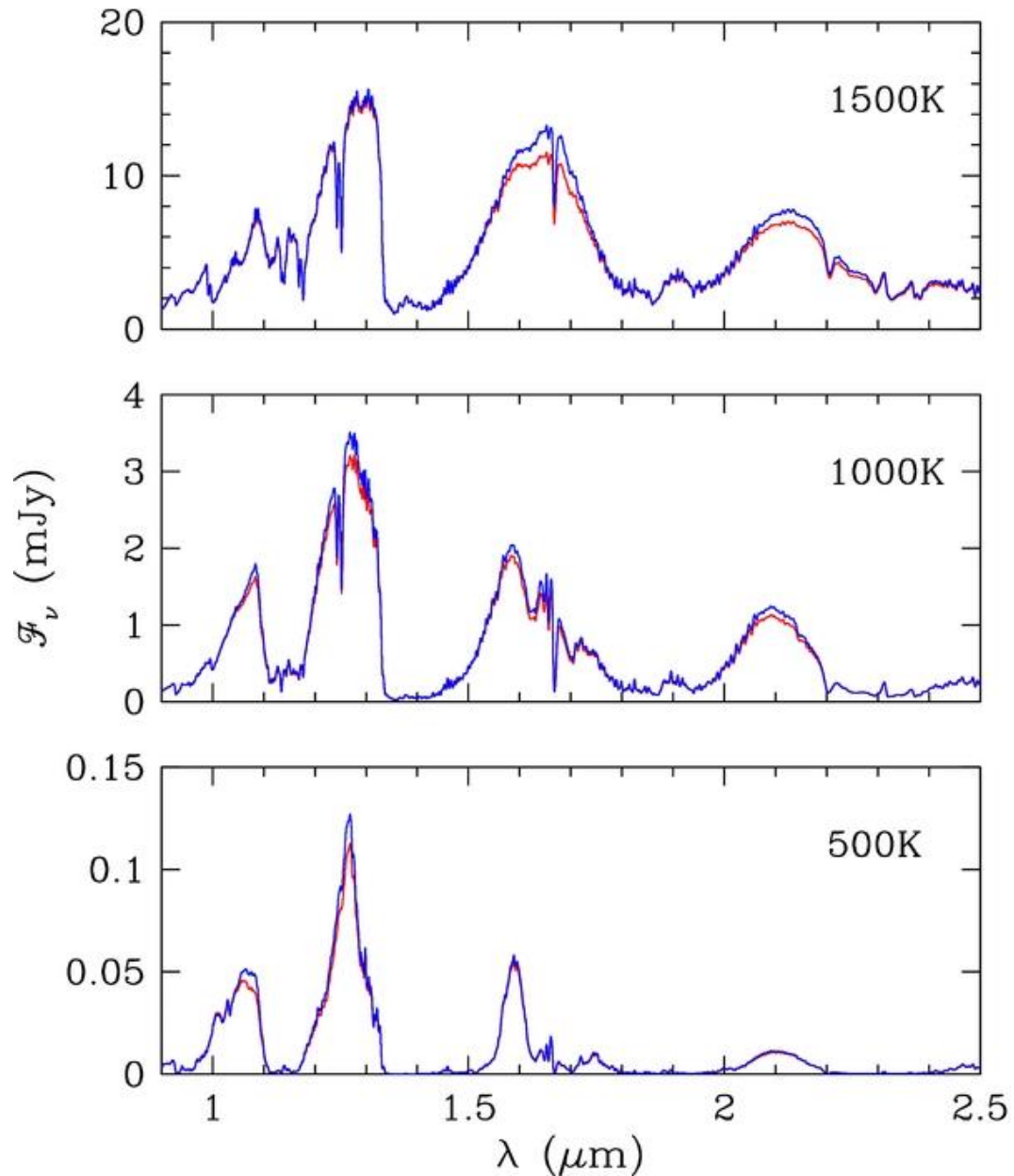


Figure 5.9 High-resolution near-infrared spectrum of the embedded stellar source SSV 13. The structure of the $v = 2 \rightarrow 0$ band head in $^{12}\text{C}^{16}\text{O}$ is evident. The smooth curve is from a theoretical model that employs an isothermal slab at 3500 K. Note that the spectrum here represents only a portion of the R -branch.



Effect of the new $\text{H}_2\text{-H}_2$ and $\text{H}_2\text{-He}$ CIA opacity on synthetic spectra of brown dwarfs. The spectra shown are *cloudless* models with $T_{\text{eff}} = 1500, 1000, \text{ and } 500 \text{ K}$, with $\log g = 5$ (cgs) and solar metallicity. The spectra computed with the new CIA opacities are shown in blue. The red lines show spectra computed with the older CIA opacity and the same (T, P) structures. The fluxes are calculated for $d = 10 \text{ pc}$ and are displayed at a resolving power of $R = 500$.