Hydrogen

As an example of absorption and emission by atoms/molecules

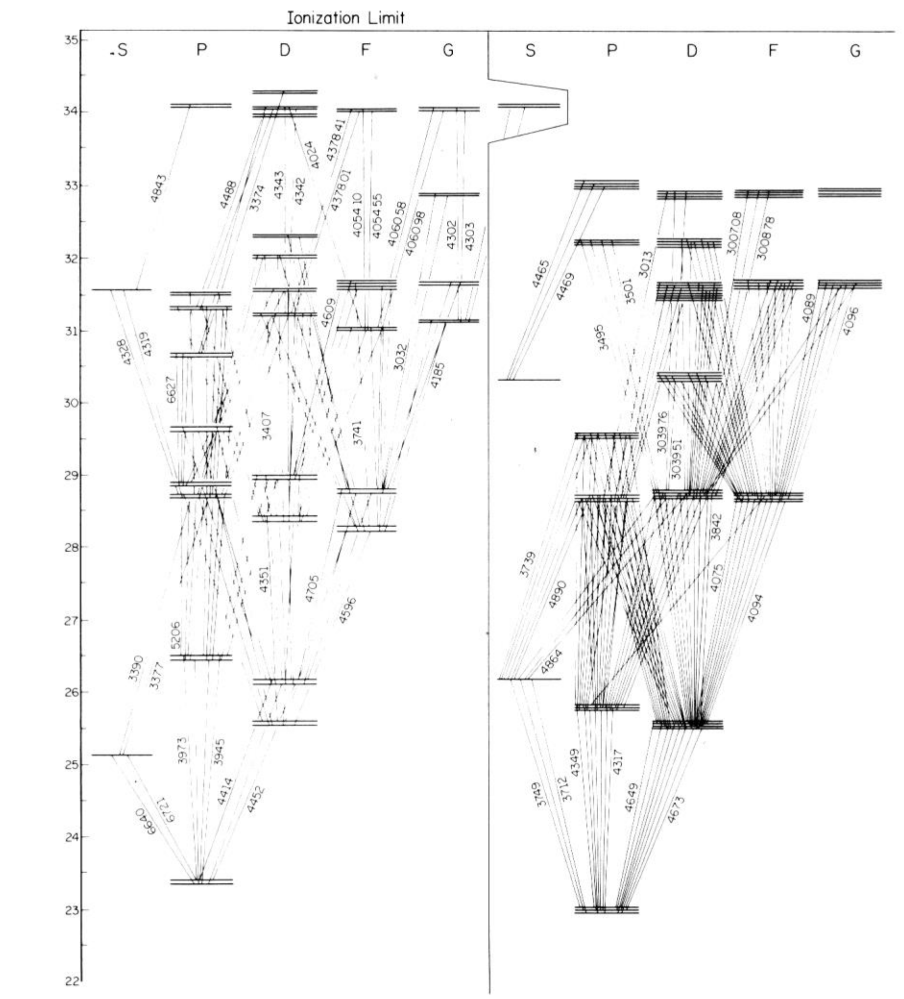


Figure 2.4. Energy levels of the O^+ ion, with the transitions of the optical O II spectrum. The levels for this ion are arranged in groups of one to four called *terms* from which arise *multiplets* of lines that are spread out in wavelength to varying degrees. See the text for a fuller explanation. A chart such as this one is often called a *term* or *Grotrian* diagram. The complexity of the electronic orbital structures of the heavier atoms is awesome. Here we present only the upper part of the diagram that produces the optical transitions. On this scale the ground state is about 40 centimeters off the bottom of the page. Below, we find levels that involve high energy ultraviolet transitions. Most of these terms involve the excitation of the outer (valence) electron only. The horizontal line at the top represents the ionization energy, above which the excited electron is lost to the atom, resulting in O^{+2}. If two electrons can be excited at the same time we can get energy levels above the ionization limit, adding to the complexity of the diagram. Diagram by the author, from *A Mupltiplet Table of Astrophysical Interest* by C. E. Moore, US Govt. Printing Office, 1945.

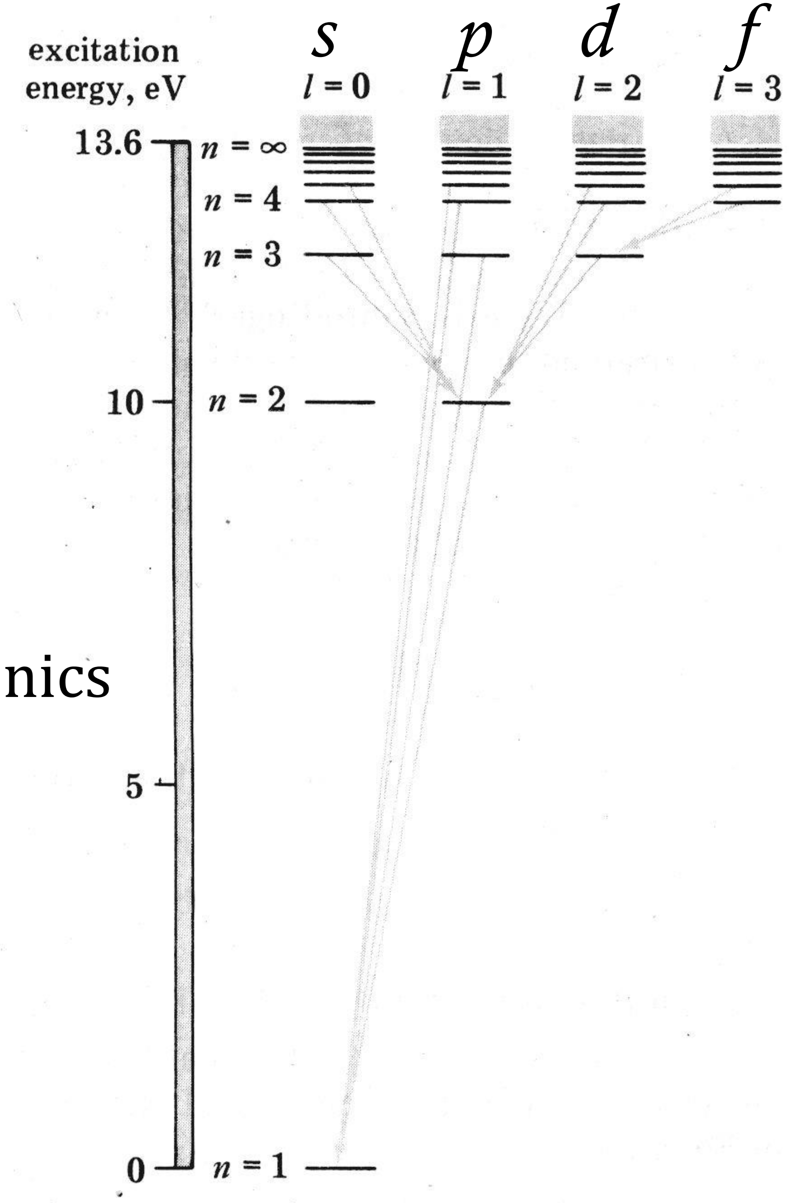
Complexity of the energy level diagram

Here is the example of O II transitions

Kaler

TABLE 6.2 THE SYMBOLIC DESIGNATION OF ATOMIC STATES IN HYDROGEN

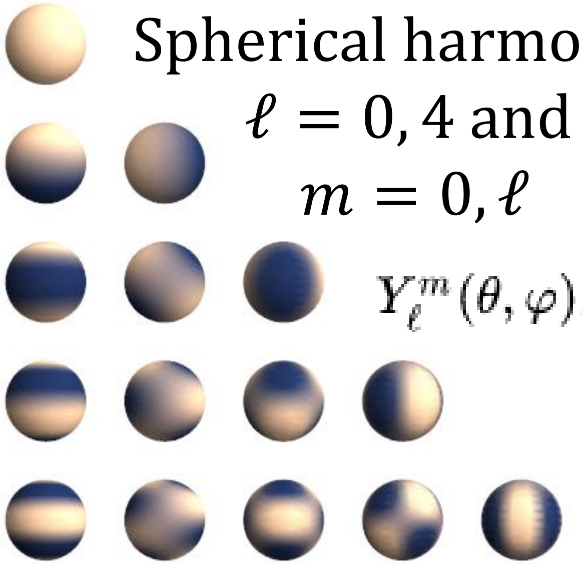
	$l=0$	$l=1$	$l=2$	$l=3$	$l=4$	$l=5$
$n=1$	1s					
$n=2$	2s	2p				
$n=3$	3s	3p	3d			
$n=4$	4s	4p	4d	4f		
$n=5$	5s	5p	5d	5f	5g	
$n=6$	6s	6p	6d	6f	6g	6h



Selection Rules

For an allowed transition

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



Spherical harmonics $\ell = 0, 4$ and $m = 0, \ell$

https://en.wikipedia.org/wiki/Spherical_harmonics

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 $\mathcal{L} = S, P, D, F, \ldots,$ for orbital momentum $\mathcal{L} = 0, 1, 2, 3 \ldots$ and p ="blank" (for even parity; whether the wave function changes sign thgough 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, $n_{\mathrm{lower}} = 1$ (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 Hα, H(3p) → H(2s), λ656.28 nm

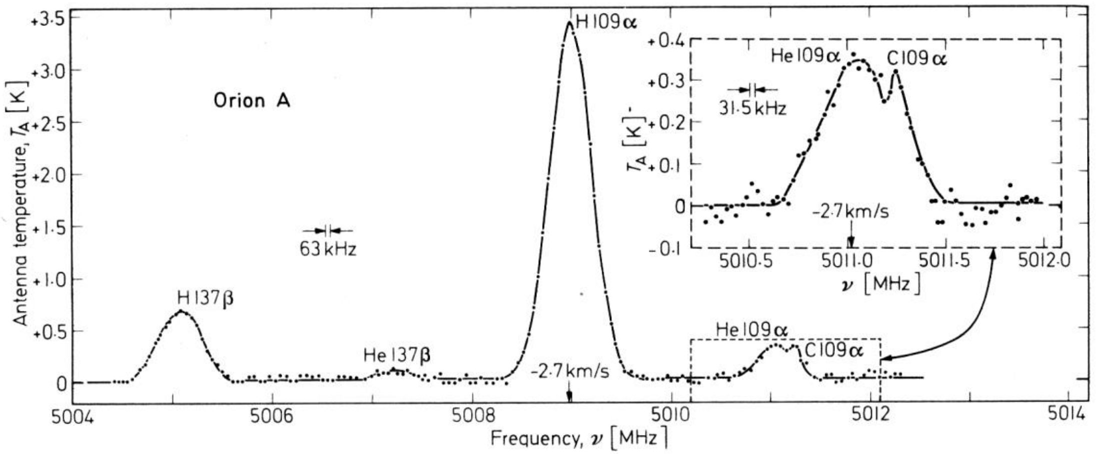


Fig. 12. Broadband spectrogram of the 109α region of the spectrum of the Orion Nebula. The frequency resolution is 63 kHz for the broadband spectrogram and 31.5 kHz for the narrow band spectrum centered on the He 109α line. (After CHURCHWELL and MEZGER, 1970, by permission of Gordon & Breach Science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

