Molecular Spectroscopy in Space

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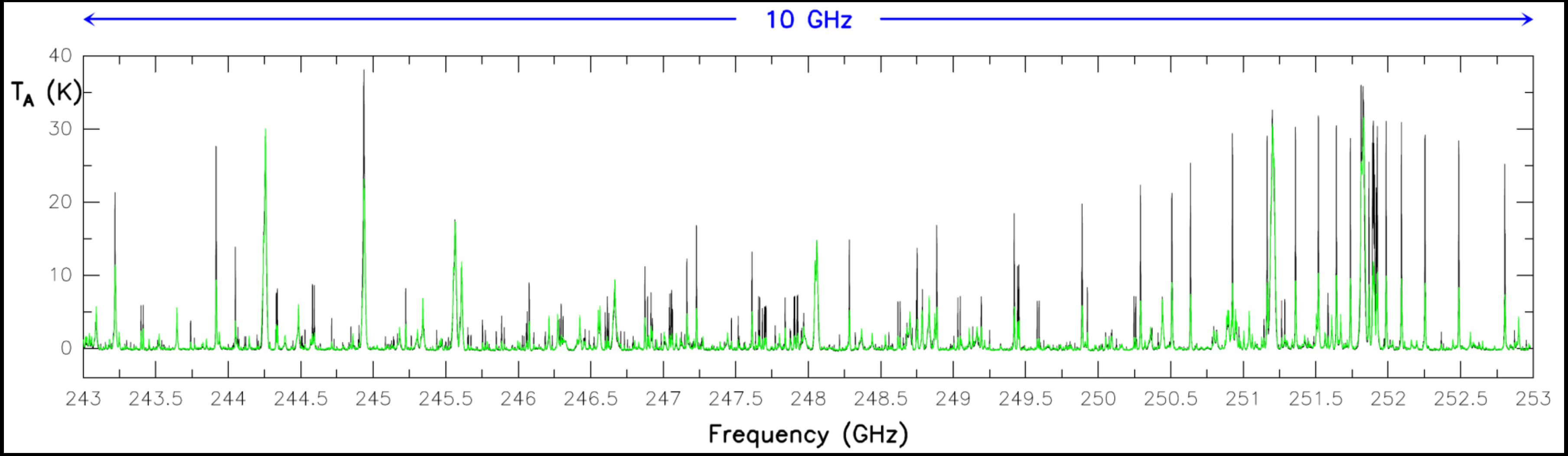
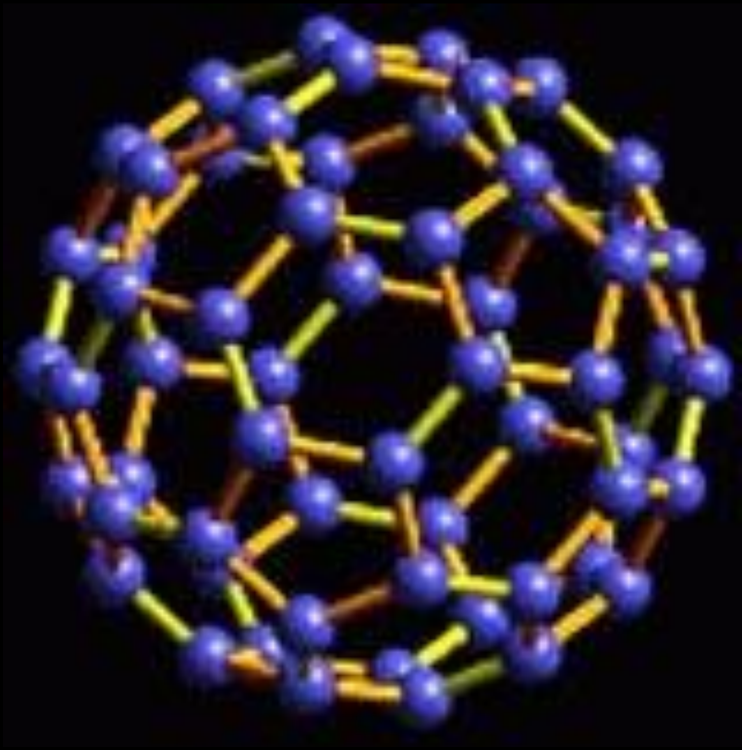


Escuela Guillermo Haro de Astrofisica Molecular, 11-21 Octubre 2016

INTRODUCTION TO MOLECULAR RADIO ASTRONOMY FROM MILLIMETER TO SUBMILLIMETER AND FAR INFRARED

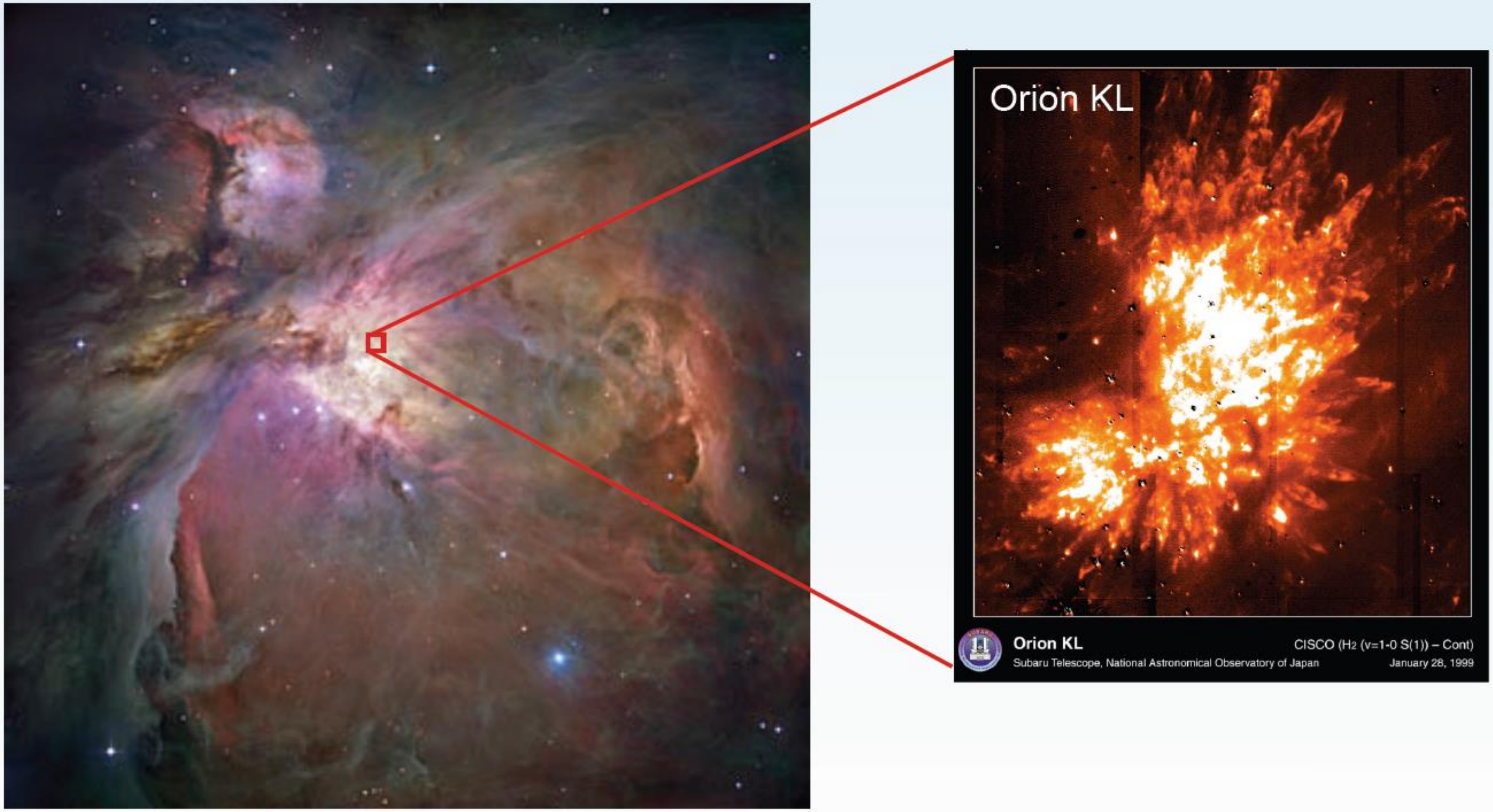
Molecular Spectroscopy

What are the mechanisms of emitting spectral lines for molecules? Which kind of transitions are allowed?



Or how to shock our students

Hot Molecular Cores



Ground Based observations of high Mass star forming regions

A&A 517, A96 (2010)
DOI: 10.1051/0004-6361/200913501

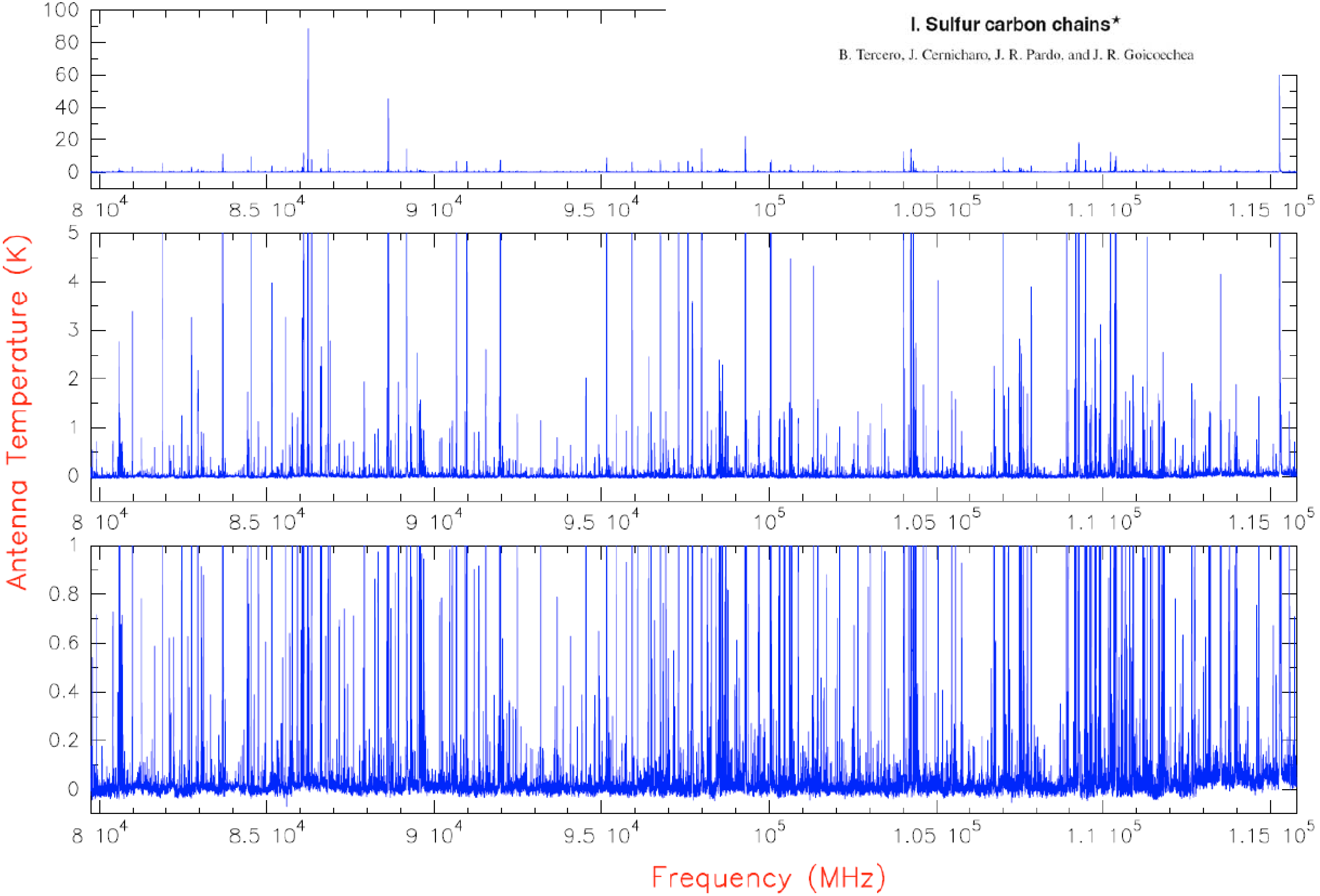
Astronomy & Astrophysics

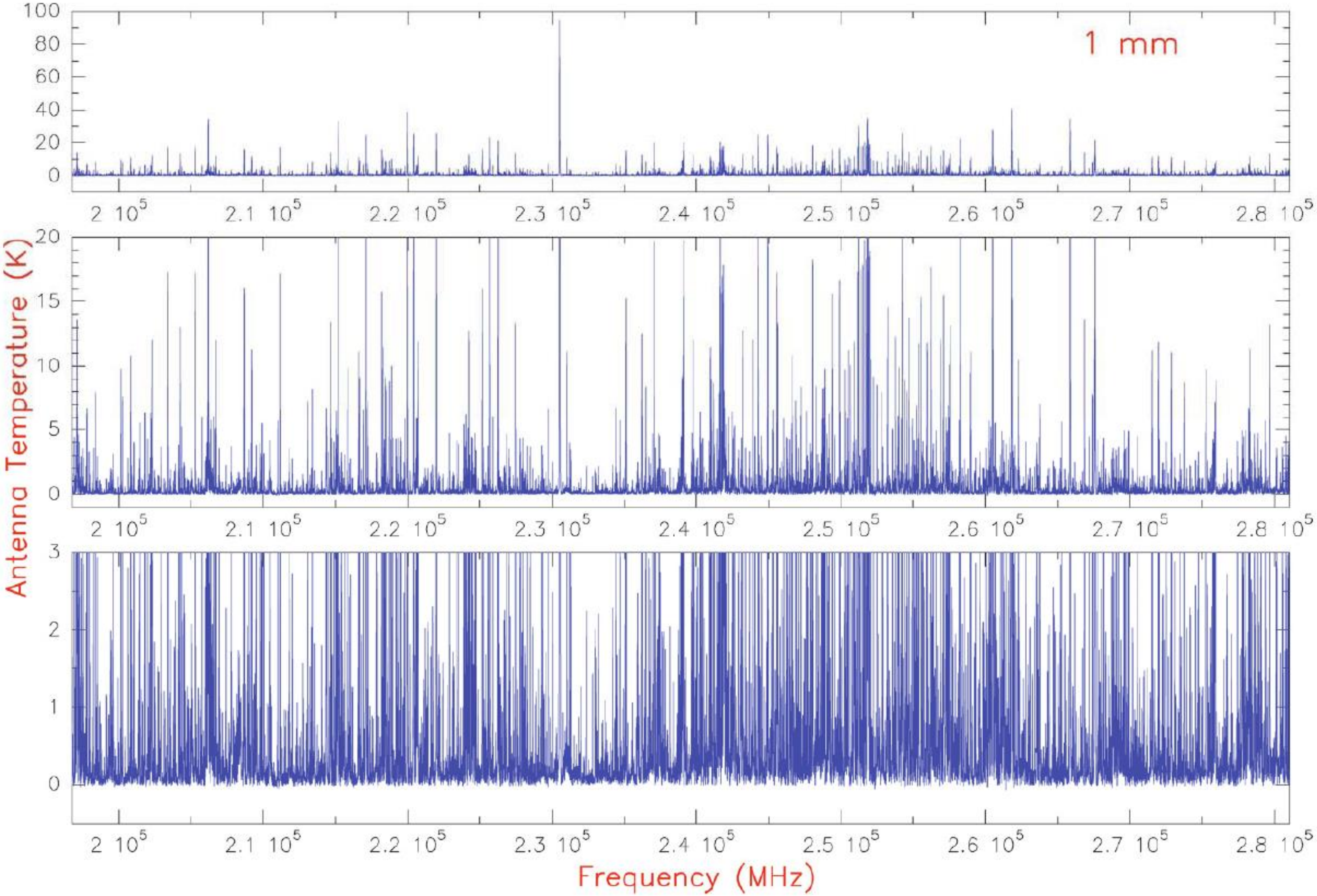
A&A 517, A

A line confusion limited millimeter survey of Orion KL

I. Sulfur carbon chains*

B. Tercero, J. Cernicharo, J. R. Pardo, and J. R. Goicoechea




1 mm
Antenna Temperature (K)
Frequency (MHz)
100
80
60
40
20
0
20
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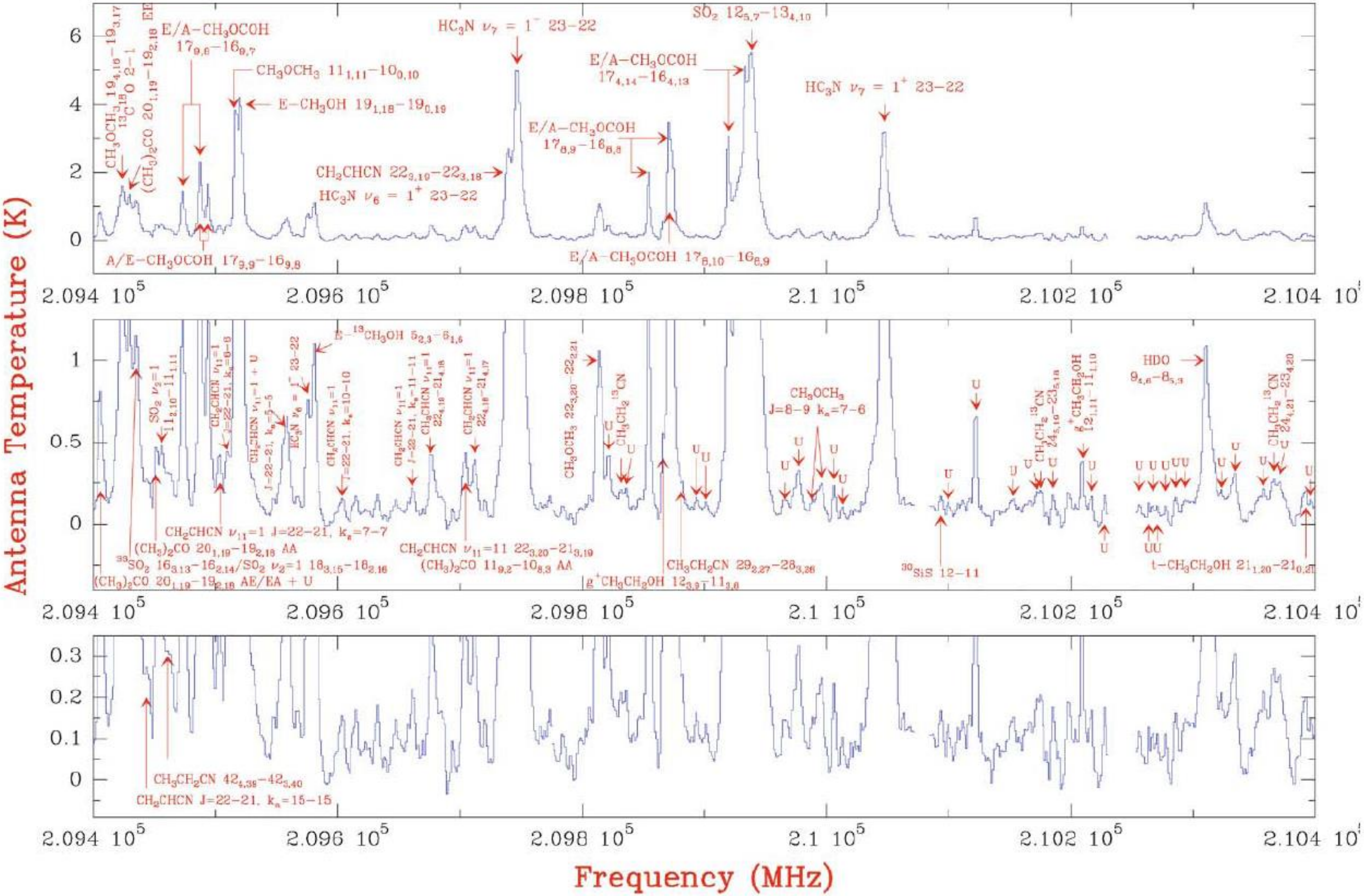
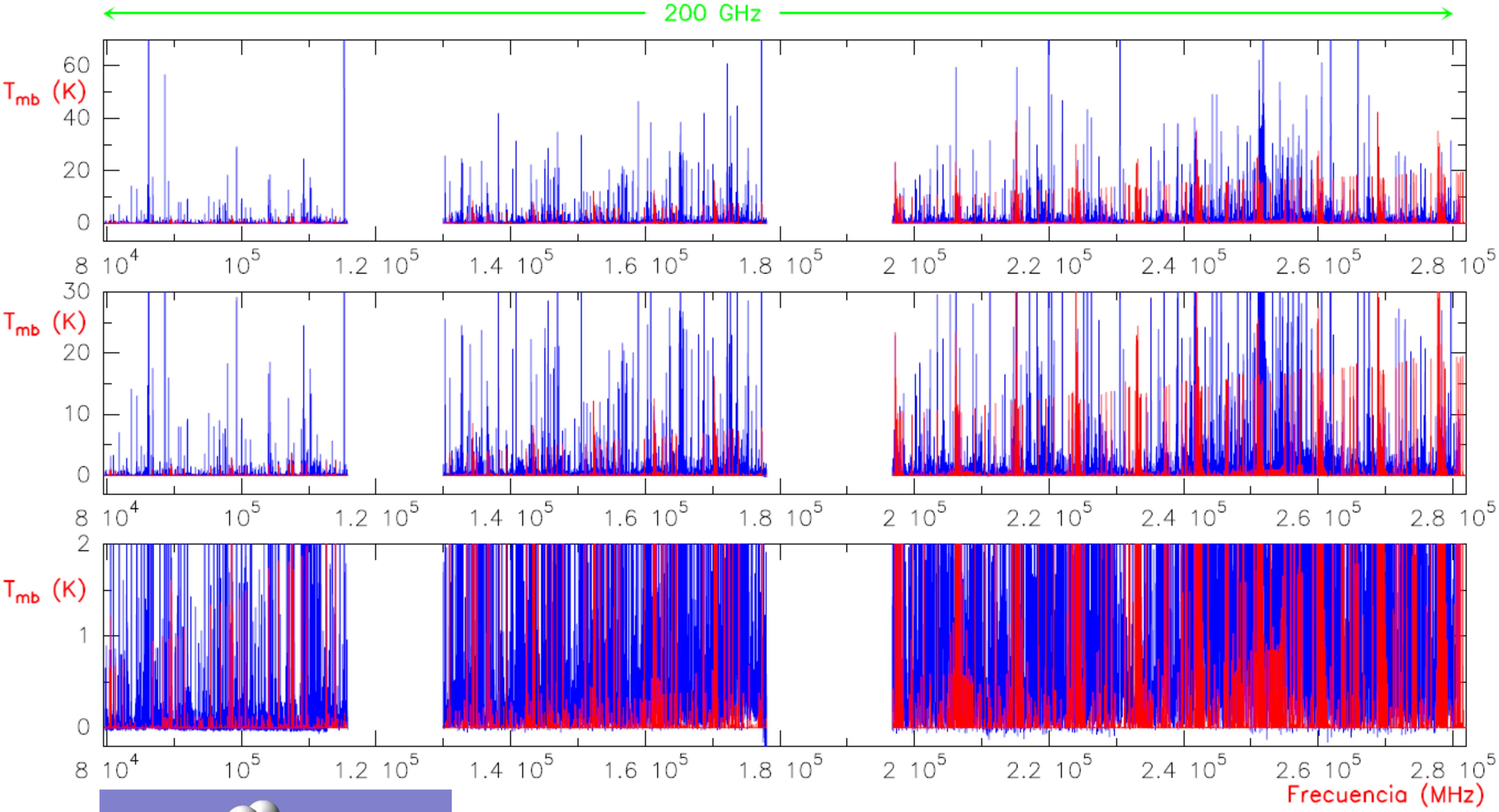
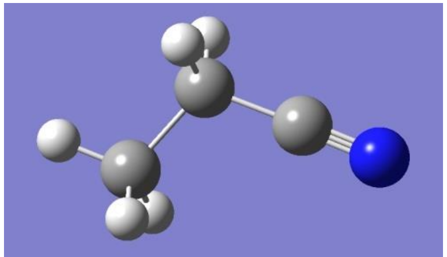
2.5 10^5
2.6 10^5
2.7 10^5
2.8 10^5

