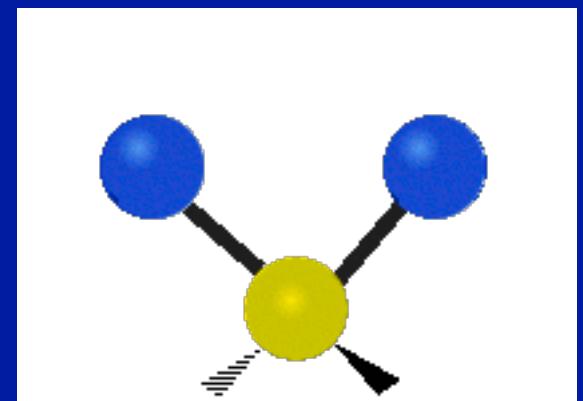
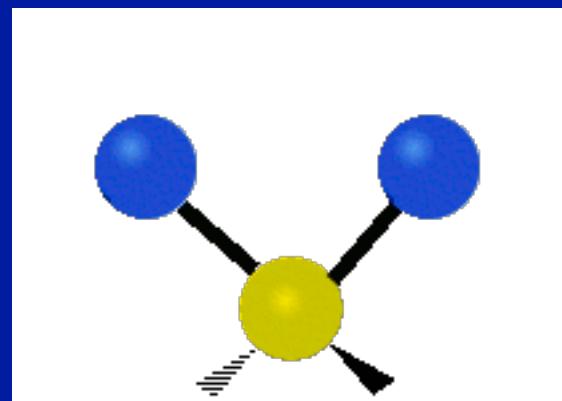
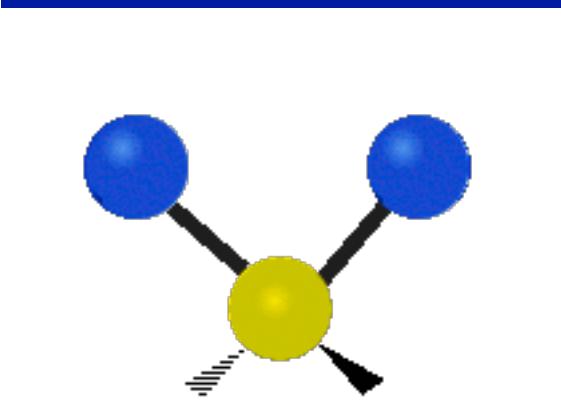
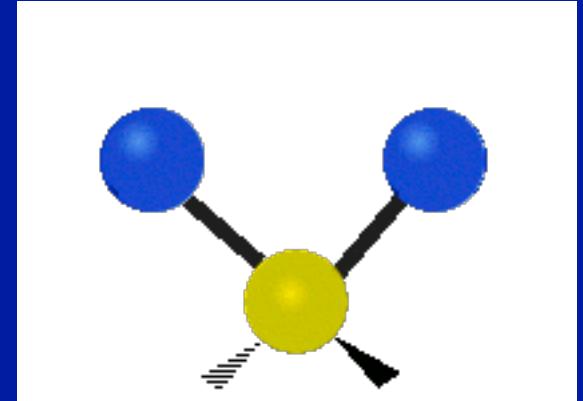
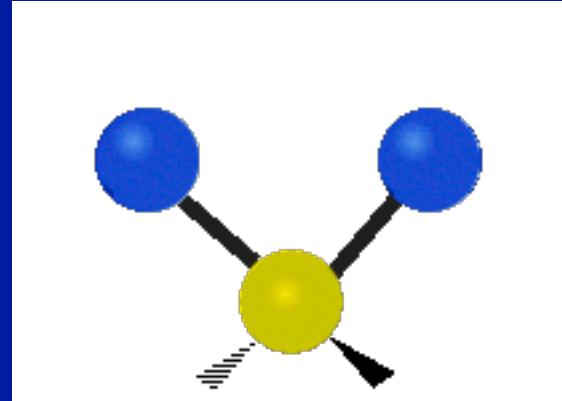
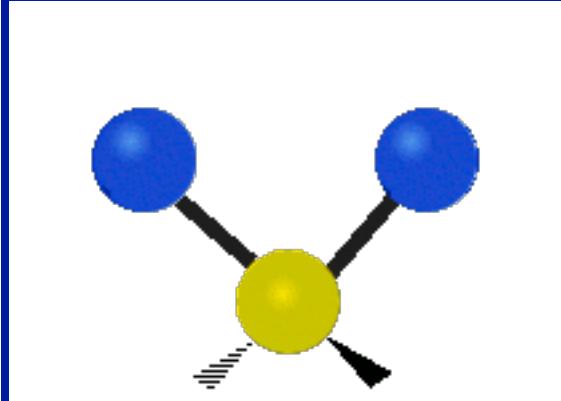


AST 515 Molecular Rotational & Vibrational Spectroscopy



$$\kappa = (2B - A - C)/(A - C)$$

$\kappa = -1$

Prolate

$\kappa = 1$

Oblate

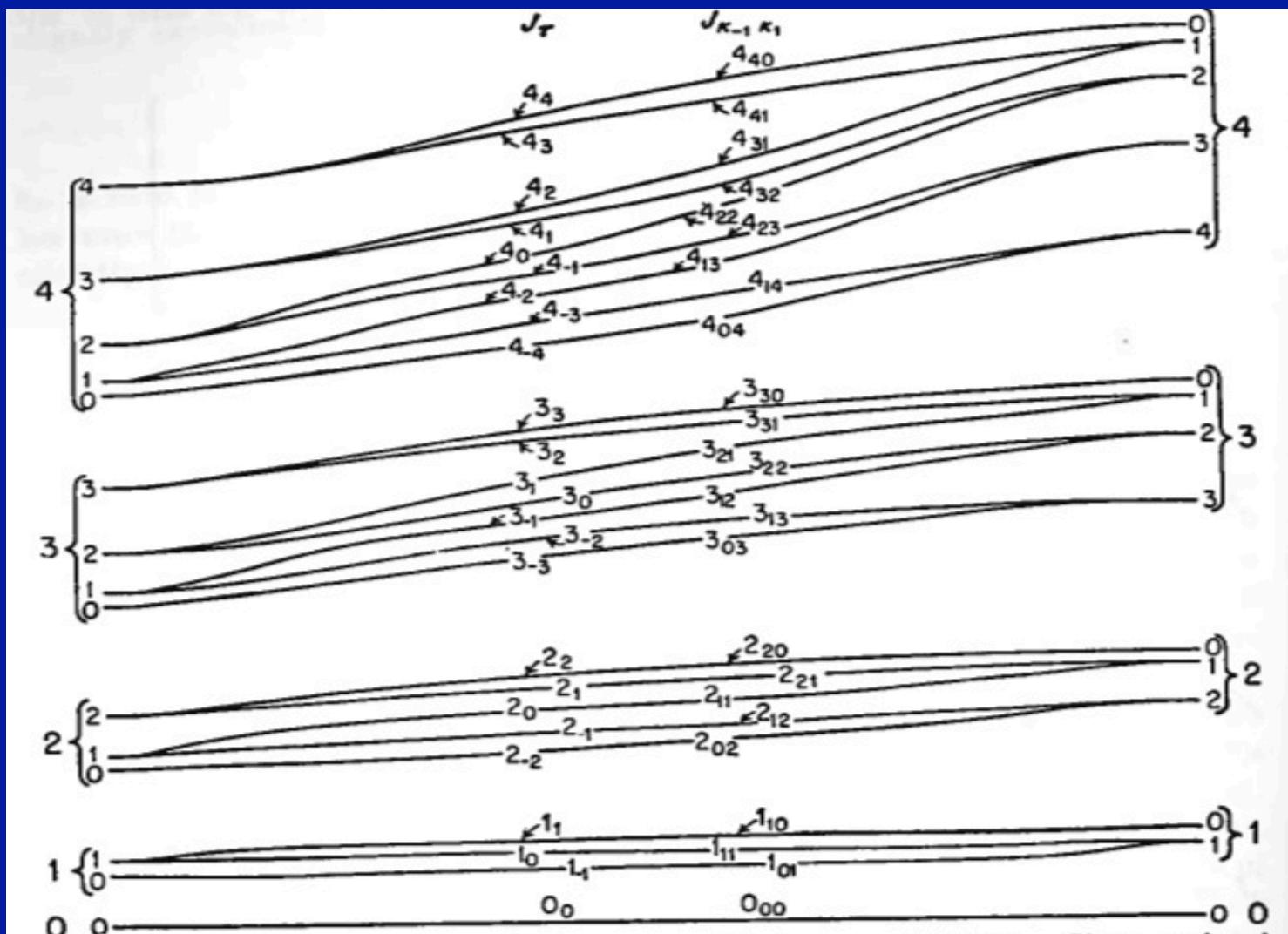


FIG. 4-1. Qualitative behavior of the asymmetric-top energy levels. The rotational constant B varies from left to right, equaling C and giving a prolate symmetric top on the left, and equaling A to give an oblate symmetric top on the right.

Asymmetric Top Selection Rules

Table 6. Selection Rules for Asymmetric Top Molecules

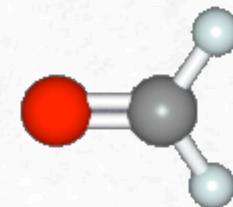
Electric Dipole	Inertia Component	Allowed Transitions $(K_{-1}K_{+1})_i \leftrightarrow (K_{-1}K_{+1})_f$	ΔK_{-1}	ΔK_{+1}
$\mu_A \neq 0$	least	$ee \longleftrightarrow eo^a$		
		$oe \longleftrightarrow oo$	$0, \pm 2, \dots$	$\pm 1, \pm 3, \dots$
$\mu_B \neq 0$	intermediate	$ee \longleftrightarrow oo$		
		$oe \longleftrightarrow eo$	$\pm 1, \pm 3, \dots$	$\pm 1, \pm 3, \dots$
$\mu_C \neq 0$	greatest	$ee \longleftrightarrow oe$		
		$eo \longleftrightarrow oo$	$\pm 1, \pm 3, \dots$	$0, \pm 2, \dots$

^ae = even and o = odd

Species Tag: 30004
 Version: 2
 Date: Nov. 1997
 Contributor: H. S. P. Müller

Species Name: H₂CO
 Formaldehyde

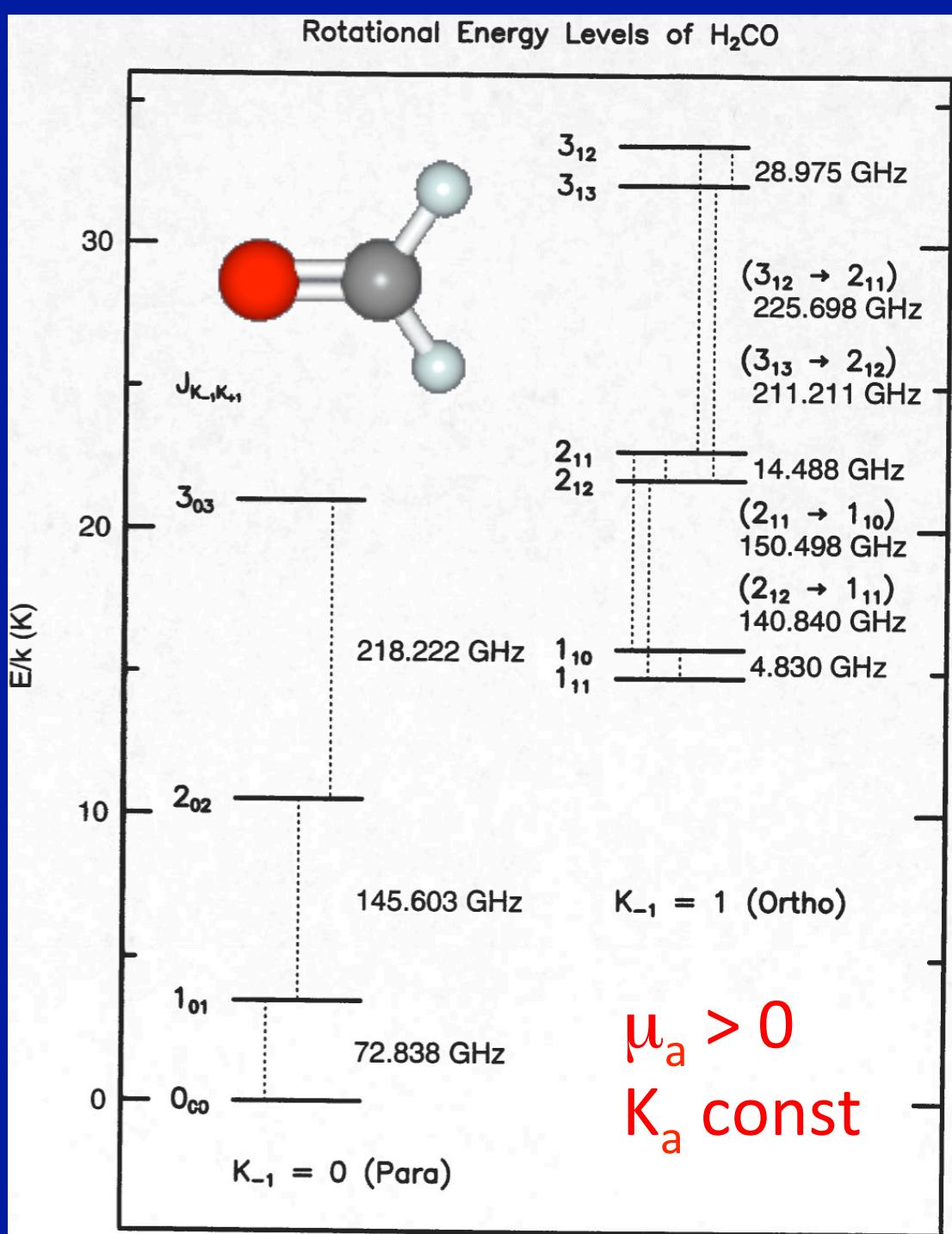
Lines Listed: 3506 Q(300.0)= 2883.014
 Freq. (GHz) < 9999 Q(225.0)= 1872.622
 Max. J: 57 Q(150.0)= 1019.971
 LOGSTR0= -20.0 Q(75.00)= 361.720
 LOGSTR1= -9.0 Q(37.50)= 128.649
 Isotope Corr.: 0. Q(18.75)= 44.681
 Egy. (cm⁻¹) > 0.0 Q(9.375)= 13.801
 μ_a = 2.331 A= 281970.58
 μ_b = B= 38833.987
 μ_c = C= 34004.244



The experimental data was reported by (1) R. Bocquet *et al.*, 1996, J. Mol. Spect. 177, 154.

The dipole moment was measured by (2) K. Kondo and T. Oka, 1960, J. Phys. Soc. Jap. 15, 307.