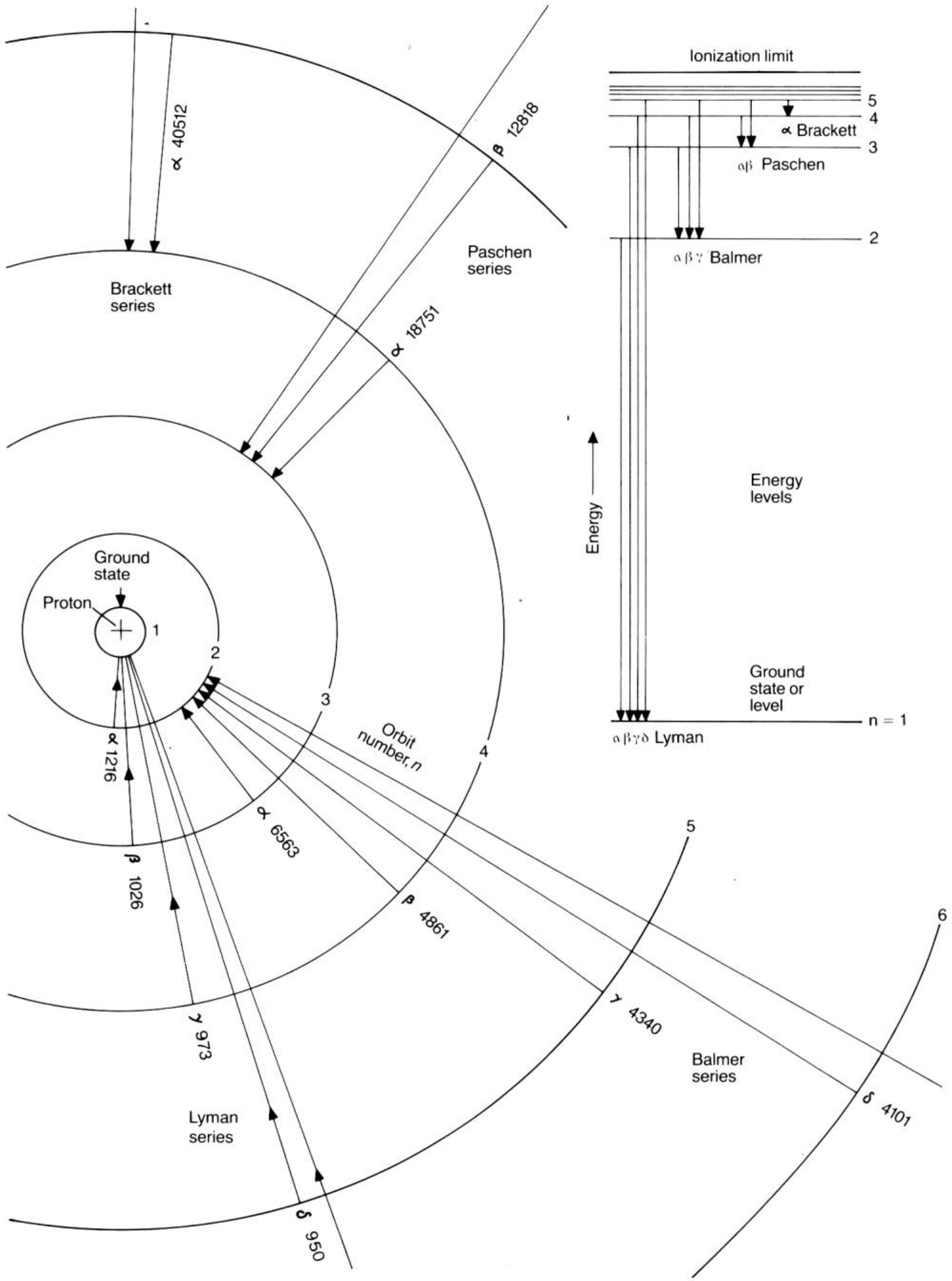
H109α

Table 11. The wavelengths in Å of the $m \to n$ 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 (He II)[1]. Here the wavelengths are in Å where 1 Å $=10^{-8}$ 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

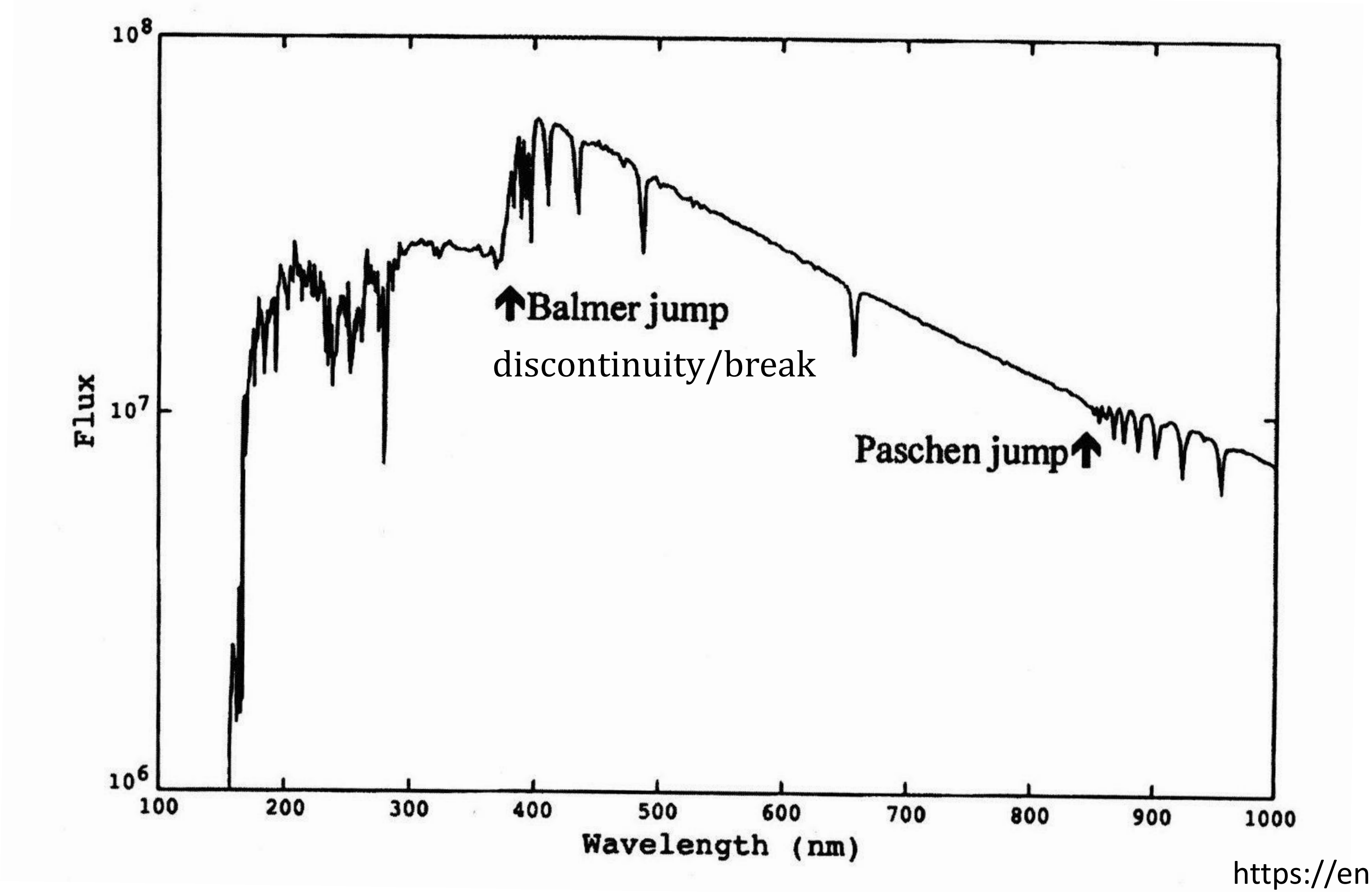
Continuum/limit

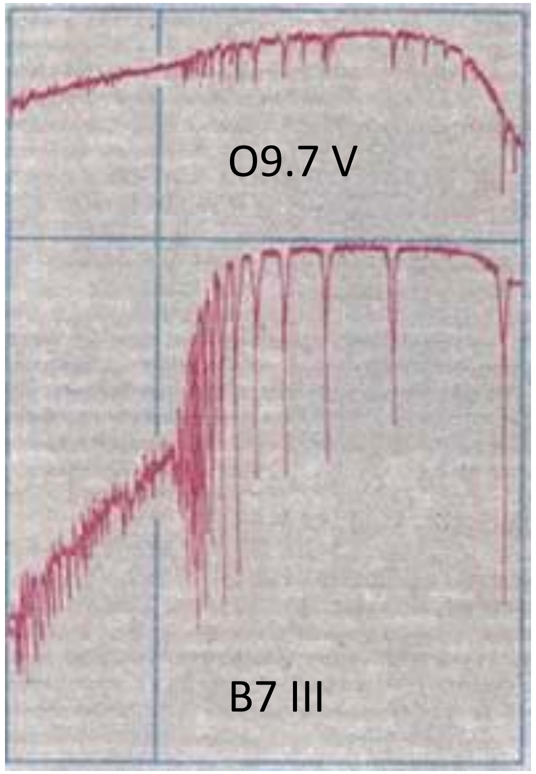
[1] Data from WIESE, SMITH, and GLENNON (1966).



α 40512
β 12818
Paschen series
Brackett series
α 18751
Ground state
Proton
1
2
3
4
5
6
Orbit number, n
α 1216
β 1026
α 6563
β 4861
γ 973
γ 4340
Balmer series
δ 4101
Lyman series
δ 950
Ionization limit
5
4
α Brackett
3
αβ Paschen
2
αβγ Balmer
Energy
Energy levels
Ground state or level
n = 1
αβγδ Lyman