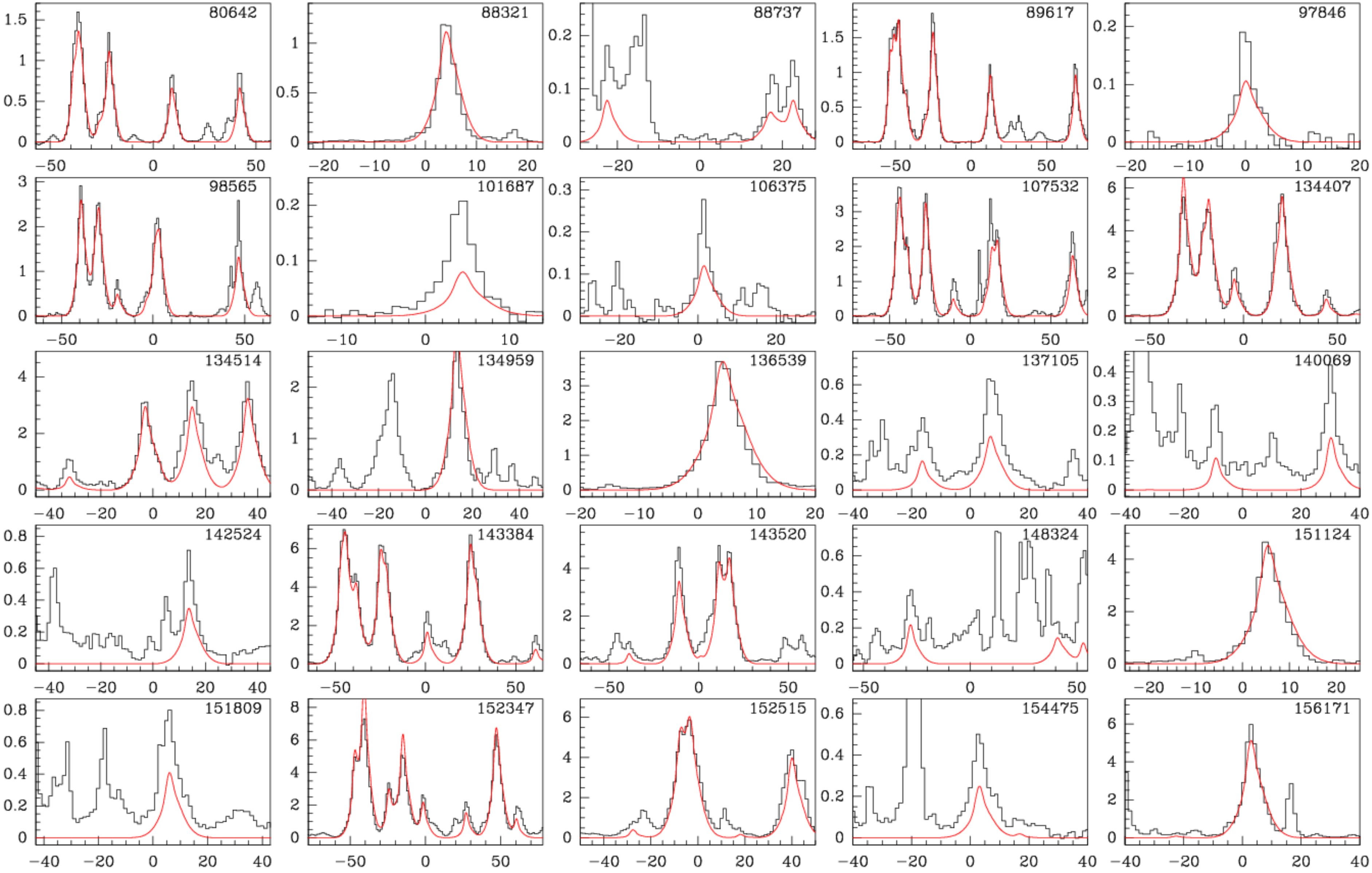


LINE CONFUSION LIMIT REACHED. WHAT TO DO ?
ALMA WILL BE 8 times more sensitive than the 30-m radio telescope

Ethyl Cyanide (The Contaminator), CH_3CH_2CN



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101687
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134407
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−50
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−40
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−20
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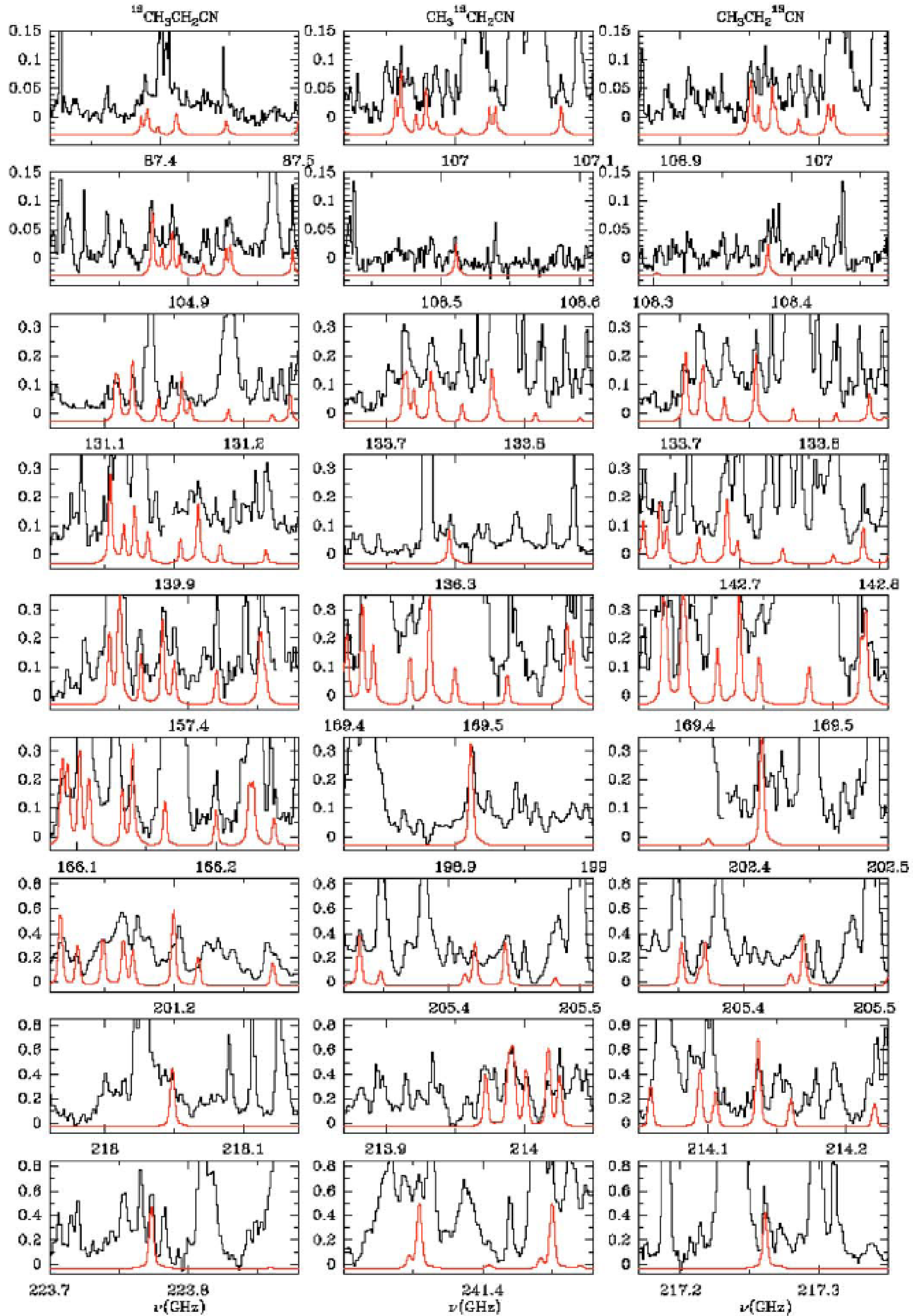


Collaboration with L. Margules, I. Kleiner et al. ➔

More than 800 lines from the isotopes of CH_3CH_2CN

Around 600 lines from the vibrational excited states of ethyl cyanide

More than 400 lines from those of CH_3OCOH

Around 800-1000 lines identified every 2 years in Orion. All lines above confusion limit could be identified around 2020 !!!

Belen started her PhD based on this line survey in 2006.

When combined with HEXOS data=> Work for a long period

ALMA ?

Sym. Species	No	Approximate type of mode	Freq. Value	Infrared Value
a'	1	CH_3 d-str	3001	3001 VS
a'	2	CH_2 s-str	2955	2955 VS
a'	3	CH_3 s-str	2900	2900 S
a'	4	CN str	2254	2254 VS
a'	5	CH_3 d-deform	1465	1465 S
a'	6	CH_2 scis	1433	1433 S
a'	7	CH_3 s-deform	1387	1387 M
a'	8	CH_2 wag	1319	1319 M
a'	9	C-CN str	1077	1077 S
a'	10	CC str	1005	1005 M
a'	**11**	**CH_3 rock**	**836**	836 W
a'	**12**	**CCC deform**	**545**	545 M
a'	**13**	**CCN bend**	**226**	226 M
a	14	CH_3 d-str	3001	3001 VS
a	15	CH_2 a-str	2849	2849 S
a	16	CH_3 d-deform	1465	1465 S
a	17	CH_2 twist	1256	1256 VW
a	18	CH_3 rock	1022	
a	**19**	**CH_2 rock**	**786**	786 M
a	**20**	**CCN bend**	**378**	378 M
a	**21**	**Torsion**	**222**	

Possible vibrational levels of CH_3CH_2CN in Orion:

$\nu_{21}, \nu_{20}, \nu_{19}, \nu_{11}, \nu_{12}, \nu_{13}$

$\nu_{21}+\nu_{20}, \nu_{21}+\nu_{19}, \nu_{21},$

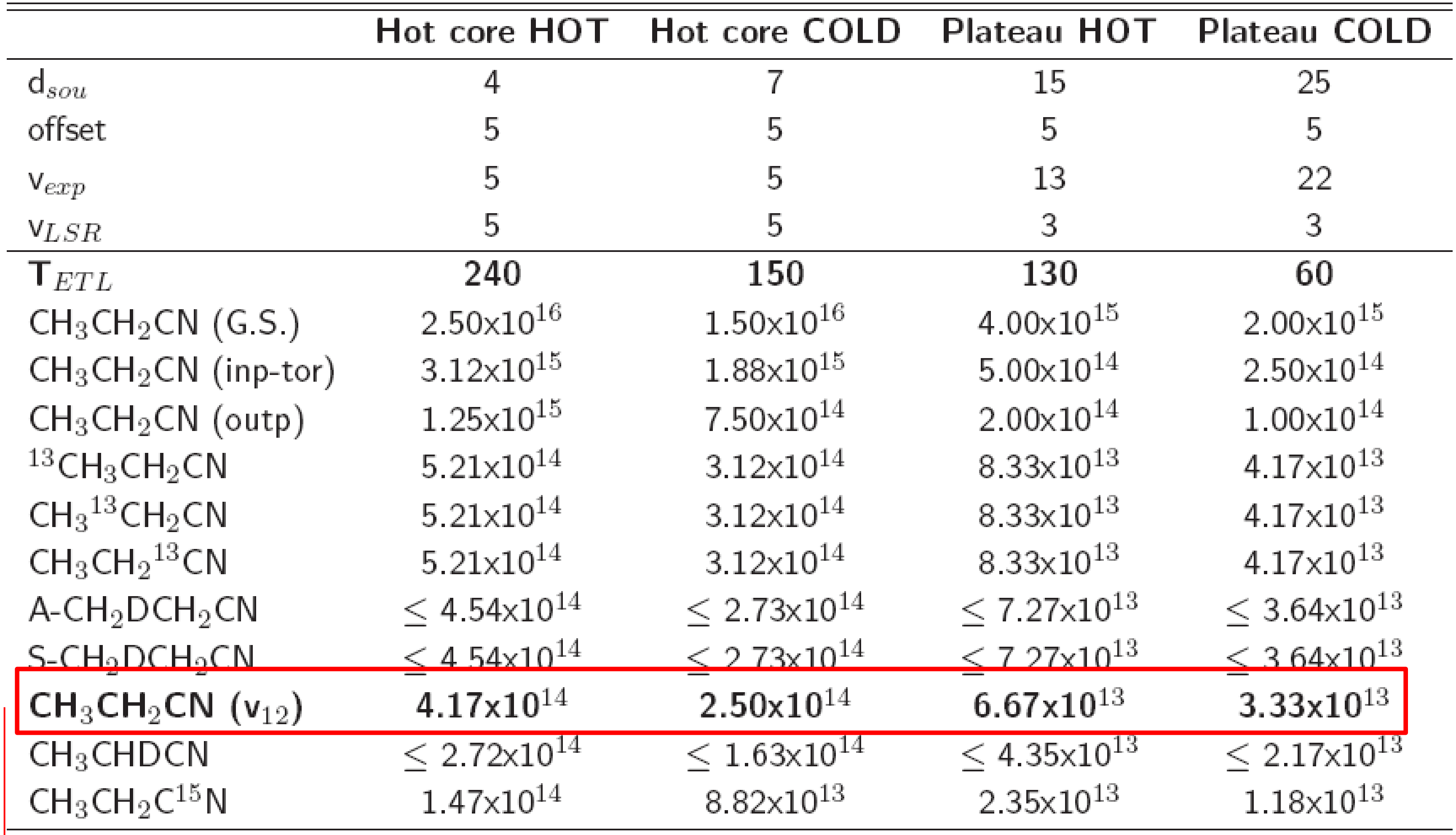
$\nu_{12}+\nu_{13}$, ……

For a vibrational temperature of 350 K all these levels will have a contribution larger than the isotopes ^{13}C !!!

Close collaboration with J.L. Alonso (Valladolid, Spain) and J. Pearson (JPL)

many of these levels have been detected (in progress for all levels below 1000 cm^{-1})

Strong perturbations, complex Hamiltonians



	Hot core HOT	Hot core COLD	Plateau HOT	Plateau COLD
d_{sou}	4	7	15	25
offset	5	5	5	5
v_{exp}	5	5	13	22
v_{LSR}	5	5	3	3
T_{ETL}	**240**	**150**	**130**	**60**
CH_3CH_2CN (G.S.)	$2.50\text{x}10^{16}$	$1.50\text{x}10^{16}$	$4.00\text{x}10^{15}$	$2.00\text{x}10^{15}$
CH_3CH_2CN (inp-tor)	$3.12\text{x}10^{15}$	$1.88\text{x}10^{15}$	$5.00\text{x}10^{14}$	$2.50\text{x}10^{14}$
CH_3CH_2CN (outp)	$1.25\text{x}10^{15}$	$7.50\text{x}10^{14}$	$2.00\text{x}10^{14}$	$1.00\text{x}10^{14}$
$^{13}CH_3CH_2CN$	$5.21\text{x}10^{14}$	$3.12\text{x}10^{14}$	$8.33\text{x}10^{13}$	$4.17\text{x}10^{13}$
$CH_3{}^{13}CH_2CN$	$5.21\text{x}10^{14}$	$3.12\text{x}10^{14}$	$8.33\text{x}10^{13}$	$4.17\text{x}10^{13}$
$CH_3CH_2{}^{13}CN$	$5.21\text{x}10^{14}$	$3.12\text{x}10^{14}$	$8.33\text{x}10^{13}$	$4.17\text{x}10^{13}$
A-CH_2DCH_2CN	$\lesssim 4.54\text{x}10^{14}$	$\lesssim 2.73\text{x}10^{14}$	$\lesssim 7.27\text{x}10^{13}$	$\lesssim 3.64\text{x}10^{13}$
S-CH_2DCH_2CN	$\lesssim 4.54\text{x}10^{14}$	$\lesssim 2.73\text{x}10^{14}$	$\lesssim 7.27\text{x}10^{13}$	$\lesssim 3.64\text{x}10^{13}$
CH_3CH_2CN (v_{12})	**$4.17\text{x}10^{14}$**	**$2.50\text{x}10^{14}$**	**$6.67\text{x}10^{13}$**	**$3.33\text{x}10^{13}$**
CH_3CHDCN	$\lesssim 2.72\text{x}10^{14}$	$\lesssim 1.63\text{x}10^{14}$	$\lesssim 4.35\text{x}10^{13}$	$\lesssim 2.17\text{x}10^{13}$
$CH_3CH_2C^{15}N$	$1.47\text{x}10^{14}$	$8.82\text{x}10^{13}$	$2.35\text{x}10^{13}$	$1.18\text{x}10^{13}$

What is the role of vibrationally excited molecules in chemistry ? Slow reactions involving ground state species could become very fast using the vibrational energy reservoir to overpass possible activation barriers. See Agúndez et al (2010, ApJ, 713, 662) for C^+ and $H_2(v=1)$

E_{vib}=800 K

Line frequencies: public and private catalogs

WARNING: Frequency predictions can be very uncertain for frequency ranges outside the observed domains in the laboratories

Astronomers use molecular databases to search for molecules and to identify molecular lines (JPL, CDMS, MADEX)

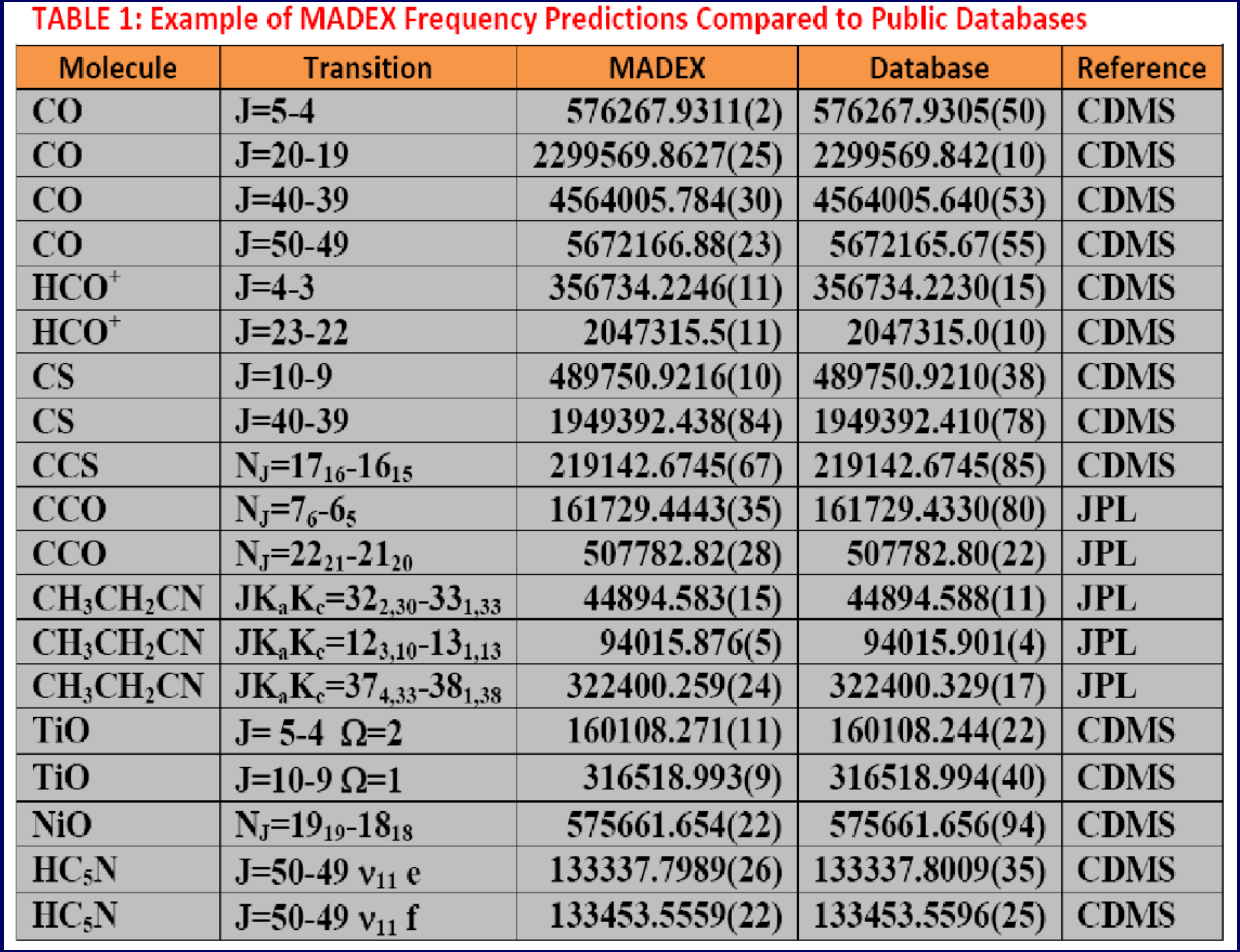
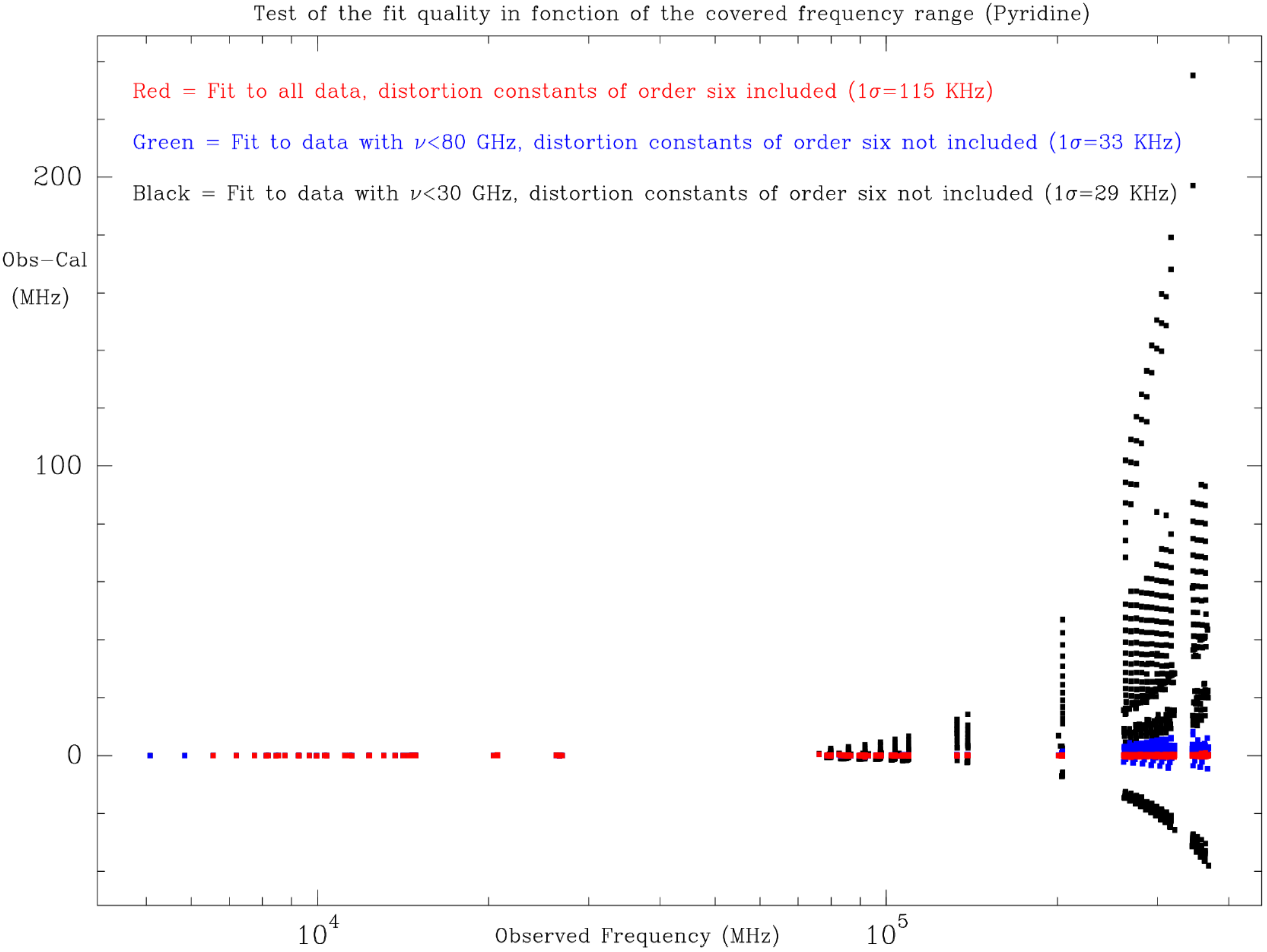
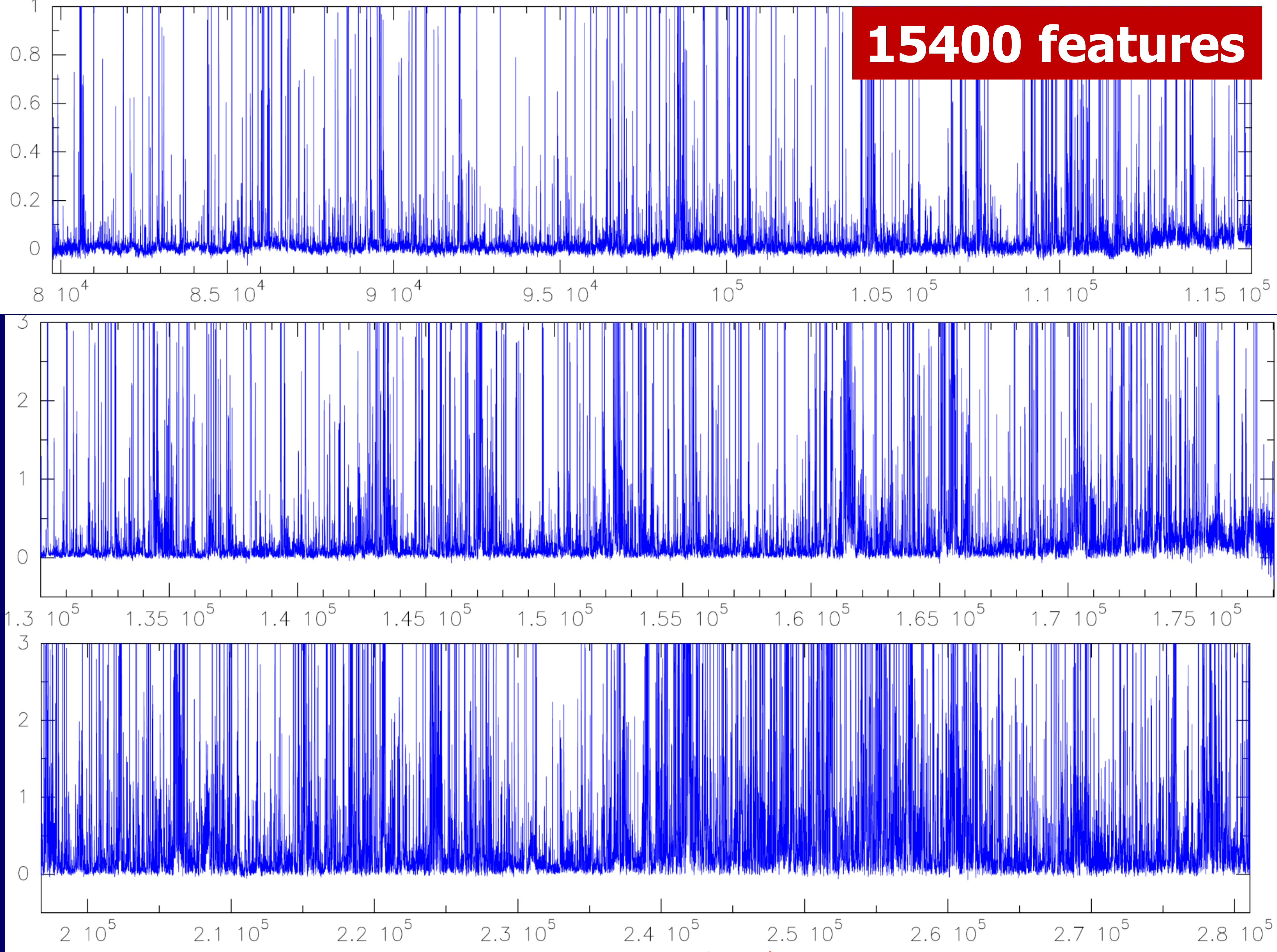


