Lecture 14. The H_2 and CO Molecules

1. Introduction
2. The H_2 Molecule
3. The CO Molecule
4. Summary

References
Shull & Beckwith, ARAA 20 163 1982

General

Herzberg, Molecular Spectra & Molecular Structure, Vol. 1 (1950)

Herzberg, The Spectra & Structure of Simple Free Radicals,
        (Cornell, 1971), esp. Parts I & II

Huber & Herzberg, Constants of Diatomic Molecules (1979)

Townes & Schawlow, "Microwave Spectroscopy" (Dover 1975)

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1. Introduction

- The CNM HI is located in a thin disk.
- Young stars are found within an even thinner disk.
- The study of the dense ISM will reveal that:

  Molecular clouds found within the thin disk are closely associated with recent star formation

- The H_2 and CO Molecules are the two most abundant of the 150 known interstellar molecules.
- They have played important roles in establishing the facts about recent star formation in the Milky Way.
- An additional reason for detailed discussion of H_2 and CO is that they are relatively simple and provide an entry to the complexities of molecular spectroscopy
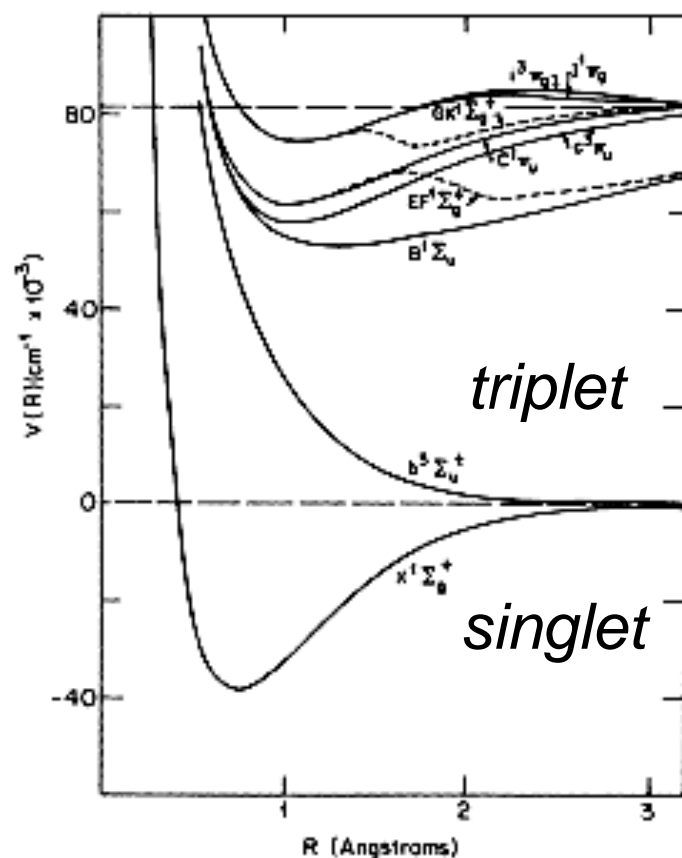
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2. The H_2 Molecule

a. Symmetry Considerations: Spin Exchange

The two electrons have total spin $S = 0$ & 1, which are anti-symmetric and symmetric under exchange. The Exclusion Principle requires the corresponding spatial wave functions to have the opposite symmetry.

There are two basic types of potential curves, **singlet and triplet**. Two asymptote to two ground state H atoms, one attractive and one repulsive (next slide)

The triplet state has higher kinetic energy and less (attractive) Coulomb energy because of its odd spatial wave function.

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Potential Energy Curves for H$_2$

triplet

singlet

*potential energy curves
that asymptote to two ground
state H atoms at zero energy*

Shull & Beckwith, ARAA 20 163 1982
(review of the basic astrophysics of H$_2$)

b. Symmetry Considerations: Proton Exchange

The protons can have spin $I = 0$ &1, which are anti-symmetric and symmetric under exchange. The Exclusion Principle requires overall anti-symmetry on exchange. This primarily affects the pure rotational states: For a homonuclear diatomic rotor, the wave function is an ordinary spherical harmonic $Y_{JM}(\theta, \phi)$. On exchange, it goes into $(-1)^J Y_{JM}$. Thus even J states go with $I = 0$ ("para" H_2) states and odd J states with $I = 1$ ("ortho" H_2).

para H_2 $I = 0$ **ortho H_2 $I = 1$**

J=4 ---------------- 1707 K

                                                        J=3 -------------- 1024

J= 2 --------------- 512 K

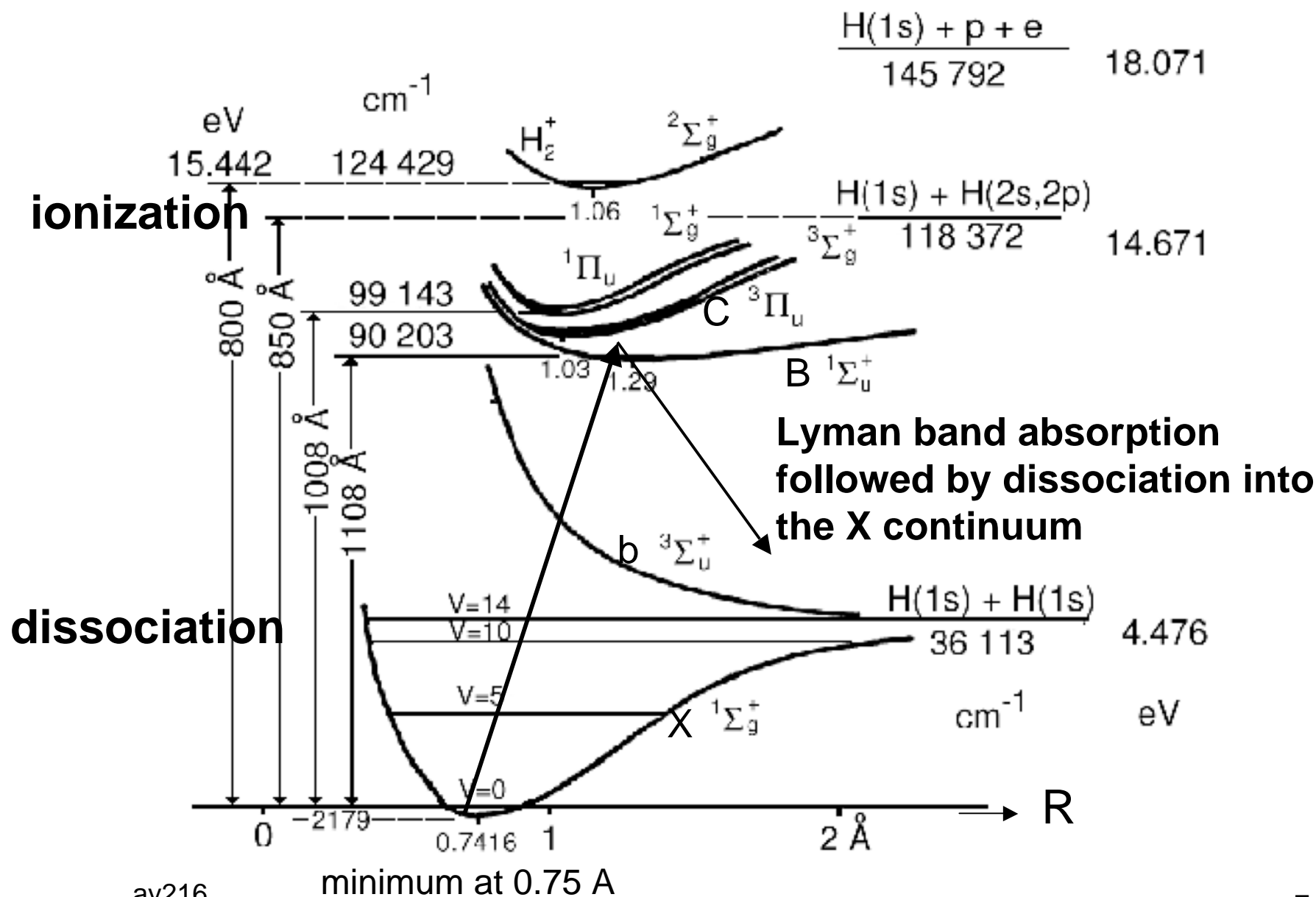   J=1 -------------- 171 K
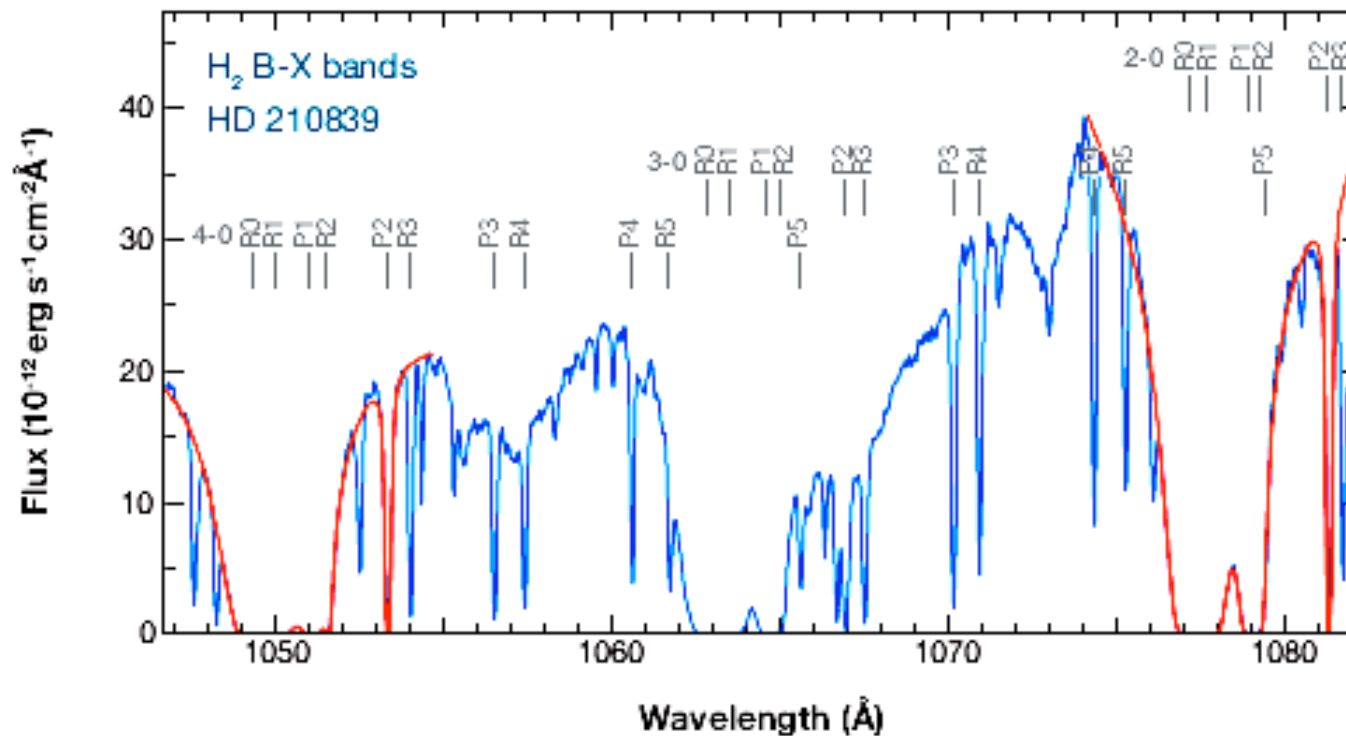
J = 0 -------------- 0 K