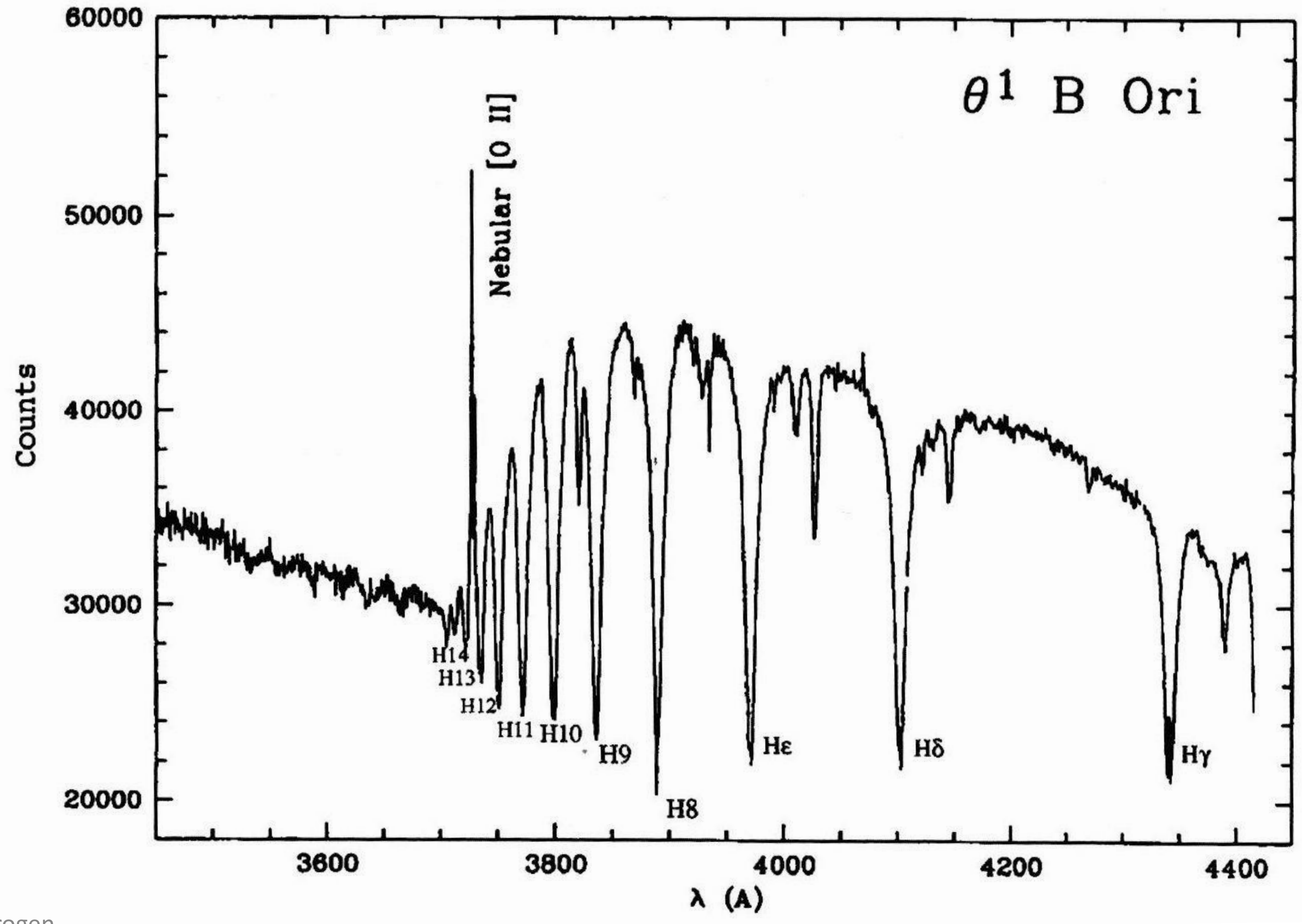
Model spectrum of an A5 star





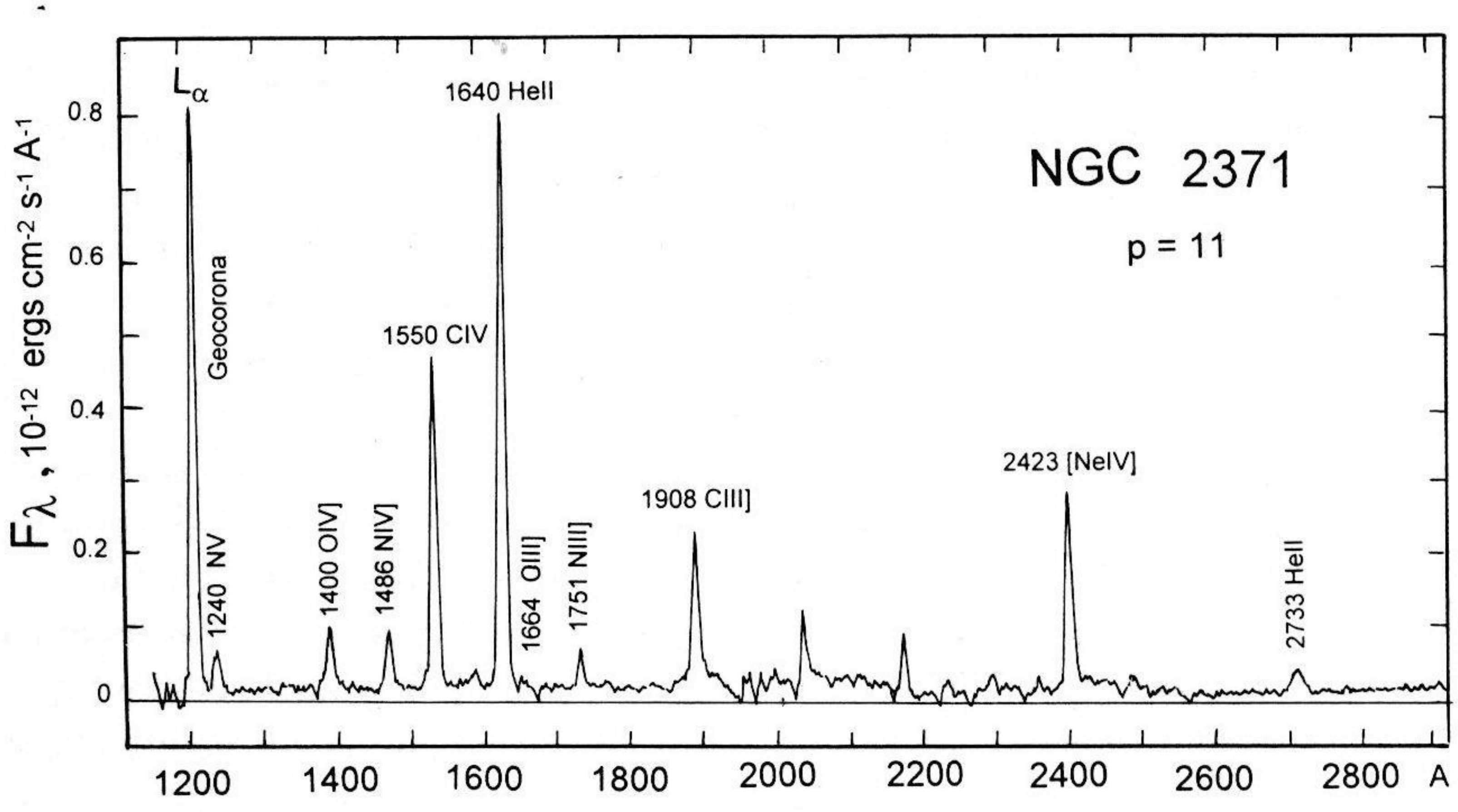
https://en.wikipedia.org/wiki/Balmer_jump

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

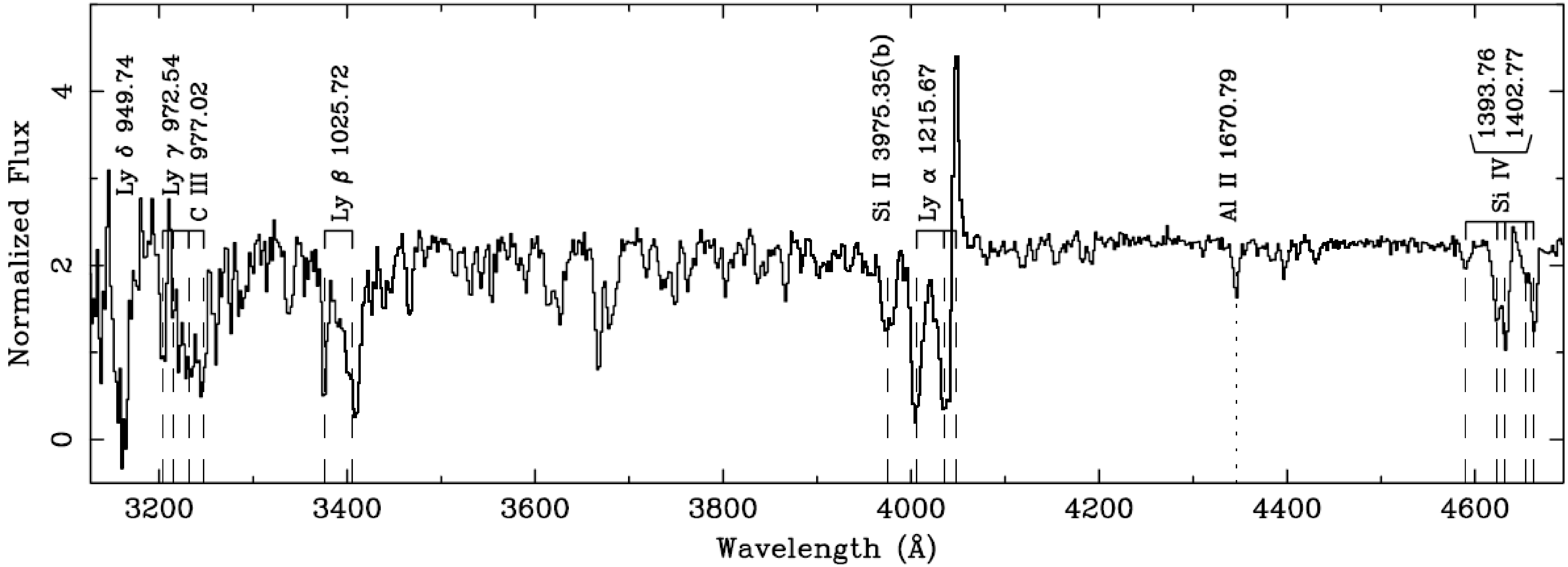


Tennyson

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



Tennyson
Mirabal+03

Brackett-alpha of the protostar Orion-BN object

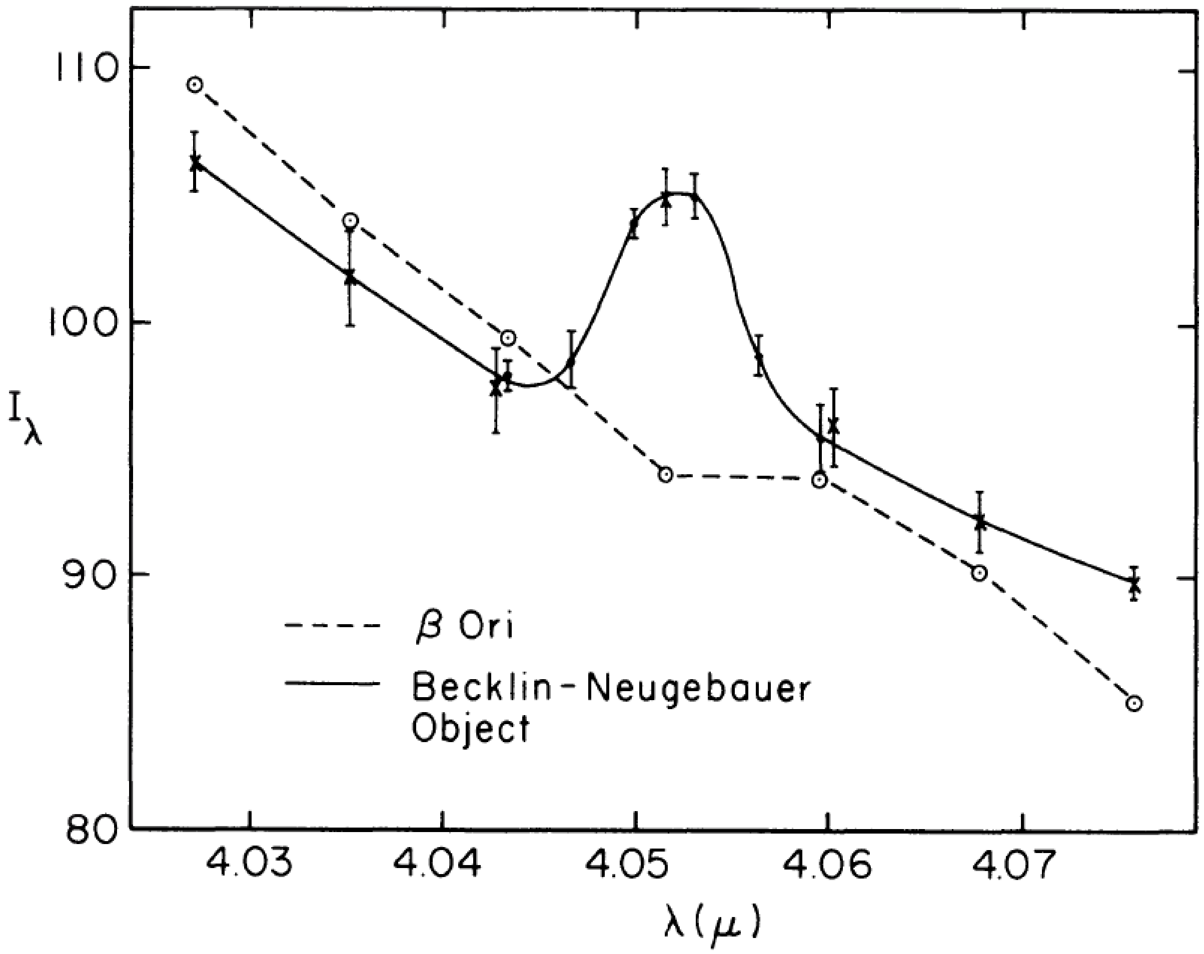


FIG. 1.—Spectra of the BN object and β Ori. The two independent sets of data for the BN object are indicated by dots and X's.