TABLE 1: Example of MADEX Frequency Predictions Compared to Public Databases

Molecule	Transition	MADEX	Database	Reference
CO	J=5-4	576267.9311(2)	576267.9305(50)	CDMS
CO	J=20-19	2299569.8627(25)	2299569.842(10)	CDMS
CO	J=40-39	4564005.784(30)	4564005.640(53)	CDMS
CO	J=50-49	5672166.88(23)	5672165.67(55)	CDMS
HCO^+	J=4-3	356734.2246(11)	356734.2230(15)	CDMS
HCO^+	J=23-22	2047315.5(11)	2047315.0(10)	CDMS
CS	J=10-9	489750.9216(10)	489750.9210(38)	CDMS
CS	J=40-39	1949392.438(84)	1949392.410(78)	CDMS
CCS	$N_J=17_{16}-16_{15}$	219142.6745(67)	219142.6745(85)	CDMS
CCO	$N_J=7_6-6_5$	161729.4443(35)	161729.4330(80)	JPL
CCO	$N_J=22_{21}-21_{20}$	507782.82(28)	507782.80(22)	JPL
CH_3CH_2CN	$JK_aK_c=32_{2,30}-33_{1,33}$	44894.583(15)	44894.588(11)	JPL
CH_3CH_2CN	$JK_aK_c=12_{3,10}-13_{1,13}$	94015.876(5)	94015.901(4)	JPL
CH_3CH_2CN	$JK_aK_c=37_{4,33}-38_{1,38}$	322400.259(24)	322400.329(17)	JPL
TiO	J= 5-4 Ω=2	160108.271(11)	160108.244(22)	CDMS
TiO	J=10-9 Ω=1	316518.993(9)	316518.994(40)	CDMS
NiO	$N_J=19_{19}-18_{18}$	575661.654(22)	575661.656(94)	CDMS
HC_5N	J=50-49 ν_{11} e	133337.7989(26)	133337.8009(35)	CDMS
HC_5N	J=50-49 ν_{11} f	133453.5559(22)	133453.5596(25)	CDMS

WARNING : CHECK CAREFULLY THE REFERENCES FOR THESE PREDICTIONS

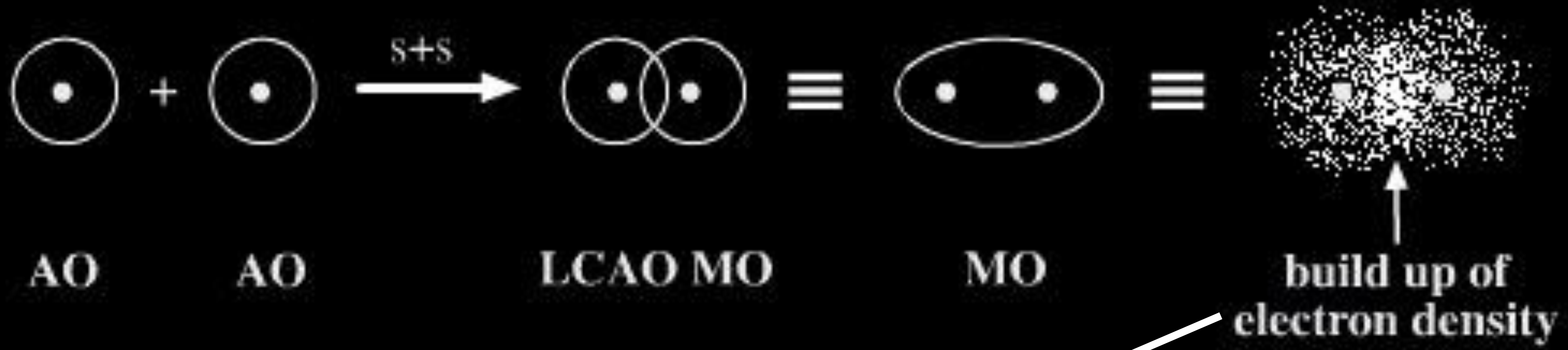

Test of the fit quality in fonction of the covered frequency range (Pyridine)
Red = Fit to all data, distortion constants of order six included (1σ=115 KHz)
Green = Fit to data with ν<80 GHz, distortion constants of order six not included (1σ=33 KHz)
Black = Fit to data with ν<30 GHz, distortion constants of order six not included (1σ=29 KHz)
Obs−Cal
(MHz)
200
100
0
10^4
10^5
Observed Frequency (MHz)

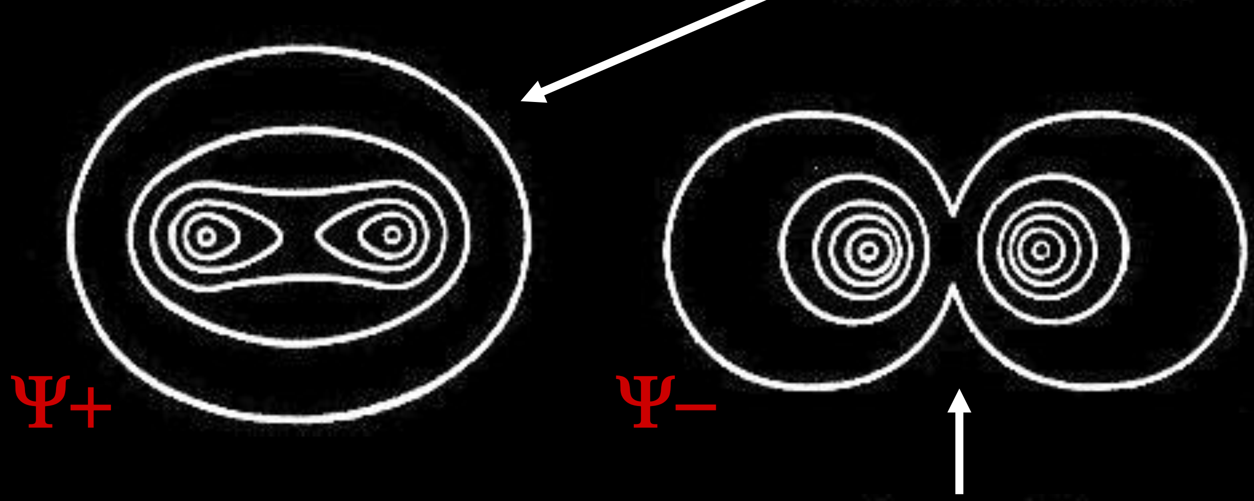


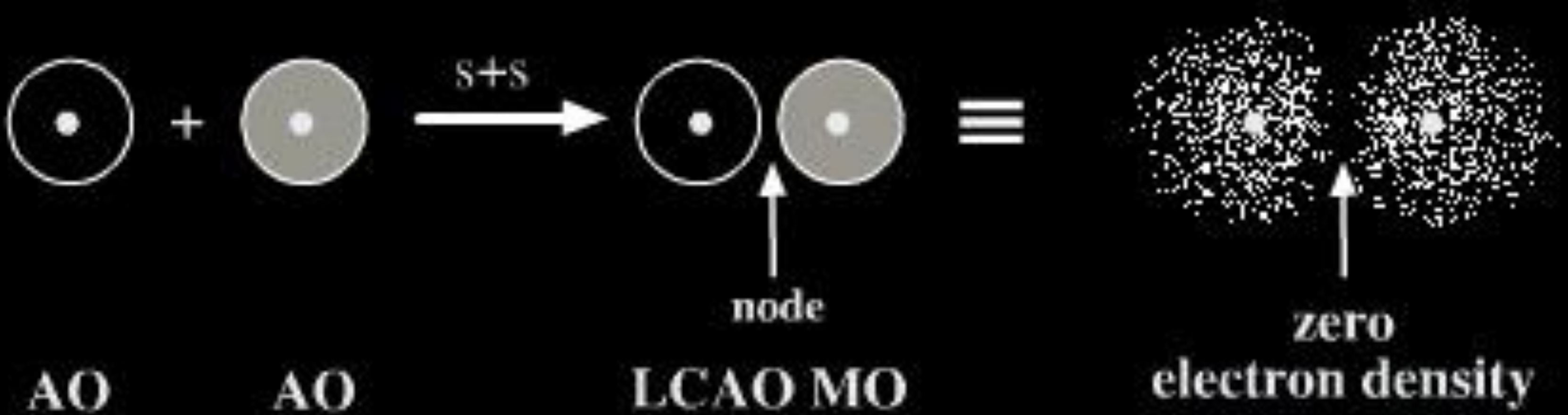
15400 features

Formation of molecules and molecular stability

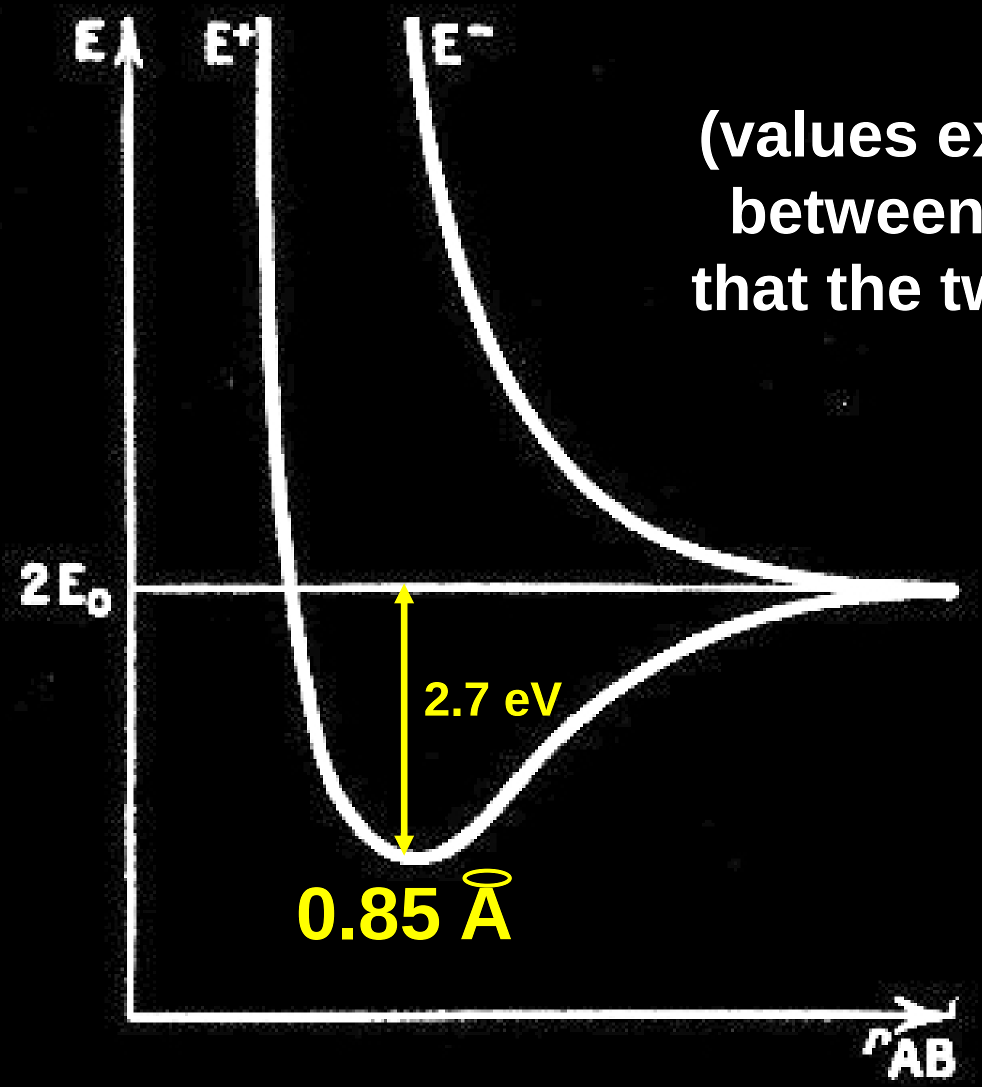
Electronic isodensity contours:







The dependency of the electronic energy of the system as a function of the internuclear distance has the following shape:



(values excluding the interaction between electrons and the fact that the two protons interact with the electrons)

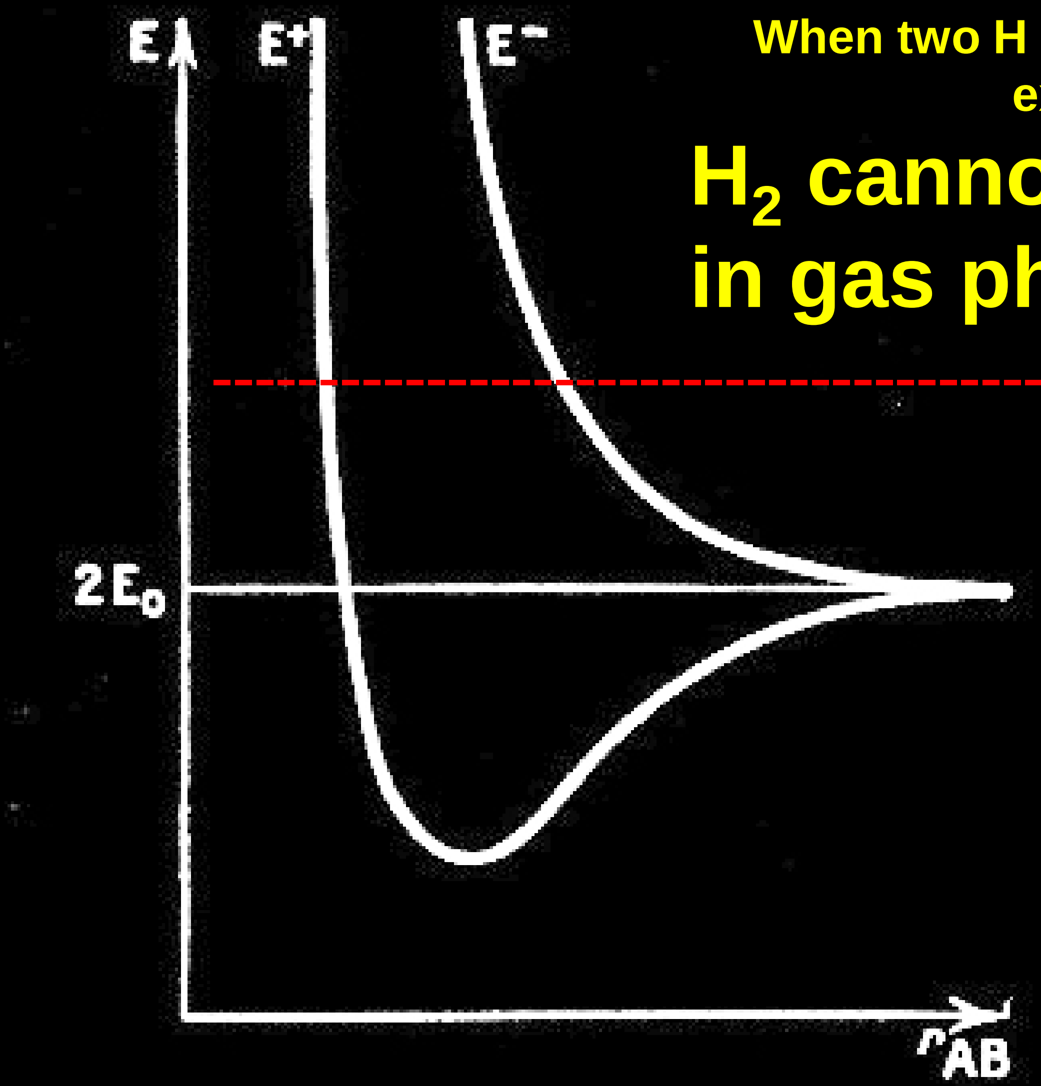
Experimental values:

0.74 Å and 4.7 eV

IMPORTANT:

When two H atoms collide they have some extra kinetic energy

H_2 cannot be formed in gas phase in the ISM !!!



$E(H_A+H_B)$

3-body collisions are required

(3rd body will carry out the excess of energy)

Once a molecule is formed…

ONCE A MOLECULE IS FORMED THE INTERNAL ENERGY IS HIGHLY DIVERSIFIED

Electronic: Energy of the electronic orbitals

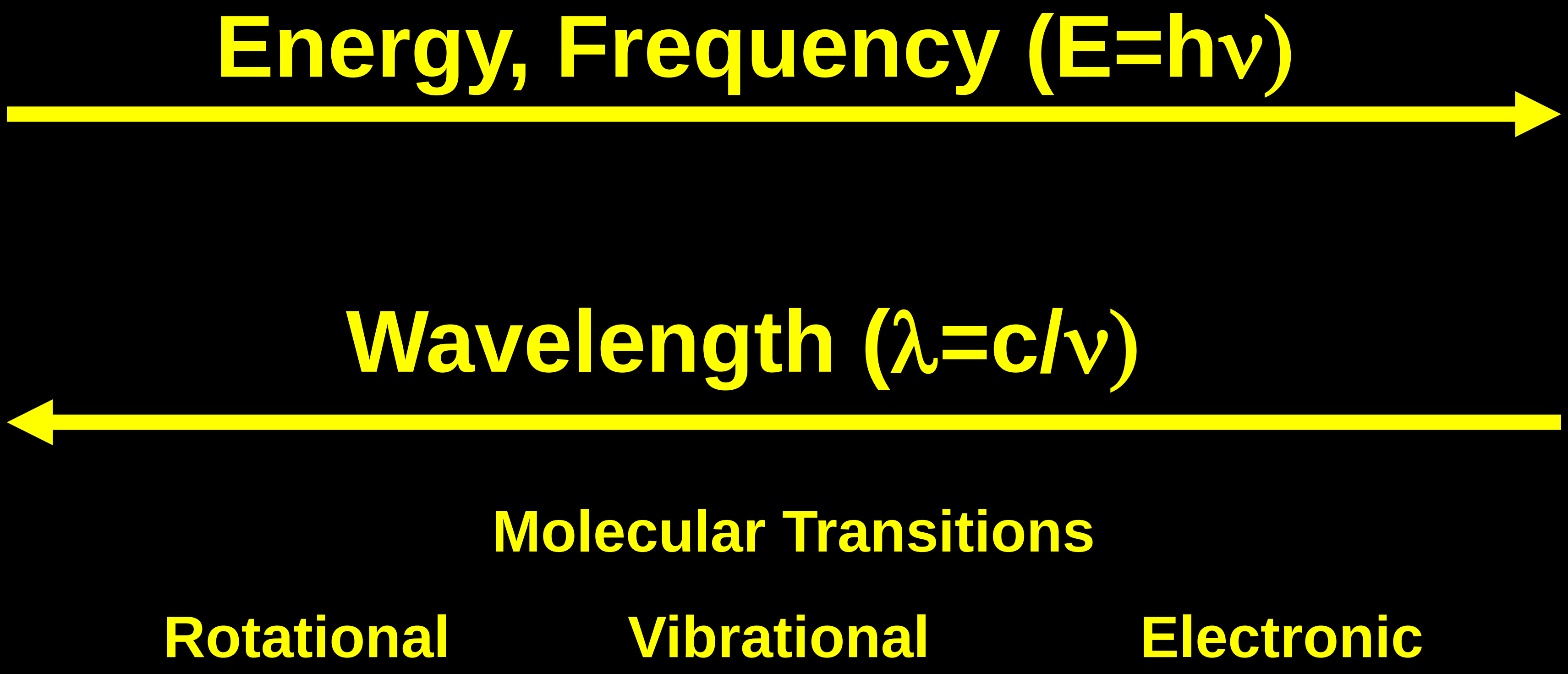
Vibrational: Energy of the vibrations of the nuclei around the equilibrium position

Rotational: Energy associated to the rotation of an electric dipole.

Other: unpaired electron spins or nuclear spins can couple with the angular momentum of the electric dipole rotation. Internal magnetic dipoles can couple with external magnetic fields, etc…

MOST OF THESE ARE TREATED AS PERTURBATIONS OF THE ROTATIONAL ENERGY

There is a hierarchy in the energies needed for transitions



Energy, Frequency ($E=h\nu$)

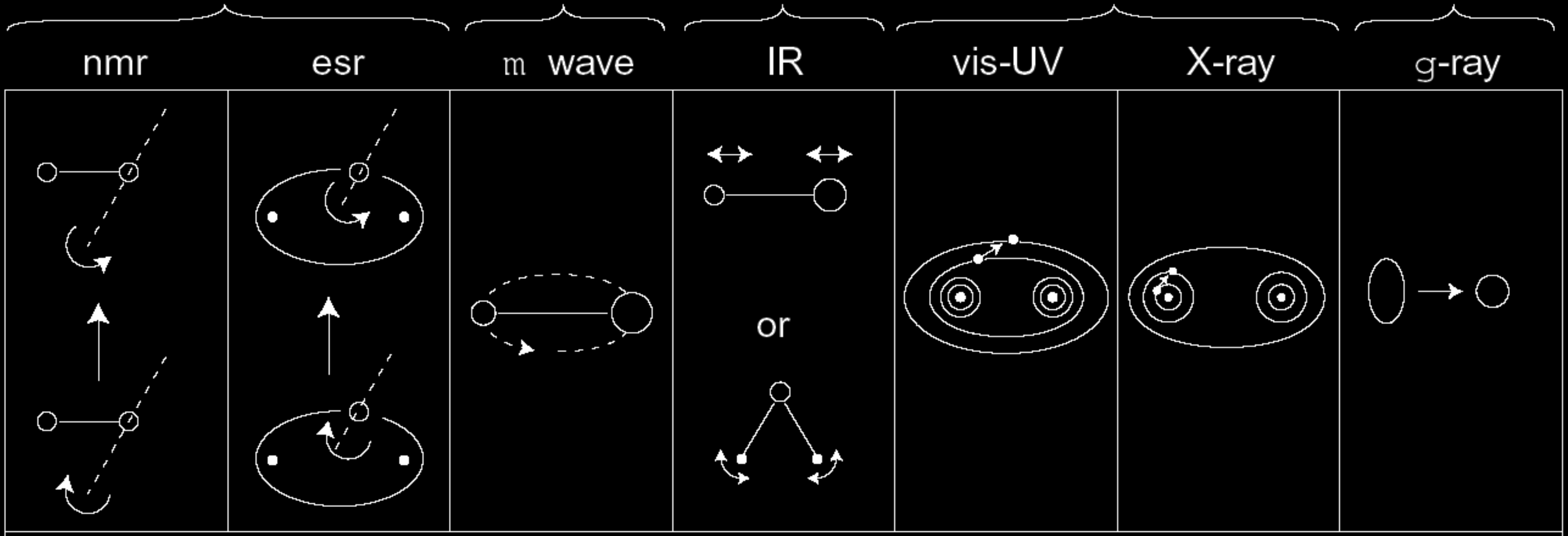
Wavelength ($\lambda=c/\nu$)

Molecular Transitions

Rotational Vibrational Electronic

However, the quantum mechanical problem is relatively simple only for very small molecules.