c. Electronic Levels

• With quantum numbers, $S = 0$, $I = 0$, $\Lambda = 0$, $J = 0$, the ground state is X $^1\Sigma^+_g$. It has 30 vibrational levels, each with an infinite number of rotational states.

• The next two singlet levels are B $^1\Sigma^+_g$ and C $^1\Pi^+_u$. Their potential curves asymptote to separated 1s and 2s,p H Atoms (above the dissociation energy into two H(1s) atoms).

• Levels B & C are connected to ground by allowed electric-dipole transitions (analogs of HI Ly-α). These **Lyman and Werner bands** start at 1108 Å and 1040 Å, and are spread more or less uniformly across the FUV band from the HI Lyman edge at 911.7 Å to the threshold at 1108 Å.

• Typical oscillator strengths are ~ 10^{-2}.

• The Lyman and Werner bands were first detected in a rocket experiment by Carruthers and then extensively observed in diffuse clouds by the UV satellites Copernicus and FUSE.

Electronic Level Diagram fr H$_2$

$\frac{H(1s) + p + e}{145\ 792}$ 18.071

eV   cm^{-1}

15.442 124 429   H$_2^+$ $^2\Sigma_g^+$

ionization   1.06 $^1\Sigma_g^+$ $\frac{H(1s) + H(2s,2p)}{118\ 372}$ 14.671

$^3\Sigma_g^+$

99 143 $^1\Pi_u$

90 203   C $^3\Pi_u$

1.03 1.29   B $^1\Sigma_u^+$

Lyman band absorption followed by dissociation into the X continuum

b $^3\Sigma_u^+$

V=14   H(1s) + H(1s)
V=10   36 113   4.476

dissociation

V=5   X $^1\Sigma_g^+$ cm^{-1} eV

V=0

R

0 −2179   0.7416 1   2 Å

minimum at 0.75 A

800 Å   850 Å   1008 Å   1108 Å

Observations of the Lyman Band Lines

FUSE FUV spectrum of a bright star showing absorption by the Lyman bands of H_2. The red curve is a fit by Rachford, ApJ 577 221 2002.

Lyman Band Absorption Towards AGN
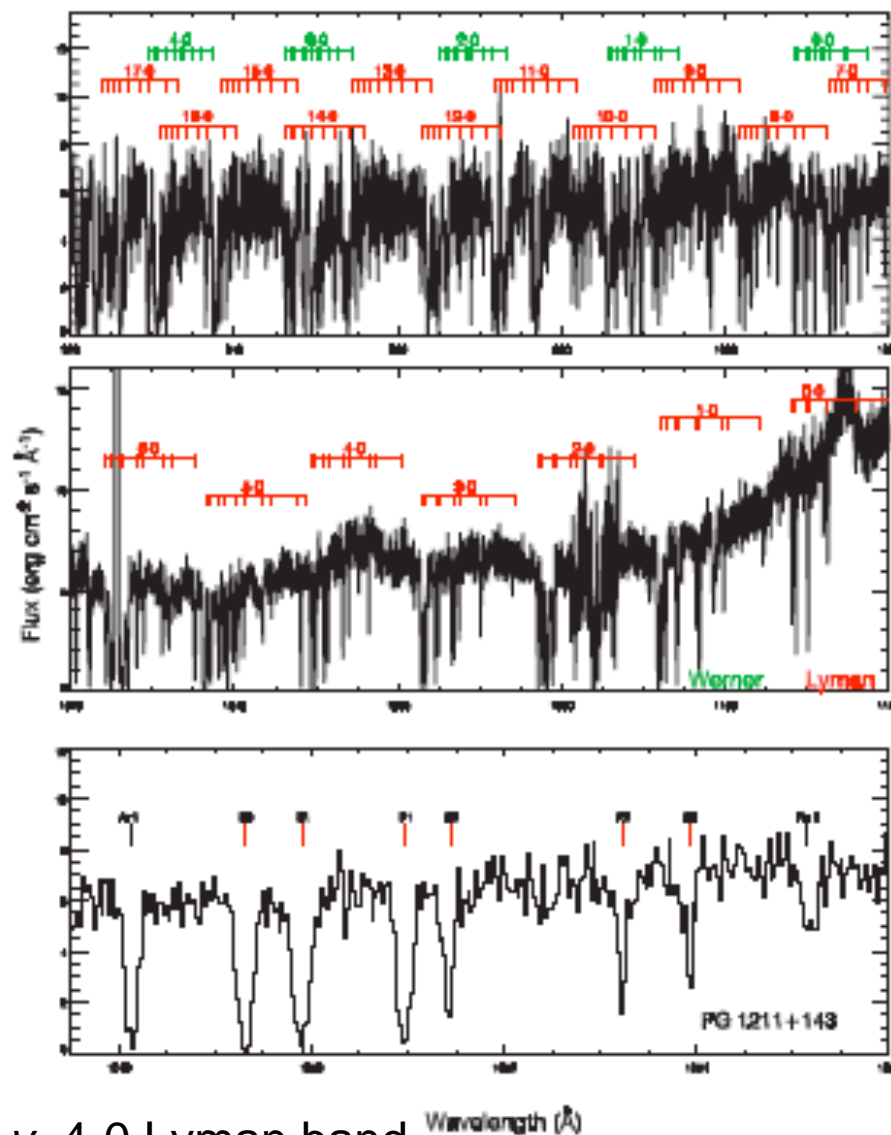
Spectra on varying wavelength scales;
Top - 920-1020 Å
Middle - 1020-1120 Å
Bottom - 1046-1146 Å