Grasdalen 1976

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

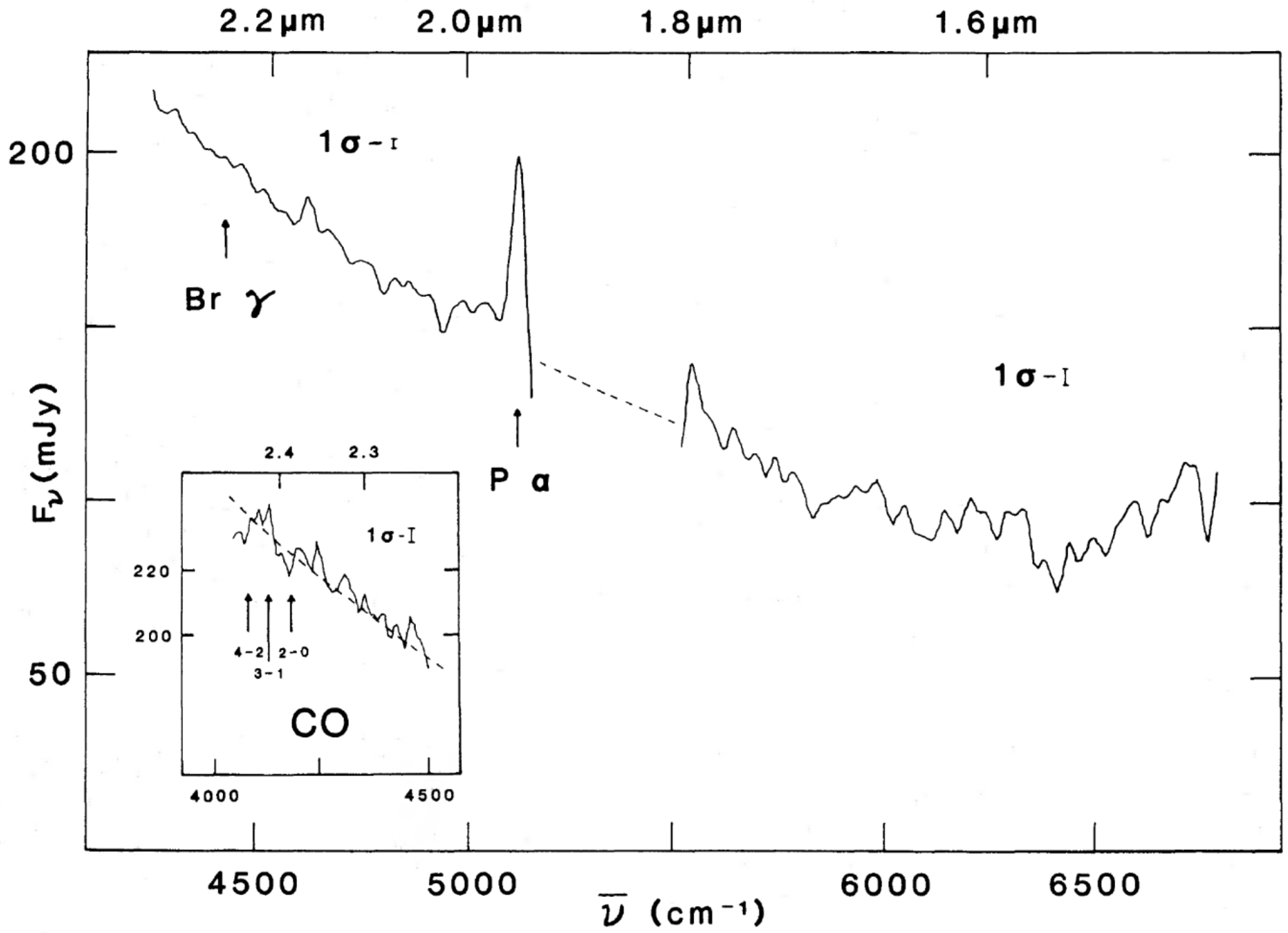


FIG. 1.—The near-infrared spectrum of Mrk 231. These data have been smoothed to a resolution of 54 cm^{-1}. The dashed line represents the portion of the spectrum in which atmospheric transmission drops below 50% and has therefore been omitted. The weak emission feature at 4620 cm^{-1} is the result of insufficient correction for the Brγ absorption line in the A type calibration star GC 18704. (*inset*) The 4000–4400 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.

Cutri+84

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

For H91α, i.e., $n = 92 \rightarrow 91$

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

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

This is called a "radio recombination line".

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

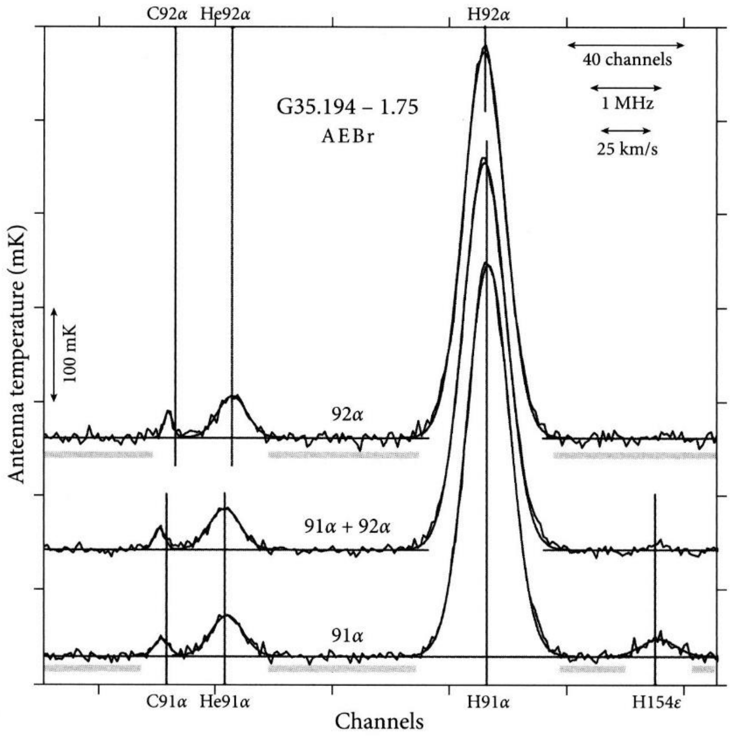


Figure 7.2. Observed recombination-line spectra from the 91α and 92α transitions of hydrogen, helium, and carbon observed in an HII region [84].

Considering reduced mass,

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

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

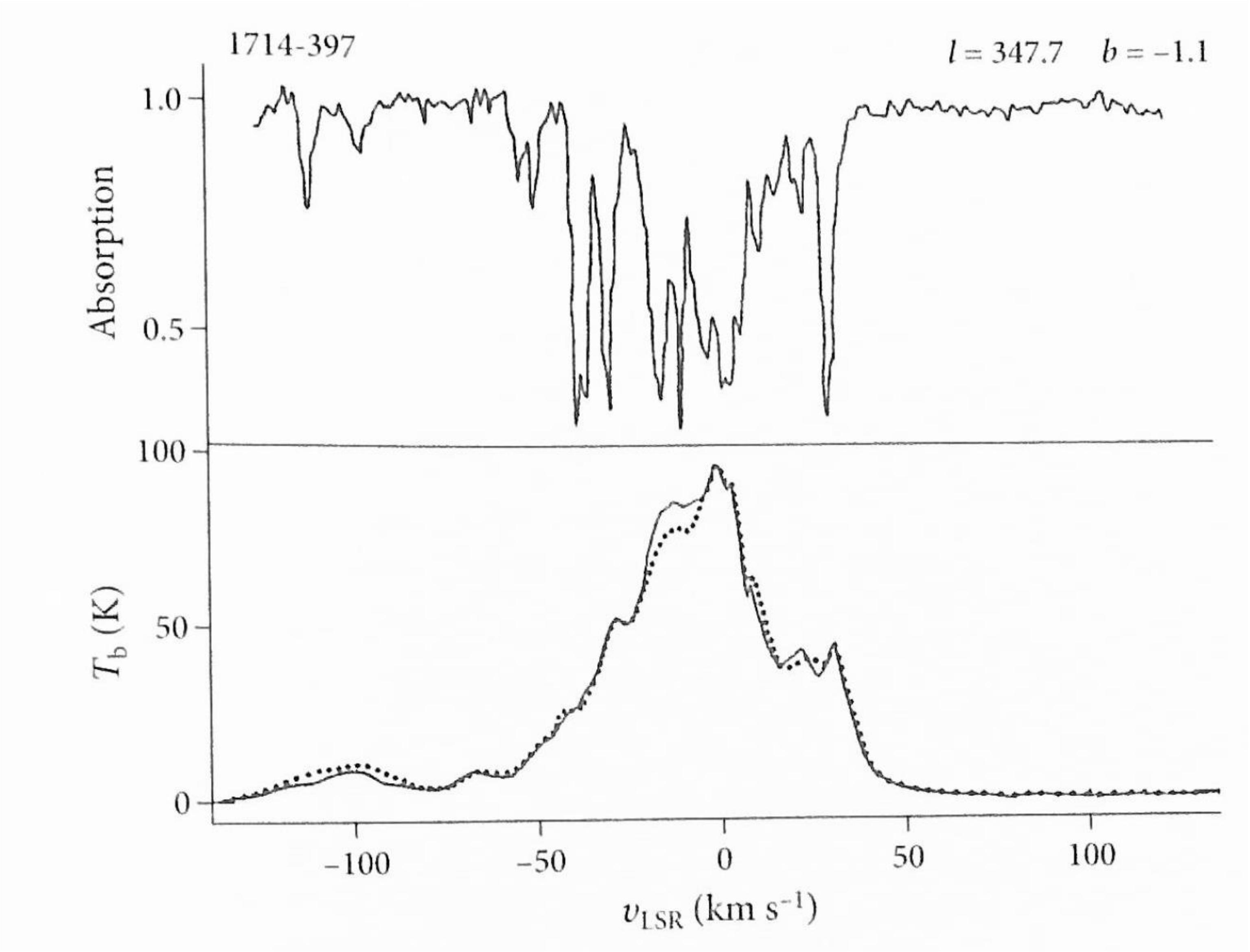
$$F = 0 \text{ (spin opposite) or } F = 1 \text{ (spin parallel)}$$

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

Including the nucleus,

$\boldsymbol{J} =$ **[electronic angular momentum]**$/\hbar$
$\boldsymbol{I} =$ **[nuclear angular momentum]**$/\hbar$
$\boldsymbol{F} =$ **[total angular momentum]**$/\hbar$