Frequency	Unc.	Log(Int.)	E_l (cm ⁻¹)	g_u	J_u	K_a	K_c	J_l	K_a	K_c
211211.4680	.0100	-2.3879	3	15.2369	21	-30004	303	3	1	3
218222.1920	.0100	-2.7693	3	7.2864	7	-30004	303	3	0	3
218475.6320	.0100	-3.0917	3	40.0402	7	-30004	303	3	2	2
218760.0660	.0100	-3.0906	3	40.0426	7	-30004	303	3	2	1
225697.7750	.0100	-2.3318	3	15.7202	21	-30004	303	3	1	2
281526.9290	.0100	-2.0074	3	22.2822	27	-30004	303	4	1	4
290623.4050	.0100	-2.4132	3	14.5655	9	-30004	303	4	0	4
291237.7800	.2000	-2.6044	3	47.3278	9	-30004	303	4	2	3
291380.4880	.1000	-2.4462	3	88.2382	27	-30004	303	4	3	2
291384.2640	.1000	-2.4461	3	88.2383	27	-30004	303	4	3	1
291948.0600	.2000	-2.6024	3	47.3397	9	-30004	303	4	2	2
300836.6350	.0100	-1.9524	3	23.2487	27	-30004	303	4	1	3
351768.6450	.0300	-1.7287	3	31.6729	33	-30004	303	5	1	5
362736.0480	.0300	-2.1465	3	24.2597	11	-30004	303	5	0	5
363945.8940	.0300	-2.2875	3	57.0425	11	-30004	303	5	2	4
364103.2490	.0300	-2.8594	3	155.1694	11	-30004	303	5	4	2
364103.2490	.0300	-2.8594	3	155.1694	11	-30004	303	5	4	1
364275.1410	.1000	-2.0129	3	97.9576	33	-30004	303	5	3	3
364288.8840	.1000	-2.0128	3	97.9578	33	-30004	303	5	3	2
365363.4280	.0300	-2.2842	3	57.0780	11	-30004	303	5	2	3
375893.2160	.0300	-1.6752	3	33.2835	33	-30004	303	5	1	4





$$\psi_{tot} = \psi_e \psi_v \psi_r \psi_n$$

2 H nuclei ($I = 1/2$) \Rightarrow F-D Statistics \Rightarrow Total \Rightarrow -

Electronic $^1\Sigma_g^+$ \Rightarrow +

Vibrational $v = 0$ \Rightarrow +

Nuclear \Rightarrow **3 sym. (ortho)** + OR

1 antisym. (para) -

Rotational \Rightarrow ee & eo \Rightarrow + \Rightarrow PARA

\Rightarrow oo & oe \Rightarrow - \Rightarrow ORTHO

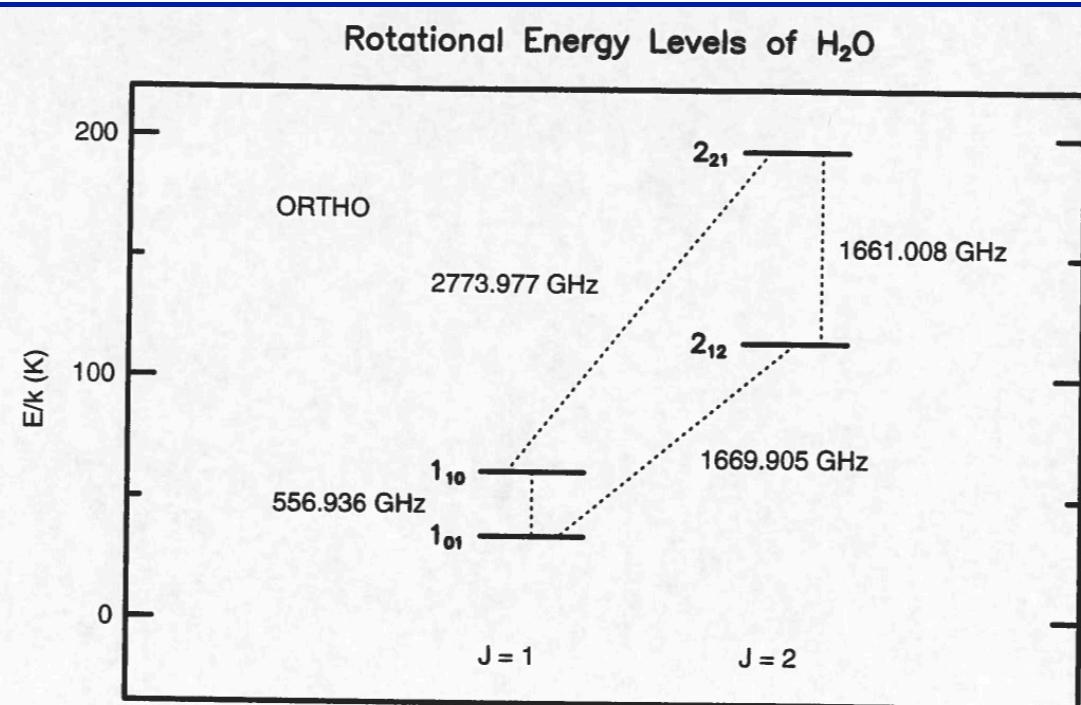
Asymmetric Top Rotation Symmetry

Table 7. Behavior of Rotational Wavefunction with π rotation about the Principle Axes

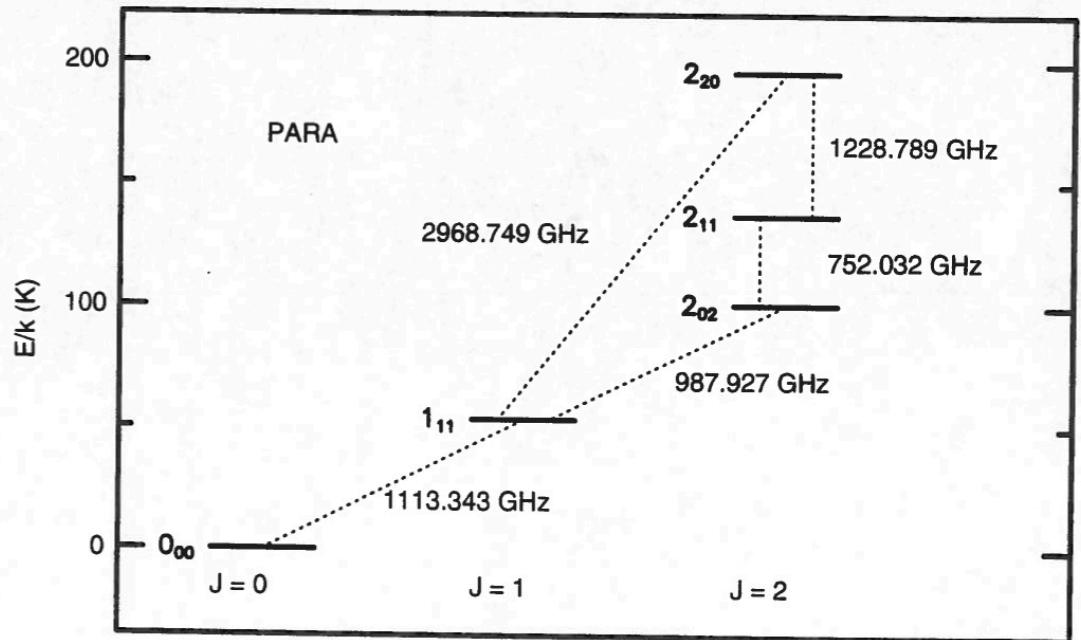
$K_{-1}K_{+1}$ ^a	$J_{K_{-1}K_{+1}}$ Symmetry ^b		
	A	B	C
ee	+	+	+
eo	+	-	-
oo	-	+	-
oe	-	-	+

^ae = even and o = odd

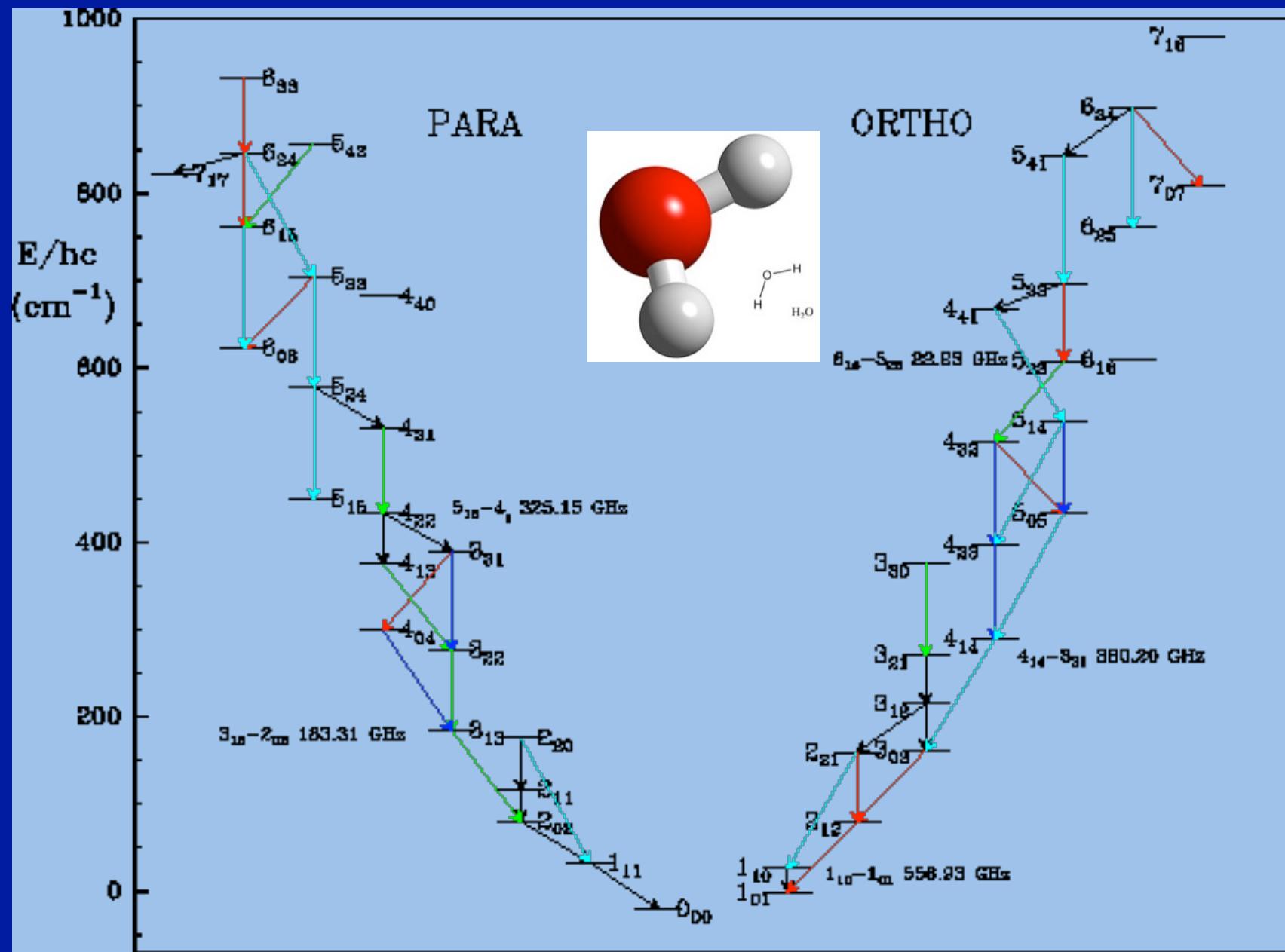
^b+ = symmetric and - = antisymmetric for rotational of π about the principle axes A, B, or C.

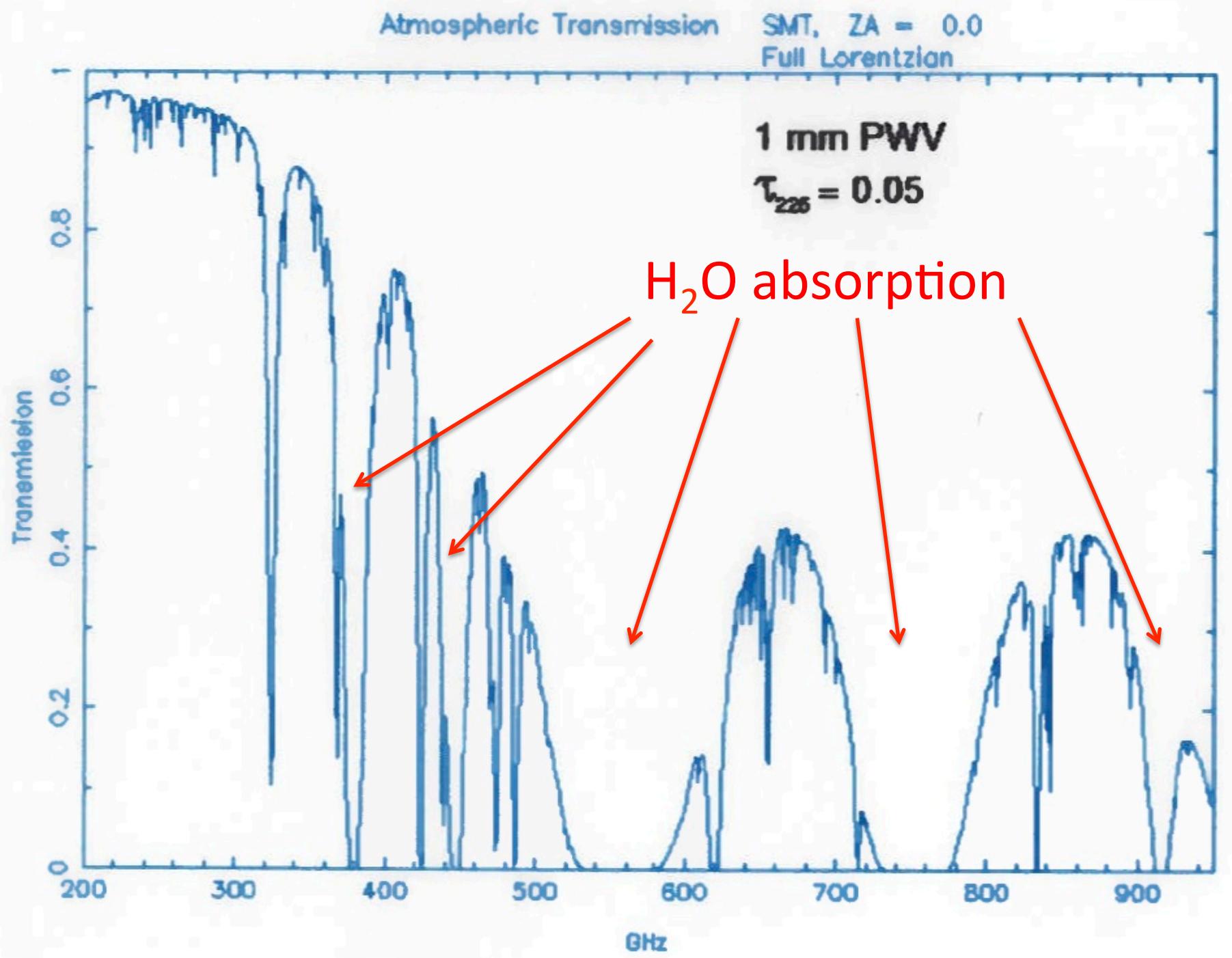


$\mu_b > 0 \longrightarrow K_a \text{ and } K_c \text{ change}$



More H₂O Energy Levels







$$\Psi_{tot} = \psi_e \ \psi_v \ \psi_r \ \psi_n$$

2 H nuclei ($I = 1/2$) \Rightarrow F-D Statistics \Rightarrow Total \Rightarrow -

Electronic $^1\Sigma_g^+$ \Rightarrow +

Vibrational $v = 0$ \Rightarrow +

Nuclear \Rightarrow **3 sym. (ortho)** + **OR**

1 antisym. (para) -

Rotational \Rightarrow **ee & oo** \Rightarrow + \Rightarrow **PARA**

\Rightarrow **eo & oe** \Rightarrow - \Rightarrow **ORTHO**

Asymmetric Top Rotation Symmetry

Table 7. Behavior of Rotational Wavefunction with π rotation about the Principle Axes

$K_{-1}K_{+1}$ ^a	$J_{K_{-1}K_{+1}}$ Symmetry ^b		
	A	B	C
ee	+	+	+
eo	+	-	-
oo	-	+	-
oe	-	-	+

^ae = even and o = odd

^b+ = symmetric and - = antisymmetric for rotational of π about the principle axes A, B, or C.