Overview of the entire spectrum



Change of Spin: nmr, esr

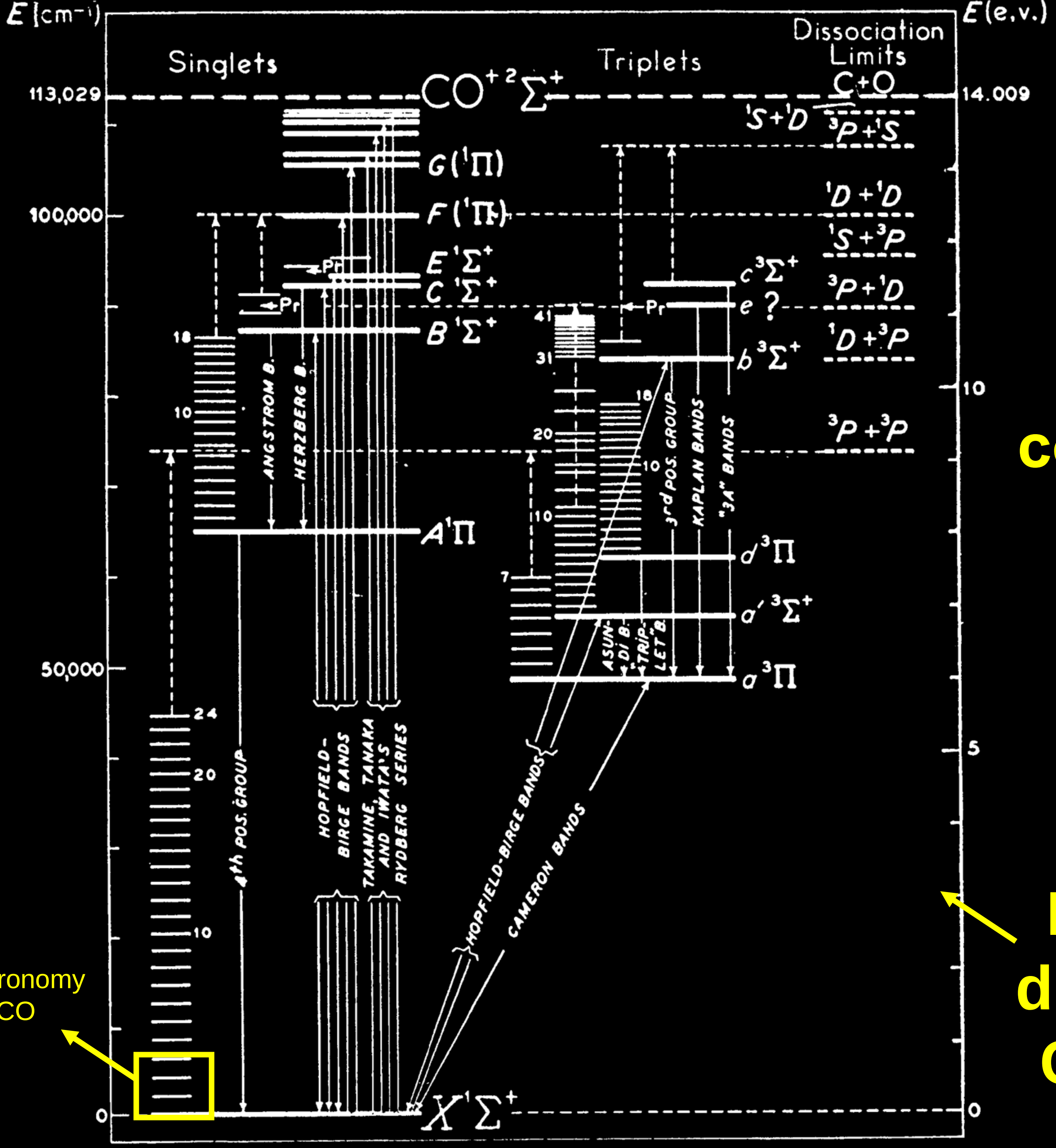
Change of Orientation: m wave

Change of Configuration: IR

Change of Electron Distribution: vis-UV, X-ray

Change of Nuclear Configuration: g-ray

	10^{-2}	1	100	10^4	cm^{-1}	10^6	wavenumber	10^8
10 m	100 cm	1 cm	100 mm	1 mm		10 nm	wavenumber	10 pm
$13 \cdot 10^6$	$3 \cdot 10^8$	$3 \cdot 10^{10}$	$3 \cdot 10^{12}$	$3 \cdot 10^{14}$	Hz	$3 \cdot 10^{16}$	frequency	$3 \cdot 10^{18}$
10^{-3}	10^{-1}	10	10^3	10^5	joules/mole	10^7	energy	10^9



Radioastronomy with CO

Well, the whole thing can be very complicated…

Energy level diagram of the CO molecule

How to characterize molecules spectroscopically from astronomical data?

- Looking for species difficult to be produced in the laboratory
- We proceed exactely in the same way than in the laboratory
- We identify the lines that we believe are produced by a molecular species (harmonic relations between the frequencies for linear molecules for example)
- We assign quantum numbers to these lines
- We check for hyperfine structure (N, H, ^{17}O, ^{33}S,…)
- We fit a Hamiltonian to the observed lines
- What accuracy can be obtained ?

Frequency accuracy

- Normally lines are gaussians with linewidths in dark clouds <0.5 km/s which means an accuracy in velocity determination of 0.05 km/s.
- This velocity accuracy corresponds to a relative frequency uncertainty of 1.7 10^{-7}
- In some sources the linewidths can be as narrow as 0.15 km/s.
- Additional uncertainty due to precision on the velocity of the source (0.2 km/s or 6.7 10^{-7} relative frequency error)

C_6H an example of a molecule fully characterize in space

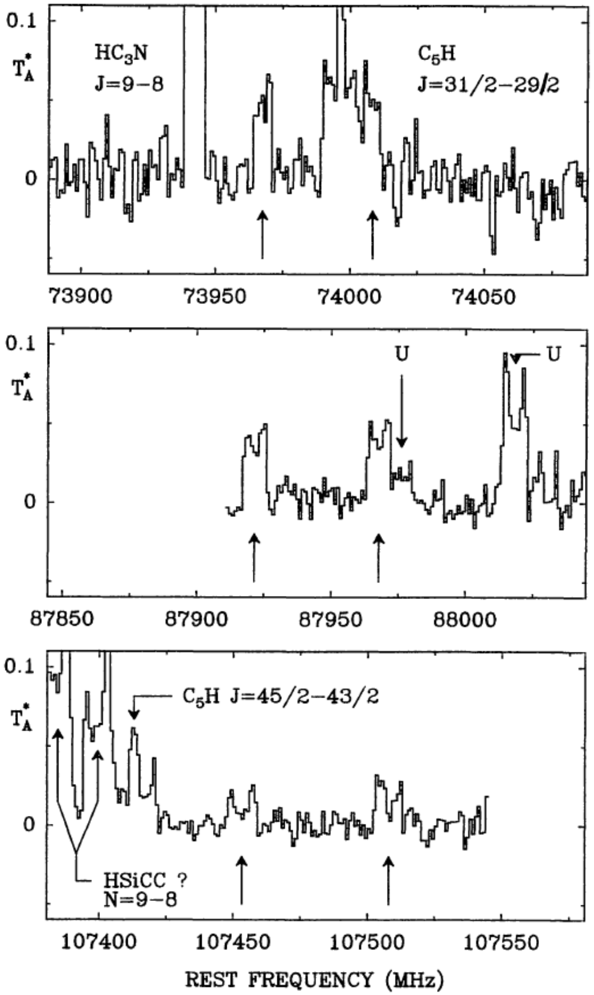
Astron. Astrophys. 181, L1–L4 (1987)

ASTRONOMY
AND
ASTROPHYSICS

Letter to the Editor

C_6H: astronomical study of its fine and hyperfine structure

J. Cernicharo[1,2], M. Guélin[2], K. M. Menten[3], and C. M. Walmsley[3]



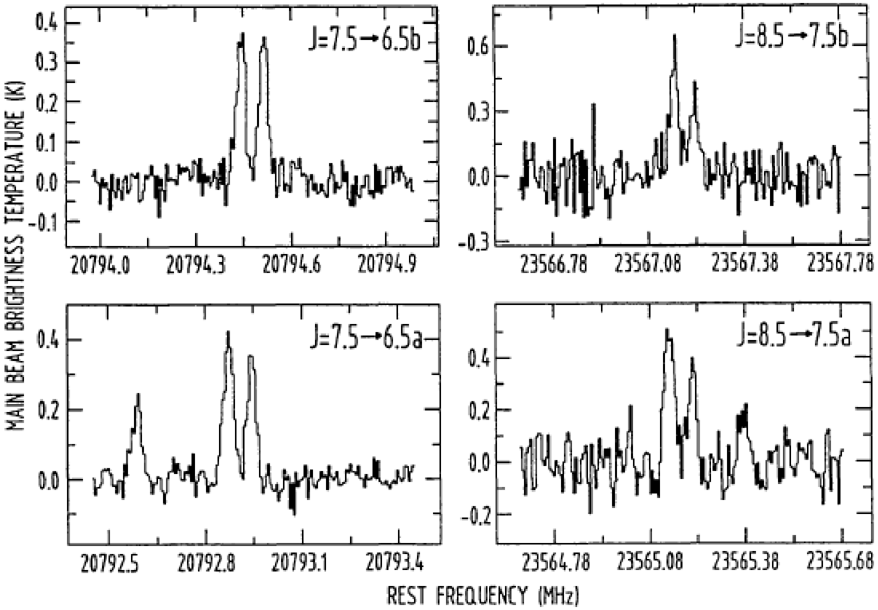


Figure 2 : *The main hyperfine components of the* $J = 15/2 \rightarrow 13/2$, *and* $J = 17/2 \rightarrow 15/2$ *rotational transitions of the* $^2\Pi_{3/2}$ *state of* C_6H *, observed towards TMC1 with the Effelsberg telescope.*

TABLE 1

C_6H LINES OBSERVED TOWARDS IRC+10216

		$C_6H\ ^2\Pi_{3/2}$			$C_6H\ ^2\Pi_{1/2}$		
Ju	Λ	Obs. Freq. (MHz)	$\int T_A dv$ $\mathrm{Kkms^{-1}}$	O−C⁺ (MHz)	Obs. Freq. (MHz)	$\int T_A dv$ $\mathrm{Kkms^{-1}}$	O−C⁺ (MHz)
26.5	a	73460.7(10)	1.70(20)	−1.57	73967.7(3)	1.30(16)	+0.09
26.5	b	73481.2(10)	1.50(19)	−0.15	74008.5(3)	1.30(16)	−0.02
29.5	a	81778.1(4)	1.50(10)	+0.22	—		
29.5	b	81801.1(4)	1.21(10)	−0.23	82384.5(5)	1.10(20)	+0.28
30.5	a	84550.0(4)	1.21(8)	+0.31	85131.1(4)	1.37(15)	+0.28
30.5	b	84574.7(5)	1.09(8)	+0.06	85176.0(4)	1.45(15)	+0.05
31.5	a	—			87921.7(3)	1.19(20)	+0.19
31.5	b	87348.3(4)	1.30(20)	+0.25	87967.7(3)	1.31(20)	+0.00
32.5	a	90093.0(3)	1.56(10)	−0.32	90712.2(3)	1.09(15)	+0.15
32.5	b	90121.4(3)	1.44(10)	−0.15	90759.3(3)	1.21(18)	−0.00
33.5	a	92865.2(3)	1.48(13)	+0.13	93502.2(10)	0.90(20)	−0.26
33.5	b	92894.9(3)	1.52(14)	−0.10	93550.9(5)	1.20(18)	+0.03
34.5	a	95636.6(4)	1.22(14)	−0.25	96292.5(3)	1.12(25)	−0.28
34.5	b	—			96342.4(3)	1.28(20)	−0.09
35.5	a	98408.9(3)	1.29(7)	+0.33	99083.2(5)	0.97(10)	+0.10
35.5	b	98441.7(3)	1.11(8)	−0.21	99133.8(5)	1.05(20)	−0.11
36.5	a	101180.3(3)	1.20(30)	+0.06	101873.6(10)	0.75(12)	+0.32
36.5	b	101215.0(15)	0.70(30)	−0.48	101925.2(7)	0.78(12)	−0.11
37.5	a	103951.9(4)	1.25(19)	−0.14	—		
37.5	b	103989.0(4)	0.90(20)	−0.01	—		
38.5	a	—			107453.2(3)	0.66(10)	−0.14
38.5	b	106762.7(3)	1.00(20)	+0.12	107507.9(4)	0.58(10)	−0.00
39.5	a	—			110243.4(10)	0.76(15)	+0.12
39.5	b	—			110229.8(10)	0.74(20)	+0.71
41.5	a	115038.4(7)	0.52(6)	−0.30	—		
41.5	b	115084.0(7)	0.42(6)	+0.54	—		

+) O−C is the observed minus calculated frequency (from the rotational constants of Table 3 "best fit")

TABLE 2

THE $^2\Pi_{3/2}$ TRANSITIONS OF C_6H OBSERVED TOWARDS TMC1

Transition J–J'	Λ$	F–F'	Frequency* MHz	$\int T_B dv$ $\mathrm{Kkms^{-1}}$	Δv $\mathrm{kms^{-1}}$	Notes
			20792.588	0.114	0.49	U line
7.5−6.5	*a*	8−7	20792.872	0.224	0.52	
		7−6	20792.944	0.167	0.43	R.I.⁺=1:0.75
7.5−6.5	*b*	8−7	20794.441	0.181	0.46	
		7−6	20794.511	0.178	0.45	R.I.=1:0.98
8.5−7.5	*a*	9−8	23565.141	0.253	0.45	
		8−7	23565.213	0.253	0.45	R.I.=1:0.52
8.5−7.5	*b*	9−8	23567.162	0.232	0.39	
		8−7	23567.224	0.147	0.41	R.I.=1:0.63

*)The typical uncertainty on the frequencies is 20 KHz; it includes a of 0.3 km s^{-1} uncertainty on the LSR velocity of TMC1. The spectral resolution of the observations is 6 KHz.
+)R.I. is the integrated intensity ratio of the hf components.
$)Transitions between lower (higher) energy Λ components are designated *a* (*b*) −Brown et al., 1975−

TABLE 3

ROTATIONAL CONSTANTS OF C_6H

		γ set to zero	"best fit"
A_{eff}	(MHz)	-387372 (100)	-430792 (10000)
B_o	(MHz)	1391.2052 (15)	1391.1918 (30)
D_o	(Hz)	49 (1)	43.2 (12)
γ_{eff}	(MHz)	0.0	-147 (30)
p+2q	(MHz)	27.34 (50)	27.65 (80)
q	(MHz)	1.363 (15)	1.43 (2)
p_d+2q_d	(kHz)	-2.61 (15)	-2.69 (26)
q_d	(Hz)	-11 (10)	-10 (8)

The values in parenthesis denote two standard deviations.

SiC a molecule found in space and in laboratory

The Astrophysical Journal, 341:L25–L28, 1989 June 1

ASTRONOMICAL AND LABORATORY DETECTION OF THE SiC RADICAL

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Received 1989 January 30; accepted 1989 March 7

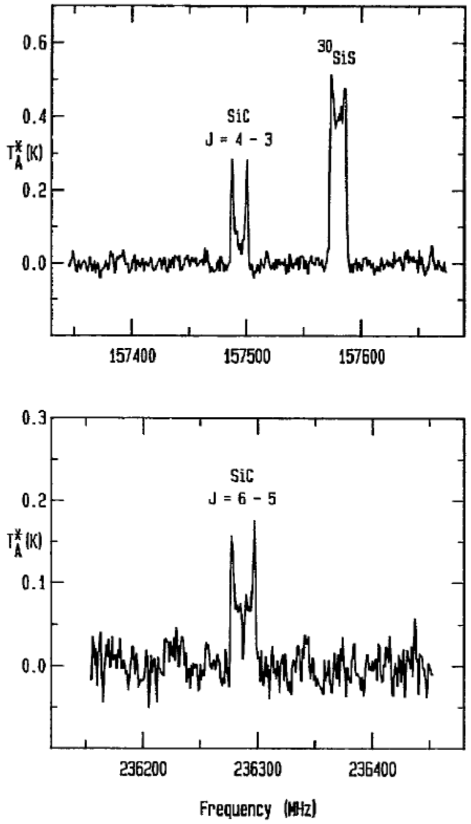

Fig. 2.—The two most intense lines of SiC observed toward IRC +10216 with the IRAM 30 m telescope. Each is from the lowest lying $^3\Pi_2$ rotational ladder and is the sum of two unresolved Λ-components. The spectral resolution is 1 MHz; the frequency scale assumes an LSR source velocity of -26.5 km s^{-1}.

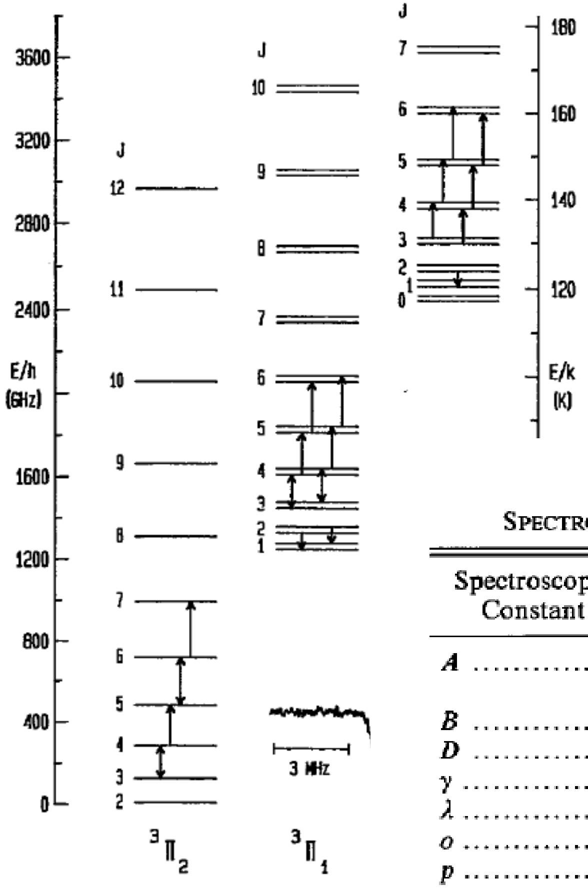

TABLE 2

Spectroscopic Constants of SiC in the $X\ ^3\Pi$ State

Spectroscopic Constant	Measured (MHz)	Calculated (MHz)
A	-1248200 ± 130 $(-41.64$ cm$^{-1})$	-1120000[a] $(-37.3$ cm$^{-1})$
B	20297.582 ± 0.001	20270.9[b]
D	0.04051 ± 0.00001	0.043[c]
γ	186 ± 2	...
λ	-1159 ± 1	...
o	26705 ± 60	...
p	132 ± 1	...
q	-1.185 ± 0.001	...

NH_3D^+ an example of molecule characterized in the laboratory from astronomical input

The Astrophysical Journal Letters, 771:L10 (4pp), 2013 July 1 doi:10.1088/2041-8205/771/1/L10

DETECTION OF THE AMMONIUM ION IN SPACE*

J. Cernicharo[1], B. Tercero[1], A. Fuente[2], J. L. Domenech[3], M. Cueto[3], E. Carrasco[3], V. J. Herrero[3],
I. Tanarro[3], N. Marcelino[4], E. Roueff[5], M. Gerin[6], and J. Pearson[7]

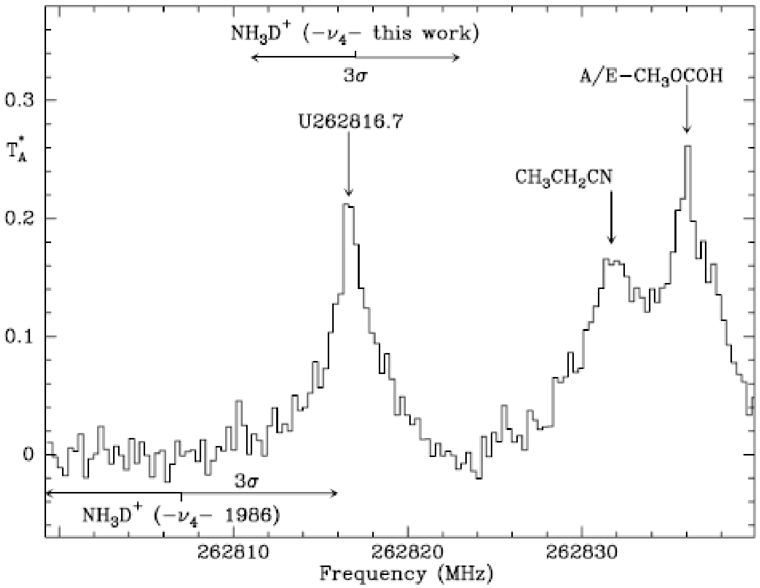

Figure 1. Observed spectrum toward Orion-IRc2 around the expected frequency of the $J_K = 1_0\text{–}0_0$ line of the deuterated ammonium ion. Identification of all other lines in this frequency range is indicated. The predicted frequency and its 3σ error bar are indicated at the bottom for the Nakanaga & Amano (1986) measurements and at the top for our new laboratory data (Domenech et al. 2013).

$$\text{Vel (km/s)}=-(\nu-\nu_0)/\nu_0 \times c$$

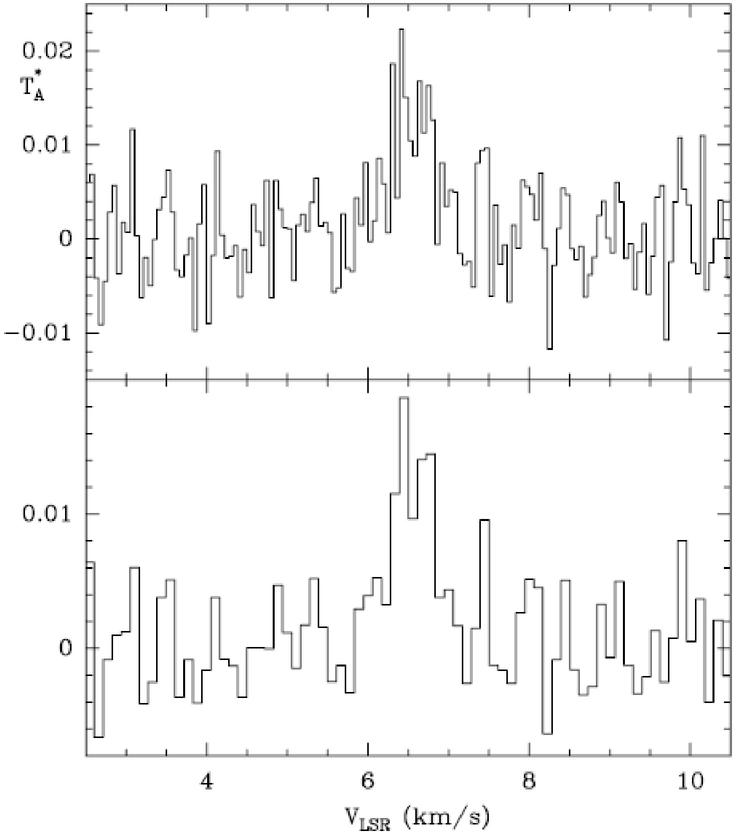

Figure 2. Observed spectrum toward B1-bS ($\alpha_{2000} = 03^h33^m21^s.34$, $\delta_{2000} = 31^\circ07'26''.7$) at the expected frequency of NH_3D^+ $J_K = 1_0\text{–}0_0$ transition. The upper panel contains the raw data resulting from a total integration time of 51 hr with a spectral resolution of 48.8 KHz (0.054 km s^{-1}). The bottom panel shows the same data smoothed to 98 KHz. For a LSR velocity of the source of 6.5 km s^{-1}, the derived line frequency for the observed feature is 262816.73 ± 0.1 MHz.