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



Condon & Ransom
Fig 7.17

H I absorption

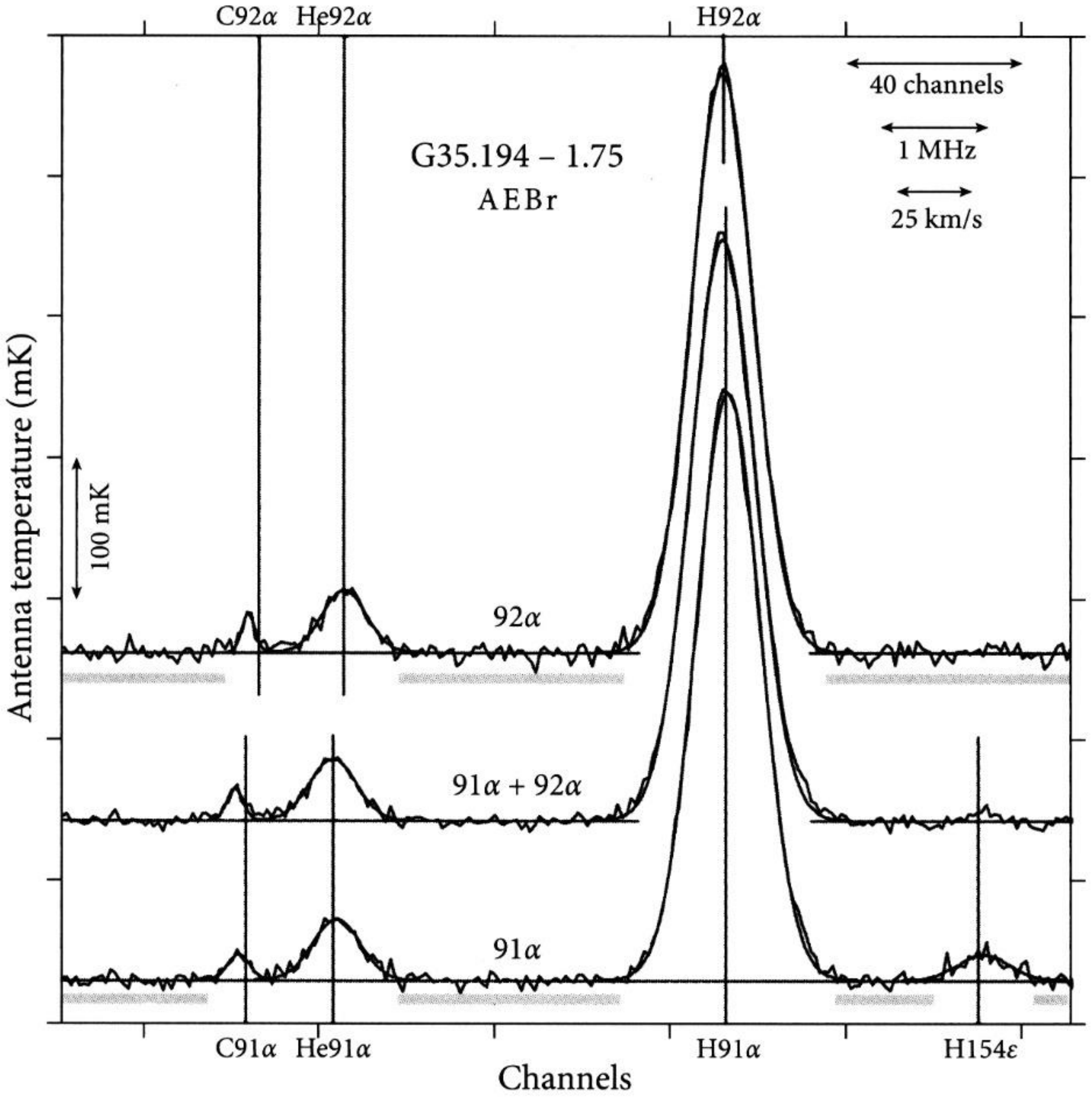
- For $n = 2, \ell = 1$, and with spin, a total angular momentum of $\ell(\ell+1)\hbar^2 = 2\hbar^2$
  3 substates, $\hbar, 0, -\hbar$, $m = 1, 0, -1$ (magnetic quantum number)

  Fine structure, $\Delta\mathcal{E}$ very small, $\sim 10^{-5}$ eV

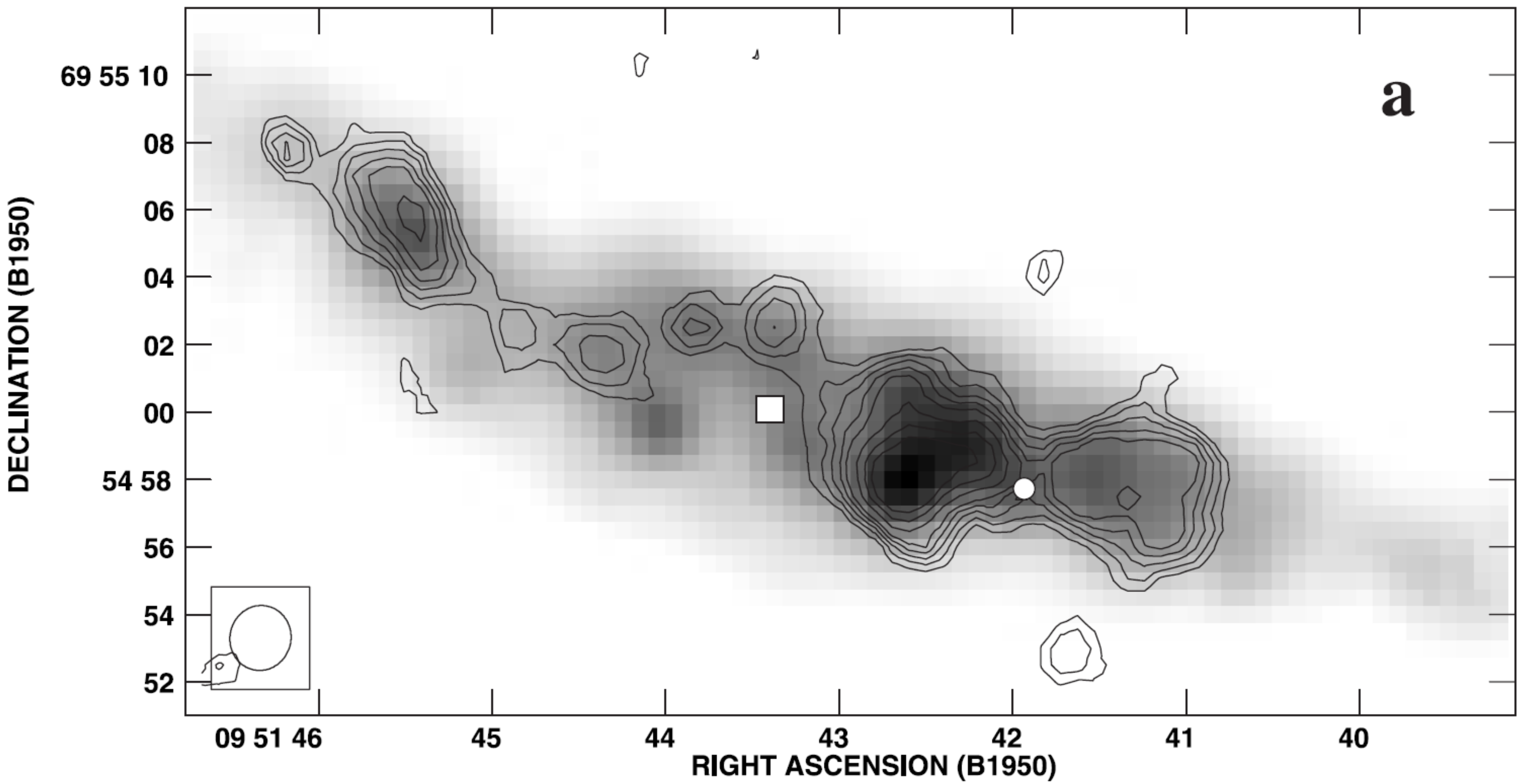
  But with an external **B** field → **Zeeman splitting**

With a field of 10 μG, 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)



C92α
He92α
H92α
40 channels
1 MHz
25 km/s
G35.194 – 1.75
AEBr
Antenna temperature (mK)
100 mK
92α
91α + 92α
91α
C91α
He91α
H91α
H154ε
Channels



VLA M82 imaged in H92α the recombination line (contours) and 8.3 GHz continuum (gray scale)

Rodrigeuz-Rico+04

H^- (negative H ion)

$$H + e^- \longrightarrow H^- + h\nu$$

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^-

$\mathcal{E}_{\text{binding}}(\text{H}^-) = 0.75$ 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

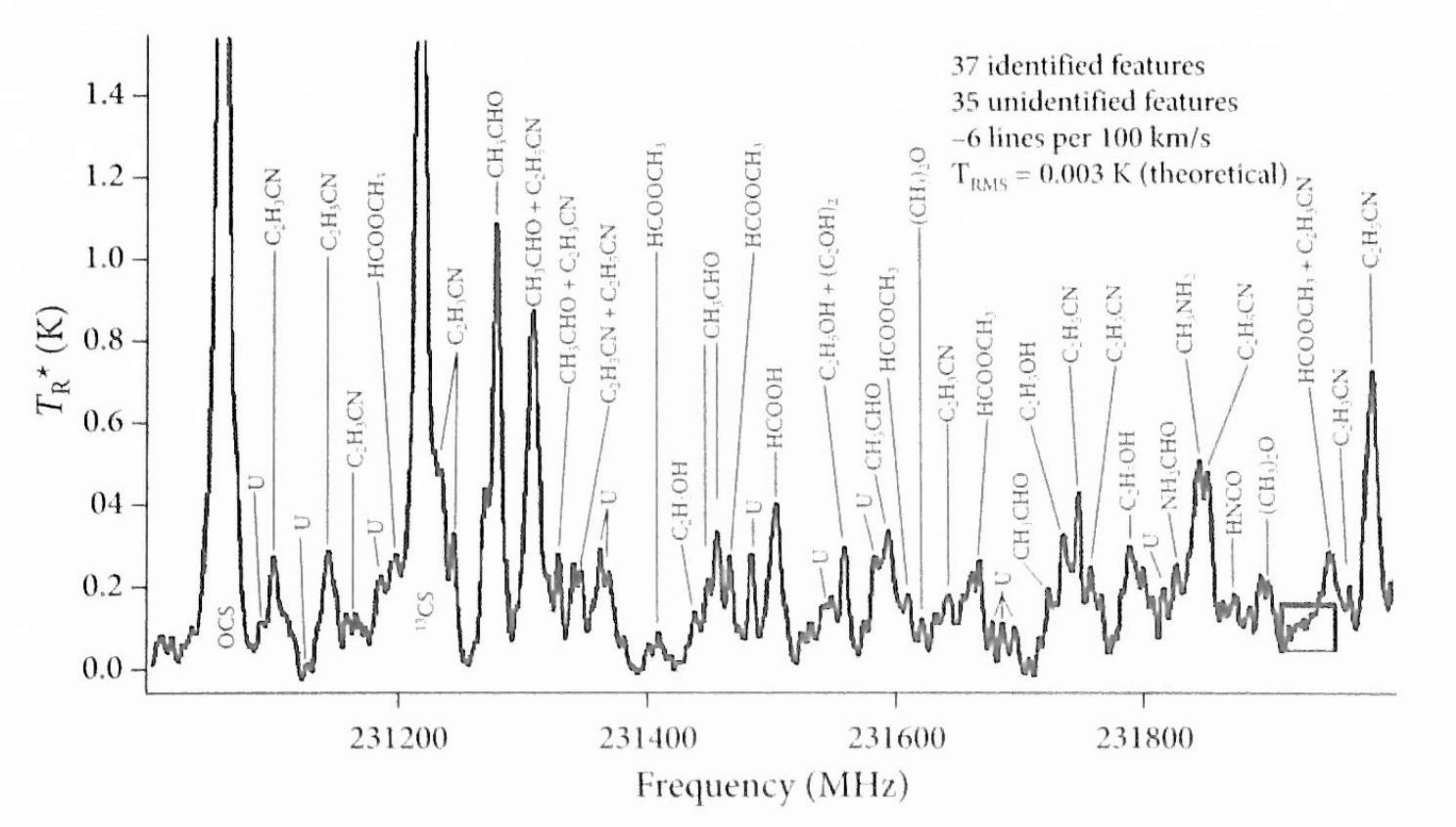
An atom has only electronic transitions.