$$\Psi_{tot} = \psi_e \psi_v \psi_r \psi_n$$

2 O nuclei ($I = 0$) \Rightarrow B-E Statistics \Rightarrow Total $\Rightarrow +$

Electronic $^1\Sigma_g^+$ \Rightarrow **+**

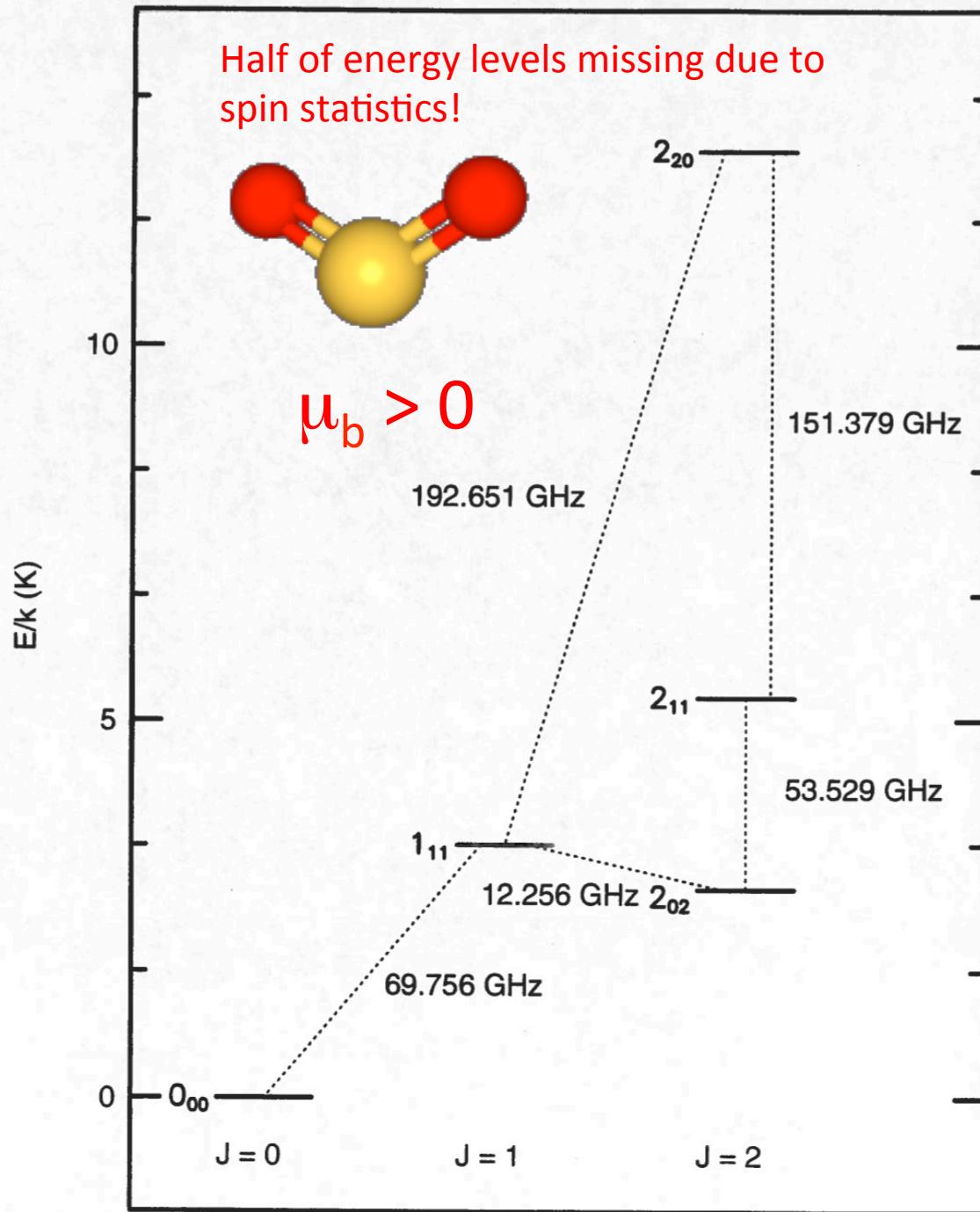
Vibrational $v = 0$ \Rightarrow **+**

Nuclear \Rightarrow **ONLY sym.** **+**

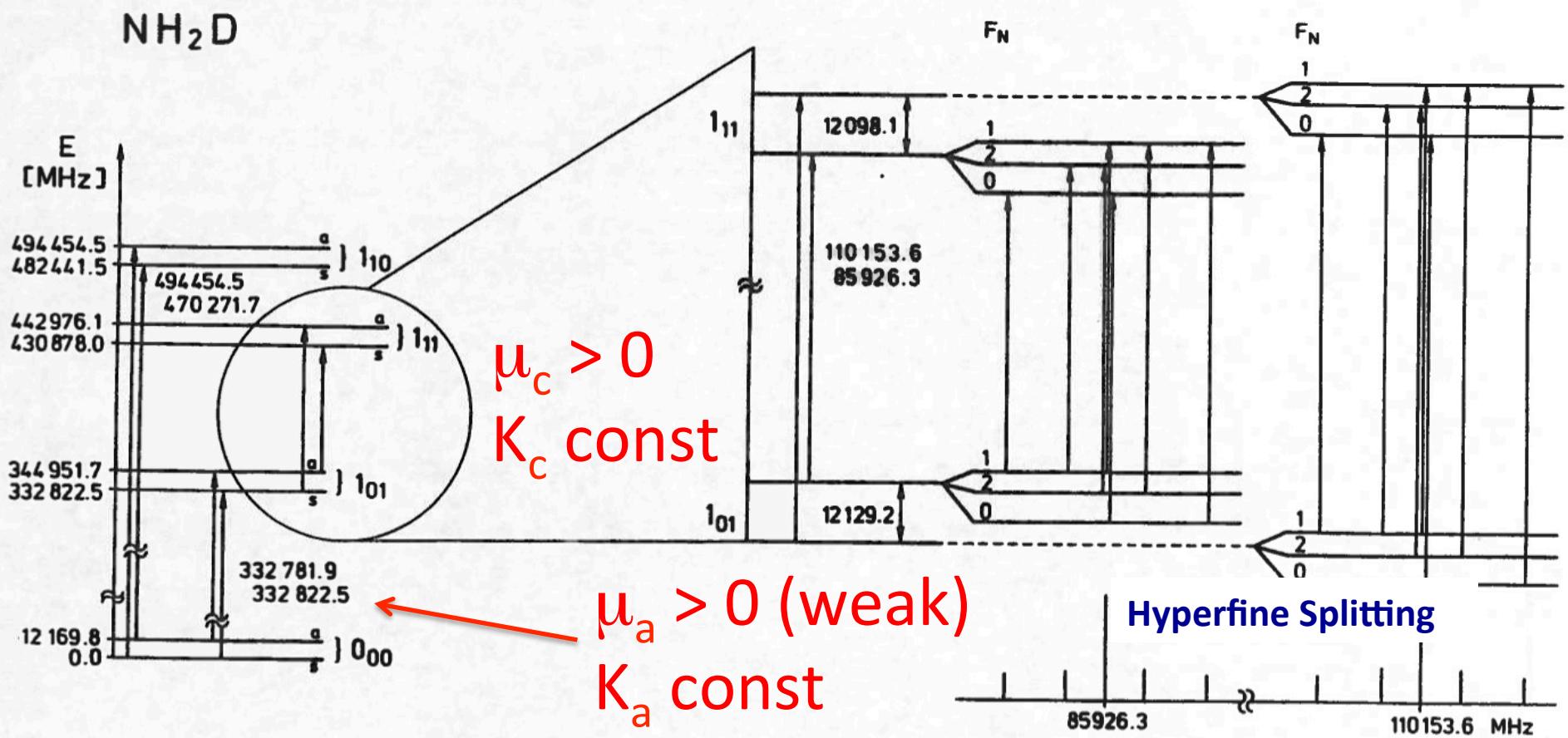
Rotational \Rightarrow **ee & oo** \Rightarrow **+** \Rightarrow **EXIST**

\Rightarrow **eo & oe** \Rightarrow **-** \Rightarrow **DON'T EXIST!**

Rotational Energy Levels of SO₂

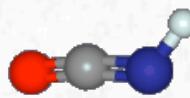


Asymmetric Top w/ Inversion



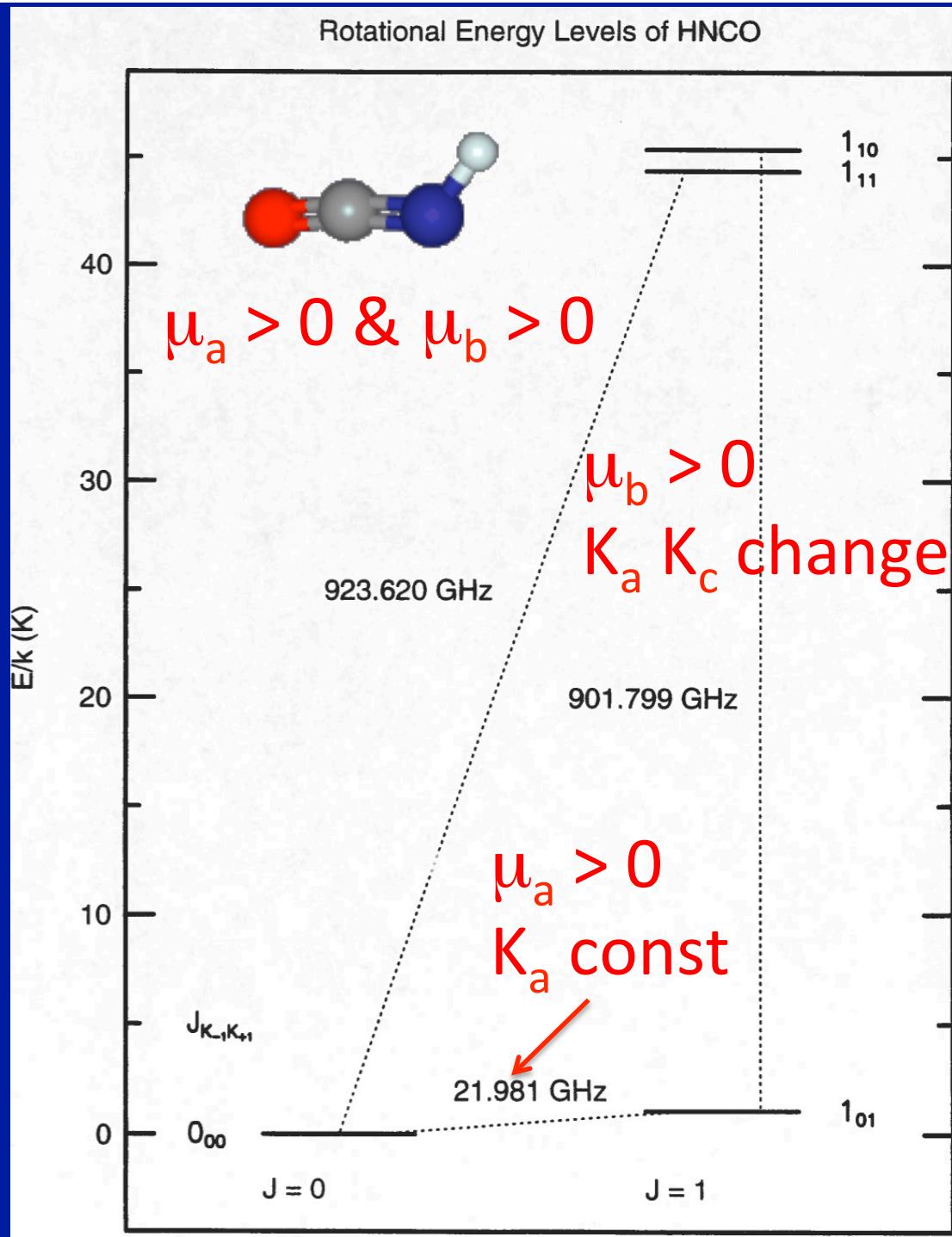
Species Tag: 43002
 Version: 1
 Date: July 1987
 Contributor: R. L. Poynter

Species Name: HNCO
 Isocyanic acid



Lines Listed:	6078	$Q(300.0) =$	7785.741
Freq. (GHz) <	2997	$Q(225.0) =$	5123.892
Max. J:	47	$Q(150.0) =$	2802.206
LOGSTR0=	-10.0	$Q(75.00) =$	992.888
LOGSTR1=	-10.0	$Q(37.50) =$	352.614
Isotope Corr.:	0.0	$Q(18.75) =$	129.479
Egy. (cm^{-1}) >	0.0	$Q(9.375) =$	56.351
$\mu_a =$	1.6020	A=	912711.435(197)
$\mu_b =$	1.3500	B=	11071.0098(9)
$\mu_c =$		C=	10910.5763(10)

Frequency	Unc.	Log(Int.)	$E_l (\text{cm}^{-1})$	g_u	J _u	K _a	K _c	F	J _l	K _a	K _c	F	
923620.0141	0.1963	-2.9079 3	0.0000	3	43002	304	1	1	1	1	0	0	0 1
923620.2329	0.1962	-2.6861 3	0.0000	5	43002	304	1	1	1	2	0	0	0 1
923620.5611	0.1969	-3.3850 3	0.0000	1	43002	304	1	1	1	0	0	0	1
901798.2443	0.1954	-3.3554 3	0.7332	3	43002	304	1	1	0	1	1	0	1 1
901798.6226	0.1951	-3.1336 3	0.7332	5	43002	304	1	1	0	2	1	0	1 1
901798.8414	0.1952	-3.1336 3	0.7332	3	43002	304	1	1	0	1	1	0	1 2
901799.1901	0.1955	-3.2305 3	0.7332	1	43002	304	1	1	0	0	1	0	1 1
901799.2197	0.1951	-2.6564 3	0.7332	5	43002	304	1	1	0	2	1	0	1 2
901799.7371	0.1955	-3.2305 3	0.7332	3	43002	304	1	1	0	1	1	0	1 0



Ethyl Cyanide – $\text{CH}_3\text{CH}_2\text{CN}$ – “Weed”