The Astrophysical Journal Letters, 771:L11 (5pp), 2013 July 1 doi:10.1088/2041-8205/771/1/L11

IMPROVED DETERMINATION OF THE 1_0–0_0 ROTATIONAL FREQUENCY OF NH_3D^+ FROM THE HIGH-RESOLUTION SPECTRUM OF THE ν_4 INFRARED BAND

J. L. Doménech[1], M. Cueto[1], V. J. Herrero[1], I. Tanarro[1], B. Tercero[2], A. Fuente[3], and J. Cernicharo[2]

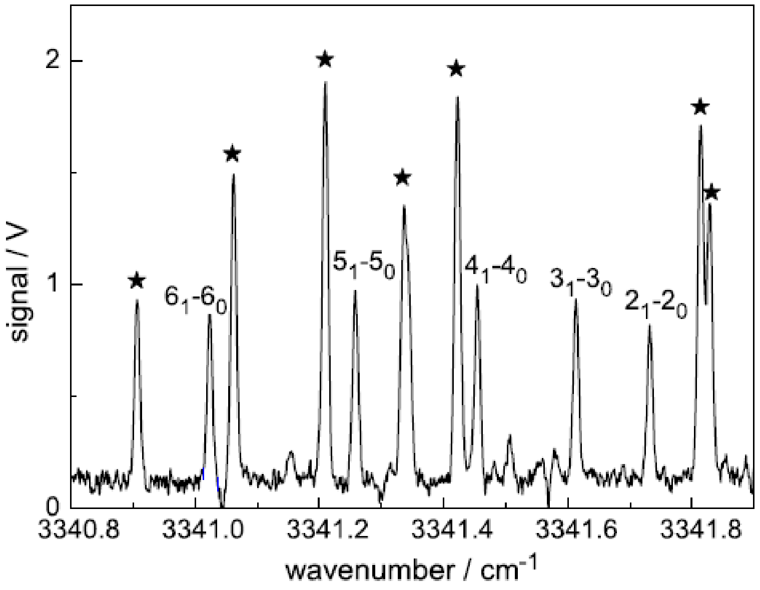

Figure 1. Portion of the ν_4 band of NH_3D^+ near the band center. The labeled lines belong to the $(J, K' = 1) \leftarrow (J, K'' = 0)$ progression (${}^rQ_0(J)$ in branch notation) and are the same as those shown in figure 1 of N&A (1986). Lines marked with an asterisk belong to NH_4^+.

Table 2

Constants Derived from the Fit

Constants (cm^{-1})	This Work	N&A (1986)
A''	5.852[a]	5.852[a]
B''	4.3834351(294)	4.38327(5)
D''_J	$6.1363(373) \times 10^{-5}$	$5.87(9) \times 10^{-5}$
D''_{JK}	$1.4689(293) \times 10^{-4}$	$1.52(6) \times 10^{-4}$
D''_K	0.0[a]	0.0[a]
ν_0	3341.07498(17)	3341.0764(3)
A'	5.818834(37)	5.81871(9)
B'	4.3640729(278)	4.36391(5)
D'_J	$5.4024(339) \times 10^{-5}$	$5.13(10) \times 10^{-5}$
D'_{JK}	$9.705(296) \times 10^{-5}$	$1.02(7) \times 10^{-4}$
D'_K	$3.801(91) \times 10^{-5}$	$3.1(3) \times 10^{-5}$
ζ	0.0582020(76)	0.058191(14)[b]
η_J	$-4.2581(686) \times 10^{-4}$	$-4.23(13) \times 10^{-4}$
η_K	$1.744(74) \times 10^{-4}$	$1.76(18) \times 10^{-4}$
q_+	$-3.393(98) \times 10^{-4}$[c]	$2.93(19) \times 10^{-4}$

HMgNC an example of molecule found in laboratory as the result of a collaboration between spectroscopists and astronomers

THE ASTROPHYSICAL JOURNAL, 775:133 (4pp), 2013 October 1 doi:10.1088/0004-637X/775/2/133

LABORATORY AND ASTRONOMICAL DISCOVERY OF HYDROMAGNESIUM ISOCYANIDE*

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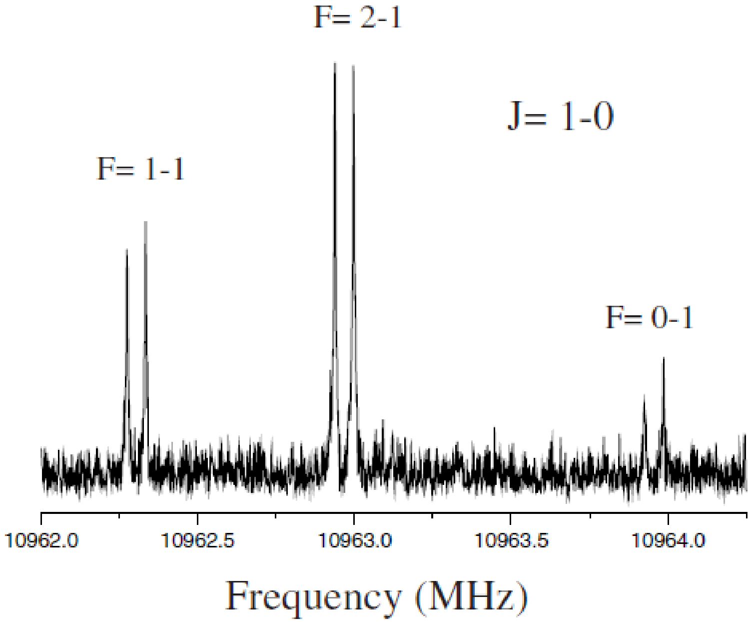

Figure 1. $J = 1$–0 rotational transition of HMgNC, observed in this work near 11 GHz. The nuclear quadrupole coupling hyperfine structure is clearly resolved. This spectrum represents one scan at steps of 0.3 MHz with 600 averages phase-coherently coadded in each point.

Table 1
Laboratory and Space Frequencies for the Observed Transitions of HMgNC

J_u	F_u	J_l	F_l	ν (MHz)	Unc (MHz)	$\nu_o - \nu_c$ (KHz)
1	1	0	1	10962.305	0.002	0.2
1	2	0	1	10962.966	0.002	0.3
1	0	0	1	10963.954	0.002	−1.8
2	2	1	2	21924.979	0.002	−1.2
2	1	1	0	21925.089	0.002	−1.5
2	2	1	1	21925.643	0.002	2.5
2	3	1	2	21925.688	0.002	0.5
2	1	1	1	21926.741	0.002	0.4
3		2		32888.284	0.003	Predicted
4		3		43850.716	0.009	Predicted
5		4		54812.866	0.019	Predicted
6		5		65774.663	0.035	Predicted
7		6		76736.036	0.058	Predicted
8		7		87697.500	0.400	584.5
10		9		109616.700	0.400	−210.4
12		11		131533.900	1.000	−182.6
13		12		142490.900	1.000	−533.8
14		13		153447.868	0.489	Predicted
15		14		164403.313	0.603	Predicted
16		15		175357.701	0.733	Predicted
17		16		186310.959	0.881	Predicted
18		17		197263.018	1.048	Predicted
19		18		208213.806	1.233	Predicted

Notes. The $J = 1$–0 and $J = 2$–1 lines have been observed in the laboratory with an accuracy of 2 KHz. The lines $J = 8$–7, 10–9, 12–11, and 13–12 have been observed in IRC+10216. Predictions obtained with the derived rotational constants are provided for lines with $E_{\rm upp} < 100$ K.

Metal Halides an example of an astronomical challenge for their identification when frequencies were already available from laboratory

(The origin of MADEX !!!)

Astron. Astrophys. 183, L10–L12 (1987)

Letter to the Editor

ASTRONOMY AND ASTROPHYSICS

Metals in IRC+10216: detection of NaCl, AlCl, and KCl, and tentative detection of AlF

J. Cernicharo[1,2] and M. Guélin[1]

4 series of harmonically Related lines found in IRC+10216

B and D derived for these species from astronomical data

1 year thinking in slightly asymetric species because D was too large (factor 10)

At that time all molecules found in space had covalent bonds……

TABLE 1

METAL HALIDES LINES IN IRC+10216

Obser. Freq. (MHz)	$\int T_A^* dv$ K kms^{-1}	Transition	Obs-Lab[1)] (MHz)
NaCl			
91169.7 (3)	1.91 (20)	$J = 7 - 6$	−0.2
104189.8 (3)	1.24 (14)	$J = 8 - 7$	0.1
130223.4 (3)	1.93 (9)	$J = 10 - 9$	−0.2
143237.0 (4)	1.47 (23)	$J = 11 - 10$	−0.4
156248.6 (2)	1.52 (13)	$J = 12 - 11$	0.0
169258.3 (10)	1.54 (30)	$J = 13 - 12$	1.1
Na^{37}Cl			
101961.9 (5)	0.68 (9)	$J = 8 - 7$	0.3
AlCl			
87457.9 (5)	0.73 (20)	$J = 6 - 5$	0.3
102032.4 (5)	0.82 (10)	$J = 7 - 6$	0.5
145744.2 (3)	2.42 (10)	$J = 10 - 9$	−0.4
160311.9 (3)	3.56 (35)	$J = 11 - 10$	−0.2
Al^{37}Cl			
142322.5 (5)	1.10 (20)	$J = 10 - 9$	0.7
156546.8 (10)	1.52 (30)	$J = 11 - 10$	−0.4
KCl			
99928.5 (10)	0.43 (15)	$J = 13 - 12$	−0.9
107611.3 (10)	0.25 (13)	$J = 14 - 13$	−0.1
130650.2 (6)	0.51 (11)	$J = 17 - 16$	−0.2
146002.1 (10)	0.39 (6)	$J = 19 - 18$	−1.1
153678.7 (10)	0.71 (12)	$J = 20 - 19$	1.3
161349.4 (15)	1.00 (40)	$J = 21 - 20$	−0.6
AlF			
98926.6 (5)	0.97 (10)	$J = 3 - 2$	−0.1
131898.0 (10)	0.80 (18)	$J = 4 - 3$	−0.7
164867.7 (6)	1.90 (40)	$J = 5 - 4$	−0.1

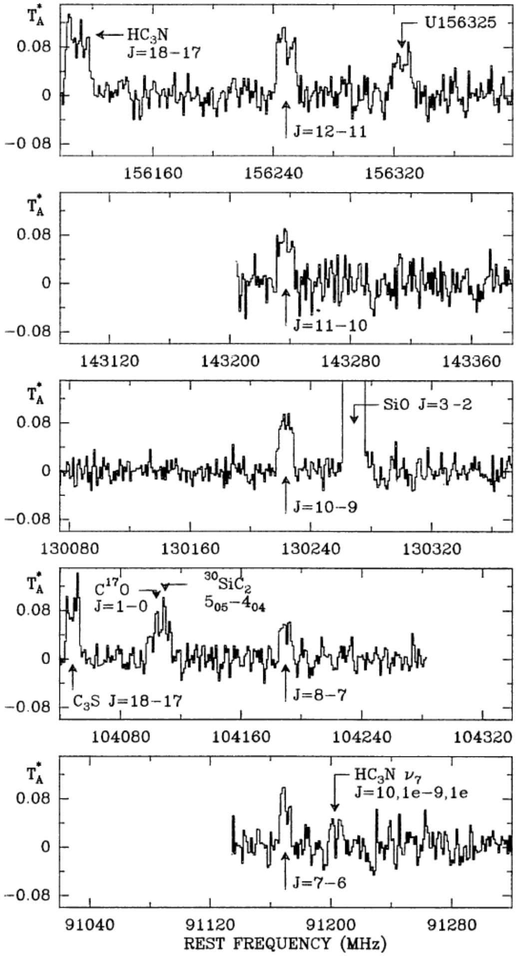

Fig. 1: Five spectra, observed toward IRC+10216 with the IRAM 30m telescope, showing the J=7–6 to 12–11 rotational transitions of NaCl. The HC$_3$N line in the upper spectrum lies in the upper sideband of the receiver and has been rejected by 15 dB.

G. Herzberg, "Atomic Spectra and Atomic Structure"

G. Herzberg, "Spectra of Diatomic Molecules"

G. Herzberg, "Infrared and Raman Spectra"

G. Herzberg, "Electronic Spectra of Polyatomic Molecules"

G. Herzberg, "The Spectra and Structures of Simple Free Radicals An Introduction to Molecular Spectroscopy"

G. M. Barrow, "Introduction to Molecular Spectroscopy"

H. B. Dunford, "Elements of Diatomic Molecular Spectra"

R. N. Dixon, "Spectroscopy and Structure"

W G Richards and P R Scott "Structure and Spectra of Molecules",.

C N Banwell and E M McCash, "Fundamentals of Molecular Spectroscopy",.

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Gordy and Cook, Microwave Molecular Spectra, Wiley

Townes and Schalow, Microwave Spectroscopy, Dover

ROTATIONAL SPECTRUM OF LINEAR MOLECULES (basic concepts)

From a "classical" point of view of quantum theory a molecule has a rotational energy proportional to the square of the angular momentum, J^2. Hence the energy levels should have a dependency on J given by

$$E(J) \propto J(J+1)$$

The frequencies of the transitions (allowed transitions have $\Delta J = \pm 1$) could be given by

$$v(J \Rightarrow J-1) \propto J$$

From a classical point of view the angular momentum of the molecule is given by $I\omega$, where I is the momentum of inertia of the molecule,

$$I = \mu r^2$$

where μ is the reduced mass, $\mu = M_1M_2/(M_1+M_2)$, and r is the separation between the nuclei.

In this “classical” approximation for the energy of a rigid molecule the energies can be written as

$$E(J) = B\,J(J+1)$$

and the frequencies as

$$\nu = 2\,B\,(J_l+1) = 2\,B\,J_u$$

The constant B, the rotational constant, is given by

$$B = (\,h / 8\,\pi^2\,I\,) = 505379.05 / I(\mathrm{ua}\ \text{Å}^2)\ \mathrm{MHz}$$

The rotational constant has units of Hz and is often given in MHz or in wavenumbers

$$1\mathrm{cm}^{-1} = 29979.2459\ \mathrm{MHz} \approx 30\ \mathrm{GHz} \approx 1.4388\ \mathrm{K}$$

This simple expresion for the energy works fine for heavy molecules. However, when the accuracy of the observations is large it is observed that the frequencies of succesive rotational transitions do not follow this simple approximation.

¿ WHY ?

Because when molecules are rotating the nuclei are submitted to centrifugal forces which increase the distance between them and increase the momentum of inertia.

The distance between the nuclei is defined by the molecular orbitals. We need a potential U(r) describing the energy of the system as a function of the internuclear distance.

As the movement of the nuclei is much slower than those of the electrons we could consider that the electronic energy of the molecule is indepent of the vibration and of the rotation.

This approximation (Born-Oppenheimer) allows to separate the total energy into electronic, vibrational and rotational energies, i.e., the total energy of the molecule could be written as a sum of terms depending on $(m_e/M_N)^{½}$.

The problem is to find the potential energy of the molecules, U(r), describing in a reasonable way the variation of energy as a function of the internuclear distance.

The empirical expression used in spectroscopy to fit the ro-vibrational spectra of diatomic molecules is

$$F_{vJ} = \omega_e(v + \tfrac{1}{2}) - \omega_e x_e(v + \tfrac{1}{2})^2 + \omega_e y_e(v + \tfrac{1}{2})^3 + \omega_e z_e(v + \tfrac{1}{2})^4 + B_v J(J + 1) - D_e J^2(J + 1)^2 + H_e J^3(J + 1)^3 + \cdots$$

$$B_v = B_e - \alpha_e(v + \tfrac{1}{2}) + \gamma_e(v + \tfrac{1}{2})^2 \;\ldots$$

From the spectroscopic constants it is possible to derive important information, through the Morse or Dunham expression for the potential energy, on the dissociation energy, equilibrium distance, etc.

The spectra of diatomic molecules

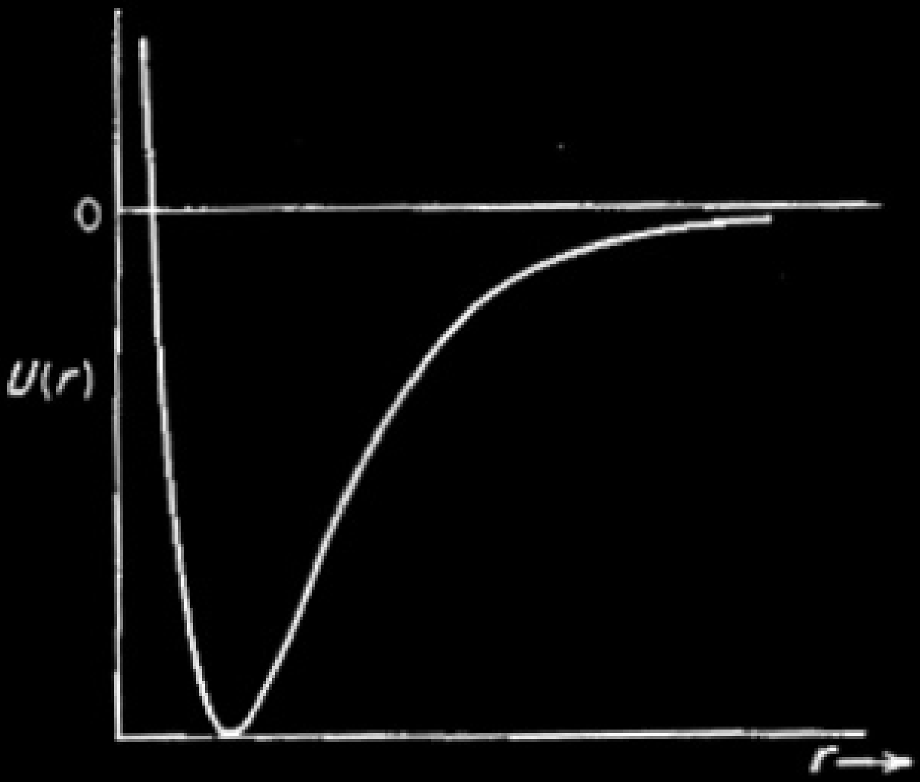
The quantum treatment of rotation, vibration and electronic movements

Potential Surfaces

As the movement of the nuclei is much slower than those of the electrons we could consider that the electronic energy of the molecule is independent of the vibration and rotation.

(Born-Oppenheimer approximation)

Problem: finding the potential energy of the molecule, U(r), describing in a reasonable way the variation of energy as a function of the internuclear distance for a given electronic state. The solution of the Schrödinger equation will depend on this potential.



Morse Potential : $U(r) = D(1 - e^{-a(r-r_e)})^2$

D = dissociation energy of the molecule
r_e = equilibrium distance between nuclei
a = a constant

The wave equation is then :

$$\frac{d^2S}{dr^2} + \left[-\frac{J(J+1)}{r^2} + \frac{8\pi^2\mu}{h^2}\left(W - D - De^{-2a(r-r_e)} + 2De^{-a(r-r_e)}\right)\right] S = 0$$

Making the following changes:

$y = e^{-a(r-r_e)}$ and $A = J(J+1)\dfrac{h^2}{8\pi^2\mu r_e^2}$

We obtain :

$$\frac{d^2S}{dy^2}+\frac{1}{y}\frac{dS}{dy}+\frac{8\pi^2\mu}{a^2h^2}\left(\frac{W-D}{y^2}+\frac{2D}{y}-D-\frac{Ar_e^2}{y^2r^2}\right)S=0$$

For A = 0, i.e., J=0 it is possible to find an analitycal solution. In the general case the solution is given by:

Harmonic oscillator

anharmonicity

Centrifugal distortion

$$\frac{W_{Jv}}{h}=\boxed{\omega_e(v+\tfrac{1}{2})-x_e\omega_e(v+\tfrac{1}{2})^2}+\boxed{J(J+1)B_e}-\boxed{D_eJ^2(J+1)^2}-\underline{\alpha_e(v+\tfrac{1}{2})J(J+1)}$$

Vibrational terms

Undisturbed rotation

Higher order corrections

Where:

$$\omega_e=\frac{a}{2\pi}\sqrt{\frac{2D}{\mu}}\qquad x_e=\frac{h\omega_e}{4D}\qquad B_e=\frac{h}{8\pi^2I_e}$$

$$D_e=\frac{h^3}{128\pi^6\mu^3\omega_e^2r_e^6}=\frac{4B_e^3}{\omega_e^2}$$

$$\alpha_e=\frac{3h^2\omega_e}{16\pi^2\mu r_e^2D}\left(\frac{1}{ar_e}-\frac{1}{a^2r_e^2}\right)=6\sqrt{\frac{x_eB_e^3}{\omega_e}}-\frac{6B_e^2}{\omega_e}$$

There is another potential proposed by Dunham. It is represented by a series in (r- r_e), where r_e is the equilibrium distance

$$U = a_0\xi^2(1 + a_1\xi + a_2\xi^2 + \cdot\cdot\cdot) + B_eJ(J + 1)(1 - 2\xi + 3\xi^2 - 4\xi^3$$

Where $\xi = (r-r_e)/r_e$ and $B_e = h/8\pi^2\mu r_e^2$

The solution can be given as

$$F_{vJ} = \sum_{l,j} Y_{lj}(v + \tfrac{1}{2})^l J^j (J + 1)^j$$

Where the terms Y_{lj} are the Dunham coefficients

…these terms can be calculated easily….

$$\begin{aligned}
Y_{00} &= B_e/8(3a_2 - 7a_1^2/4) \\
Y_{10} &= \omega_e[1 + (B_e^2/4\omega_e^2)(25a_4 - 95a_1a_3/2 - 67a_2^2/4 \\
&\quad + 459a_1^2a_2/8 - 1155a_1^4/64)] \\
Y_{20} &= (B_e/2)[3(a_2 - 5a_1^2/4) + (B_e^2/2\omega_e^2)(245a_6 - 1365a_1a_5/2 \\
&\quad - 885a_2a_4/2 - 1085a_3^2/4 + 8535a_1^2a_4/8 + 1707a_2^3/8 \\
&\quad + 7335a_1a_2a_3/4 - 23{,}865a_1^3a_3/16 - 62{,}013a_1^2a_2^2/32 \\
&\quad + 239{,}985a_1^4a_2/128 - 209{,}055a_1^6/512)] \\
Y_{30} &= (B_e^2/2\omega_e)(10a_4 - 35a_1a_3 - 17a_2^2/2 + 225a_1^2a_2/4 \\
&\quad - 705a_1^4/32) \\
Y_{40} &= (5B_e^3/\omega_e^2)(7a_6/2 - 63a_1a_5/4 - 33a_2a_4/4 - 63a_3^2/8 \\
&\quad + 543a_1^2a_4/16 + 75a_2^3/16 + 483a_1a_2a_3/8 - 1953a_1^3a_3/32 \\
&\quad - 4989a_1^2a_2^2/64 + 23{,}265a_1^4a_2/256 - 23{,}151a_1^6/1024)
\end{aligned}$$

and obviously, there is a relation between the Dunham coefficients and those obtained with the Morse potential

$$\begin{array}{lll}
Y_{10} \approx \omega_e & Y_{20} \approx -\omega_e x_e & Y_{30} \approx \omega_e y_e \\
Y_{01} \approx B_e & Y_{11} \approx -\alpha_e & Y_{21} \approx \gamma_e \\
Y_{02} \approx -D_e & Y_{12} \approx -\beta_e & Y_{40} \approx \omega_e z_e \\
Y_{03} \approx H_e & &
\end{array}$$

IN SUMMARY: The empirical expression used in spectroscopy to fit the ro-vibrational spectra of diatomic molecules is

$$F_{vJ} = \omega_e(v + \tfrac{1}{2}) - \omega_e x_e(v + \tfrac{1}{2})^2 + \omega_e y_e(v + \tfrac{1}{2})^3 + \omega_e z_e(v + \tfrac{1}{2})^4 \\ + B_v J(J + 1) - D_e J^2(J + 1)^2 + H_e J^3(J + 1)^3 + \cdots$$

$$B_v = B_e - \alpha_e(v + \tfrac{1}{2}) + \gamma_e(v + \tfrac{1}{2})^2 \;.\;.\;.$$

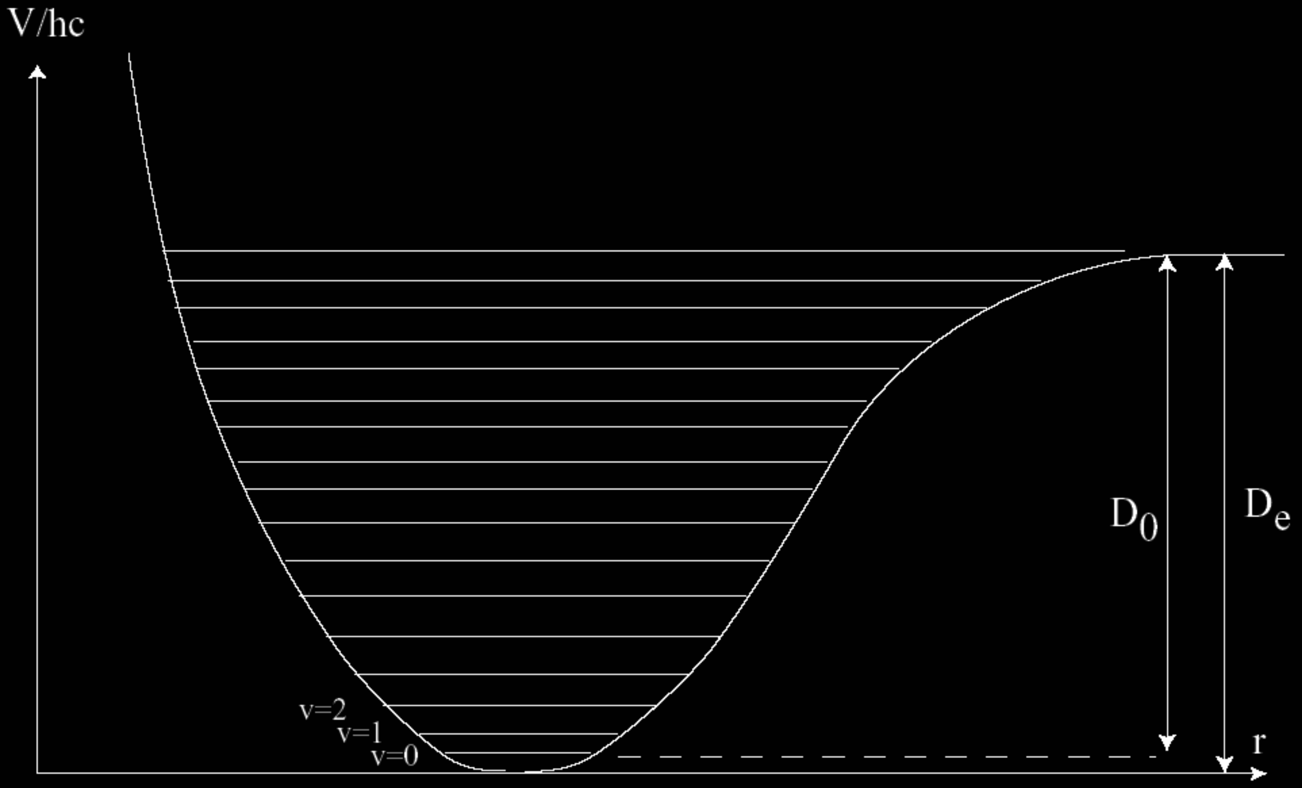
INVERSE PROBLEM: From spectroscopic measurements it Is possible to fit spectroscopic constants and from them it is possible to derive important information, through the Morse or Dunham expression for the potential energy, on the dissociation energy, equilibrium distance, etc.