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**.



1.3 mm spectrum of SgrB2(N) near the Galactic center by known and unknown species

Condon & Ransom
Fig 7.16

Example molecular transitions

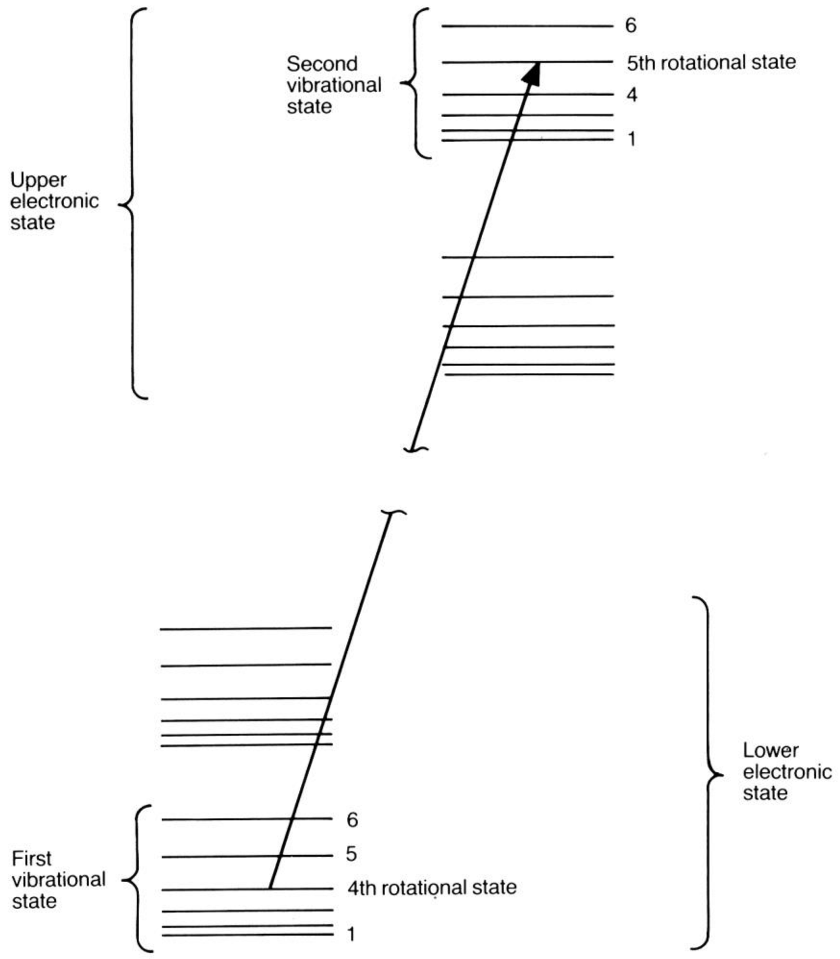


Figure 2.5. Molecular spectra. Two electronic states are shown. Each is divided into vibrational states, of which only the lowest two are drawn. Each of these is split again into rotational states, for which only the lowest six are illustrated. A single molecular absorption line is shown arising from 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.

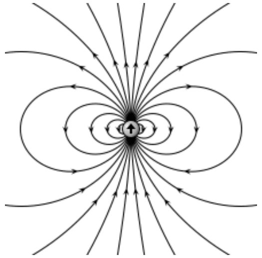
Kaler

H_2 (dihydrogen, molecular hydrogen)

- It is the 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**, cold H_2 is 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.

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

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

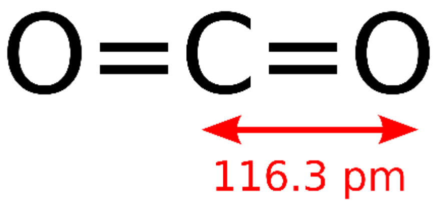


Zero electric dipole moment

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

H_2, a homonuclear molecule (i.e., consisting of only one type of atoms), has no dipole moment, so can only radiate in less probable transitions, e.g., quadrupole, 10^{-9} times weaker.
Ortho- spins of protons parallel; para- spins antiparallel

CO_2 has no pure rotation spectrum.



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

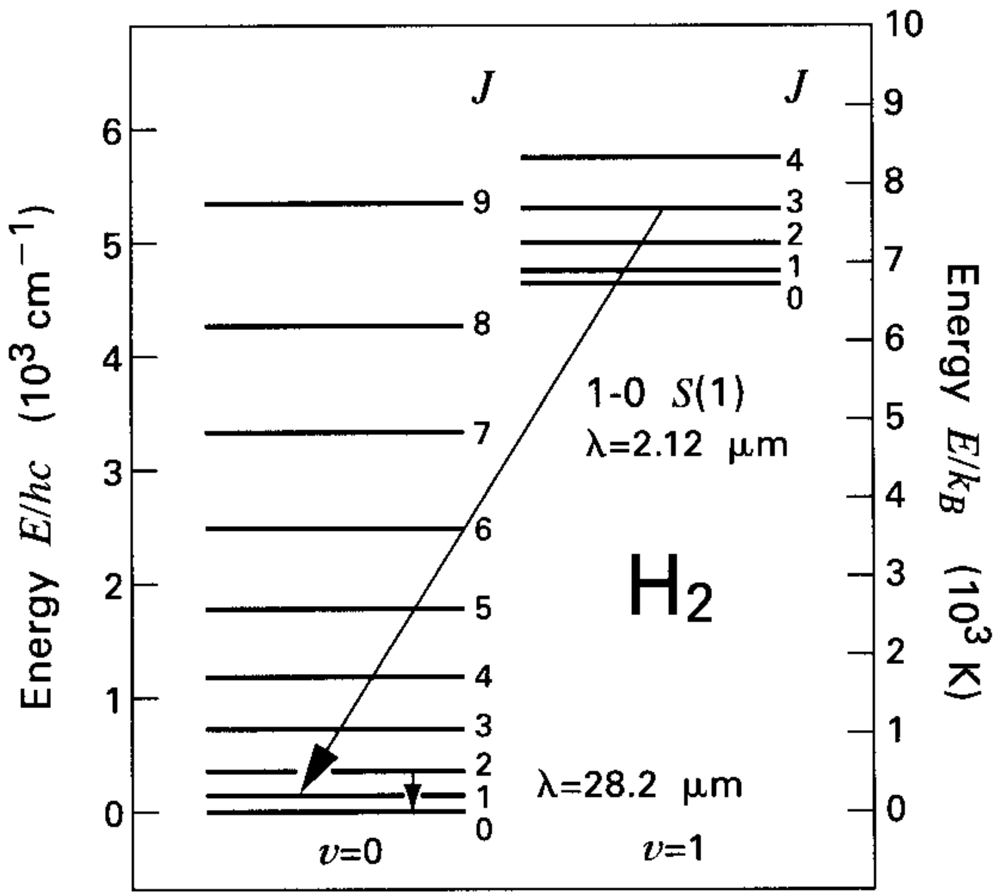


Figure 5.4 Rotational levels of H_2 for the first two vibrational states. Within the $v = 0$ state, the $J = 2 \rightarrow 0$ transition at 28.2 μm is displayed. Also shown is the transition giving the 1-0 S(1) rovibrational line at 2.12 μm. Note that two different energy scales are used.

Stahler & Palla

CO molecules

- Simple and most abundant next to H_2
- Strong $\mathcal{E}_{\text{dissociation}}$ =11.16 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.
- $^{12}C^{16}O$ easiest to detect; isotopes $^{13}C^{16}O$, $^{12}C^{18}O$, $^{12}C^{17}O$, $^{13}C^{18}O$ useful as diagnosing tools
- Low critical density for excitation → CO used to study large-scale distribution of clouds, as a tracer of H_2, $n(\text{CO}) \approx 10^{-4} n(\text{H}_2)$

$$n^*_{NH_3} \approx 10^3 \text{ cm}^{-3} \qquad n^*_{HCN} \approx 10^5 \text{ cm}^{-3} \text{ (for } J = 1 \rightarrow 0)$$

'Conversion factor', $N(H_2)/I_{CO} = 2 \times 10^{20}$ [K km s^{-1}]$^{-1}$

- $^{12}C^{16}O$ almost always **optically thick**.
  so brightness temperature ≈ 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
  $N_H = 10^6 \, N_{^{13}CO}$

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

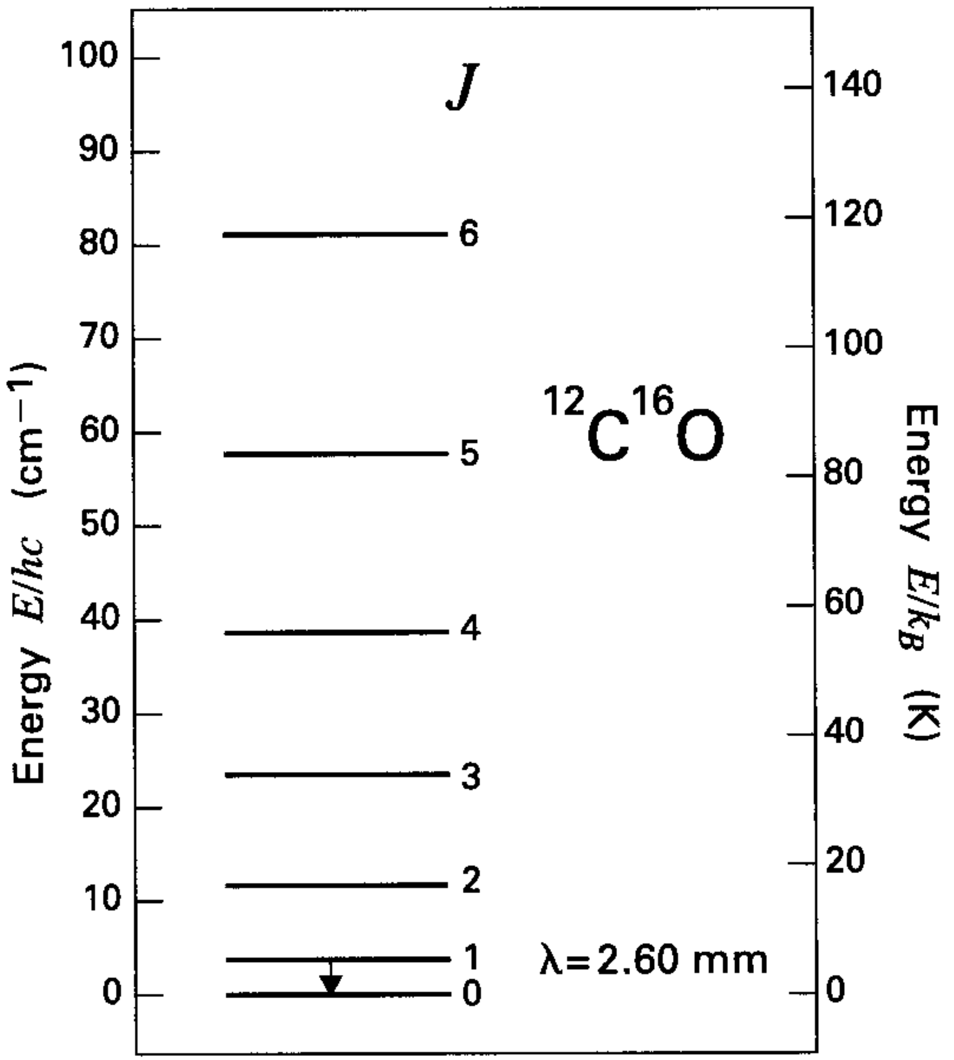


Figure 5.6 Rotational levels of $^{12}C^{16}O$ within the ground ($v = 0$) vibrational state. The astrophysically important $J = 1 \rightarrow 0$ transition at 2.60 mm is shown.