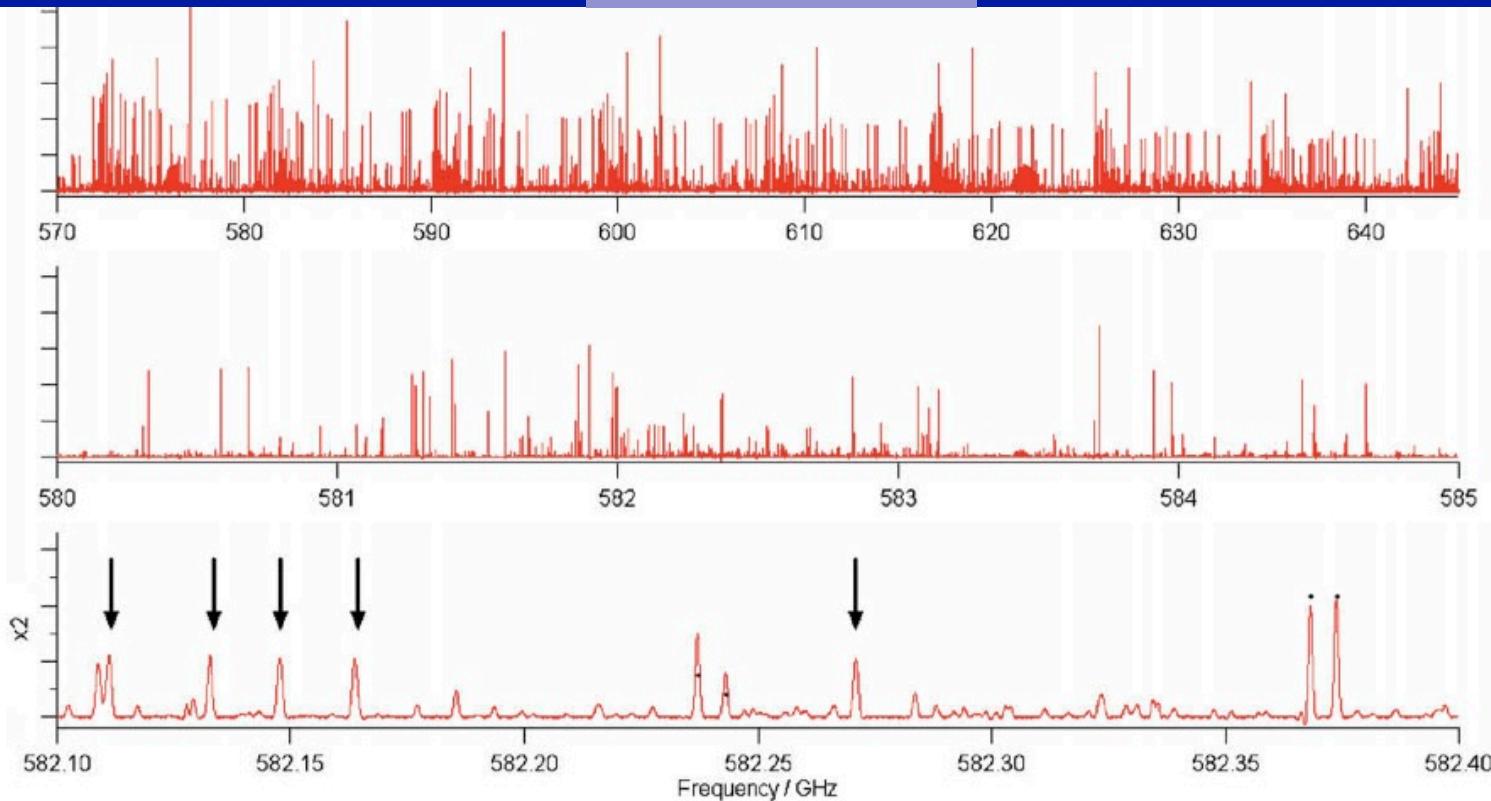
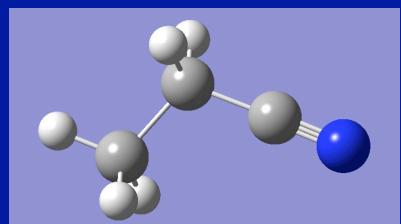


Fig. 19. Spectrum of ethyl cyanide at 300 K, shown as a series of spectral expansions. In the lower panel (expanded 2× vertically) a comparison is made with a catalog based on a quantum mechanical model (the dots indicate frequency and intensity of the catalog lines). The arrows show lines that are not in the catalog that are significantly larger than other lines that are in the catalog.

De Lucia 2010, Journal of Molecular Spectroscopy 261, 1

Vibrational Bands

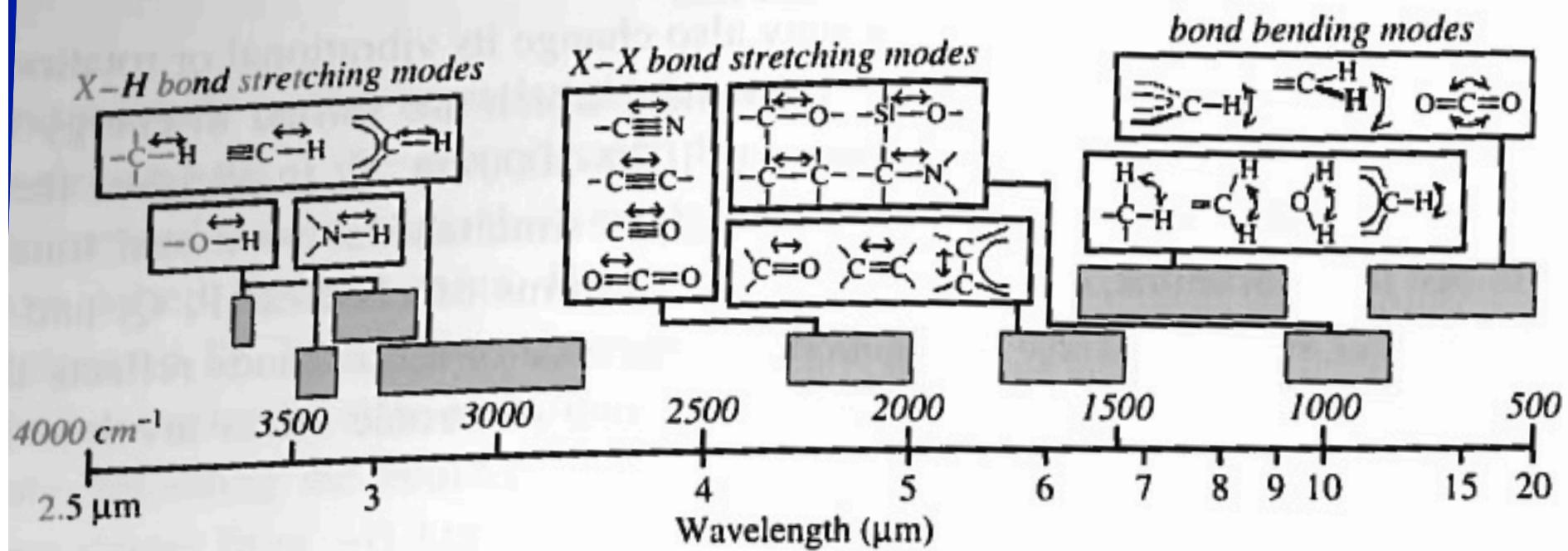


Figure 2.4 Summary of the vibrational frequencies of various molecular groups. The filled boxes indicate the range over which specific molecular groups absorb. The vibrations of these groups are schematically indicated in the linked boxes. Figure kindly provided by D. Hudgins.

Ro-vibrational transitions : CO

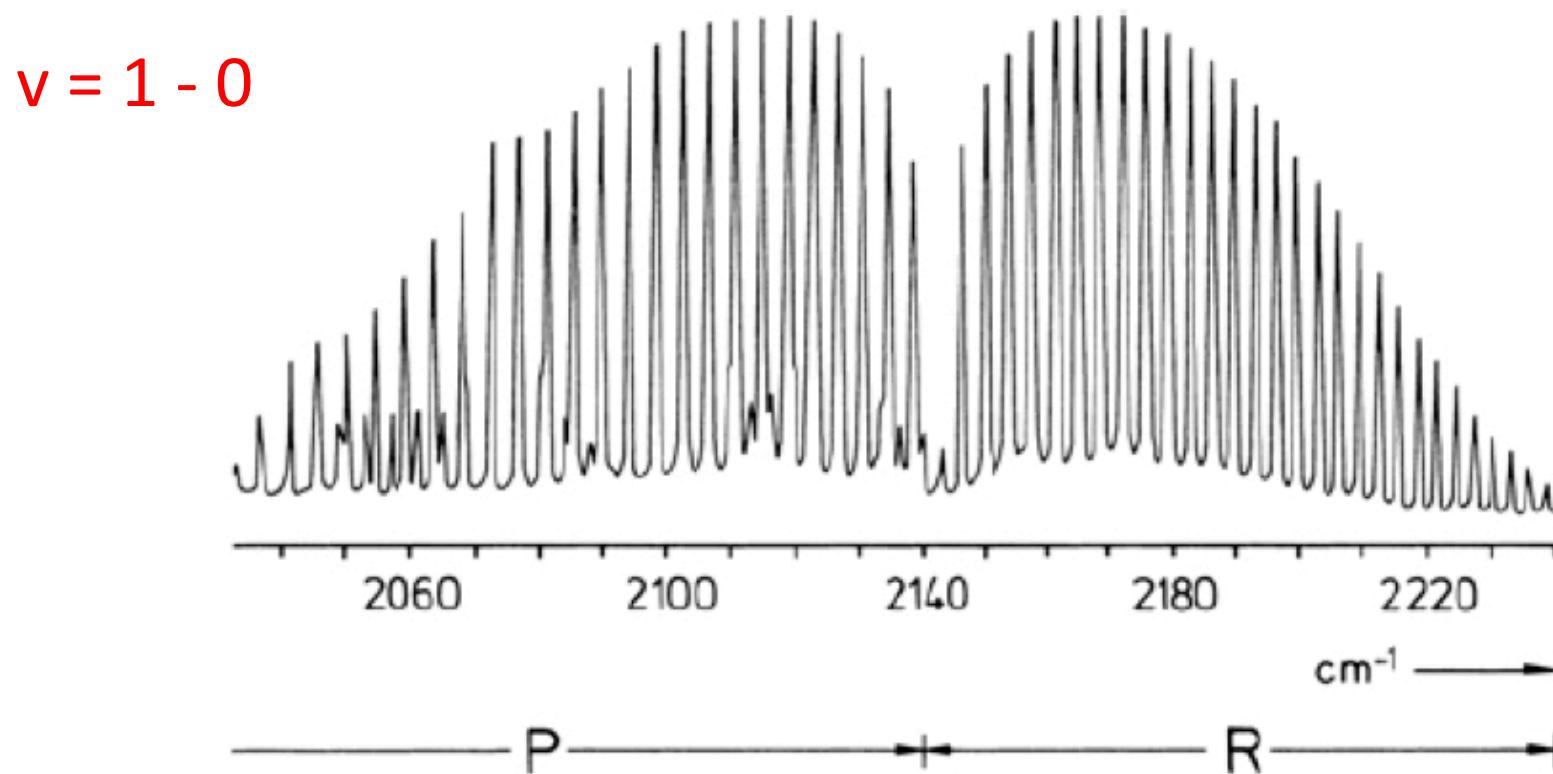
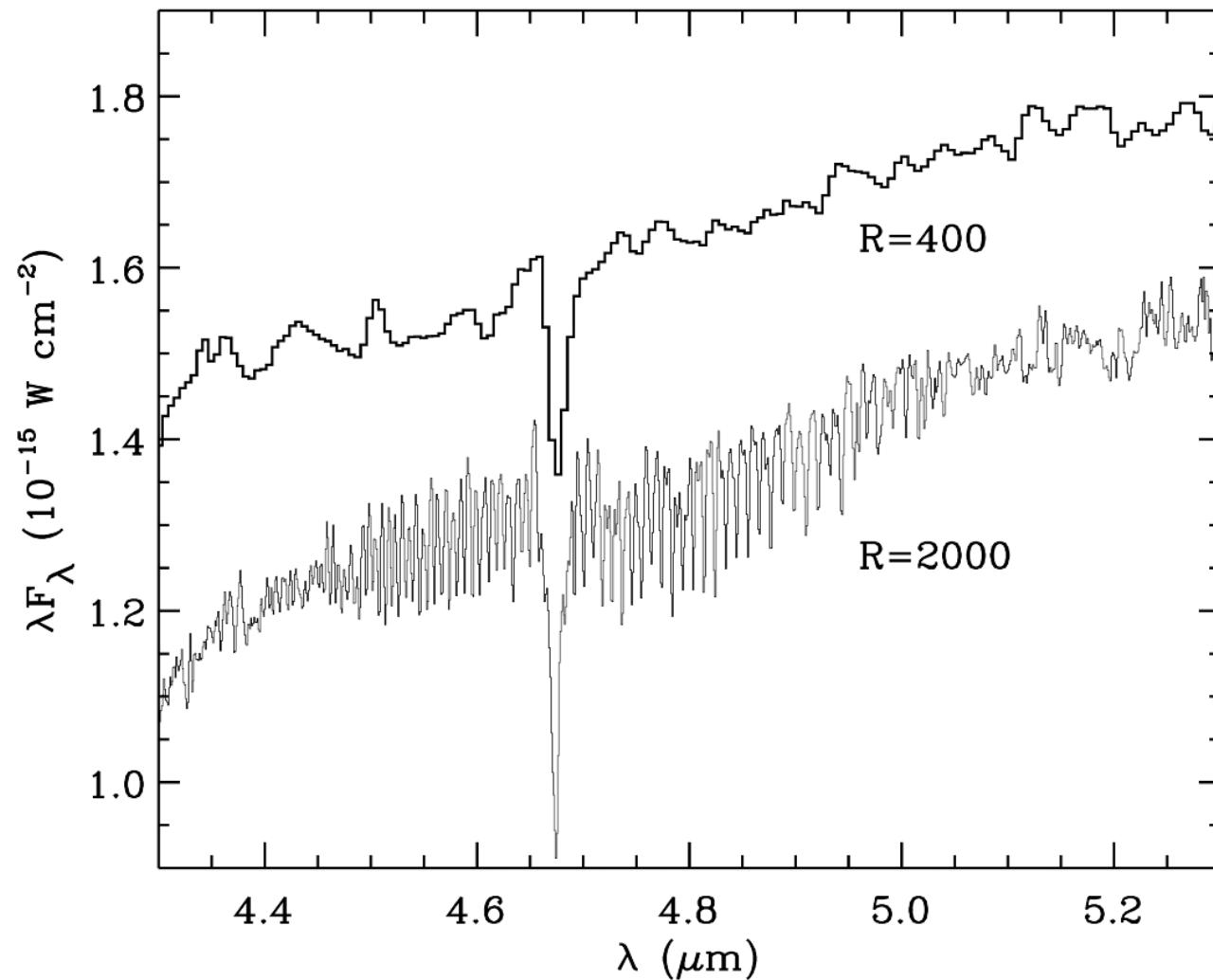


Figure 3.15: Rotational-vibrational spectrum of the CO molecule due to the fundamental vibrational transition, measured at high spectral resolution. Left and right of the center (2143.28 cm^{-1}) are the P and R branches. From Haken & Wolf (2006).