Gillmon et al., ApJ 636 891 2006
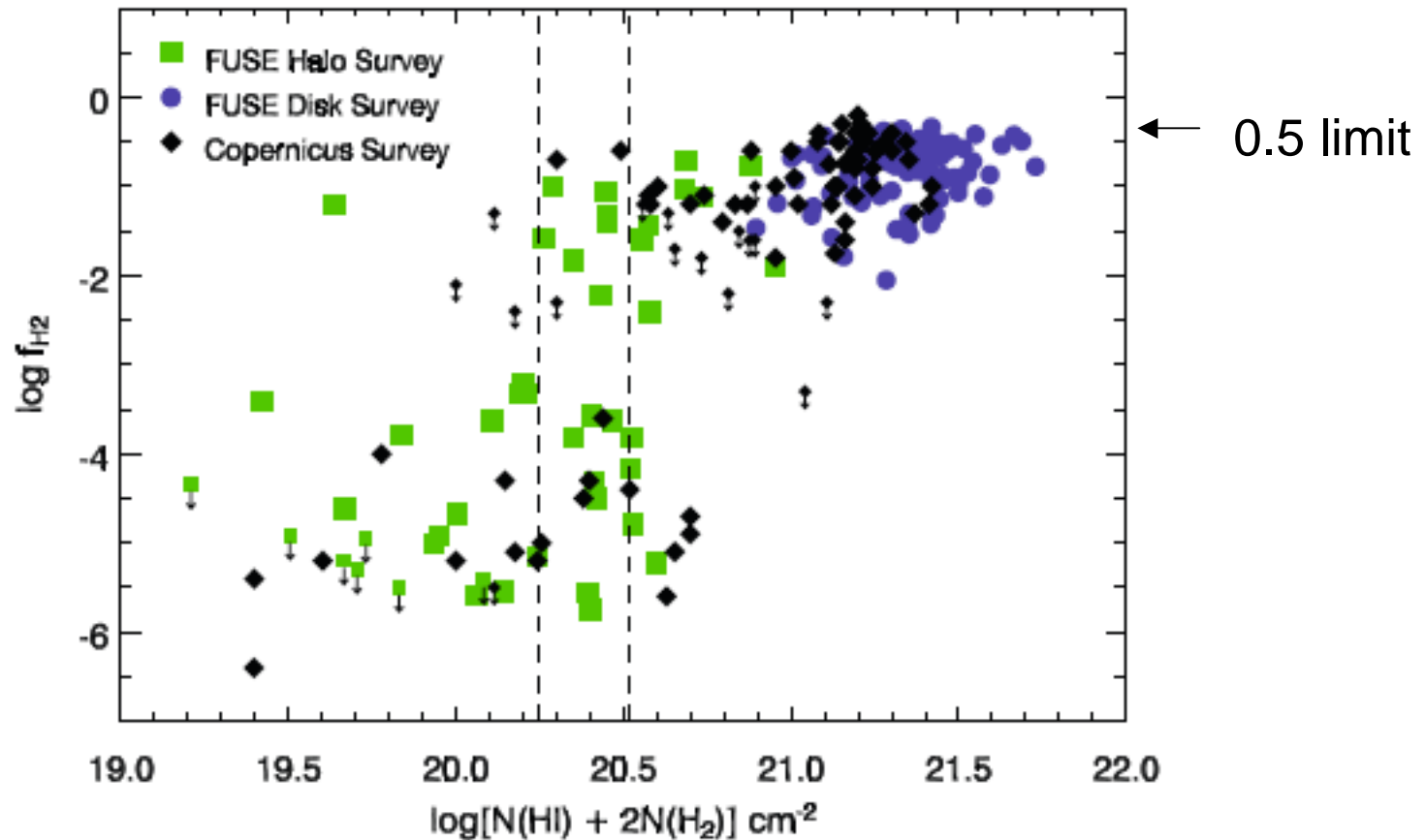"A Fuse Survey of Interstellar H_2 towards High Latitude AGN"

Analysis of spectra like these yields H_2 column densities and excitation temperatures.

blow up of *v*=4-0 Lyman band

FUSE and Copernicus Survey Results
Gillmon et al (2006)

$\leftarrow$ 0.5 limit

$$F = \frac{2N(\mathrm{H}_2)}{N(\mathrm{H}) + 2N(\mathrm{H}_2)} \quad \text{vs.} \quad N(\mathrm{H}) = N(\mathrm{H}) + 2N(\mathrm{H}_2)$$

The 1/2 transition occurs near $N_{\mathrm{H}} = 2.4 \times 10^{20}$ cm^{-2}

Lyα Pumped Fluorescence of H₂

Lyα is often a strong line covering several Å. It can overlap many Lyman band H₂ lines. The fluorescence is sensitive to T and the abundance of H₂. It can be used as a thermometer.
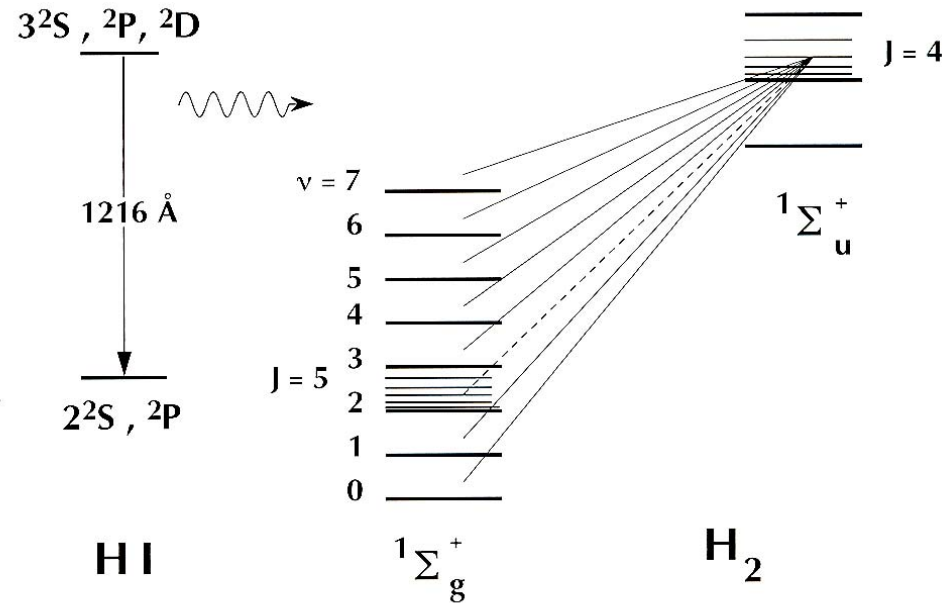
Fig. 4.10. Fluorescence of H₂ with Lyα. In order for this process to occur, the molecular hydrogen has to be both vibrationally and rotationally excited, which requires a temperature above about 1000 K

First observed in sunspot spectra by Jordan (1977), analyzed theoretically be Shull (1978), and most recently observed in the nearby T Tauri star TW Hya (Herczeg et al. 2002).