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

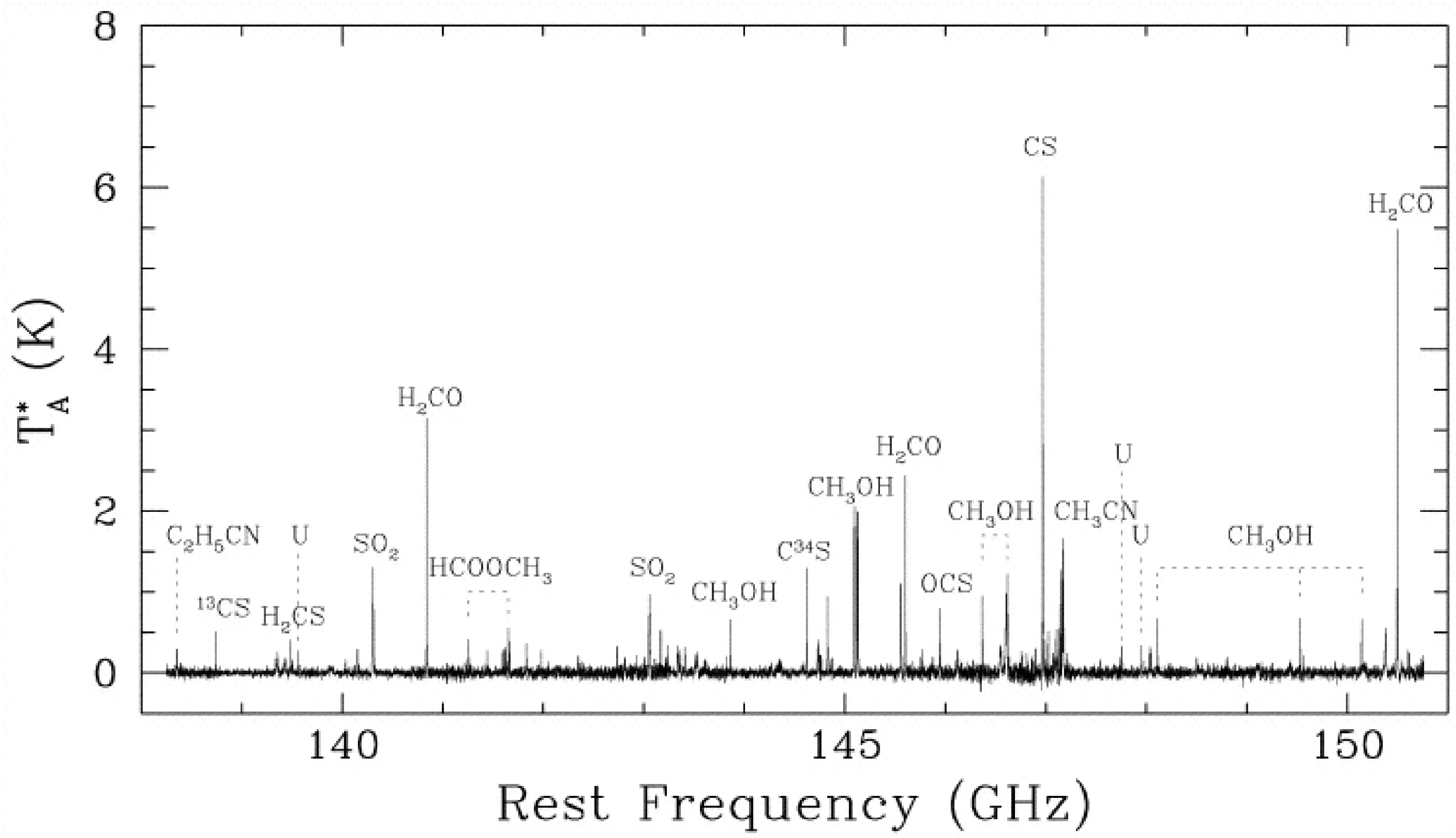
Only 5 K above the ground level … can be excited by collisions with ambient molecules or CMB photons

$J = 2 - 1$, 1.30 mm
$J = 3 - 2$, 0.87 mm

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

Stahler & Palla

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, $g_{\mathrm{U}} = 3$, $g_{\mathrm{L}} = 1$

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

Molecules in space

The Astrophysical Journal Supplement Series, 239:17 (48pp), 2018 December https://doi.org/10.3847/1538-4365/aae5d2

CrossMark

2018 Census of Interstellar, Circumstellar, Extragalactic, Protoplanetary Disk, and Exoplanetary Molecules

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Abstract

To date, 204 individual molecular species, comprised of 16 different elements, have been detected in the interstellar and circumstellar medium by astronomical observations. These molecules range in size from 2 atoms to 70, and have been detected across the electromagnetic spectrum from centimeter wavelengths to the ultraviolet. This census presents a summary of the first detection of each molecular species, including the observational facility, wavelength range, transitions, and enabling laboratory spectroscopic work, as well as listing tentative and disputed detections. Tables of molecules detected in interstellar ices, external galaxies, protoplanetary disks, and exoplanetary atmospheres are provided. A number of visual representations of these aggregate data are presented and briefly discussed in context.

Table 2

List of Detected Interstellar Molecules with Two to Seven Atoms, Categorized by Number of Atoms, and Vertically Ordered by Detection Year

2 Atoms		3 Atoms		4 Atoms	5 Atoms	6 Atoms	7 Atoms
CH	CP	H_2O	N_2O	NH_3	HC_3N	CH_3OH	CH_3CHO
CN	NH	HCO^+	MgCN	H_2CO	HCOOH	CH_3CN	CH_3CCH
CH^+	SiN	HCN	$H3^+$	HNCO	CH_2NH	NH_2CHO	CH_3NH_2
OH	SO^+	OCS	SiCN	H_2CS	NH_2CN	CH_3SH	CH_2CHCN
CO	CO^+	HNC	AlNC	C_2H_2	H_2CCO	C_2H_4	HC_5N
H_2	HF	H_2S	SiNC	C_3N	C_4H	C_5H	C_6H
SiO	N_2	N_2H^+	HCP	HNCS	SiH_4	CH_3NC	c-C_2H_4O
CS	CF^+	C_2H	CCP	$HOCO^+$	c-C_3H_2	HC_2CHO	CH_2CHOH
SO	PO	SO_2	AlOH	C_3O	CH_2CN	H_2C_6	C_6H^-
SiS	O_2	HCO	H_2O^+	l-C_3H	C_5	C_5S	CH_3NCO
NS	AlO	HNO	H_2Cl^+	$HCNH^+$	SiC_4	HC_3NH^+	HC_5O
C_2	CN^-	HCS^+	KCN	H_3O^+	H_2CCC	C_5N	
NO	OH^+	HOC^+	FeCN	C_3S	CH_4	HC_4H	
HCl	SH^+	SiC_2	HO_2	c-C_3H	HCCNC	HC_4N	
NaCl	HCl^+	C_2S	TiO_2	HC_2N	HNCCC	c-H_2C_3O	
AlCl	SH	C_3	CCN	H_2CN	H_2COH^+	CH_2CNH	
KCl	TiO	CO_2	SiCSi	SiC_3	C_4H^-	C_5N^-	
AlF	ArH^+	CH_2	S_2H	CH_3	CNCHO	HNCHCN	
PN	NS^+	C_2O	HCS	C_3N^-	HNCNH	SiH_3CN	
SiC		MgNC	HSC	PH_3	CH_3O		
		NH_2	NCO	HCNO	NH_3D^+		
		NaCN		HOCN	H_2NCO^+		
				HSCN	$NCCNH^+$		
				HOOH	CH_3Cl		
				l-C_3H^+			
				HMgNC			
				HCCO			
				CNCN			

McGuire (2018)

Table 3

List of Detected Interstellar Molecules with Eight or More Atoms, Categorized by Number of Atoms, and Vertically Ordered by Detection Year

8 Atoms	9 Atoms	10 Atoms	11 Atoms	12 Atoms	13 Atoms	Fullerenes
$HCOOCH_3$	CH_3OCH_3	$(CH_3)_2CO$	HC_9N	C_6H_6	c-C_6H_5CN	C_{60}
CH_3C_3N	CH_3CH_2OH	$HO(CH_2)_2OH$	CH_3C_6H	n-C_3H_7CN		C_{60}^+
C_7H	CH_3CH_2CN	CH_2CH_2CHO	CH_3CH_2OCHO	i-C_3H_7CN		C_{70}
CH_3COOH	HC_7N	CH_3C_5N	CH_3COOCH_3			
H_2C_6	CH_3C_4H	CH_3CHCH_2O				
CH_2OHCHO	C_8H	CH_3OCH_2OH				
HC_6H	CH_3CONH_2					
CH_2CHCHO	C_8H^-					
CH_2CCHCN	CH_2CHCH_3					
NH_2CH_2CN	CH_3CH_2SH					
CH_3CHNH	HC_7O					
CH_3SiH_3						

McGuire (2018)

https://scitechdaily.com/key-discovery-in-search-for-origin-of-life-astronomers-detect-largest-molecule-yet-in-a-cosmic-dust-trap/?fbclid=IwAR0eiaJTbzOxmxlLAyykanGgAtsyZ1NLtqUwDQMfnLgCr4ufYa-Ur7X9IY0

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

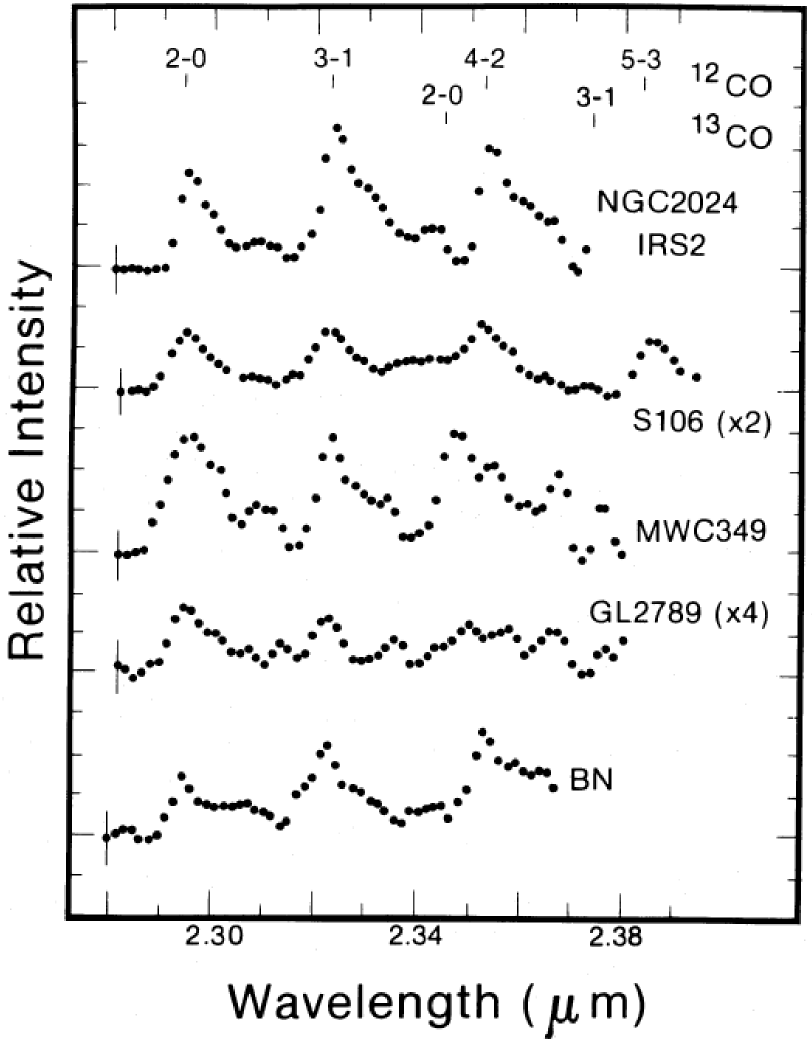


FIG. 2.—Spectra of those sources in which CO band head emission was detected. Linear baselines have been subtracted from each spectrum. The positions of the band heads are indicated at the top of the figure. Vertical scale marks are separated by 2×10^{-17} W cm^{-2} μm^{-1}. Noise levels are indicated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