Elias 29 CO ice + gas



Boogert 1999

Ro-vibrational transitions : H₂

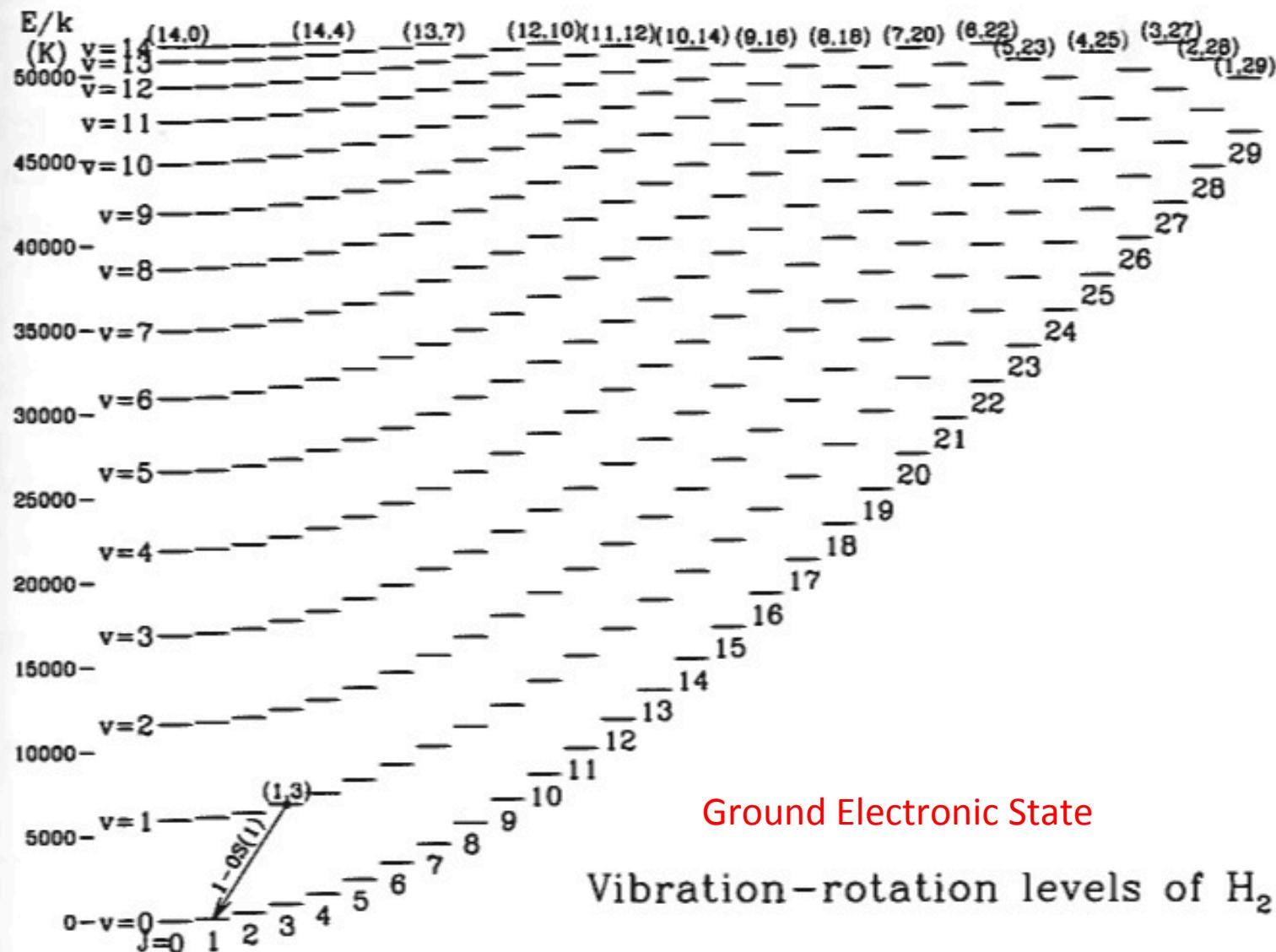
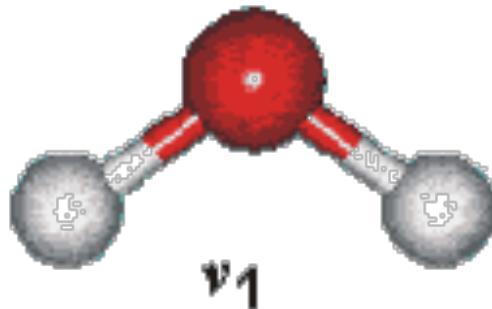


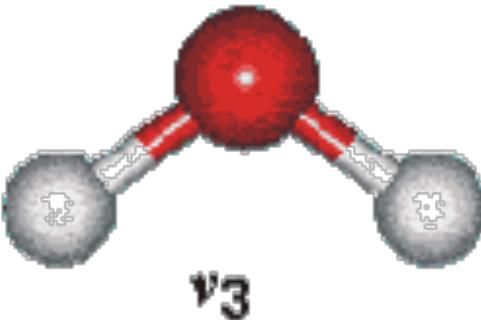
Figure 5.2 Vibration-rotation energy levels of the ground electronic state of H₂ with

Example – H₂O, CO₂, CO



symmetric stretch

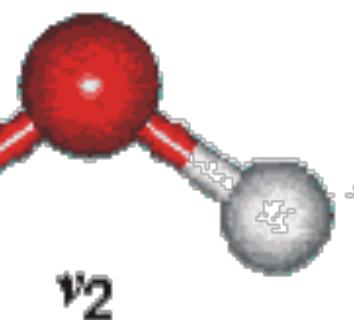
3657 cm⁻¹
2.73 μm



asymmetric stretch

H₂O

3756 cm⁻¹
2.65 μm



bend

1595 cm⁻¹
6.27 μm

CO₂

x
x

2347 cm⁻¹
4.26 μm

667 cm⁻¹
15 μm

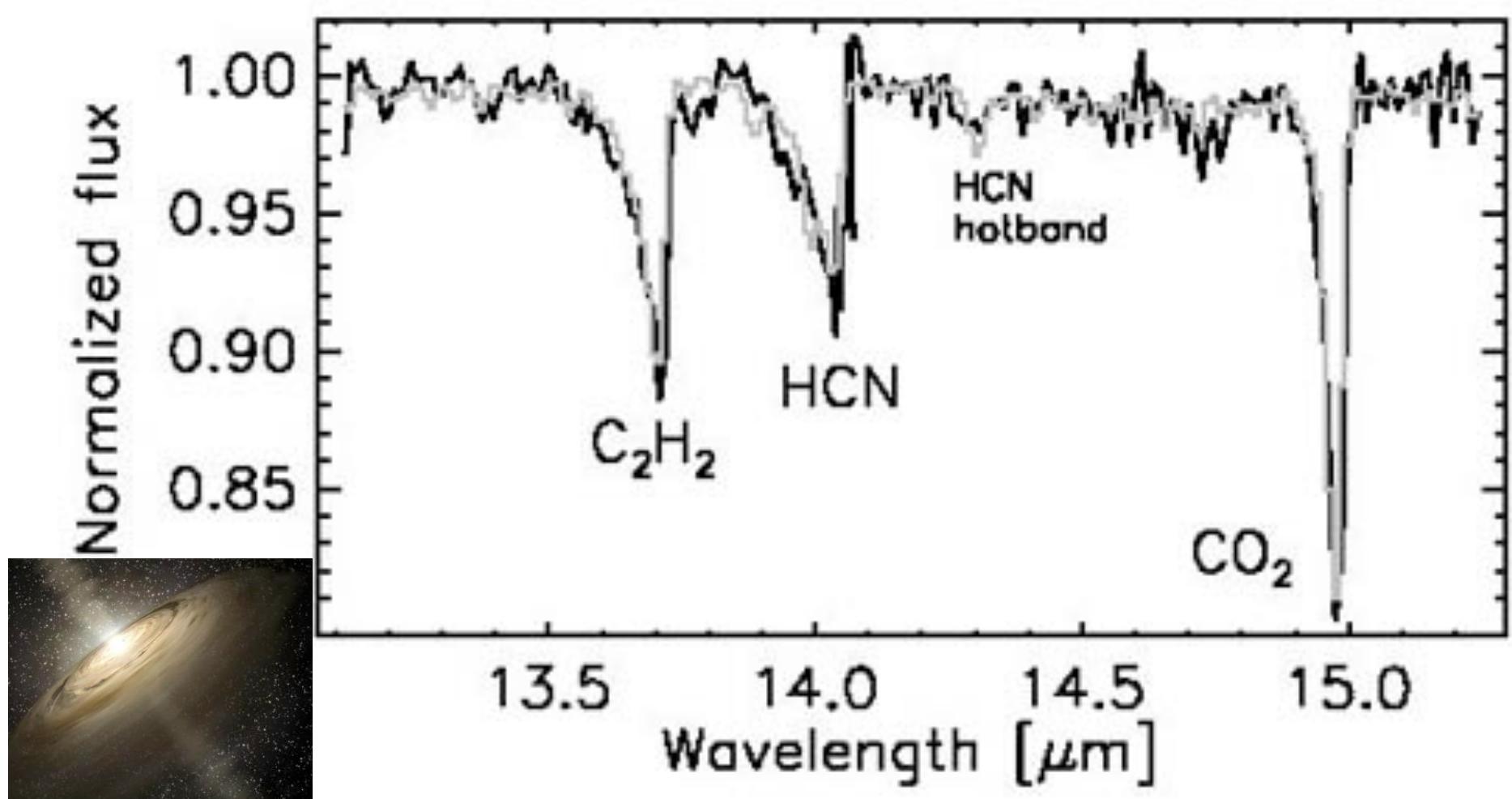
CO

2143 cm⁻¹
4.67 μm

x
x

x
x

IRS 46 Spectrum



Fazio Spitzer IRS GTO

HCO^+ vibrational states ($\nu_1 \nu_2 \nu_3$)

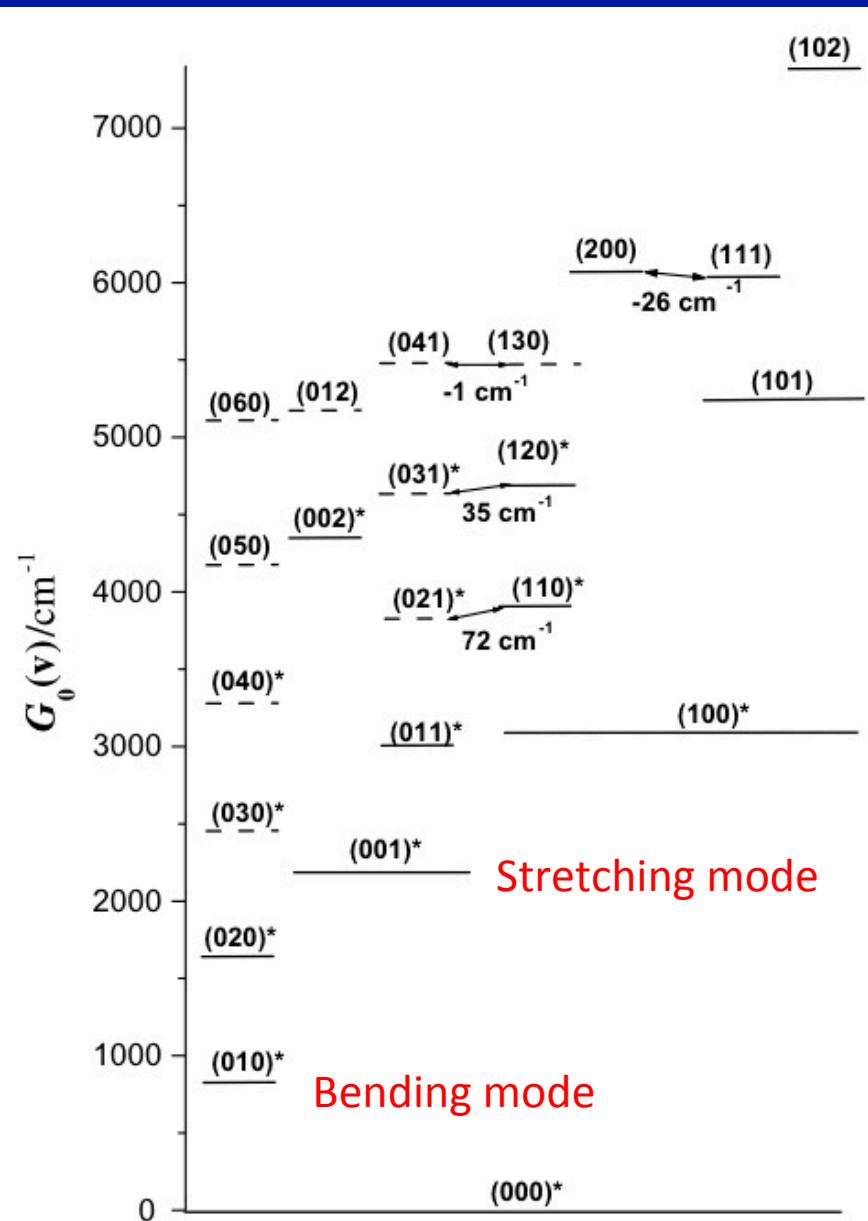
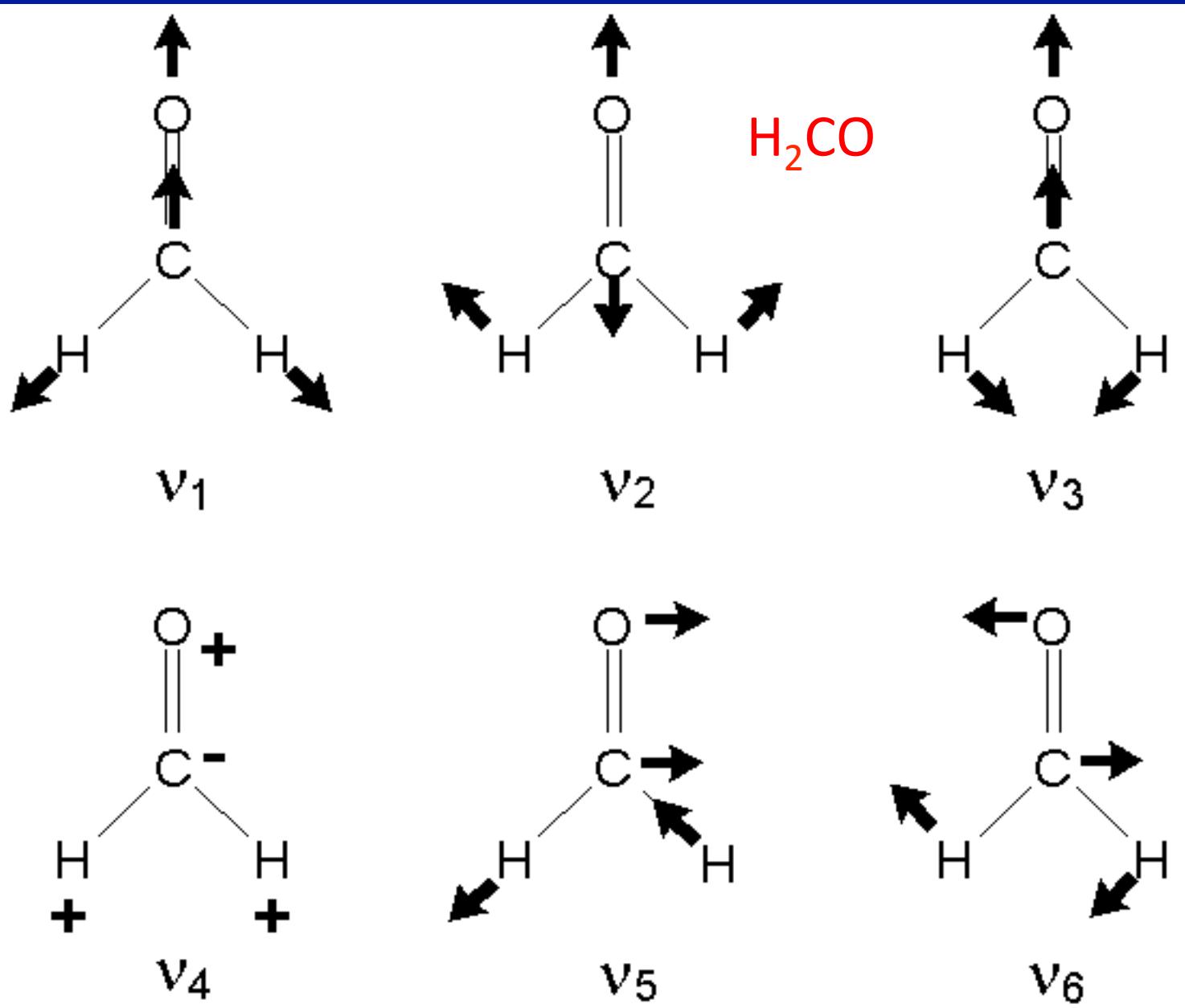