FUSE Observations of HD
Lacour et al. A&A 430 967 2005
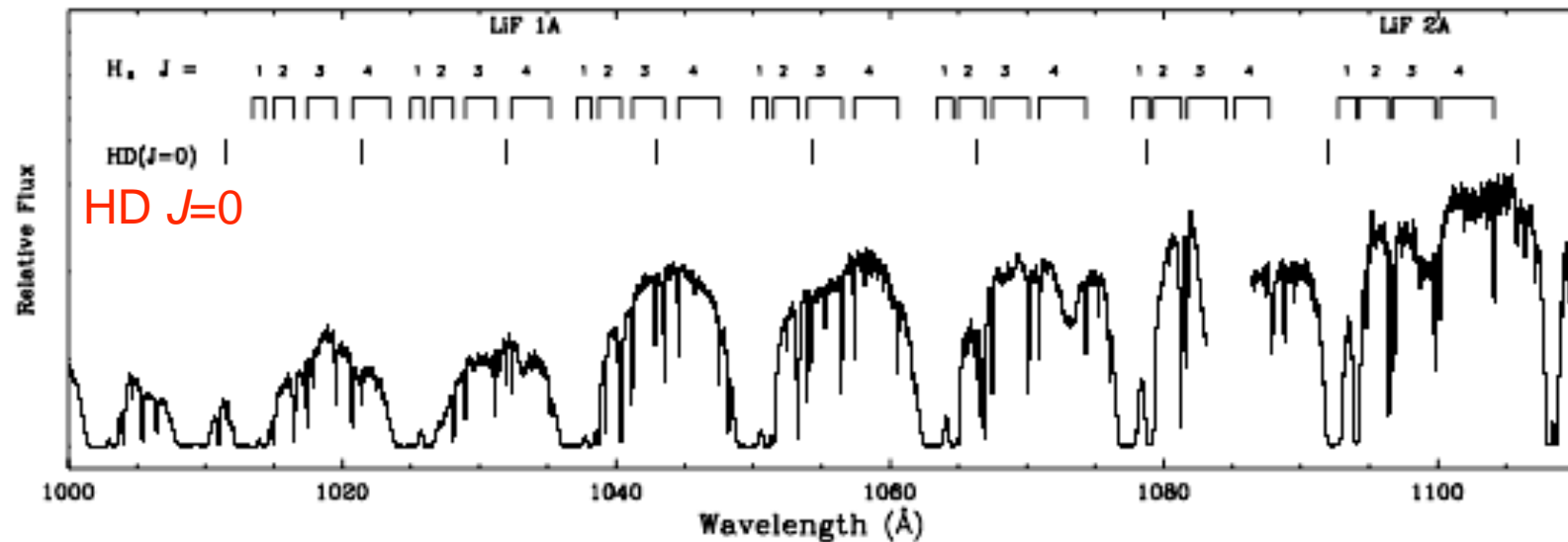
Fuse FUV absorption line spectrum of a nearby translucent cloud HD 110432 [E(B-V)=0.4]. Typical HD abundances are ~ 3×10^{-06}. Since the abundance of deuterium in the ISM is a factor of 5 or more larger, D is incompletely transformed into molecules, probably due to photodissociation. Normal hydrogen is only 55% converted into H_2 in this cloud.

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d. Near Infrared Transitions

- The ground level vibrational constant is $\omega \sim 4400$ cm^{-1} (6330 K); ro-vib transitions occur in the NIR near 2.2 μm.
- They are observed in warm regions, where they are collisionally excited, and in regions near a FUV source, where they are part of the fluorescence spectrum following absorption of a Lyman or Werner band photon.
- Neutral gas near a star-forming region is a good example.

Because H_2 has no dipole moment, these are **weak quadrupole transitions**; a favorite is the 1-0 S(1) line at 2.12 μm, corresponding to $v'=1, J'=3 \rightarrow v''=0, J''=1$.

	O	P	Q	R	S
$J' =$	$J'-2$	$J'-1$	J'	$J'+1$	$J'+2$

NIR H$_2$ Ro-Vib Lines in a Herbig-Haro Object
## Fernandes & Brand, MNRAS 274 639 1995
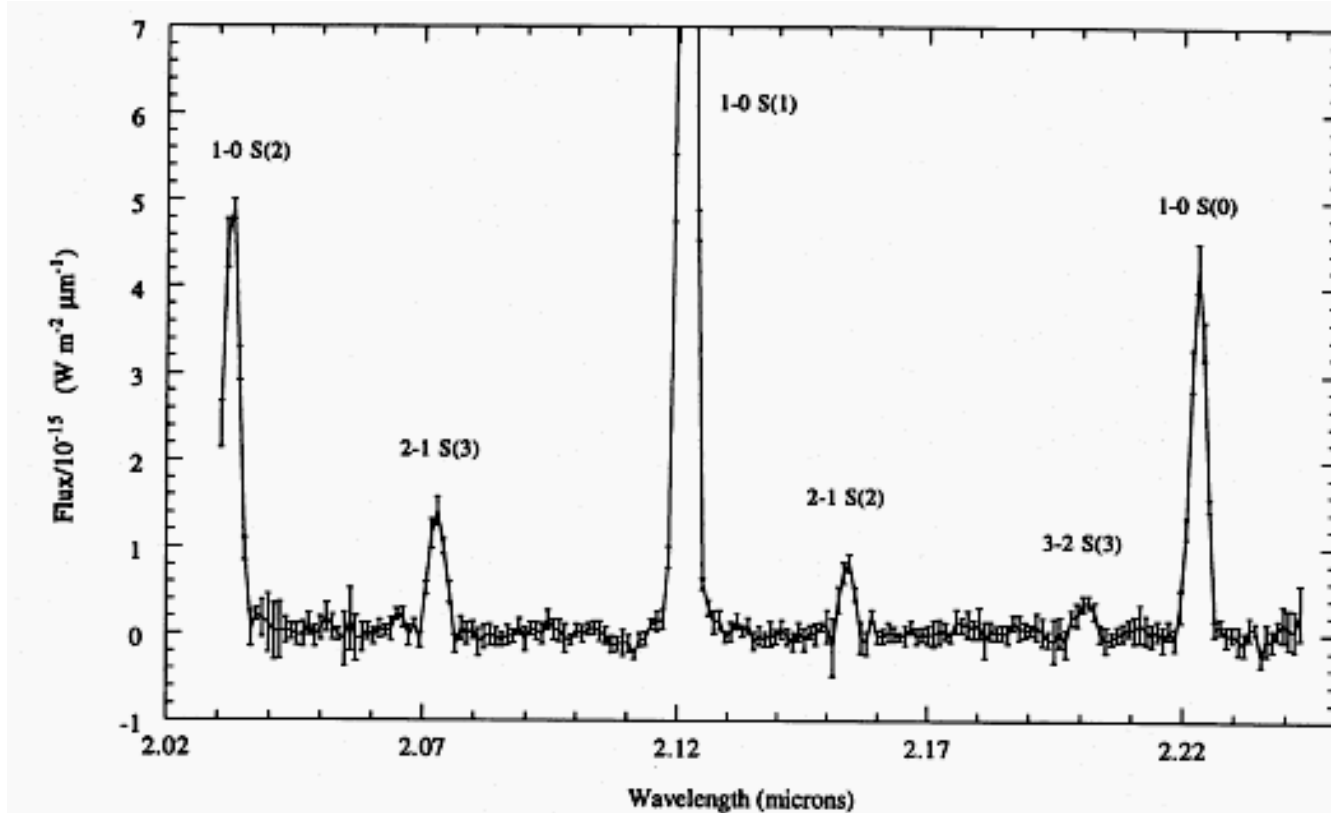
This spectrum of HH-7 was taken with the slit pointing towards the source of the outflow from the YSO SVS13 in Perseus. HH objects are believed to be due to fast winds overtaking slower material, and hey often manifest a bow-shock shock appearance. Fast shocks generate UV radiation and produce fluorescence after exciting H$_2$.
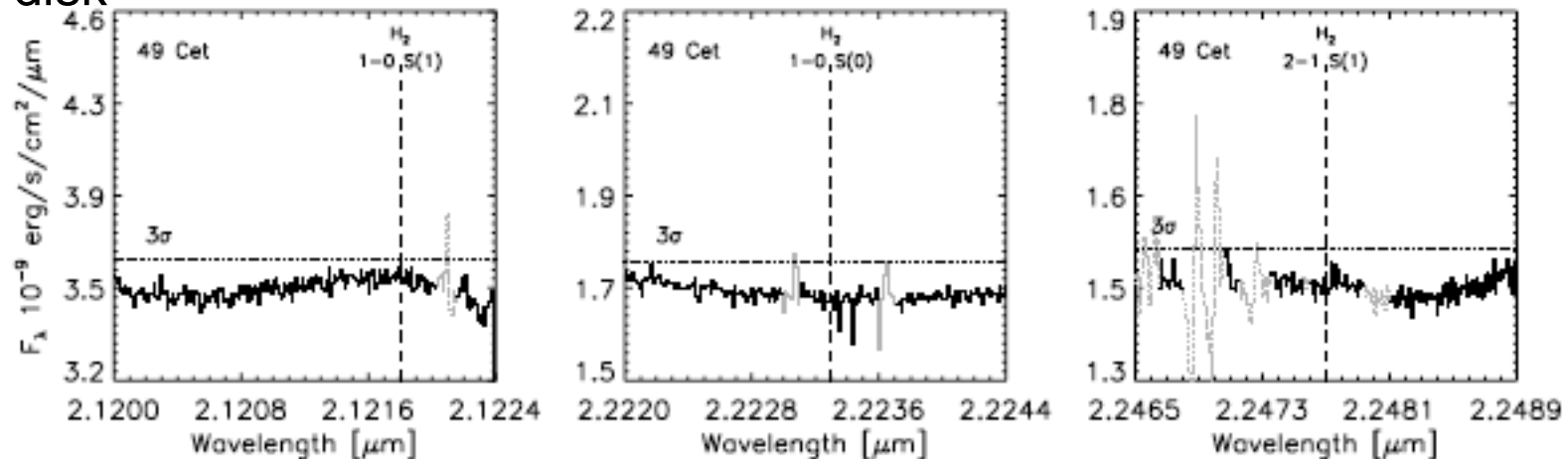
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NIR H$_2$ Ro-vib Lines in Protoplanetary Disks
Carmona et al. A&A 476 853 2007