Gaballe & Persson (1987)

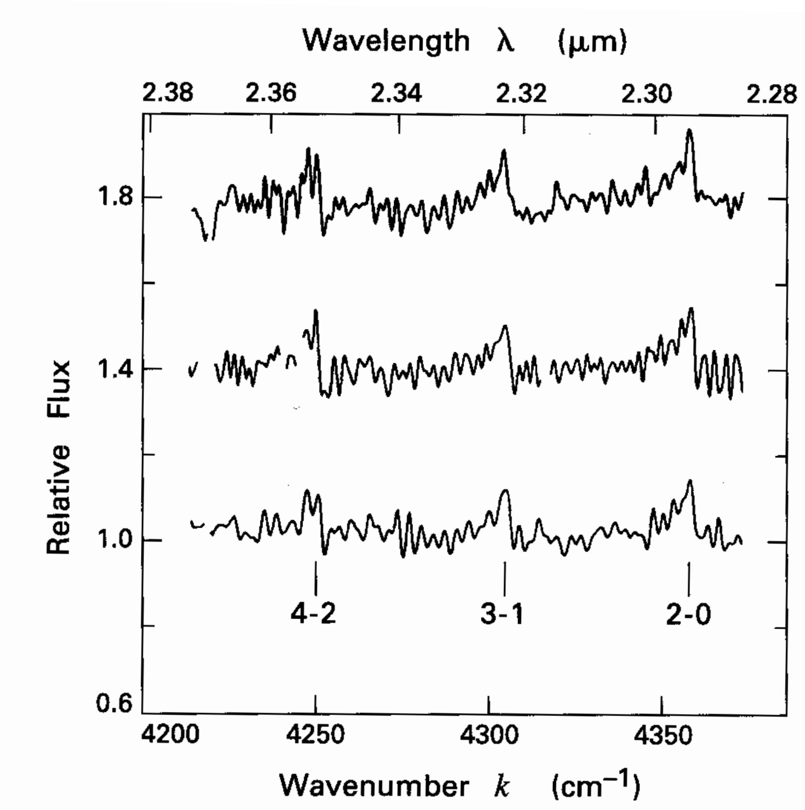
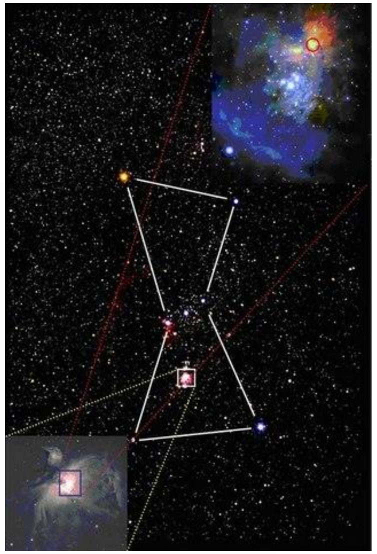
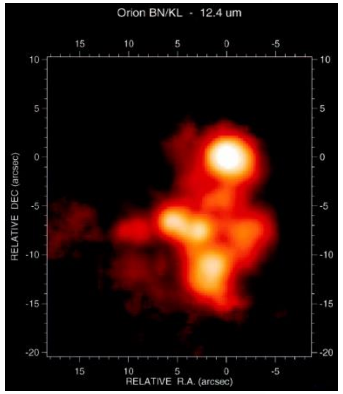


Figure 5.8 Near-infrared spectrum of the BN object in Orion, shown at three different observing times. The relative flux is plotted against the wave number k, defined here as $1/\lambda$.

Stahler & Palla





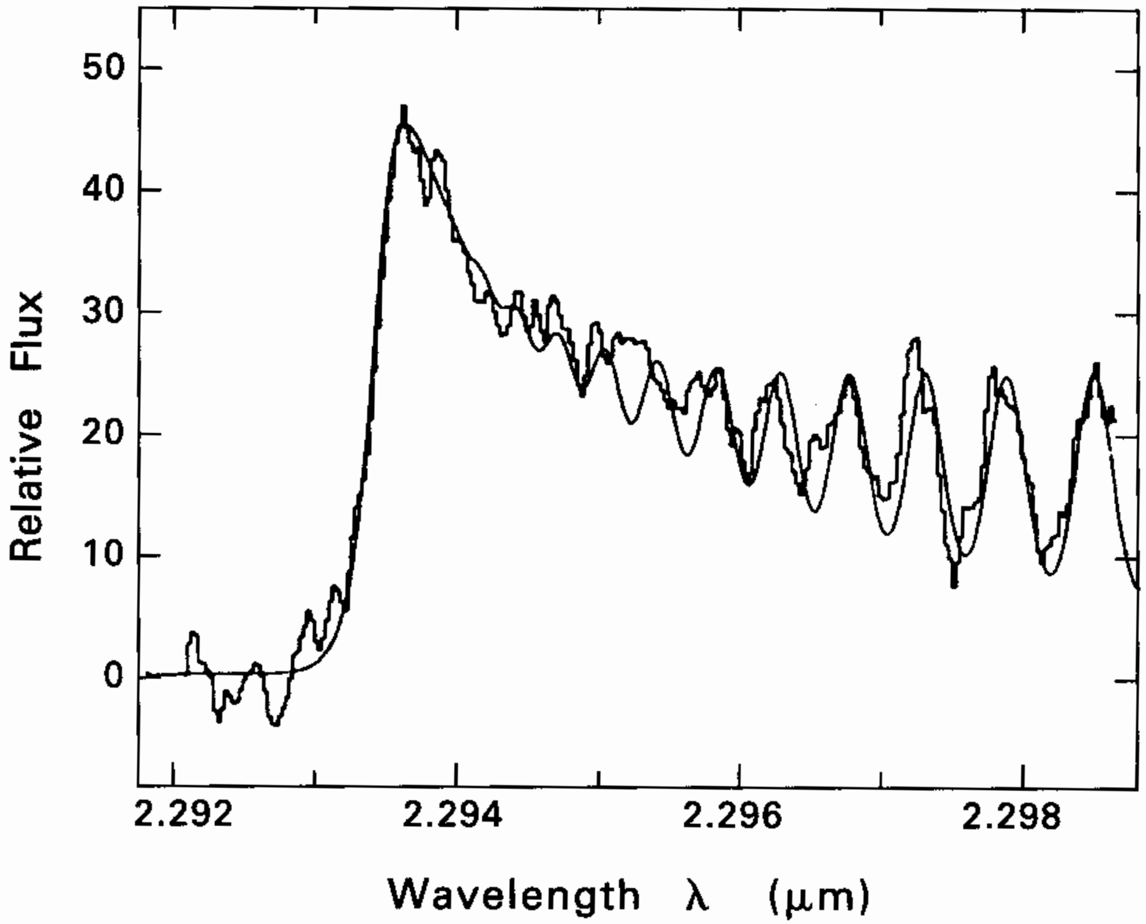
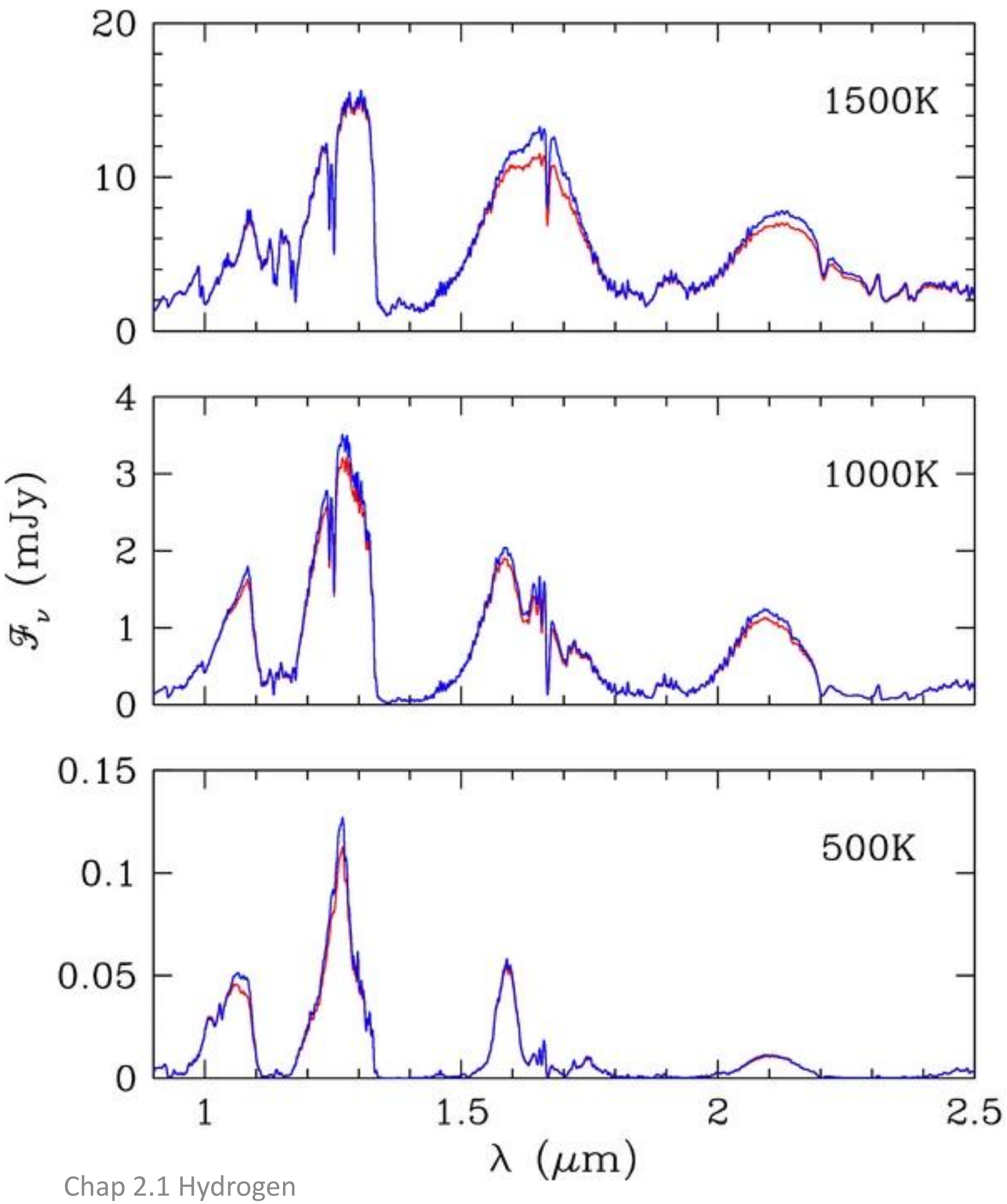


Figure 5.9 High-resolution near-infrared spectrum of the embedded stellar source SSV 13. The structure of the $v = 2 \rightarrow 0$ band head in $^{12}C^{16}O$ is evident. The smooth curve is from a theoretical model that employs an isothermal slab at 3500 K. Note that the spectrum here represents only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

Stahler & Palla



Effect of the new H_2–H_2 and H_2–He CIA opacity on synthetic spectra of brown dwarfs. The spectra shown are *cloudless* models with T_{eff} of 1500 K, 1000 K, and 500 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 pc and are displayed at a resolving power of $R = 500$.

Didier Saumon et al. 2012