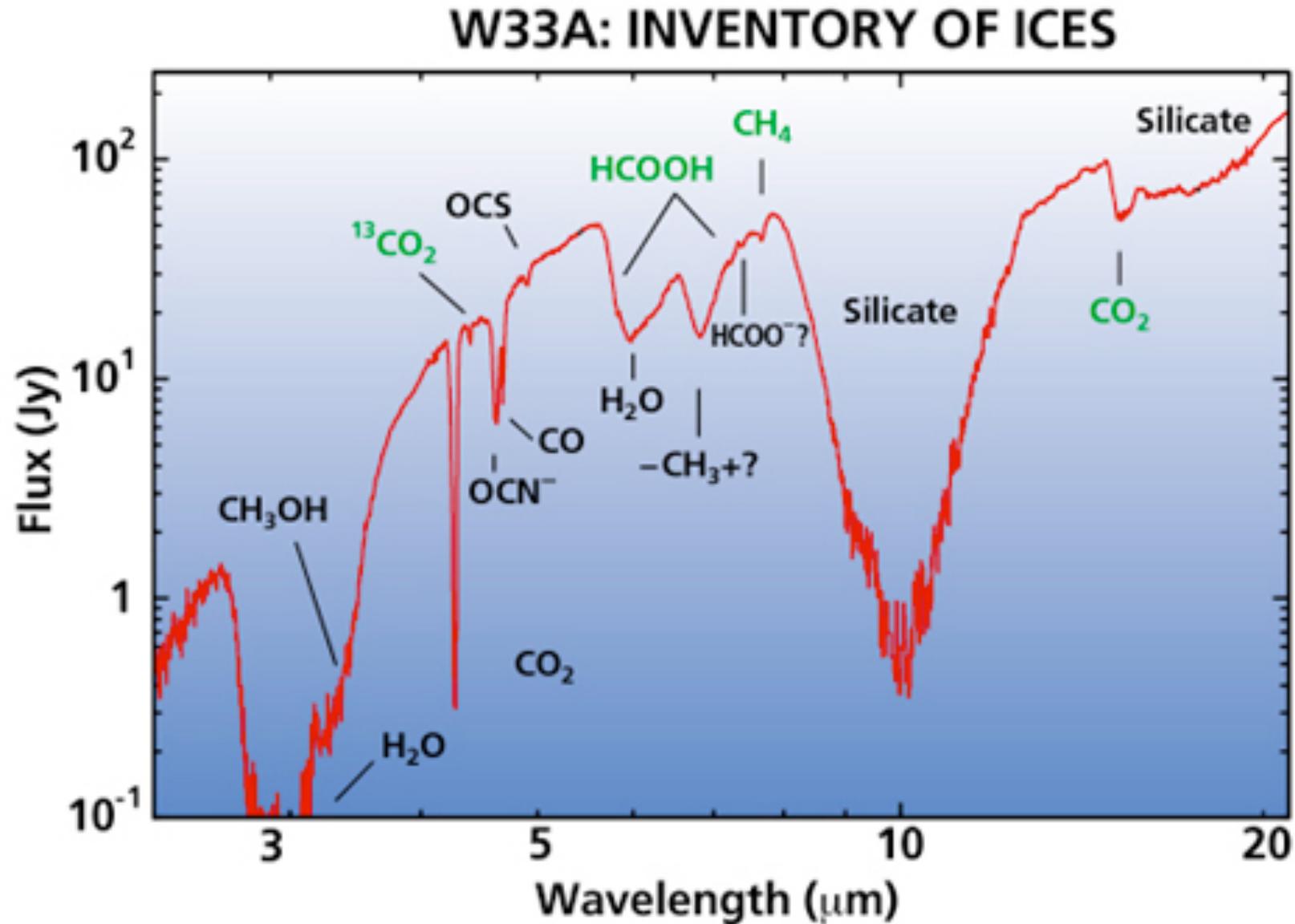
fig. 1. The low-lying vibrational states of HCO^+ . The vertical axis

Hirano et al. 2008 JMS

There are $3N_{\text{atoms}} - 6$ vibrational modes

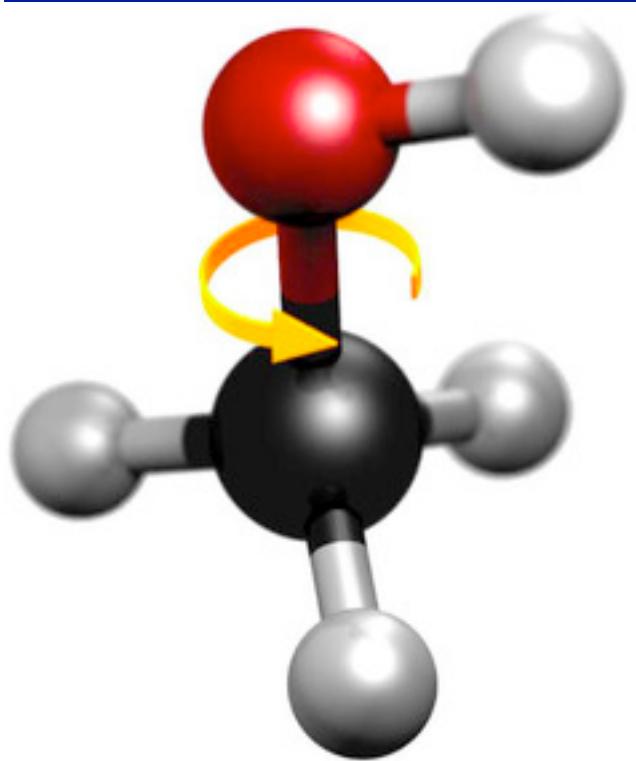


Solid State Vibrational Features



Courtesy van Dischoeck from Gibb et al. 1998

Torsion (Internal Rotation)



CH₃OH (Methanol)

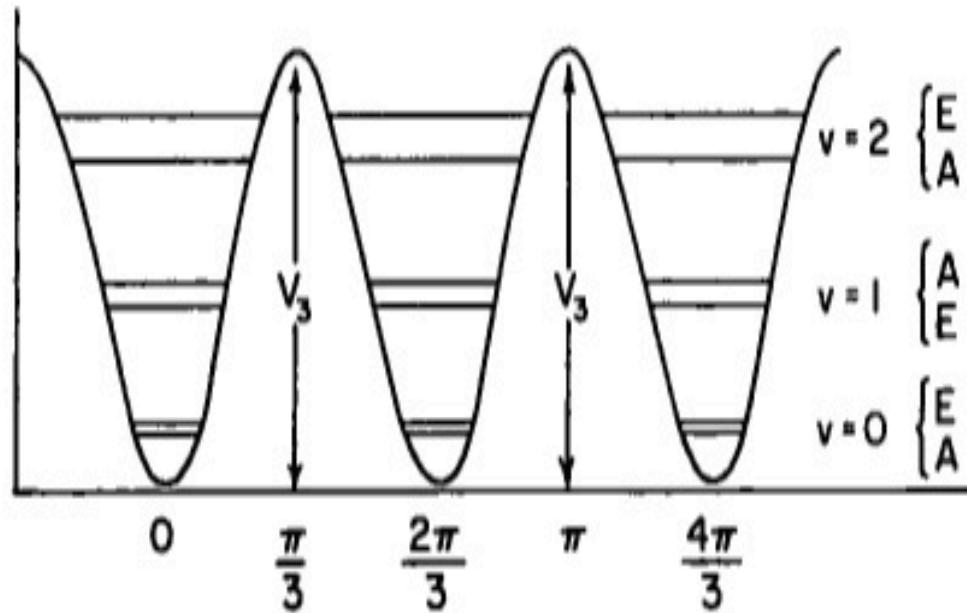
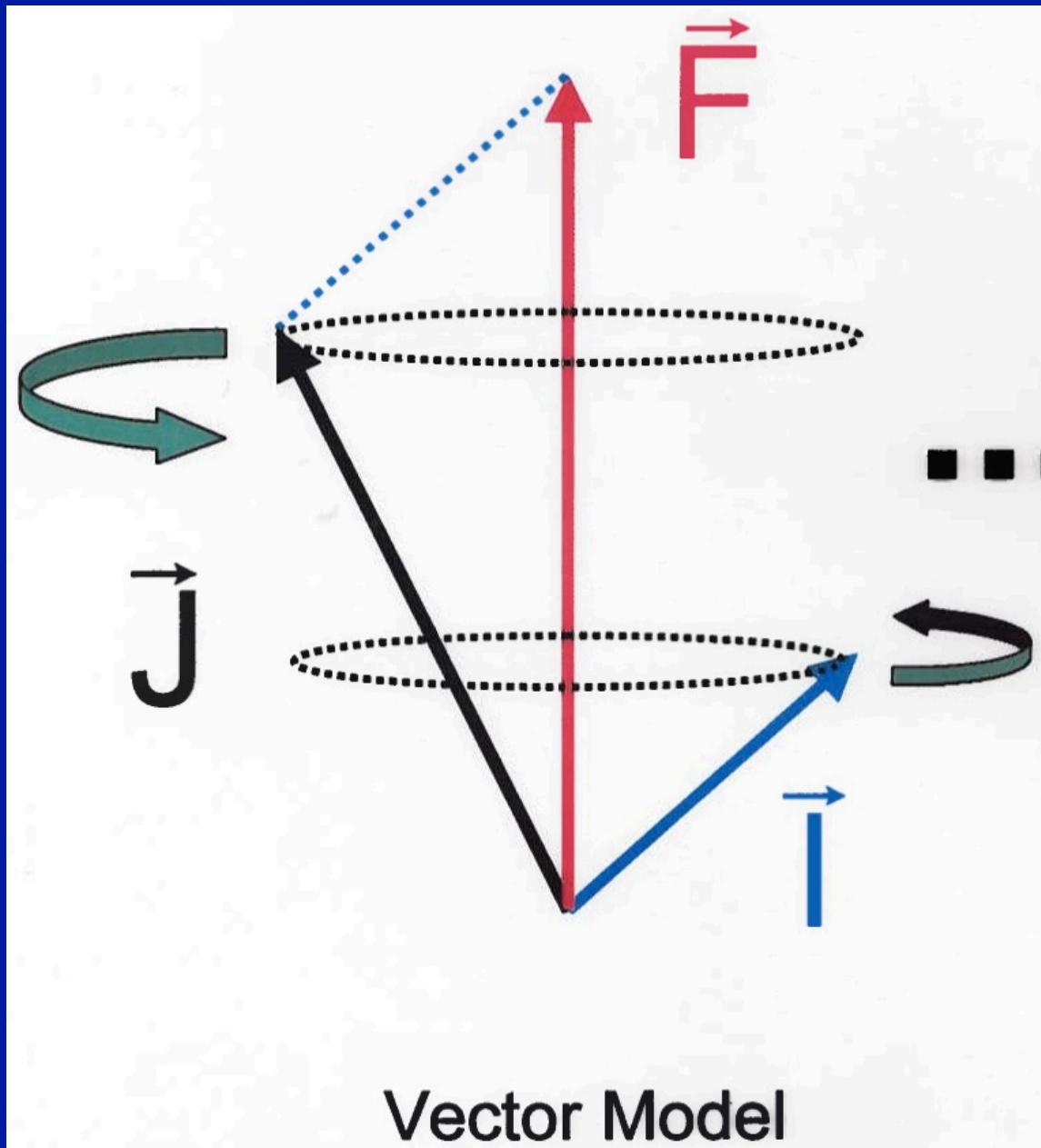


Fig. 12.3 Schematic representation of the potential function and torsional energy levels. A simple cosine potential is depicted with three identical minima and maxima. Each torsional energy level is labeled by the torsional quantum number v . The torsional sublevels are denoted by their symmetry A or E under the C_3 group.

Nuclear Spin

<i>Atomic Number</i>	<i>Element</i>	<i>Symbol</i>	<i>Mass Number</i>	<i>Mass (amu)</i>	<i>Relative Abundance (%)</i>	<i>Spin</i>
1	Hydrogen	H	1	1.00782519	99.9850	$\frac{1}{2}$
			2	2.0141022	0.01492	1
2	Helium	He	3	3.0160297	1.37×10^{-4}	$\frac{1}{2}$
			4	4.0026031	99.999863	0
3	Lithium	Li	6	6.015125	7.42	1
			7	7.016004	92.58	$\frac{3}{2}$
4	Beryllium	Be	9	9.012186	100	$\frac{3}{2}$
5	Boron	B	10	10.0129388	19.61	3
			11	11.0093053	80.39	$\frac{1}{2}$
6	Carbon	C	12	12.0000000	98.893	0
			13	13.0033544	1.107	$\frac{1}{2}$
7	Nitrogen	N	14	14.0030744	99.6337	1
			15	15.0001077	0.3663	$\frac{1}{2}$
8	Oxygen	O	16	15.9949150	99.759	0
			17	16.999133	0.0374	$\frac{5}{2}$
9	Fluorine	F	18	17.9991600	0.2039	0
			19	18.9984046	100	$\frac{1}{2}$

Hyperfine Splitting



HI 21cm Spin Flip Transition

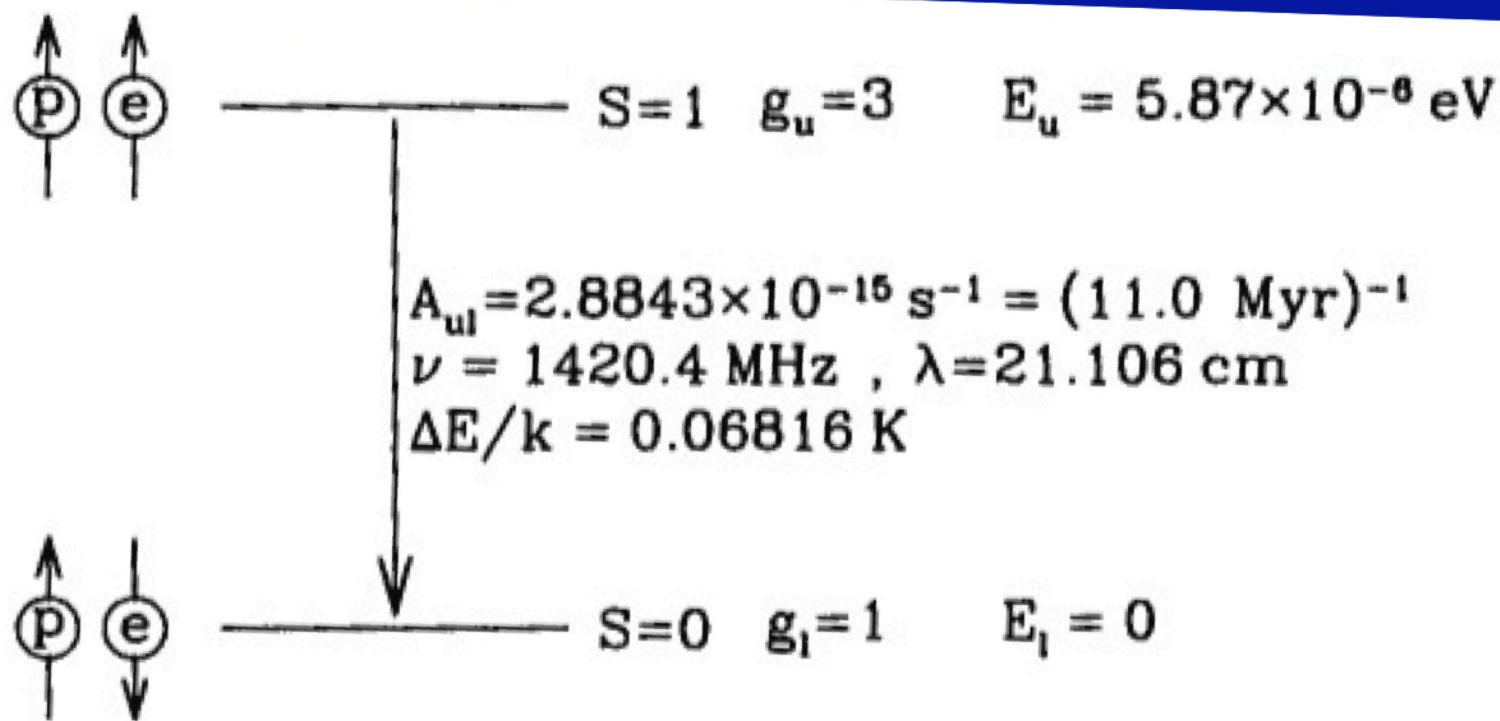


Figure 8.1 Hyperfine splitting of the $1s$ ground state of atomic H (Gould 1994).