This is the main subject of papers in journals such as the *Journal of Molecular Spectroscopy* or the *Journal of Molecular Structure*

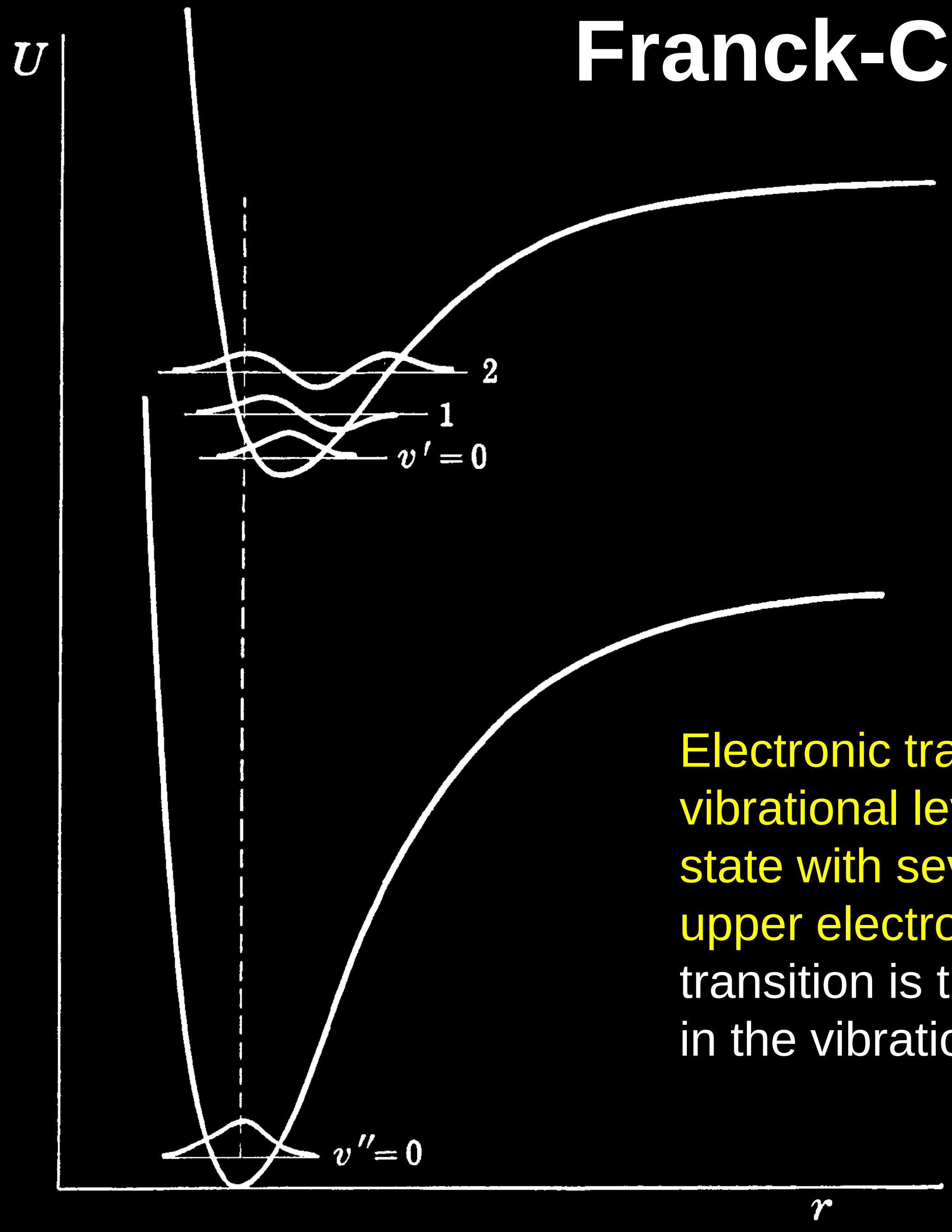
A few facts…

Continuous term spectra and dissociation

If oscillator has more energy E' than, hcD_e, then $r \rightarrow \infty$ and molecule dissociates. For $E' > hcD_e$, system has excess energy (kinetic energy) after dissociation. $\therefore \ (K.E)_{\text{atoms}} > 0$ and not quantized.



Franck-Condon Principle



Electronic transitions will connect the lowest vibrational level of the ground electronic state with several vibrational states of the upper electronic state. The most probable transition is the one having the best overlap in the vibrational eigen functions.

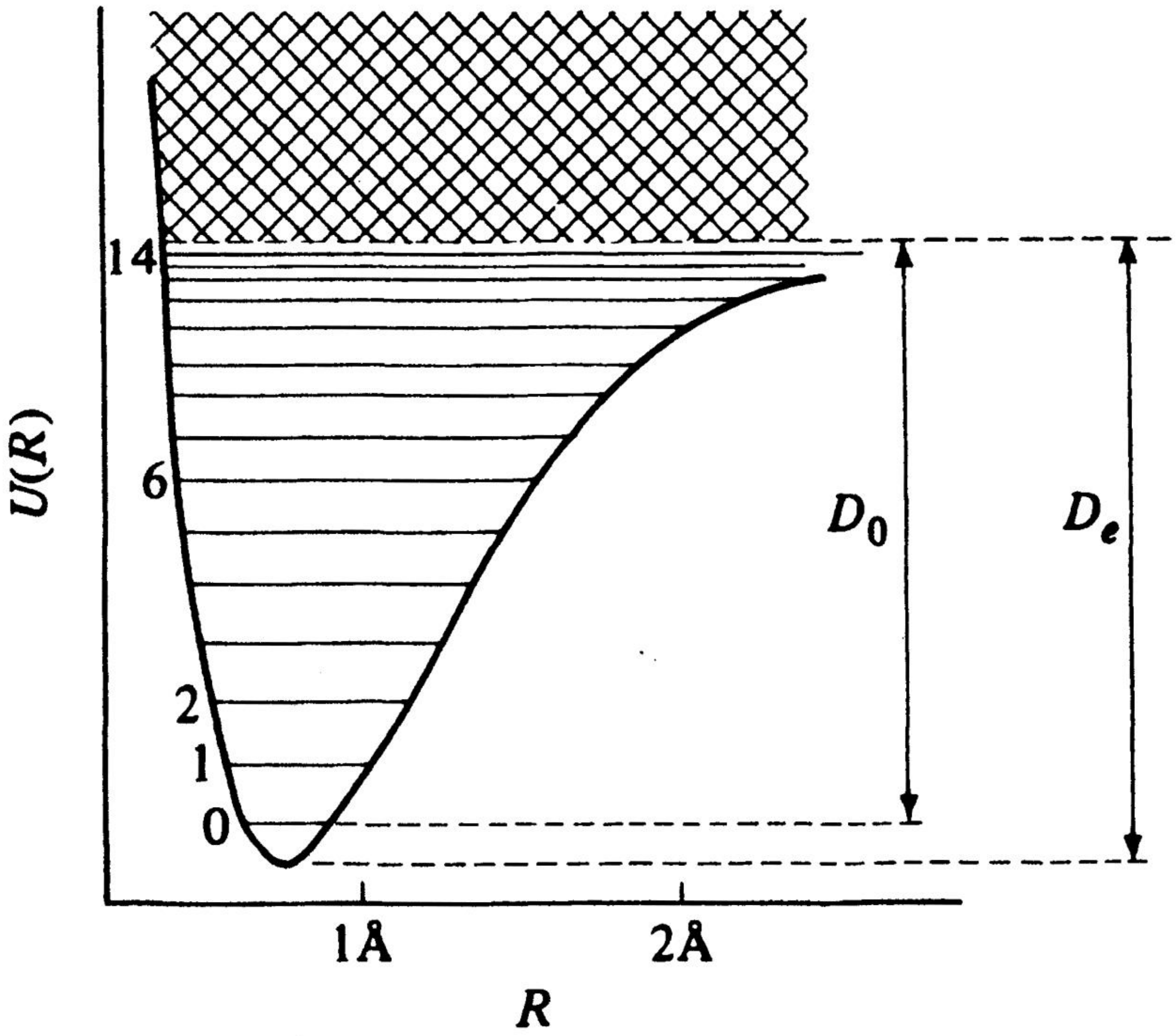
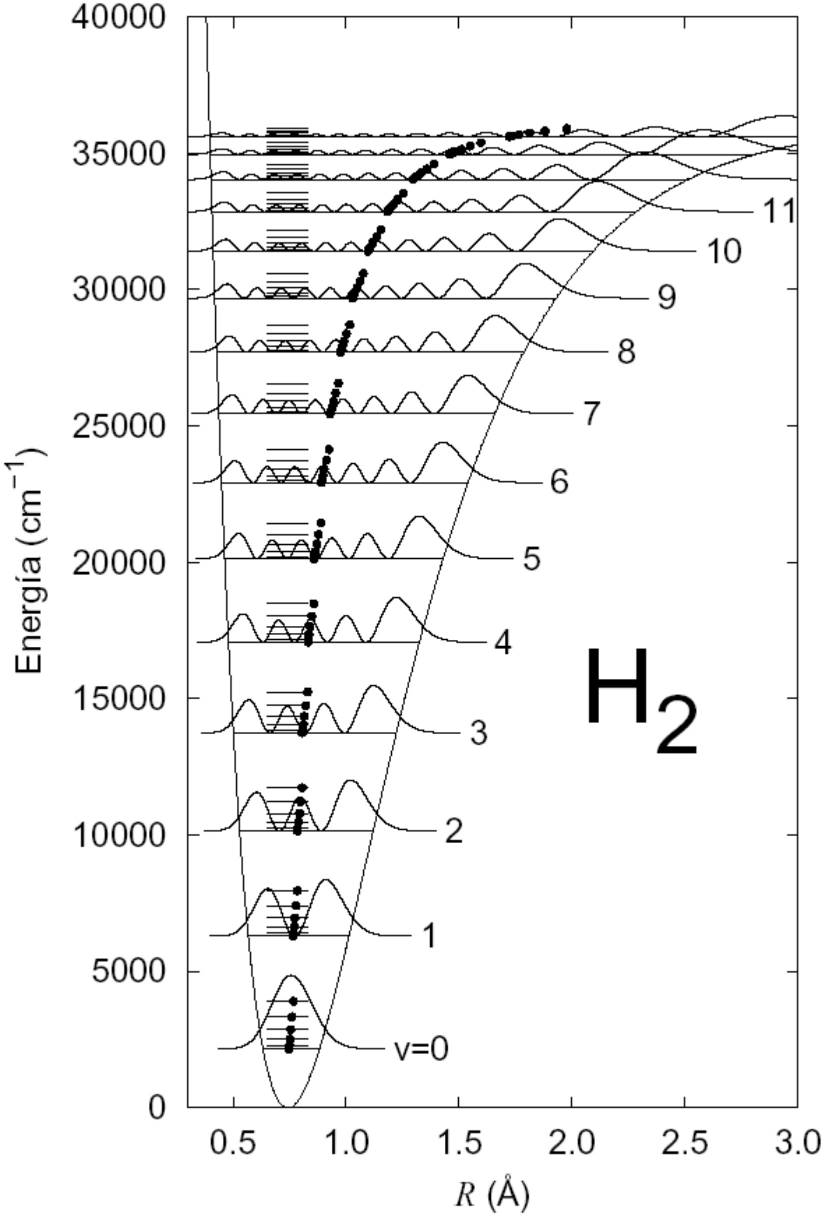


Fig. 4.4 The vibrational levels of the H_2 ground electronic state. The levels are drawn between the classical limits of vibration, but there is a small probability for vibration to extend into the classically forbidden region.



Energía vibracional:

$$E_{vib}(v) = h\nu_e\left(v+\frac{1}{2}\right) - h\nu_e x_e\left(v+\frac{1}{2}\right)^2.$$

La separación entre estados vibracionales sucesivos,

$$\frac{\Delta E_v}{h} = \frac{E_{vib}(v+1)-E_{vib}(v)}{h} = \nu_e - \nu_e x_e 2(v+1),$$

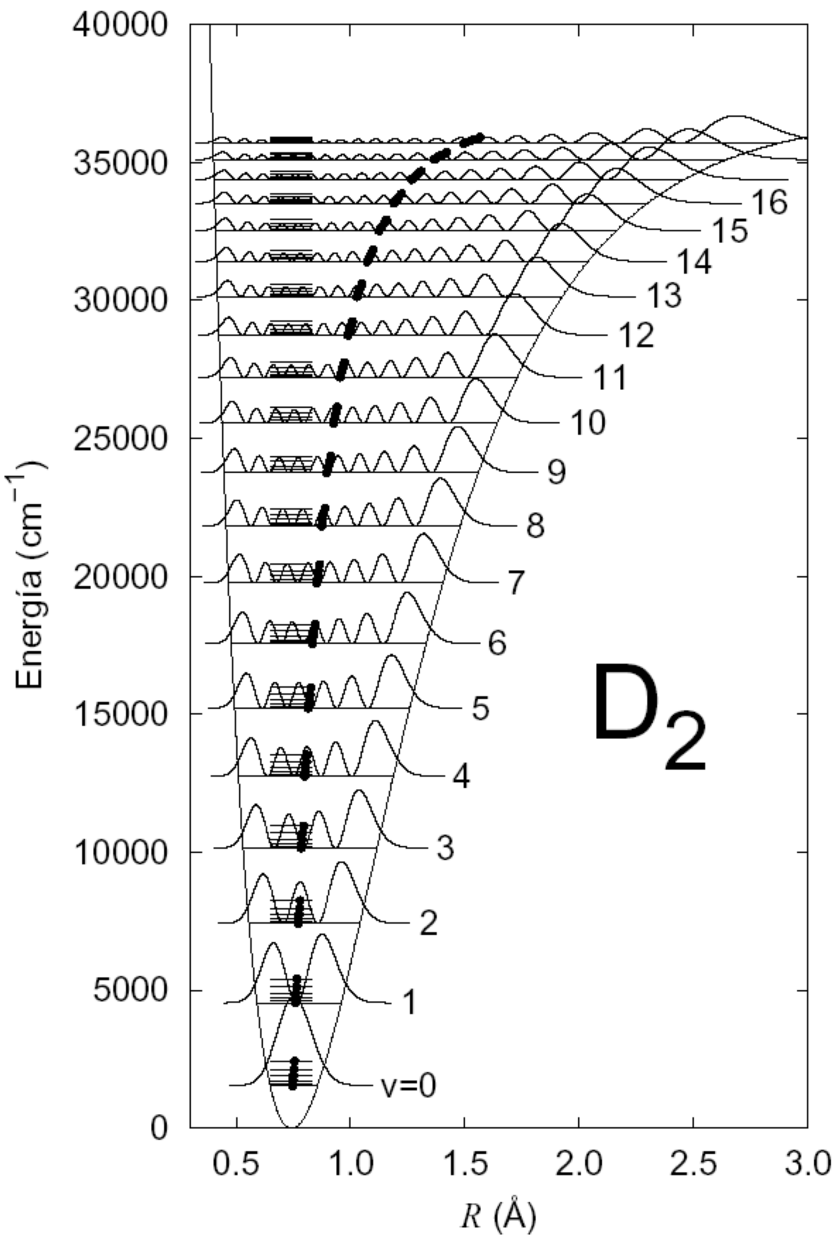
se reduce al aumentar v (Excepción: algunas moléculas con $x_e < 0$).

Separación nuclear efectiva:

$$\frac{1}{R^2_{vJ}} = \left\langle \frac{1}{R^2} \right\rangle = \left\langle \psi_v \middle| \frac{1}{R^2} \middle| \psi_v \right\rangle.$$

Constante rotacional efectiva:

$$B_v = B_e - \alpha_e\left(v+\frac{1}{2}\right) = \frac{h^2}{8\pi^2\mu R^2_{vJ}}.$$



Energía rotacional:

$$E_{rot} = hB_v J(J+1) - h\bar{D}_e\,[J(J+1)]^2$$

La separación entre estados rotacionales sucesivos,

$$\frac{\Delta E_J}{h} = \frac{E_{v,J+1} - E_{v,J}}{h} = B_v 2(J+1) - \bar{D}_e 4(J+1)^3$$

disminuye con $J\uparrow$ y $v\uparrow$.

Energía de punto cero:

$$\epsilon_0 = \frac{1}{2}h\nu_e - \frac{1}{4}h\nu_e x_e + hY_{00}.$$

Importancia relativa: Generalmente $\nu_e \gg \nu_e x_e \approx B_e \gg \alpha_e \gg \bar{D}_e$.

Constantes espectroscópicas en cm^{-1}.

		U_e	ν_e	$\nu_e x_e$	B_e	α_e	$\bar{D}_e$	R_e
H_2	$X - {}^1\Sigma_g^+$	0	4401.213	121.336	60.8530	3.0622	47.1×10^{-3}	0.74144
	$B - {}^1\Sigma_u^+$	91700.0	1358.09	20.888	20.0154	1.1845	16.25×10^{-3}	1.29282
D_2 †	$X - {}^1\Sigma_g^+$	0	3115.50	61.82	30.4436	1.0786	11.41×10^{-3}	0.74152
OH	$X - {}^2\Pi$	0	3737.761	84.8813	18.9108	0.7242	1.938×10^{-3}	0.96966
HF	$X - {}^1\Sigma^+$	0	4138.32	89.88	20.9557	0.798	2.151×10^{-3}	0.916808
N_2 †	$X - {}^1\Sigma_g^+$	0	2358.57	14.324	1.998241	0.017318	5.76×10^{-6}	1.097685
CO	$X - {}^1\Sigma^+$	0	2169.81358	13.28831	1.93128087	0.01750441	6.12147×10^{-6}	1.128323
NO	$X - {}^2\Pi_{1/2}$	0	1904.204	14.075	1.67195	0.0171	0.54×10^{-6}	1.15077
	$X - {}^2\Pi_{3/2}$	119.82	1904.040	14.100	1.72016	0.0182	10.23×10^{-6}	1.15077
	$A - {}^2\Sigma^+$	43965.7	2374.31	10.106	1.9965	0.01915	5.4×10^{-6}	1.06434
O_2 †	$X - {}^3\Sigma_g^-$	0	1580.193	11.981	1.4376766	0.01593	4.839×10^{-6}	1.20752
F_2 †	$X - {}^1\Sigma_g^+$	0	916.64	11.236	0.89019	0.013847	3.3×10^{-6}	1.41193
ICl	$X - {}^1\Sigma^+$	0	384.293	1.501	0.1141587	0.0005354	40.3×10^{-9}	2.320878
I_2	$X - {}^1\Sigma_g^+$	0	214.502	0.6147	0.037372	0.0001138	4.25×10^{-9}	2.6663

† $\nu_e y_e$: 0.562 (D_2), −0.00226 (N_2), 0.04747 (O_2), $-0.113\ \text{cm}^{-1}$ (F_2).

$\omega' \approx \omega \sqrt{\frac{\mu}{\mu'}}$ Ejemplo: H_2 y D_2 $\omega' \approx \omega \sqrt{\frac{1}{2}} = 4401.213 / 1.414 = 3112.1$ vs $3115.5\ \text{cm}^{-1}$

Breakdown of the Bohr-Oppenheimer approximation

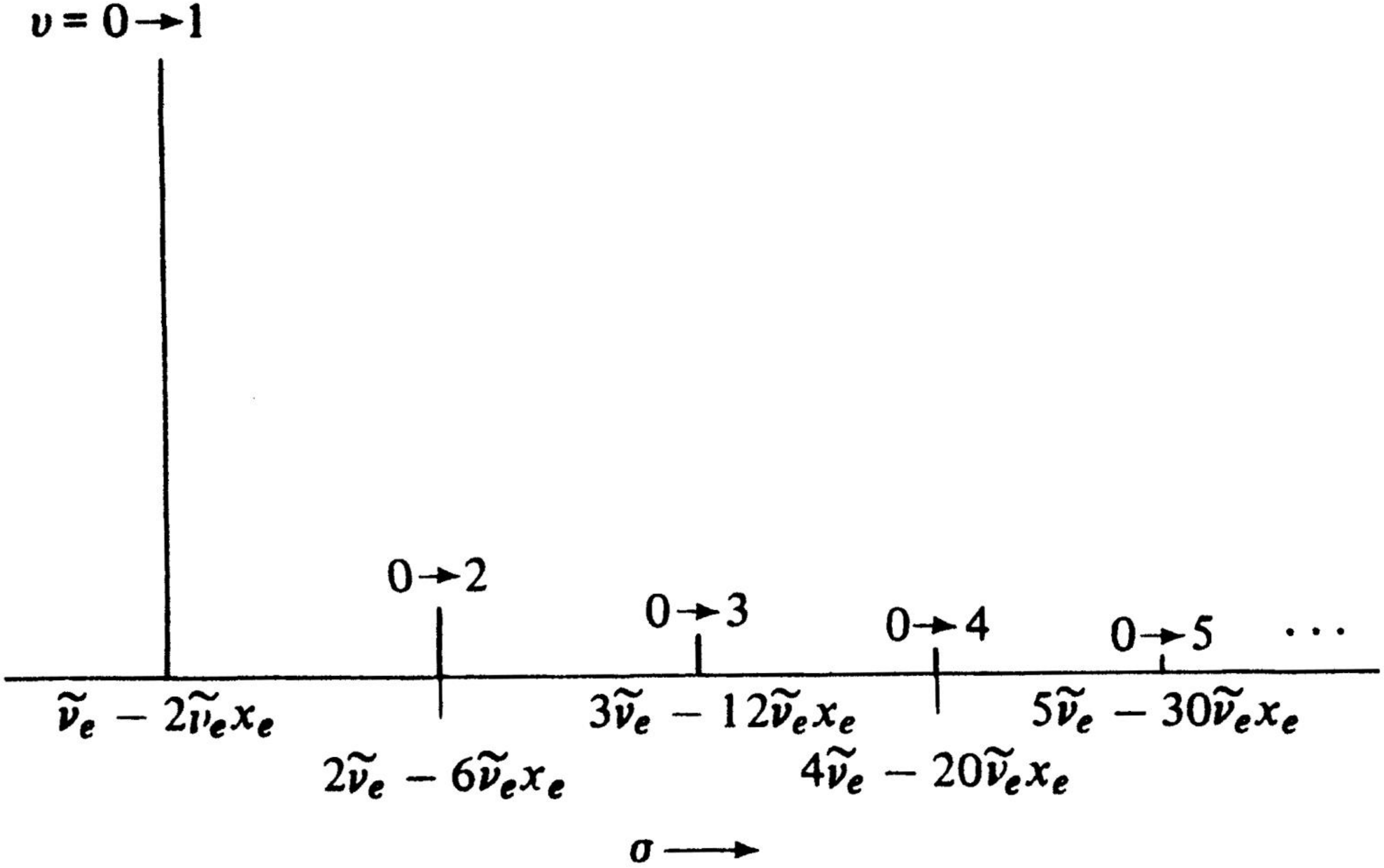


Fig. 4.7 Positions of the band origins of the infrared absorption spectrum of a diatomic molecule.