CTTS

debris disk
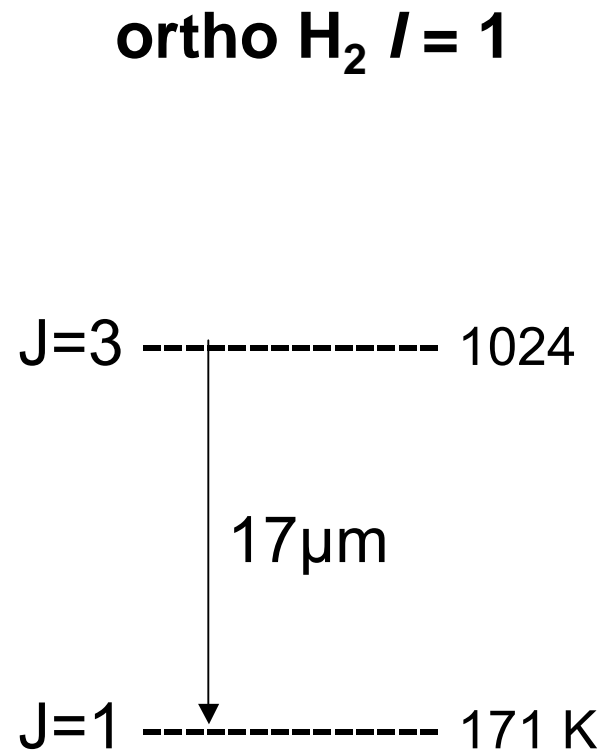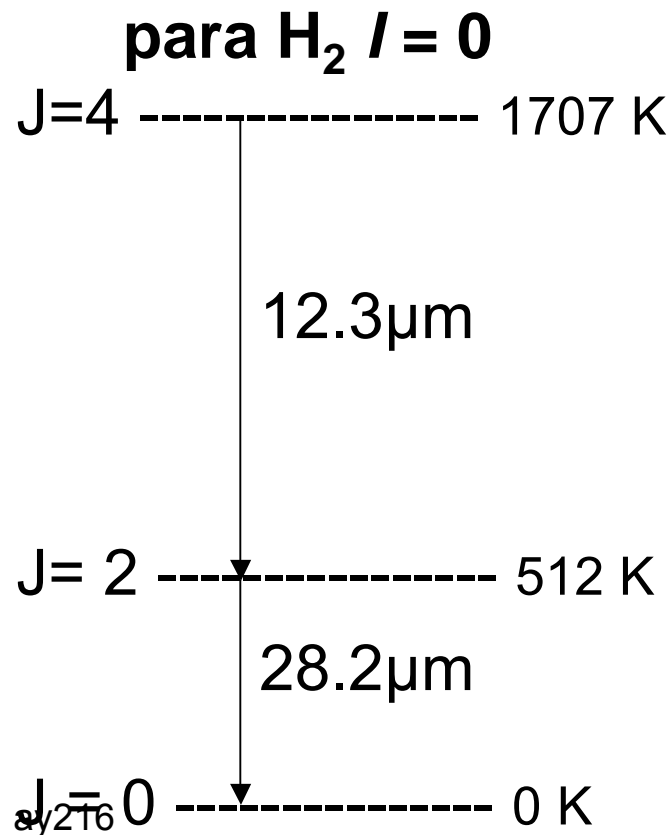

A. Carmona et al.: NIR H$_2$ emission from protoplanetary disks
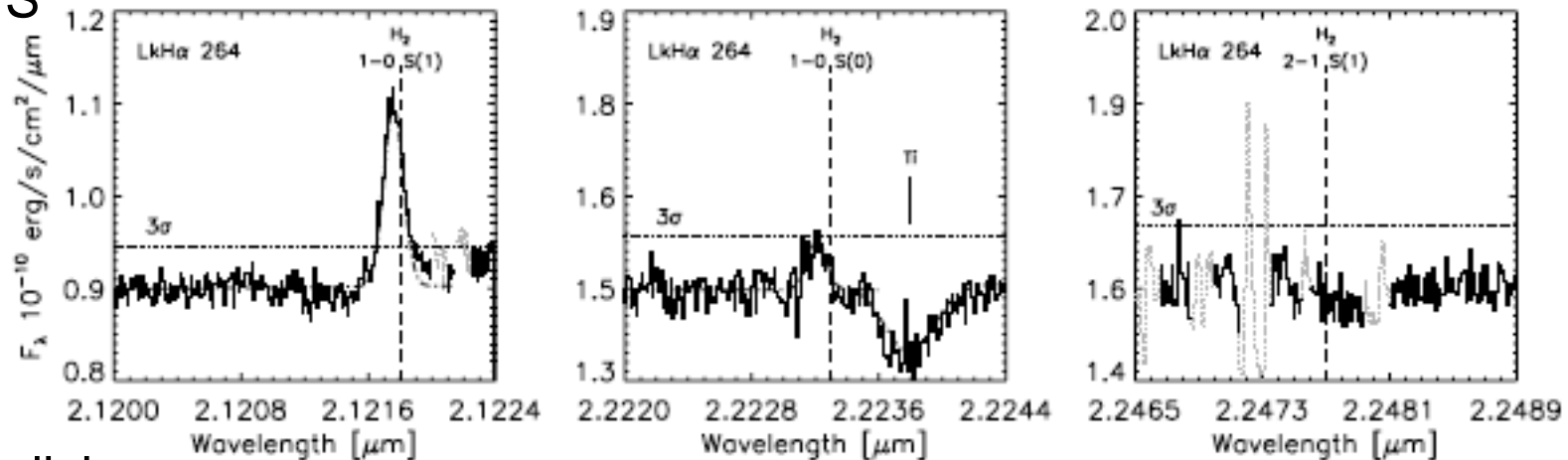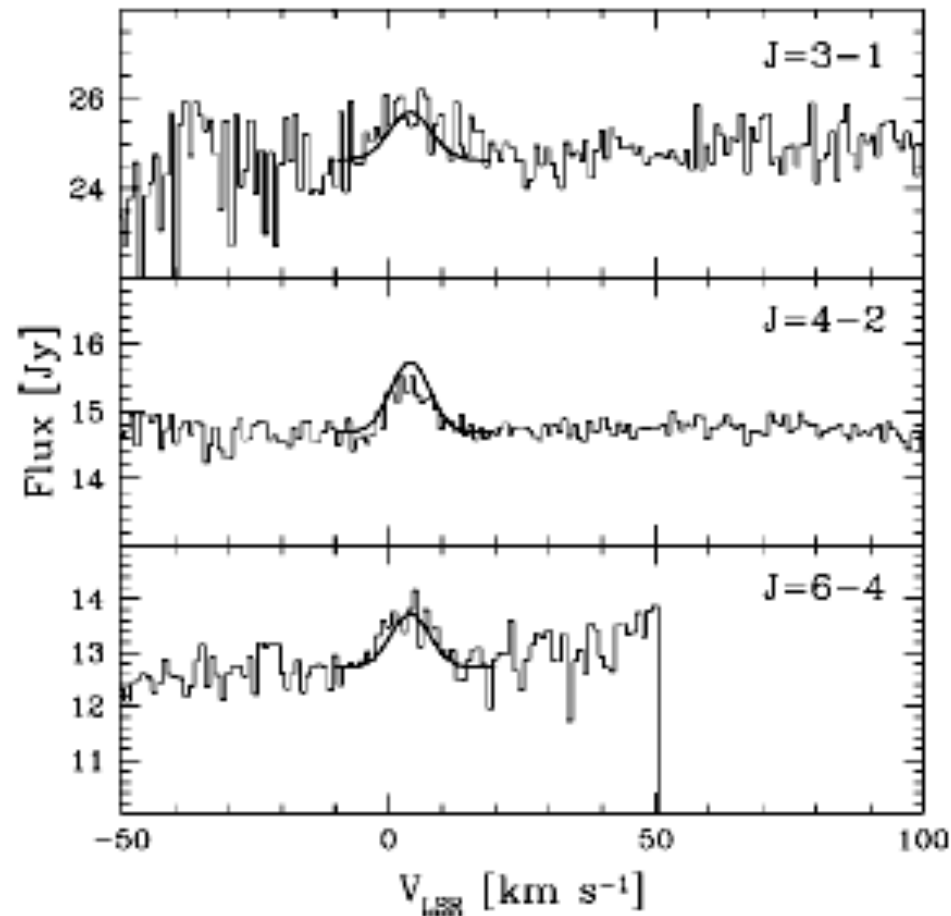
ESO VLT adaptive optics high resolution NIR spectrograph

e. Mid-Infrared Transitions

• The ground rotational constant is B = 60.85 cm^{-1} (87.6 K).
• Pure rotational transitions occur in the MIR shortwards of 28 µm; they are very weak quadrupole transitions.
• Observable in lukewarm regions (T > 300 K) by collisional excitation and by fluorescence near UV and X-ray sources.