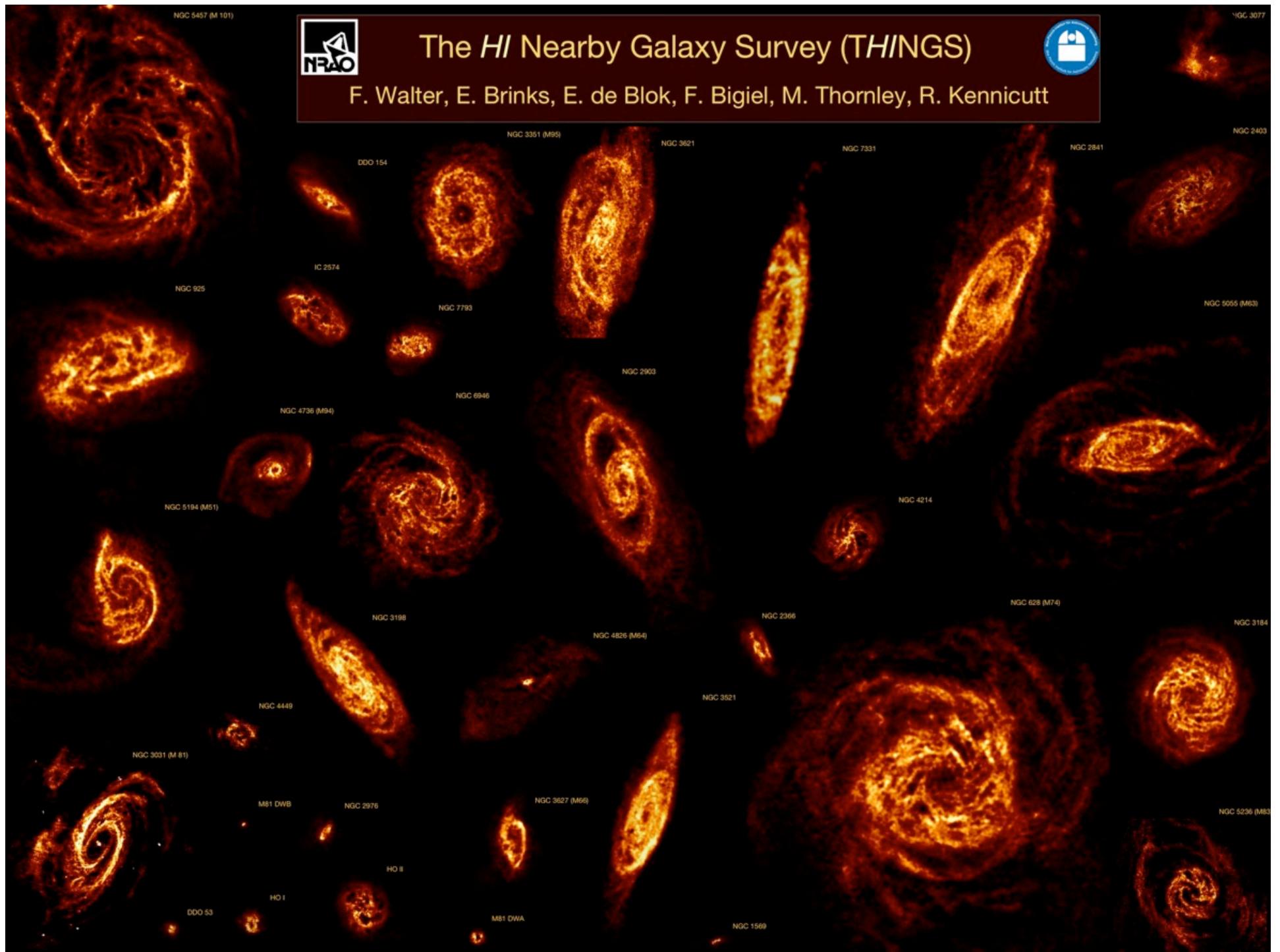
NGC 5457 (M 101)

The HI Nearby Galaxy Survey (THINGS)

F. Walter, E. Brinks, E. de Blok, F. Bigiel, M. Thornley, R. Kennicutt

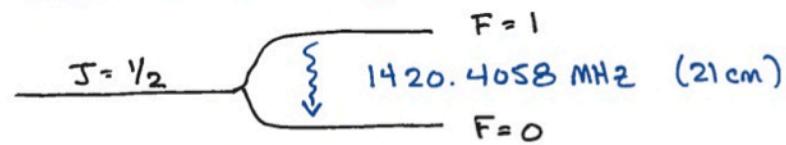


NGC 3077

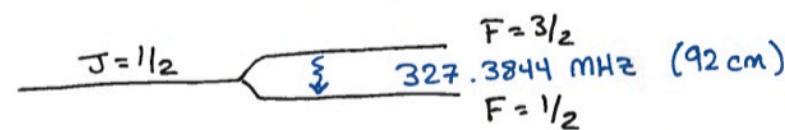


Atomic Hyperfine Transitions

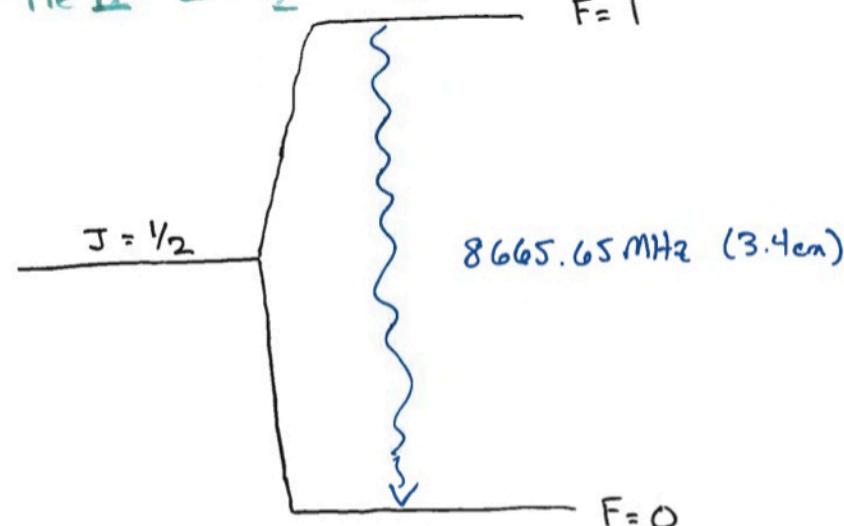
^1HI $I = \frac{1}{2}$ $^2S_{\frac{1}{2}}$



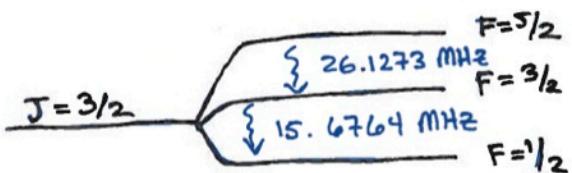
^2DI $I = 1$ $^2S_{\frac{1}{2}}$



$^3\text{He II}$ $I = \frac{1}{2}$ $^2S_{\frac{1}{2}}$

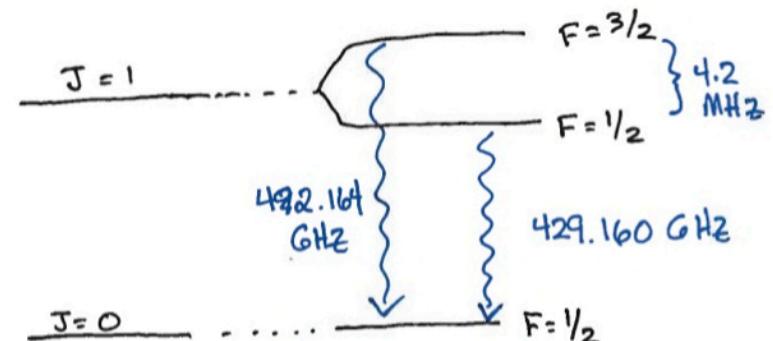
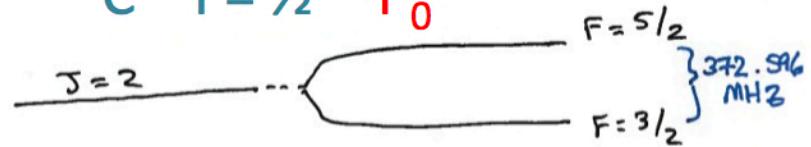


^{14}NI $I = 1$ $^4S_{\frac{3}{2}}$



Example of
Hyperfine splitting of
fine structure levels:

^{13}C $I = \frac{1}{2}$ 3P_0



OBSERVATIONS OF THE 327 MHz DEUTERIUM HYPERFINE TRANSITION

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Received 2006 September 8; accepted 2006 December 14

ABSTRACT

We report measurements of the 327 MHz line of deuterium for regions in the Galactic plane at 171° , 183° , and 195° longitude using an array of 24 stations of fixed phased-antenna elements. The anticenter region was observed using simultaneous multiple beams at each station over a period of just over 2 years from 2004 June to 2006 July. The average deuterium-to-hydrogen (D/H) ratio in the Galactic anticenter region derived from these observations is 21 ± 7 parts per million. The error is $\pm 3\sigma$ and includes the model-dependency error in conversion of the line amplitudes to the D/H ratio.

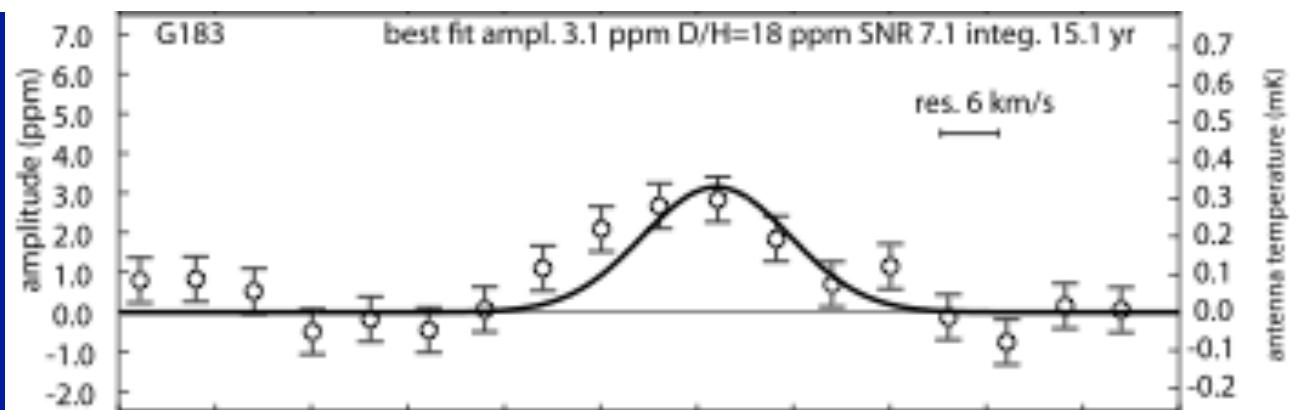


Table 2. Properties of Astrophysically Important Nuclei and Hyperfine Coupling Constants of Astrophysically Important Molecules

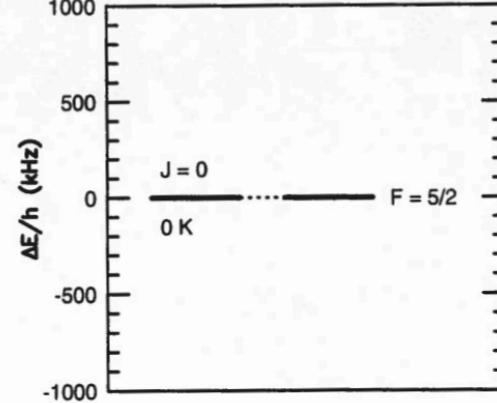
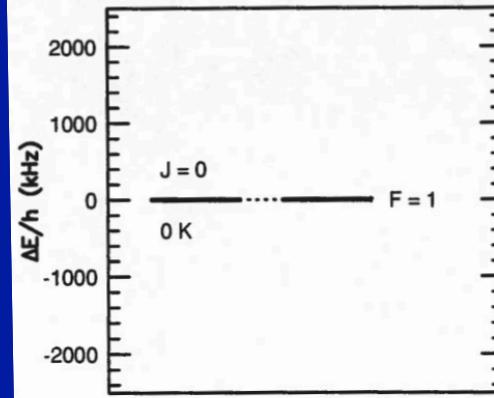
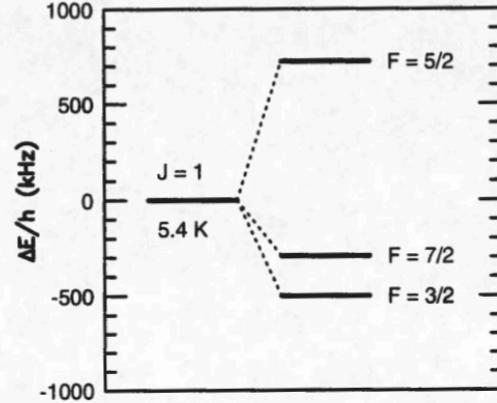
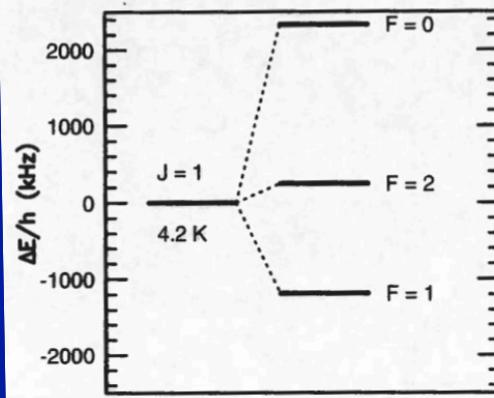
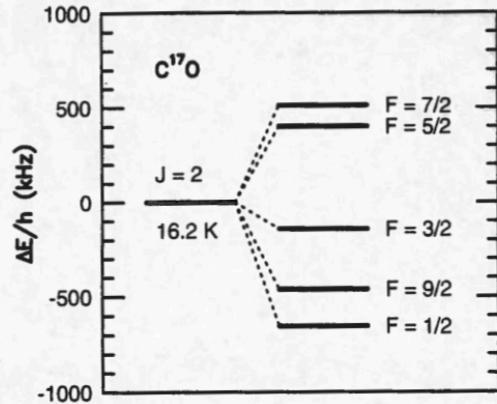
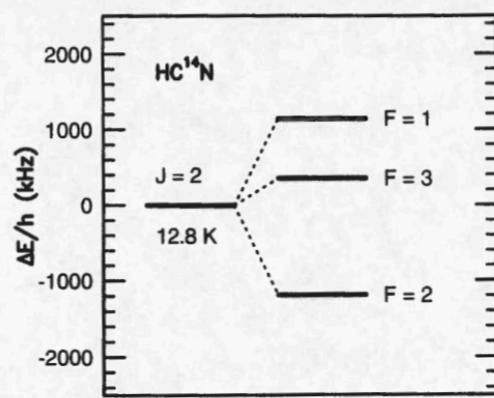
Isotope	Spin I	Magnetic Moment ^a	Quadrupole Moment ^b	Molecule	eQq (MHz)	C _I (kHz)	Ref
¹ H	$\frac{1}{2}$	+2.79278	...				
² D	1	+0.85743	+0.0028	DCN	+0.1944	-0.6	1
¹² C	0				
¹³ C	$\frac{1}{2}$	+0.7024	...				
¹⁴ N	1	+0.4036	+0.01				
				NH ₃	-4.0842		1
				HCN	-4.7091	+10.4	1
				HC ₃ N	-4.28		1
				CH ₃ CN	-4.2244		1
¹⁵ N	$\frac{1}{2}$	-0.2831	...				
¹⁶ O	0				
¹⁷ O	$\frac{5}{2}$	-1.8937	-0.026				
				C ¹⁷ O	+4.337	-30.4	2
				HC ¹⁷ O ⁺	+4.595	-20	3
¹⁸ O	0				
²⁸ Si	0				
³² S	0				
³³ S	$\frac{3}{2}$	+0.6434	-0.055				
				C ³³ S	+12.83		1
³⁴ S	(0)				

^aMagnetic Moment in nuclear magnetons. $1\mu_B = 9.274 \times 10^{-21} \text{ erg}\cdot\text{gauss}^{-1}$.