Espectro roto-vibracional: $\Delta J \neq 0$, $v \to v'$: Para la transición fundamental $v: 0 \to 1$ tenemos:

$$\begin{aligned}
&\textbf{Banda origen}: & \nu_{\text{or}} &= \nu_e - 2\nu_e x_e, \\
&\textbf{Rama P}\ (\Delta J = -1): & \nu_P(J) &= \nu_{\text{or}} - 2B_e(J+1) - \alpha_e(J-1)(J+1) + 4\bar{D}_e(J+1)^3, \\
&\textbf{Rama Q}\ (\Delta J = 0): & \nu_Q(J) &= \nu_{\text{or}} - \alpha_e J(J+1), \\
&\textbf{Rama R}\ (\Delta J = +1): & \nu_R(J) &= \nu_{\text{or}} + 2B_e(J+1) - \alpha_e(J+1)(J+3) - 4\bar{D}_e(J+1)^3,
\end{aligned}$$

$$I_{v,J \to v',J'} = I_{or}(v \to v')\, N_J \propto I_{or}(v \to v')\, \frac{hB_e}{kT}\, (2J+1)\, e^{-J(J+1)hB_e/kT},$$

Separación entre líneas sucesivas:

$$\begin{aligned}
&\textbf{Rama P}: & \Delta\nu_P(J) &= -2B_e - \alpha_e(2J-1) + 4\bar{D}_e(3J^2 - 9J + 7), \\
&\textbf{Rama Q}: & \Delta\nu_Q(J) &= -\alpha_e 2(J+1), \\
&\textbf{Rama R}: & \Delta\nu_R(J) &= +2B_e - \alpha_e(2J+5) - 4\bar{D}_e(3J^2 - 9J + 7).
\end{aligned}$$

- $\nu_P < \nu_{or} < \nu_R$ ($\nu_Q \approx \nu_{or}$ pero no es visible).
- $\Delta\nu_P(J) \approx \Delta\nu_R(J) \approx 2B_e$.
- $J \uparrow \Longrightarrow \nu_P \downarrow, \nu_R \uparrow, \Delta\nu_P(J) \downarrow, \Delta\nu_R(J) \uparrow$.
- La rama P puede presentar cabeza de banda cuando $\Delta\nu_R(J) = 0 \approx 2B_e - \alpha_e(2J_{CB} + 5)$. El fenómeno es más fácil en moléculas ligeras: $J_{CB} = 24$ (HF y OH), 108 (CO) y 211 (ICl).

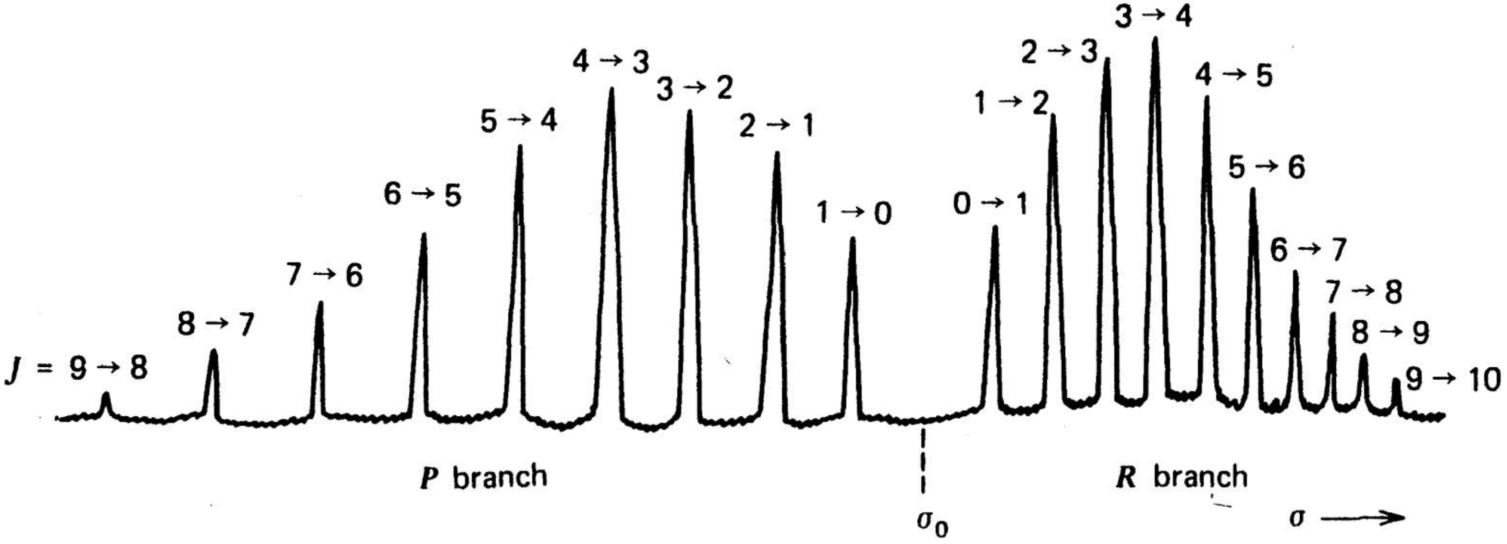


Fig. 4.9 Rotational fine structure of a vibration–rotation band of a diatomic molecule. Note the decreasing spacing with increasing J in the R branch, and the increasing spacing with increasing J in the P branch.

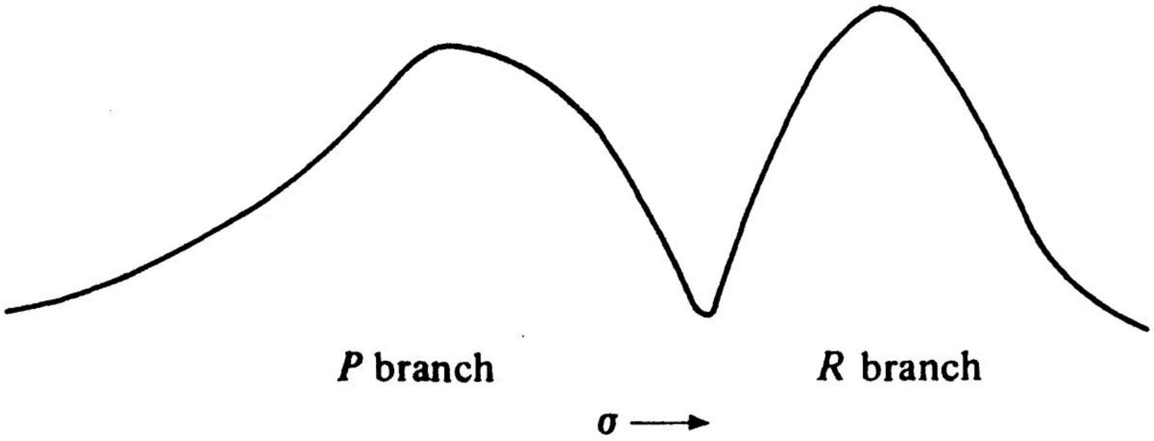
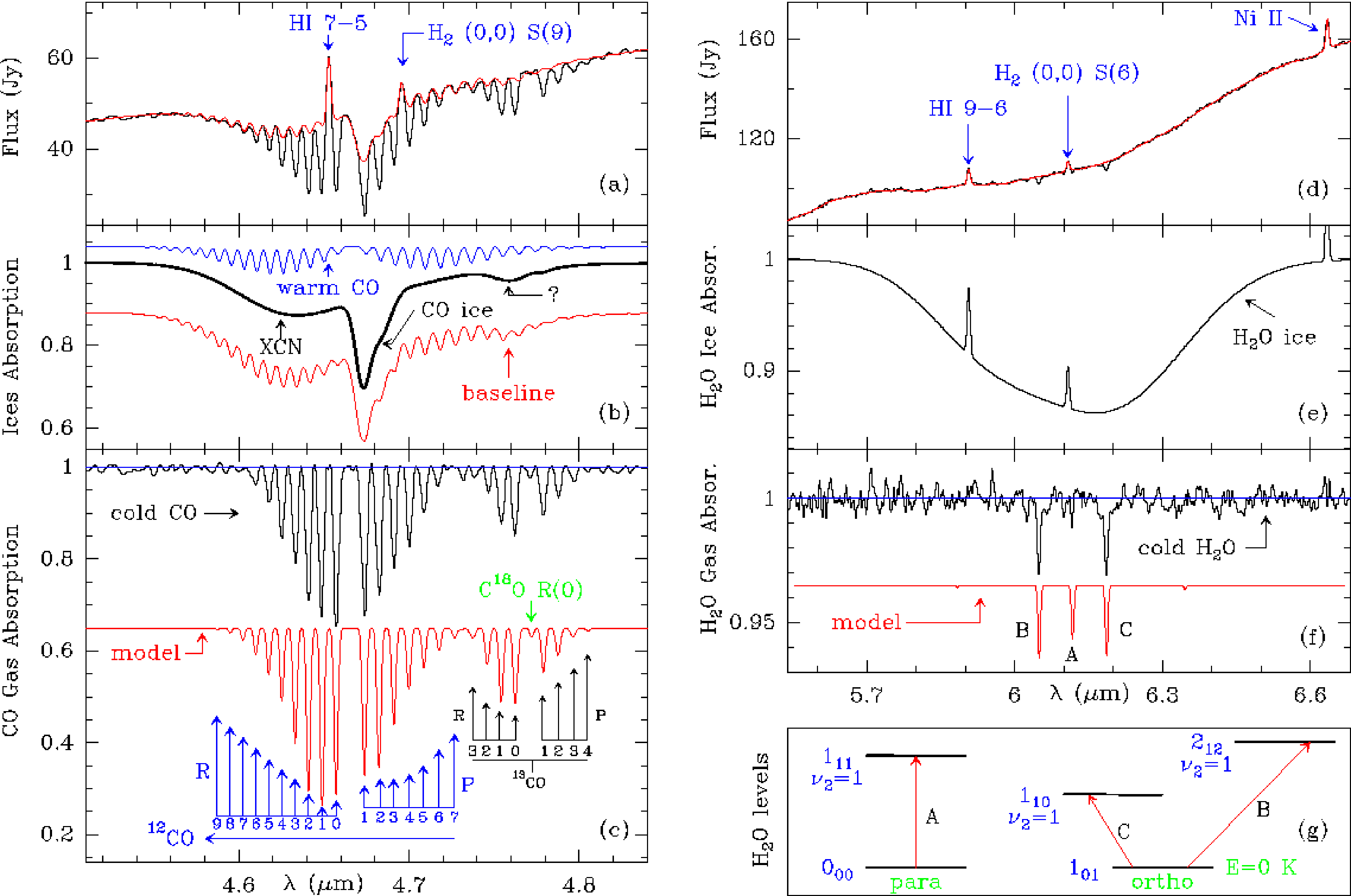


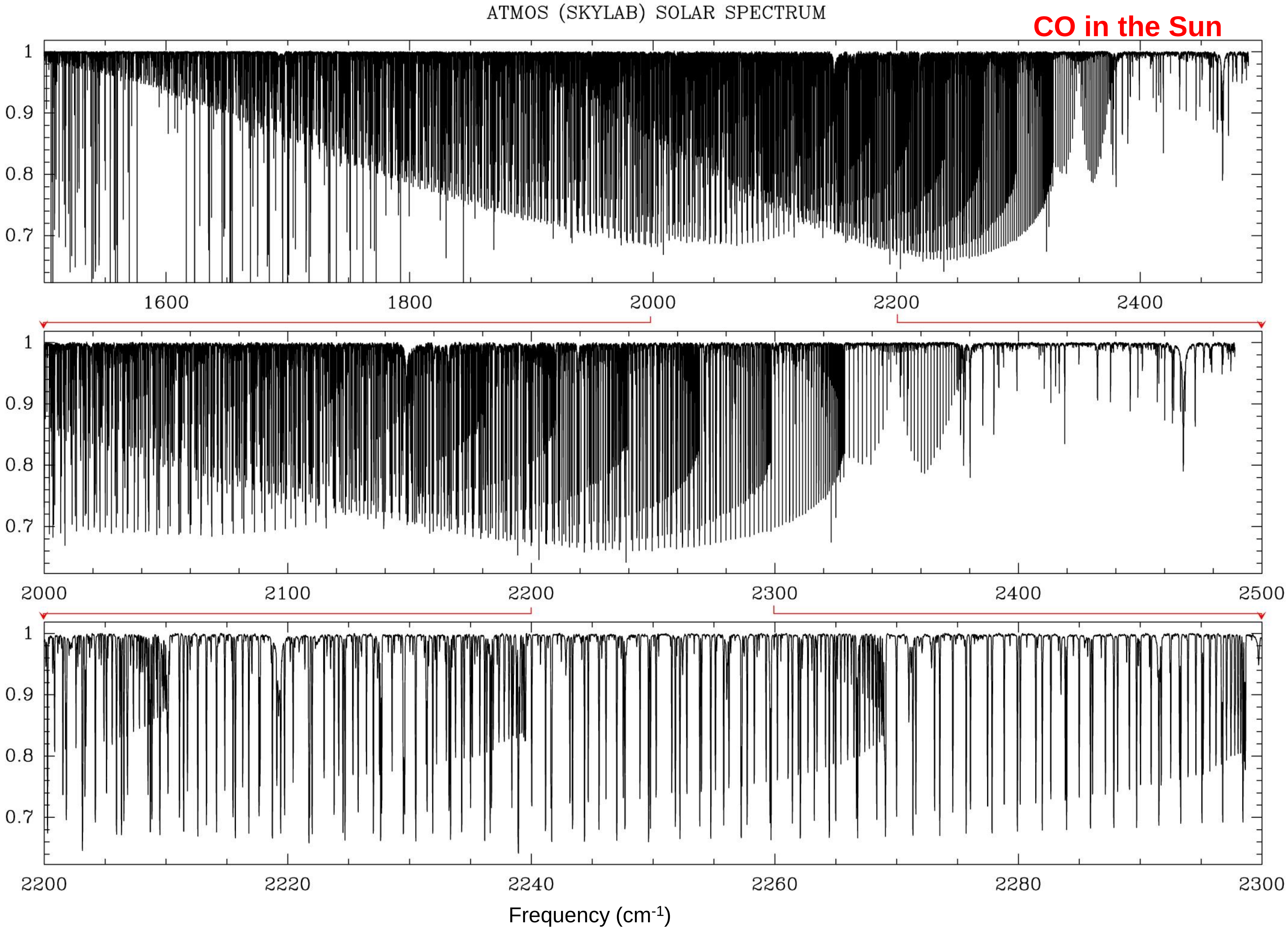
Fig. 4.10 Appearance of a vibration–rotation band of a diatomic molecule under low resolution.

Perhaps in dark clouds infrared effects are much less important. The kinetic temperature is too low to pump vibrational levels. But !!!!

(Moneti, Cernicharo & Pardo ApJ Letters,2001)



CO in the Sun



All frequencies can be computed with a few constants !

```
ROTATIONAL CONSTANTS (Yij) USED FOR FREQUENCY PREDICTIONS, LINE INTENSITIES AND ENERGIES IN MADEX
 Y10 (cm-1) =       2169.81272147  ERROR (1sigma) =             .00000356
 Y20 (cm-1) =        -13.28791503  ERROR (1sigma) =             .00000280
 Y30 (cm-1) =      1.04230043E-02  ERROR (1sigma) =        8.71724663E-07
 Y40 (cm-1) =      6.75125585E-05  ERROR (1sigma) =        1.20645180E-07
 Y50 (cm-1) =      3.26953608E-07  ERROR (1sigma) =        8.56996098E-09
 Y60 (cm-1) =     -5.79731191E-09  ERROR (1sigma) =        3.26608992E-10
 Y70 (cm-1) =     -6.26610004E-10  ERROR (1sigma) =        6.34448969E-12
 Y80 (cm-1) =      9.06043909E-12  ERROR (1sigma) =        4.92657662E-14
 Y90 (cm-1) =     -6.17053672E-14  ERROR (1sigma) =         .00000000
 Y01 (MHz) =       57898.34440307  ERROR (1sigma) =             .00015568
 Y11 (MHz) =        -524.76175591  ERROR (1sigma) =             .00041569
 Y21 (MHz) =       1.80115040E-02  ERROR (1sigma) =        2.45807930E-04
 Y31 (MHz) =      -4.71867991E-05  ERROR (1sigma) =        4.77632641E-05
 Y41 (MHz) =       8.66859871E-05  ERROR (1sigma) =        4.23503613E-06
 Y51 (MHz) =      -2.30684772E-06  ERROR (1sigma) =        1.86487796E-07
 Y61 (MHz) =       4.56008373E-09  ERROR (1sigma) =        3.96223816E-09
 Y71 (MHz) =      -4.00605025E-10  ERROR (1sigma) =        3.23262843E-11
 Y02 (MHz) =       -.18351892      ERROR (1sigma) =        2.05966918E-07
 Y12 (MHz) =       3.06017813E-05  ERROR (1sigma) =        3.10233614E-07
 Y22 (MHz) =      -5.00667407E-06  ERROR (1sigma) =        8.34577408E-08
 Y32 (MHz) =       7.70219531E-09  ERROR (1sigma) =        5.33917091E-09
 Y42 (MHz) =      -2.04206155E-09  ERROR (1sigma) =         .00000000
 Y52 (MHz) =       7.95573653E-11  ERROR (1sigma) =         .00000000
 Y03 (MHz) =       1.73912087E-07  ERROR (1sigma) =        2.10858800E-10
 Y13 (MHz) =      -4.78671372E-09  ERROR (1sigma) =        5.46158704E-11
 Y23 (MHz) =      -1.53877206E-11  ERROR (1sigma) =        9.29239351E-12
 Y33 (MHz) =       5.23188498E-13  ERROR (1sigma) =         .00000000
 Y43 (MHz) =      -4.28843372E-14  ERROR (1sigma) =         .00000000
 Y04 (MHz) =       1.56388520E-13  ERROR (1sigma) =        8.32772613E-14
 Y14 (MHz) =      -2.15397911E-14  ERROR (1sigma) =         .00000000
 Y24 (MHz) =      -1.18564210E-16  ERROR (1sigma) =         .00000000
 Y34 (MHz) =      -4.36681631E-17  ERROR (1sigma) =         .00000000
 Y44 (MHz) =       2.08681608E-18  ERROR (1sigma) =         .00000000
 Y05 (MHz) =      -1.38717863E-18  ERROR (1sigma) =         .00000000
 Y15 (MHz) =      -1.62968088E-19  ERROR (1sigma) =         .00000000
 Y25 (MHz) =      -2.75517128E-21  ERROR (1sigma) =         .00000000
 Y35 (MHz) =       7.81937501E-23  ERROR (1sigma) =         .00000000
 Y06 (MHz) =      -2.32787184E-23  ERROR (1sigma) =         .00000000
 Y16 (MHz) =      -1.19013866E-24  ERROR (1sigma) =         .00000000
 Y26 (MHz) =      -1.75689536E-25  ERROR (1sigma) =         .00000000
 Y36 (MHz) =       7.59714424E-27  ERROR (1sigma) =         .00000000
 Y07 (MHz) =      -1.24275243E-28  ERROR (1sigma) =         .00000000
 Y17 (MHz) =      -1.19610126E-29  ERROR (1sigma) =         .00000000
 Y27 (MHz) =       5.06551541E-31  ERROR (1sigma) =         .00000000
```

Cómo deciamos ayer ……

For simple molecules we can separate the vibrational and rotational parts of the wave function as another Born-Oppenheimer aproximation…

SIMPLE CASE: ROTATIONAL SPECTRUM OF DIATOMIC OR LINEAR MOLECULES

From a **"classical"** point of view of quantum theory a molecule has a rotational energy proportional to the square of the angular momentum, J^2. Hence the energy levels should have a dependency on J given by

$$\mathbf{E(J) \propto J(J+1)}$$

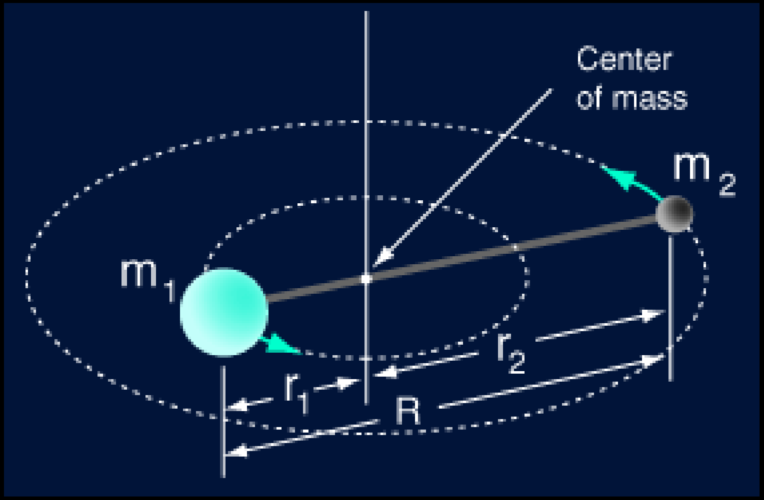
The frequencies of the transitions could be given by

$$\mathbf{\nu(J{=}{>}J\text{-}1) \propto J}$$

The angular momentum of the molecule is given by $I\omega$, where I is the momentum of inertia of the molecule,

$I = \mu\, r^2$, μ: reduded mass, r: separation between the nuclei.

In this “classical” approximation for the energy of a rigid molecule the energies can be written as



$$E(J) = B\,J(J+1)$$

and the frequencies as

$$\nu = 2\,B\,J_u$$

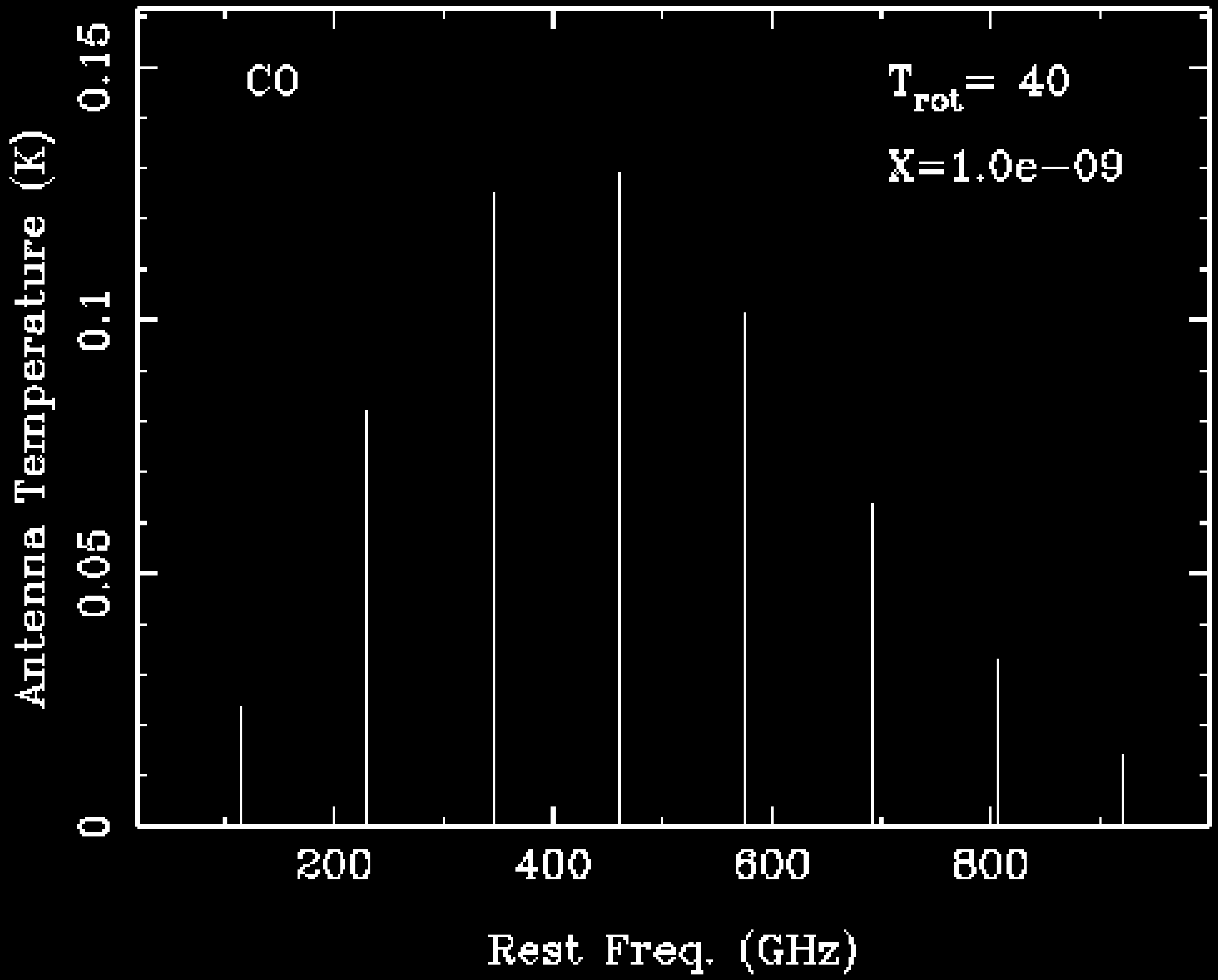
The constant B, the rotational constant, is given by

$$I = \frac{m_1 m_2 R^2}{m_1 + m_2} = \mu R^2$$

$$B = (h / 8\,\pi^2\, I)$$ [frequency units]

$$1\mathrm{cm}^{-1} = 29979.2459\ \mathrm{MHz} \approx 30\ \mathrm{GHz} \approx 1.4388\ \mathrm{K}$$

The heavier the molecule, the smaller B; the rotational spectrum will be tighter.