para H$_2$ I = 0   **ortho H$_2$ I = 1**

J=4 ---------------- 1707 K

12.3µm

J=3 ------------- 1024

17µm

J= 2 -------------- 512 K

28.2µm

J=1 ------------- 171 K

J=0 ------------- 0 K

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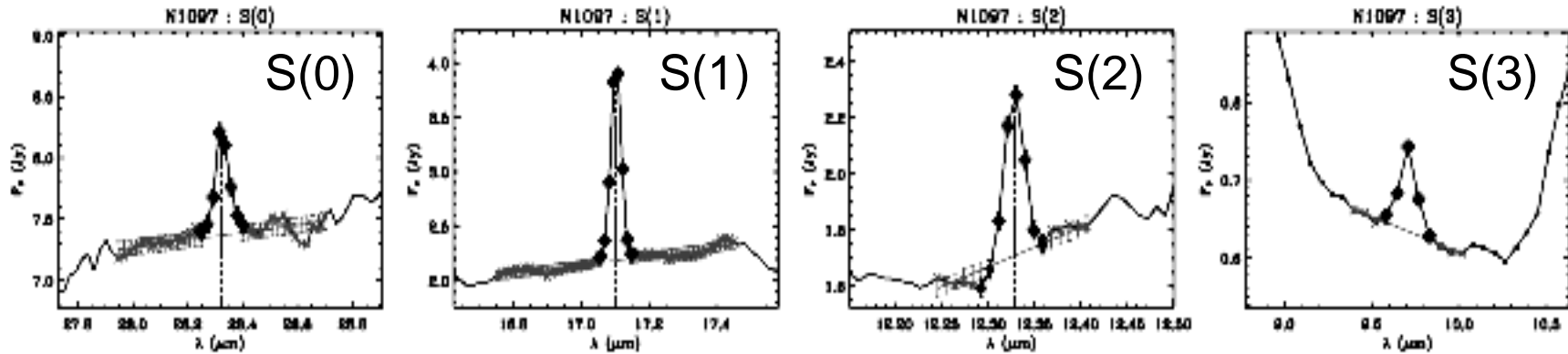# H2 Rotational Lines in a Herbig A Star Aur
Bitner e a. ApJ 661 L69 2007

TEXES (Texas Echelon Cross Echelle Spectrograph)
at Gemini North and NASA IRTF

H₂ Rotational Line Detections in AGN

Roussel et al. ApJ 669 959 2007

S(0)   S(1)   S(2)   S(3)

OBSERVED H₂ LINES

Transition $v = 0$	Short Notation	Rest λ (μm)	Spectral Order	E_u/k (K)	A (10^{-11} s^{-1})
$J = 2-0$	S(0)	28.219	LH 14	510	2.95
$J = 3-1$	S(1)	17.035	SH 12	1015	47.6
$J = 4-2$	S(2)	12.279	SH 17	1681	275.0
$J = 5-3$	S(3)	9.665	SL 1	2503	980.0
$J = 6-4$	S(4)	8.025	SL 1	3473	2640.0
$J = 7-5$	S(5)	6.910	SL 2	4585	5880.0
$J = 8-6$	S(6)	6.109	SL 2	5828	11400.0
$J = 9-7$	S(7)	5.511	SL 2	7196	20000.0

NOTE.—The rotational upper level energies were computed from the molecular constants given by Huber & Herzberg (1979), and the transition probabilities are from Black & Dalgarno (1976).

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3. The CO Molecule

Some Advantages of CO

• CO has a small but finite permanent dipole moment (0.110 Debye). Its pure rotational and rovib transitions are relatively strong compared to H_2.

• The long wavelength transitions occur in reasonably good parts of the mm and sub-mm spectrum bands.

• Its strong binding means that it is widely distributed with a roughly constant abundance, at least where most hydrogen is mainly molecular. [D(CO) = 11.09 eV compared to D(H_2)= 4.48 eV]

• It has useful isotopes, ^{13}CO, $C^{17}O$, & $C^{18}O$.

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Spectroscopic Constants in cm⁻¹

We follow Herzberg's formula for the energy levels expressed in wave numbers ($k = E/ch$):
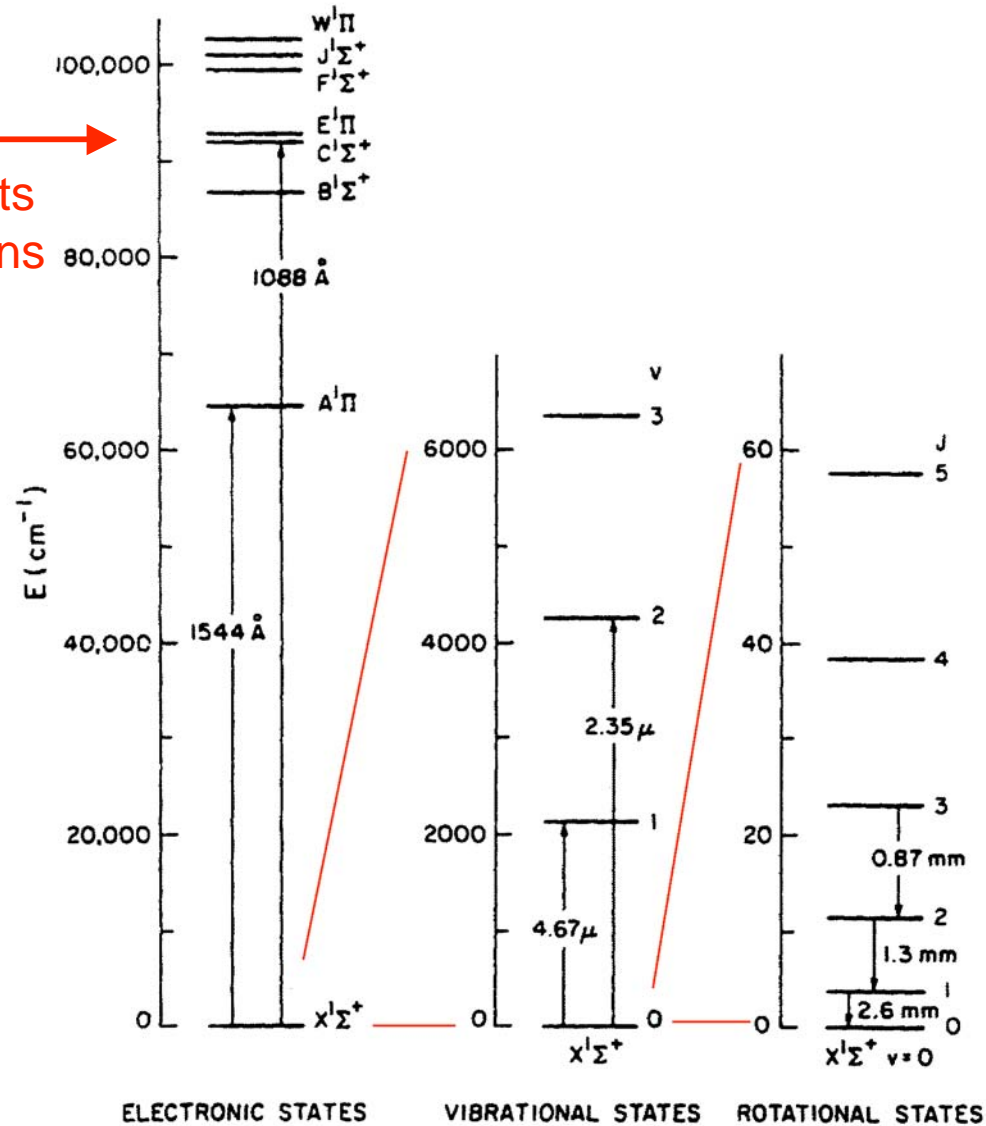
$$k = G(v) + B_v J(J+1) - D_v [J(J+1)]^2 + \cdots$$

v	0	1	2
B_v	1.922529	1.905026	1.887524
$D_v \times 10^6$	6.1206	6.1203	6.120
$G(v)$-$G(0)$		2143.272	4260.64

In Kelvin:

$B_0 = 2.766$ K   and $\theta_0 = (ch/k_B) [G(1) - G(0)] = 3084$ K.