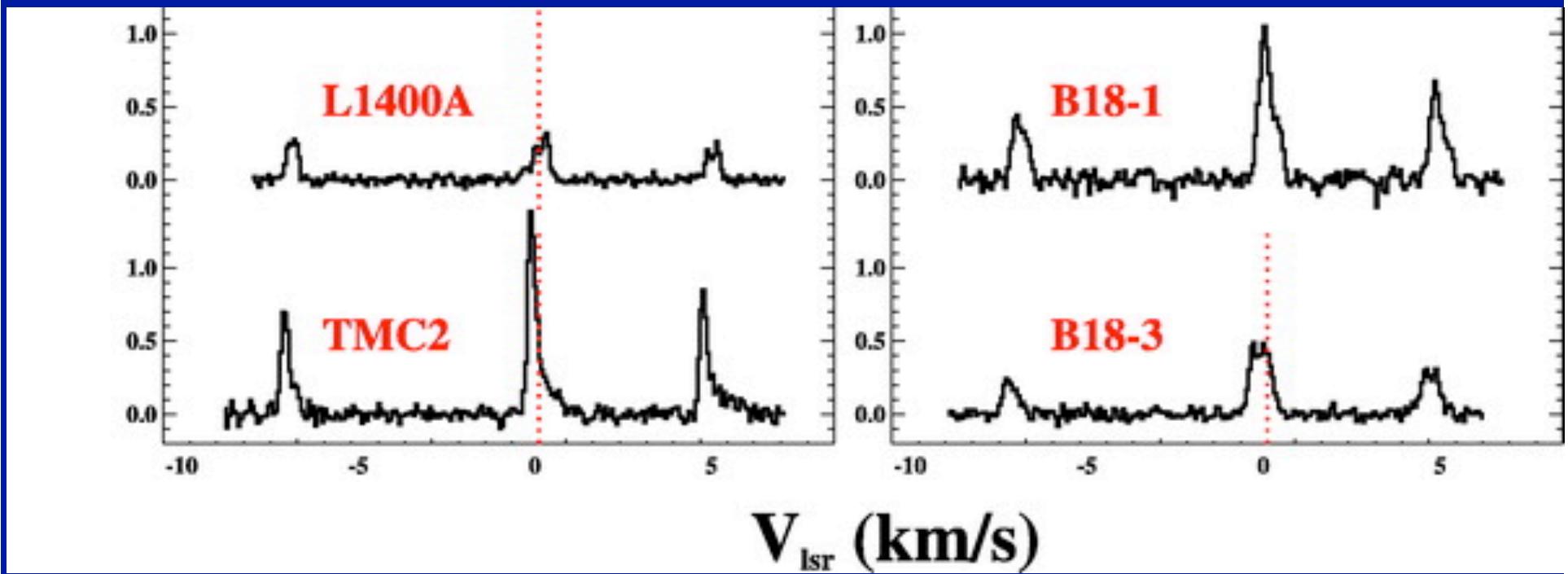
^bQuadrupole Moment in barns. $1 \text{ barn} = 10^{-24} \text{ cm}^2$.

References. — 1. Gordy & Cook 1984; 2. Frerking & Langer 1981; 3. Dore et al. 2001;

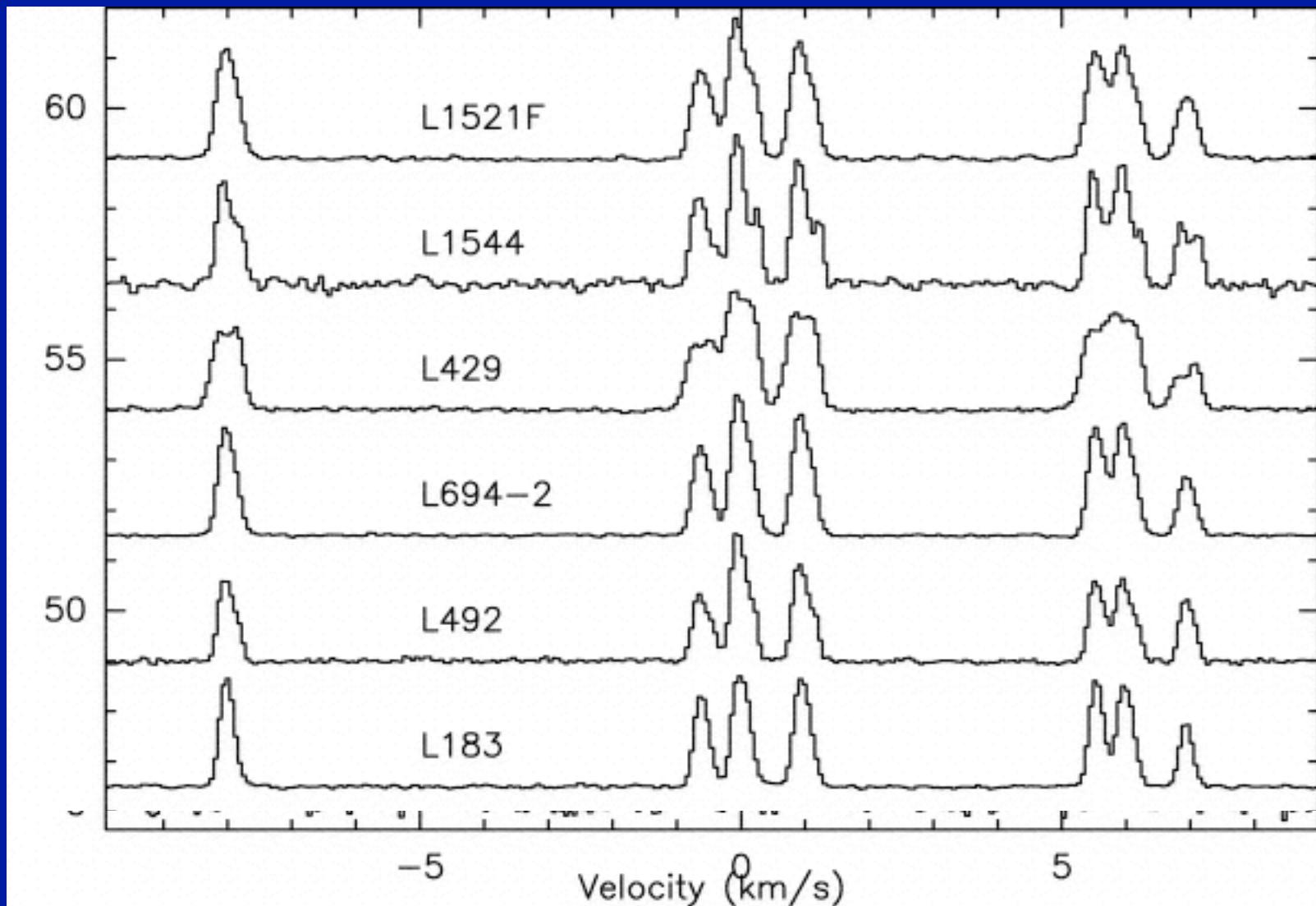
HC¹⁴N and C¹⁷O Hyperfine Energy Levels



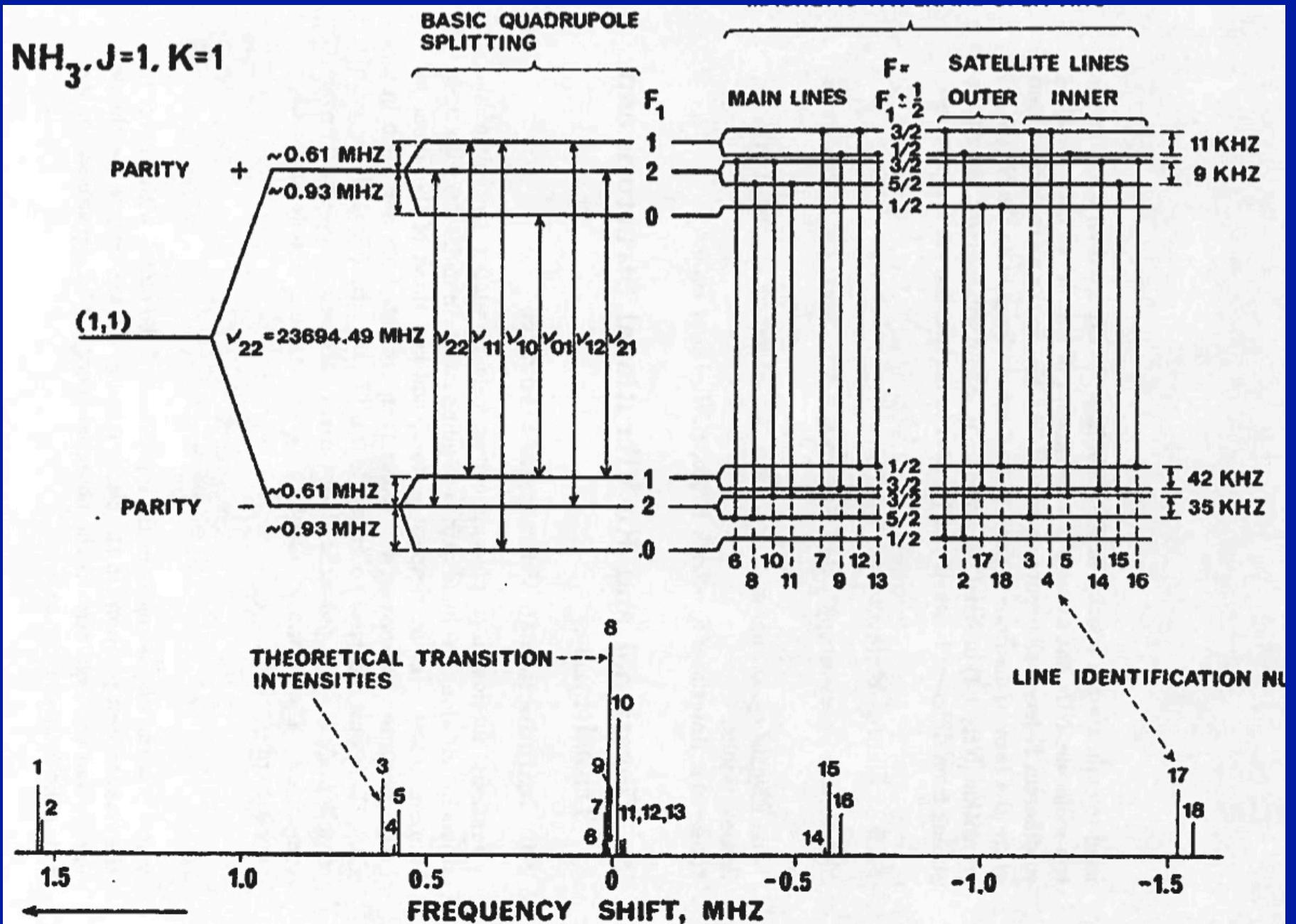
HCN 1-0 Spectra – One Coupling Nuclei



N_2H^+ 1-0 Spectra – 2 Coupling Nuclei



Ammonia Hyperfine Structure



Ammonia Hyperfine structure

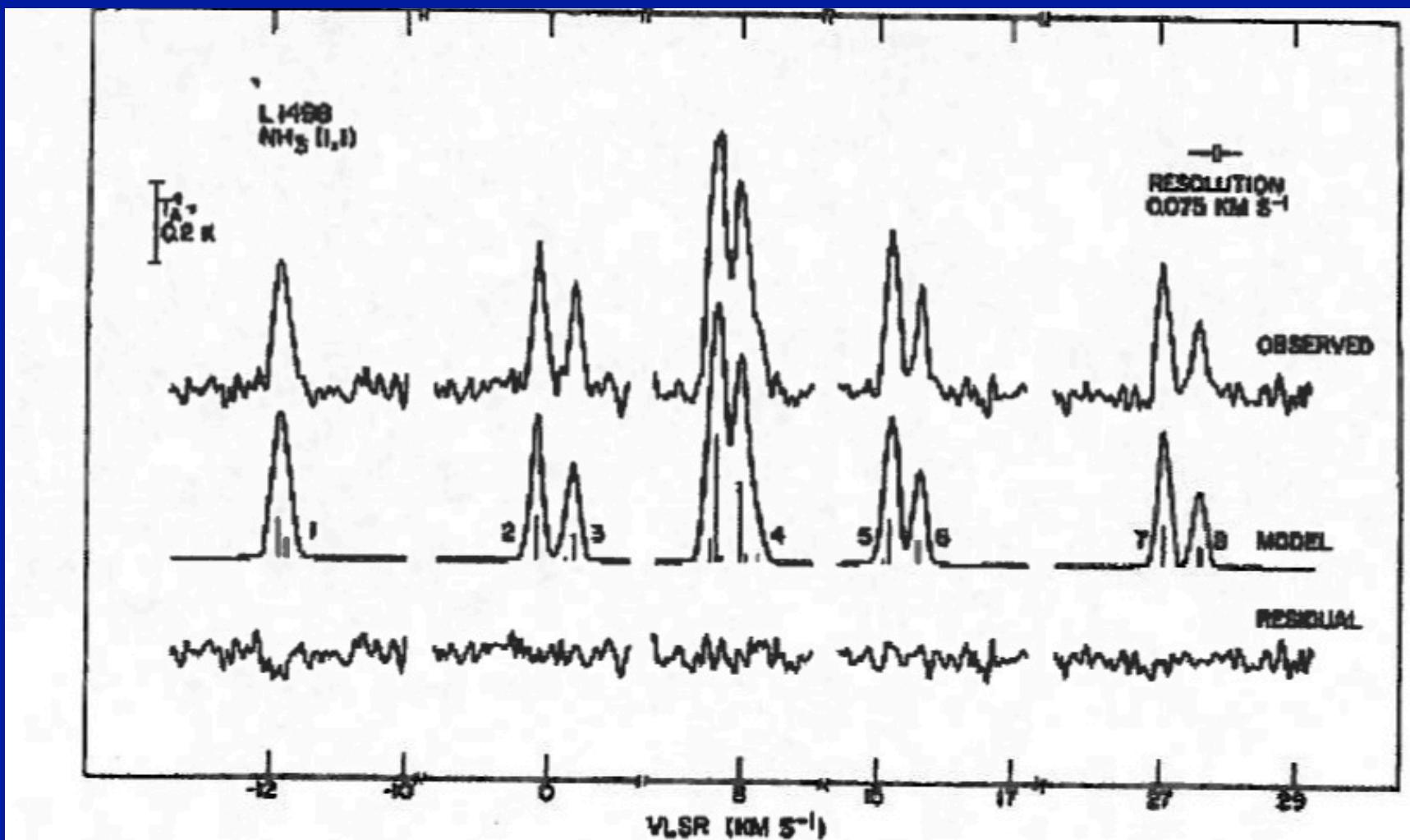


Figure 3 Observed (J, K) = (1, 1) spectrum toward L1498 (Myers & Benson 1983). The relative LTE strengths of the various hyperfine components are indicated by the vertical tick marks under the model spectrum.