Energy Levels of CO

FUV dissociation starts
with electron transitions
just below 1100 Å

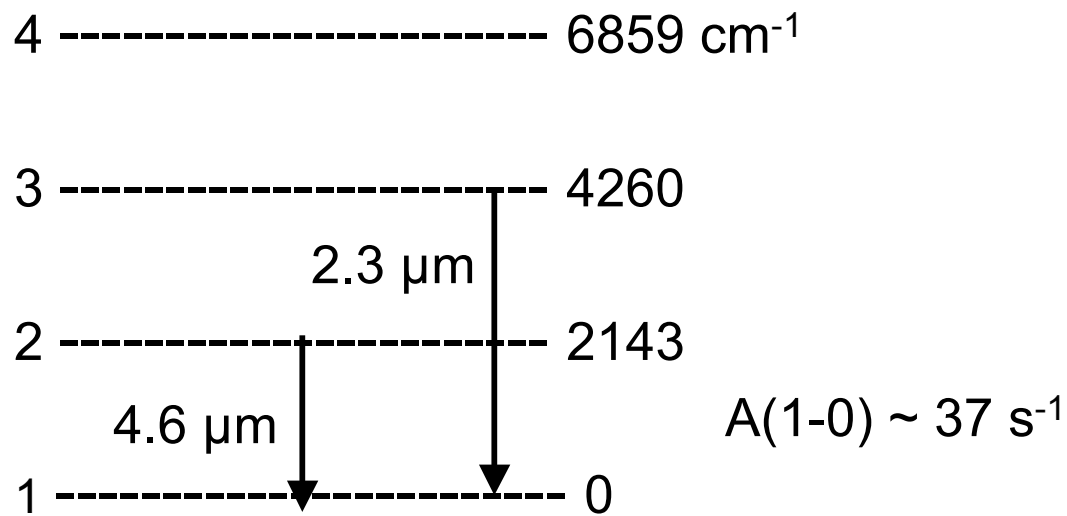ay216

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CO and H$_2$ Dissociation Energies

15.44 -------------------- IP

13.6 -------------------

11.2 -------------------

                       continuum

4.76 ------------------- Diss

0.00 -------------------

H$_2$

14.0 -------------------- IP

13.6 -------------------   **continuum**

12.0 ------------------- Diss

11.3 -------------------

0.00 -------------------

CO
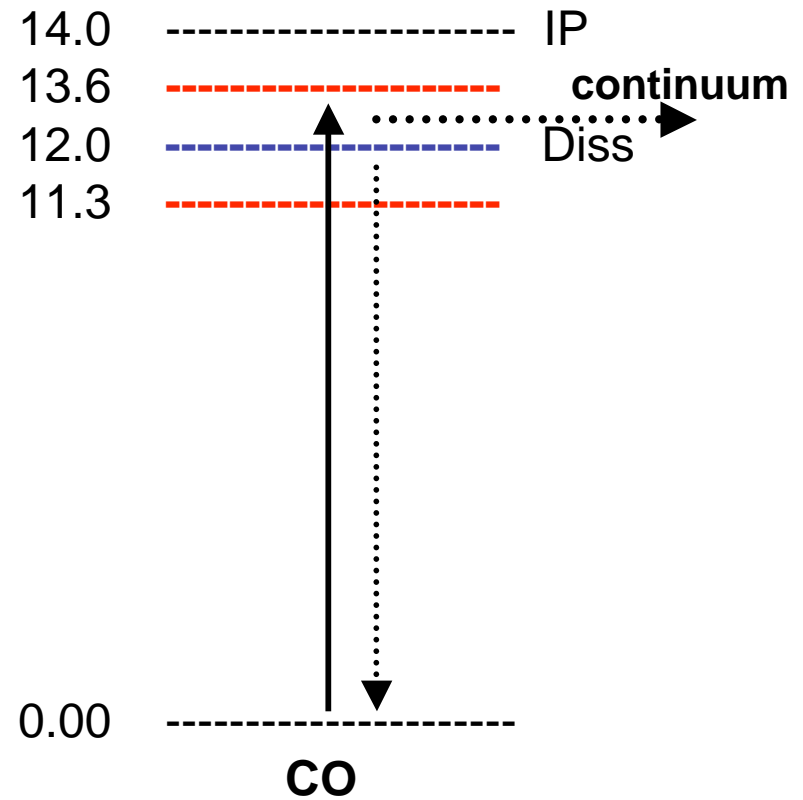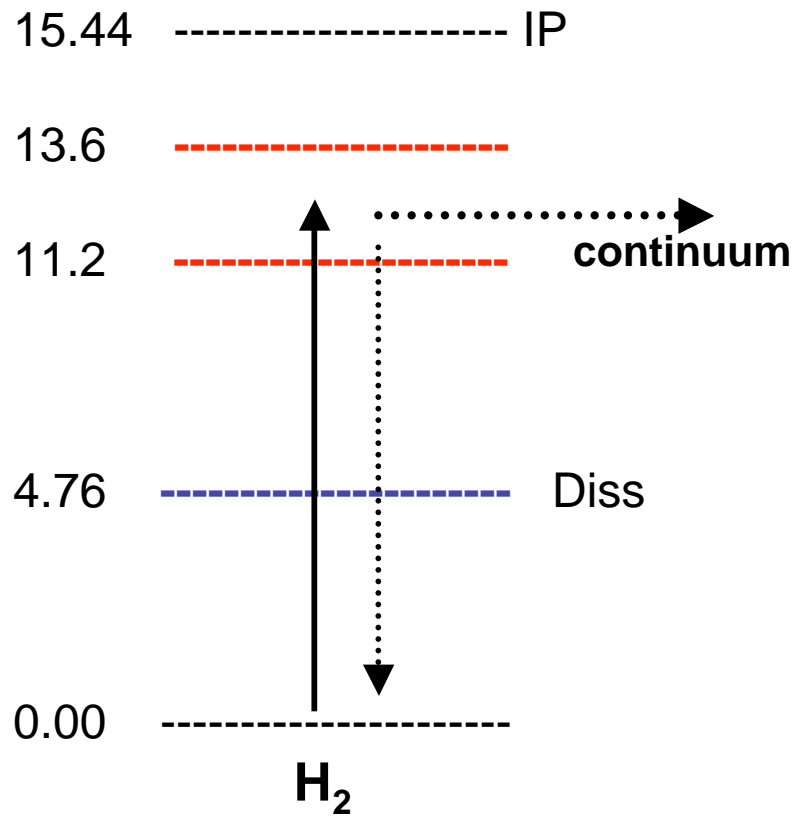
Legend: IP = Ionization Potential

        Diss = Dissociation energy

        = allowed electronic transitions in the FUV

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Summary of the CO Diagnostic Lines

a. UV – CO is something like a heavy H_2: The UV bands occur in the far UV near 1000 Å with oscillator strengths of the same order of magnitude (10^{-2}) as for H_2. They have have been detected in absorption towards diffuse clouds where the CO maximum abundance is 10^{-5}.

b. NIR $\Delta v = 1$ transitions are the *fundamental* bands
$\Delta v = 2$ transitions are the *1st overtone bands*, etc

4 --------------------- 6859 cm^{-1}

3 --------------------- 4260

2.3 µm

2 --------------------- 2143

4.6 µm   A(1-0) ~ 37 s^{-1}

1 --------------------- 0

CO 1st Overtone Band Head
Carr & Tokunaga ApJ 393 L67 1992
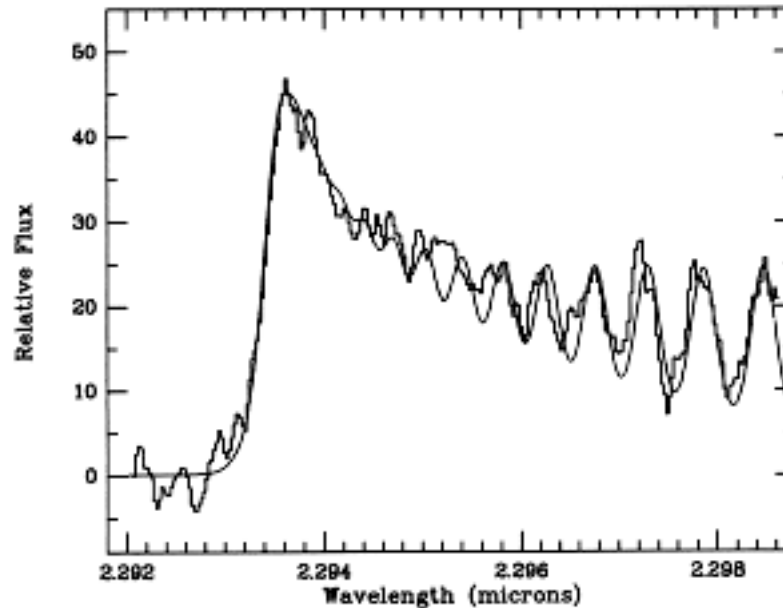
Bandhead of the v=2-0 CO ro-vib transitions
observed in the YSO SVS 13 in Perseus

The bandhead arises from the centrifugal stretching. For large enough *J* in the R-branch, the increasing trend of the low-*J* rotational energy differences is reversed. The level spacing near the bandhead become very small, and this accounts for the increase brightness that makes it relatively easy to detect CO in YSOs under the proper excitation conditions.

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Bandhead Formation for a Diatomic Molecule

The rotational constant varies with the state. Even for the same vibrational & electronic state, *B* decreases with increasing *J for large J* due to centrifugal stretching . The energy emitted in a R or P ro-vib transition for unequal *B'* & *B''* is (following Herzberg),

$$\Delta E(m) = \Delta E_0 + (B'+B'')m + (B'-B'')m^2$$

$$m = J + 1 \text{ for the R branch } \& \ m = -J \text{ for the P branch}$$

For small *m*, we get the familiar linear behavior. For a diatomic molecule in its ground vibrational & electronic state, we expect *B'* < *B''*. So for *m* > 0 (R branch), we see that there is a value of m_{bh} where *ΔE* stops increasing with *m*.

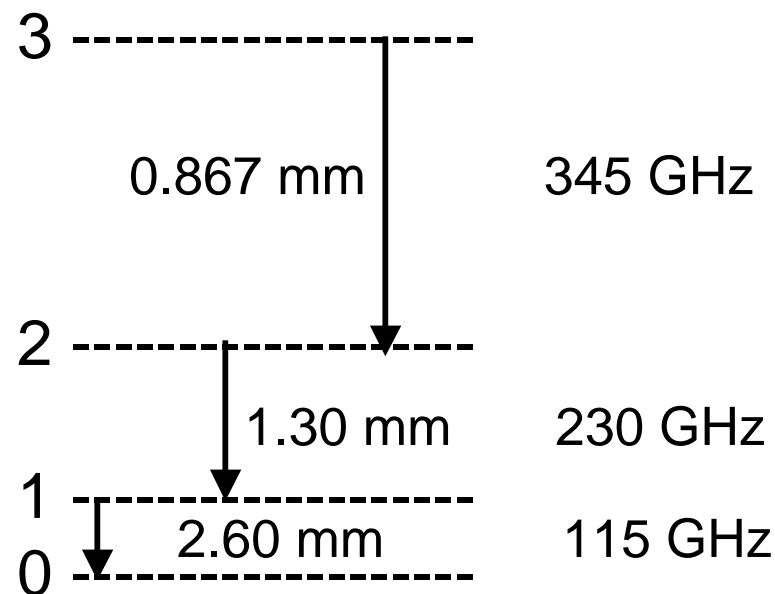$$m_{bh} = \frac{B''+B'}{B''-B'}$$

Approaching this value, the increments become small and the lines pile up, forming the *"bandhead"*.

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c. mm – pure rotational bands in the ground electronic and vibrational level. For small J

$$E_J = J(J+1)B \qquad \Delta E_J = E_J - E_{J-1} = 2BJ$$

$$B = 1.922529 \text{ cm}^{-1} \qquad 2B/k_B = 5.532 \text{ K}$$

CO is the ideal diagnostic & coolant for cool clouds with $T \sim$ 10-100 K.

CO has been detected from the ground throughout much of mm and sub-mm bands. Very dry conditions are needed at high frequencies, e.g., the Atacama desert plateau at 5525 m in N. Chile (for ALMA). The CO 9-8 1.087 THz line has been detected (Marrone et al. 2004).

3 ------------------------

0.867 mm   345 GHz

2 ------------------------

1.30 mm   230 GHz

1 ------------------------
0 ------------------------
    2.60 mm   115 GHz

$$A_{10} = 7.17 \times 10^{-8} \text{ s}^{-1} \qquad A_{J,J-1} = 3J^4/(2J+1) \, A_{10}$$

Fundamental Rotational Frequencies of CO

CO mm Frequencies in MHz by FJ Lovas
(http://www.physics.nist.gov/PhysRefData/Micro/Html/contents.html)
rounded to 6 figures and ignoring hfs

CO	115271
^{13}CO	110201
^{14}CO	105871
C^{17}O	112359
C^{18}O	109782
^{13}C^{17}O	107289
^{13}C^{18}O	104711

Rough ISM isotope ratios: ^{12}C:^{13}C = 70:1 ^{16}O:^{17}O:^{18}O= 1500:500:1

CO, H2O, and OH FIR Lines from YSOs
in a sequence of increasing age and decreasing activity
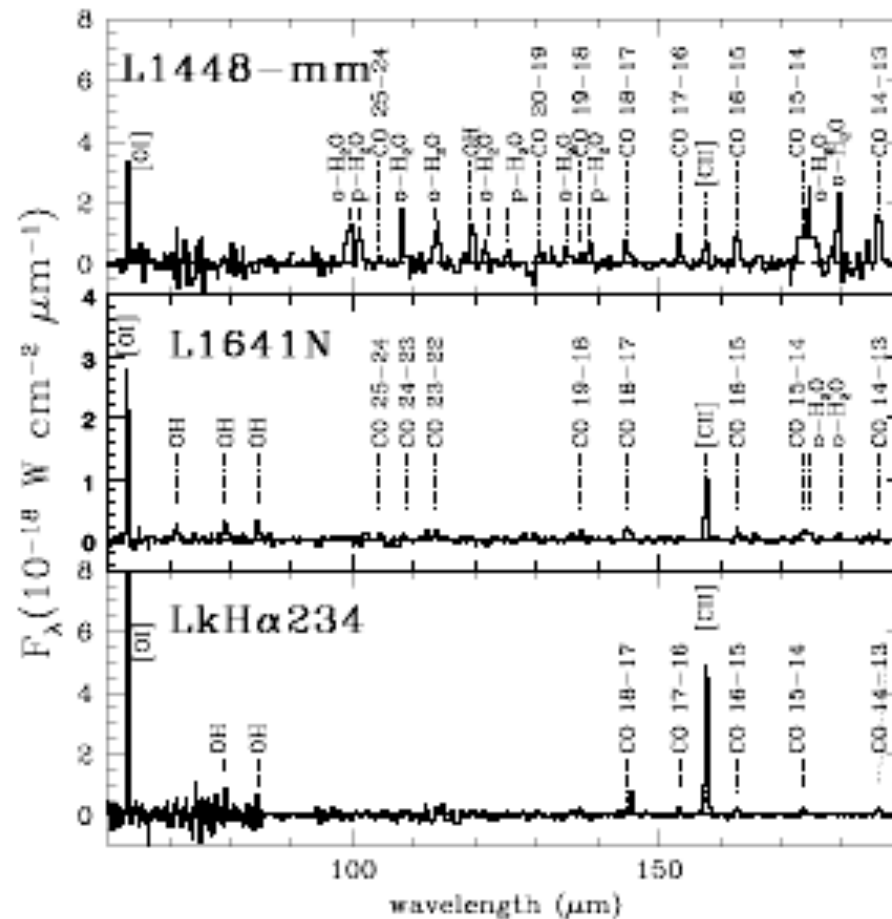
Benedettini et al. (2003)

4. Summary

We have outlined the basic spectroscopy needed to study the cooler parts of the ISM.

Many additional questions remain:

1. How are interstellar molecules formed and destroyed?
2. How are they excited?
3. What role do they play in determining the physical conditions in the ISM?
4. How do the observations of H_2, CO, and other molecules inform us about the evolution of interstellar clouds and the formation of stars?
5. What other molecules are important in these studies?