ROTATIONAL SPECTRUM OF CARBON MONOXIDE

EXAMPLES :

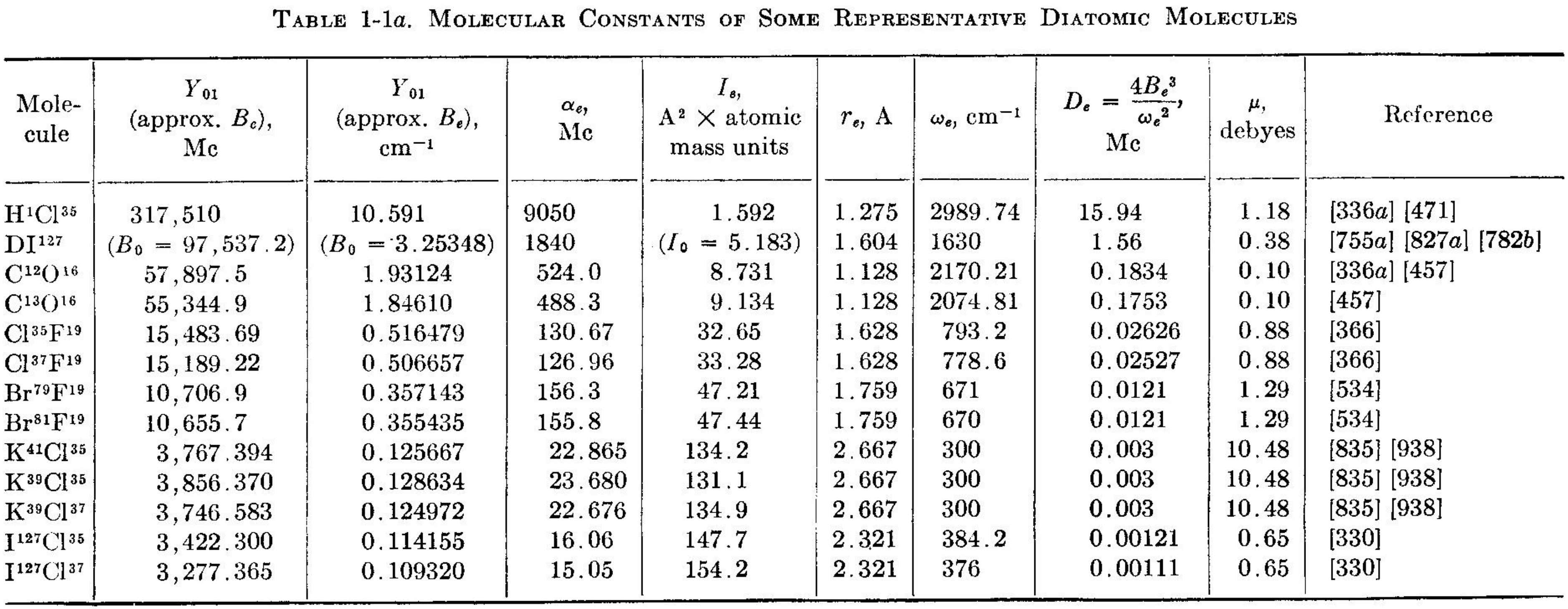
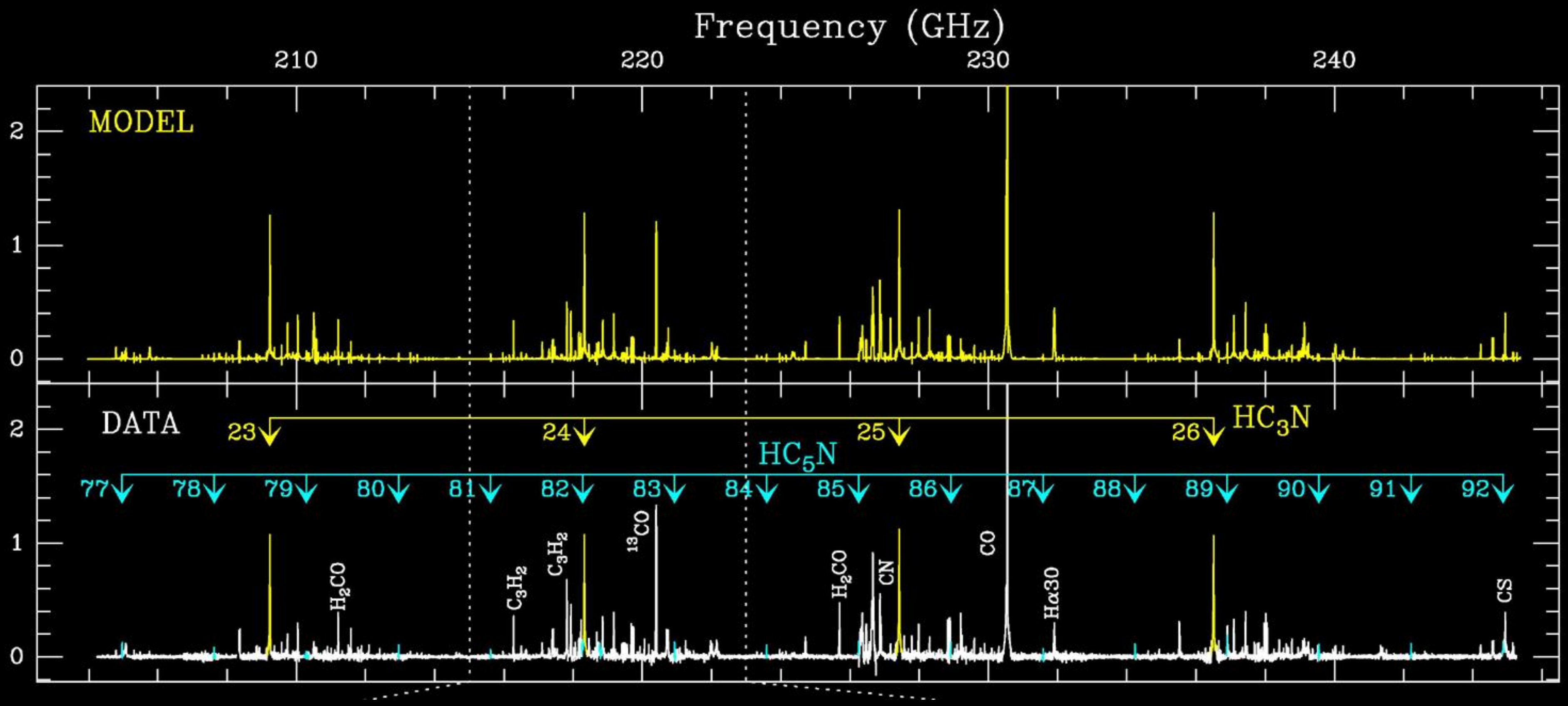


TABLE 1-1*a*. MOLECULAR CONSTANTS OF SOME REPRESENTATIVE DIATOMIC MOLECULES

Molecule	Y_{01} (approx. B_c), Mc	Y_{01} (approx. B_e), cm^{-1}	α_e, Mc	I_e, $A^2 \times$ atomic mass units	r_e, A	ω_e, cm^{-1}	$D_e = \frac{4B_e^3}{\omega_e^2}$, Mc	μ, debyes	Reference
H^1Cl^{35}	317,510	10.591	9050	1.592	1.275	2989.74	15.94	1.18	[336*a*] [471]
DI^{127}	(B_0 = 97,537.2)	(B_0 = 3.25348)	1840	(I_0 = 5.183)	1.604	1630	1.56	0.38	[755*a*] [827*a*] [782*b*]
$C^{12}O^{16}$	57,897.5	1.93124	524.0	8.731	1.128	2170.21	0.1834	0.10	[336*a*] [457]
$C^{13}O^{16}$	55,344.9	1.84610	488.3	9.134	1.128	2074.81	0.1753	0.10	[457]
$Cl^{35}F^{19}$	15,483.69	0.516479	130.67	32.65	1.628	793.2	0.02626	0.88	[366]
$Cl^{37}F^{19}$	15,189.22	0.506657	126.96	33.28	1.628	778.6	0.02527	0.88	[366]
$Br^{79}F^{19}$	10,706.9	0.357143	156.3	47.21	1.759	671	0.0121	1.29	[534]
$Br^{81}F^{19}$	10,655.7	0.355435	155.8	47.44	1.759	670	0.0121	1.29	[534]
$K^{41}Cl^{35}$	3,767.394	0.125667	22.865	134.2	2.667	300	0.003	10.48	[835] [938]
$K^{39}Cl^{35}$	3,856.370	0.128634	23.680	131.1	2.667	300	0.003	10.48	[835] [938]
$K^{39}Cl^{37}$	3,746.583	0.124972	22.676	134.9	2.667	300	0.003	10.48	[835] [938]
$I^{127}Cl^{35}$	3,422.300	0.114155	16.06	147.7	2.321	384.2	0.00121	0.65	[330]
$I^{127}Cl^{37}$	3,277.365	0.109320	15.05	154.2	2.321	376	0.00111	0.65	[330]

$m(^{13}C)=13.00335483$; $m(^{12}C)=12$; $m(O)=15.99491464$

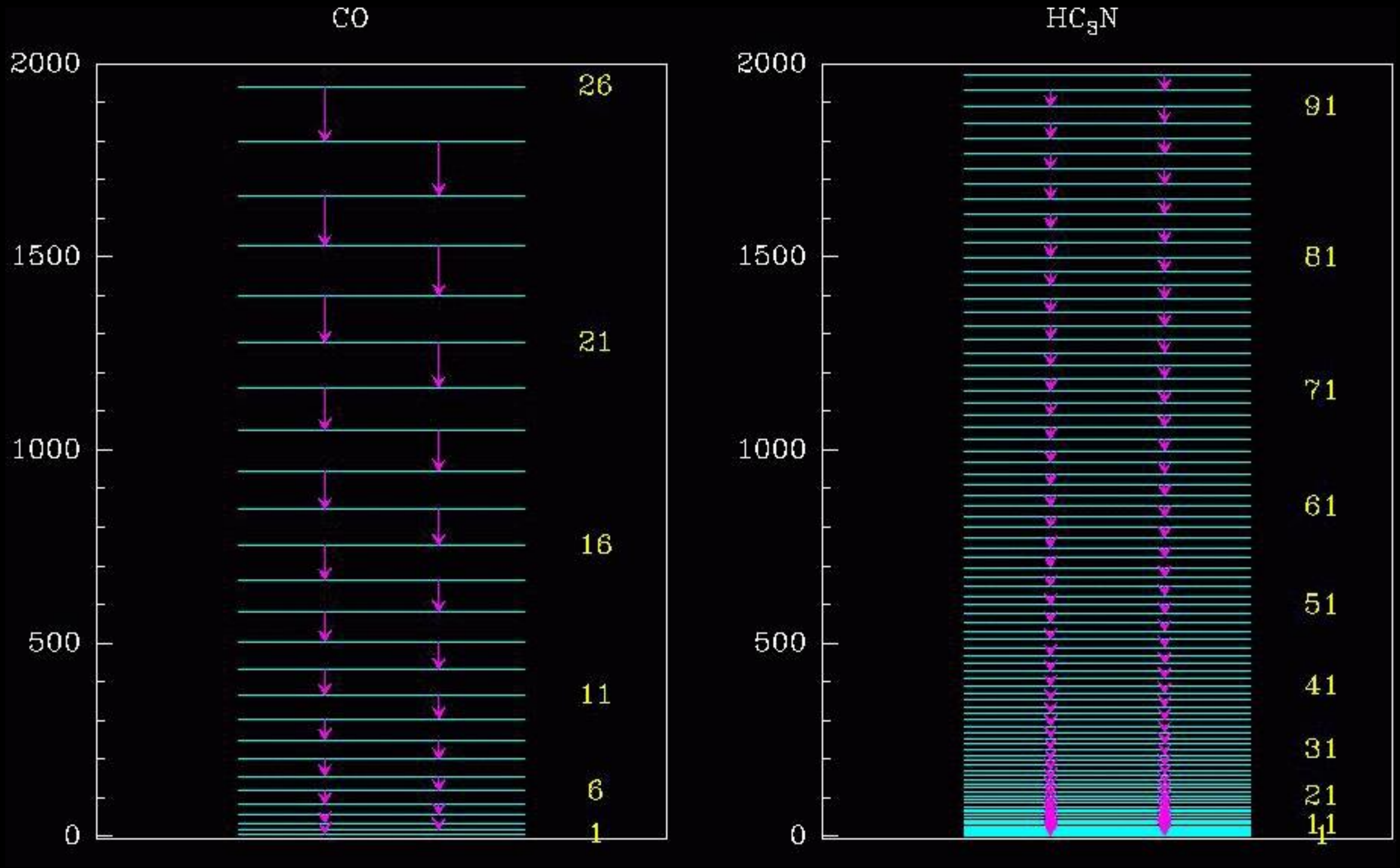
$$B_e(^{13}CO)=\mu(^{12}CO)/\mu(^{13}CO)*B_e(^{12}CO)=0.95591388*57897.5=55345.02$$



ROTATIONAL SPECTRUM OF HC_3N (linear)

ROTATIONAL SPECTRUM OF HC_5N (linear)

Spectrum Getting tighter

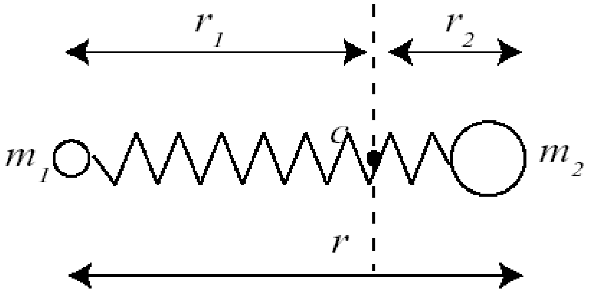


Selection rules $\Delta J=\pm1$

The Simple Harmonic Oscillator

Lecture # 2

We next consider the vibrational modes of a diatomic molecule. There are a number of different models, which describe the vibrational motion of a diatomic molecule. We shall consider firstly the simplest model and later consider more sophisticated and more accurate models. The simplest is the Simple Harmonic Oscillator Model (S.H.O.), which assumes that the nuclei of the molecule can be represented by two masses connected by a massless spring obeying Hook's law, as illustrated in the following diagram.



Frank Houwing's Lecture Notes Web site!

www.anu.edu.au/Physics/houwing/LectureNotes/ Phys3034_MolSpec/MolSpec_L2_OH.pdf

According to classical mechanics, the motion of each mass is given by the following equations.

$$m_1 \frac{d^2 r_1}{dt^2} = -k(r - r_e) \;\; ; \;\; m_2 \frac{d^2 r_2}{dt^2} = -k(r - r_e) \;\; ,$$

where k is the spring constant and r_e is the equilibrium separation for which no force is exerted by the spring. C is the centre of mass; the reduced mass is given by

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad ; \quad \text{and} \quad r_1 = \frac{\mu}{m_1} r \quad ; \quad r_2 = \frac{\mu}{m_2} r \quad .$$

The equation of motion of the reduced mass can be found by substituting for r_1 in the first equation to give

$$\mu \frac{d^2 (r - r_e)}{dt^2} = -k(r - r_e) \;\; .$$

Classically one finds that only one discrete oscillation frequency exists, given by

$$\nu'_{osc} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \quad ,$$

with the displacement from equilibrium separation given by

$$r - r_e = A \cos 2\pi\nu'_{osc}t \quad .$$

However, the energy of the vibration can take on any value since it is given by

$$E_{clas} = \frac{1}{2}kA^2,$$

That is, it is related to the amplitude of the vibration. To determine the allowed energy of vibration according to Quantum Mechanics, we again turn to the time-independent Schrödinger equation.

Writing $x = r - r_e$, the equation is written as follows:

$$\left\{ \frac{-\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2} k x^2 \right\} \Psi = E \Psi$$

Kinetic energy operator__ $\frac{-\hbar^2}{2\mu} \frac{d^2}{dx^2}$

Potential operator ______ $+\frac{1}{2} k x^2$

Eigenvalue ___________ E

Eigenfunction _________ Ψ

Using the relationship $\nu'_{osc} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$, this becomes

$$\left\{ \frac{-\hbar^2}{2\mu} \frac{d^2}{dx^2} + 2\pi^2 \mu \nu_{osc}^2 x^2 \right\} \Psi = E \Psi$$

$$\Leftrightarrow \left\{ \frac{d^2}{dx^2} + \left[\frac{2\mu E}{\hbar^2} - \left(\frac{2\pi\mu\nu_{osc}}{\hbar} \right)^2 x^2 \right] \right\} \psi = 0$$

If we now define $\alpha = \dfrac{2\pi\mu\nu_{osc}}{\hbar}$ and $\beta = \dfrac{2\mu E}{\hbar^2}$, then

$$\left\{ \frac{d^2}{dx^2} + \left(\beta - \alpha^2 x^2\right) \right\} \Psi = 0 \quad ,$$

Performing now a change of variables: $\eta = x\sqrt{\alpha}$;

$$\frac{d\Psi}{dx} = \sqrt{\alpha}\,\frac{d\Psi}{d\eta} \quad ; \quad \frac{d^2\Psi}{dx^2} = \alpha \frac{d^2\Psi}{d\eta^2}$$

the Schrödinger equation becomes

$$\left[\frac{d^2}{d\eta^2} + \left(\frac{\beta}{\alpha} - \eta^2 \right) \right] \Psi = 0$$

The solution to this differential equation is

$$\Psi(\eta) = N_{\mathrm{v}} H(\eta) e^{-\eta^2/2}$$

where $H(\eta) = \sum_{\text{even m}} C_m \eta^m$ or $H(\eta) = \sum_{\text{odd m}} C_m \eta^m$

with $C_{m+2} = \dfrac{-(\beta/\alpha - 1 - 2m)}{(m+1)(m+2)} C_m$

take $C_o \equiv 1 \qquad C_1 \equiv 2$

The function $H(\eta)$ is only bounded if the polynomial is truncated at some value of

$$m = \mathrm{v} \text{ for which } \left(\beta/\alpha - 1 - 2m\right) = 0 \ .$$

That is, if $\dfrac{\beta}{\alpha} - 1 = 2\mathrm{v}$, where $\mathrm{v} = 0, 1, 2.....$

If this is the case, the summation series terminates at term C_{v} and

$$H(\eta) = H_{\mathrm{v}}(\eta) = \quad \text{Hermite polynomial.}$$

For example, for $\mathrm{v} = 0, 1, 2, 3, 4, 5$, we have

$$H_0(\eta) = 1 \ ; \ H_1(\eta) = 2\eta \ ; \ H_2(\eta) = 4\eta^2 - 2 \ ;$$
$$H_3(\eta) = 8\eta^3 - 12\eta \ ; \ H_4(\eta) = 16\eta^4 - 48\eta^2 + 12 \ ;$$
$$H_5(\eta) = 32\eta^5 - 160\eta^3 + 120\eta \ ;$$

The discrete values for the vibrational energy is readily obtained from the boundedness condition $\frac{\beta}{\alpha} = 2v + 1.$ Since $\frac{\beta}{\alpha} = \frac{2\mu E}{\hbar^2}\frac{\hbar}{2\pi\mu \nu'_{osc}} = \frac{2E}{h\nu'_{osc}}$, this gives $E_{\mathrm{v}} = \left(\mathrm{v} + \frac{1}{2}\right) h\nu'_{osc}$, where v = 0,1,2…. In wavenumbers, the vibrational energy term for the S.H.O. is

$$G(\mathrm{v}) = \frac{E_{\mathrm{v}}}{hc} = \frac{\nu'_{osc}}{c}\left(\mathrm{v} + \frac{1}{2}\right) = \omega\left(\mathrm{v} + \frac{1}{2}\right)$$

where $\omega = \frac{\nu'_{osc}}{c}$ is the classical oscillation frequency expressed in wavenumbers, Changing back to the original variable x , we found that the wavefunction is given by

$$\Psi_{\mathrm{v}} = N_{\mathrm{v}} e^{-\alpha x^2/2} H_{\mathrm{v}}\left(\sqrt{\alpha}\, x\right)$$

We shall now consider the <u>SELECTION RULES</u> for dipole transitions between vibrational levels

$$|n\rangle = \mathrm{v}' \text{ and } |m\rangle = \mathrm{v}''.$$

We shall assume that the oscillator is oriented in the x direction. We then need to consider only the x component of the electric dipole matrix element $R_{\mathrm{x}}^{\mathrm{v'v''}}$. We shall also assume that the magnitude of the electric dipole moment is given by $M = M_o + M_1 x$ where $x = r - r_e$. Then,

$$R_x^{\mathrm{v'v''}} = M_o \int \Psi_{\mathrm{v'}}^* \Psi_{\mathrm{v''}} dx + M_1 \int x \Psi_{\mathrm{v'}}^* \Psi_{\mathrm{v''}} dx \quad .$$

The eigenfunctions Ψ_{v} must form an orthogonal basis set (as do the rotational eigenfunction Ψ_{r}). Hence, the orthogonality condition gives

$$\int \Psi_{\mathrm{v'}}^* \Psi_{\mathrm{v''}} dx = 0 \text{ because } \mathrm{v'} \neq \mathrm{v''} \ .$$

In evaluating the second integral, we put $\eta = x\sqrt{\alpha}$ which gives

$$R_x^{\mathrm{v'v''}} = \frac{M_1 N_{\mathrm{v'}} N_{\mathrm{v''}}}{\alpha} \int_{-\infty}^{\infty} \eta H_{\mathrm{v'}}(\eta) H_{\mathrm{v''}}(\eta) e^{-\eta^2} d\eta \quad .$$

The recursion formula for $H_{\mathrm{v}}(\eta)$ is as follows

$$\eta H_{\mathrm{v}}(\eta)=\frac{1}{2}H_{\mathrm{v}+1}(\eta)+\mathrm{v}H_{\mathrm{v}-1}(\eta) \quad .$$

We can therefore write

$$R_x^{\mathrm{v'v''}}=\frac{M_1 N_{\mathrm{v'}} N_{\mathrm{v''}}}{\alpha}\left[\frac{1}{2}\int H_{\mathrm{v'}} H_{\mathrm{v''}+1} e^{-\eta^2}\,d\eta+\mathrm{v''}\int H_{\mathrm{v'}} H_{\mathrm{v''}\text{-}1} e^{-\eta^2}\,d\eta\right]$$

According to the orthogonality condition, the first integral

$$\sim \int \Psi_{\mathrm{v'}}^{*}\Psi_{\mathrm{v''}+1}dx \quad \neq 0 \ \text{ only if } \ \mathrm{v'}=\mathrm{v''}+1$$

and the second integral

$$\sim \int \Psi_{\mathrm{v'}}^{*}\Psi_{\mathrm{v''}-1}dx \quad \neq 0 \ \text{ only if } \ \mathrm{v'}=\mathrm{v''}-1 \quad .$$

Hence, the selection rule for dipole transitions of the S.H.O. is

$$\Delta \mathrm{v} \pm 1$$

To determine the spectrum we again adopt the convention that E' > E'' which means that v' > v'' for pure vibration.
Hence

$$\mathrm{v}' = \mathrm{v}'' + 1\ .$$

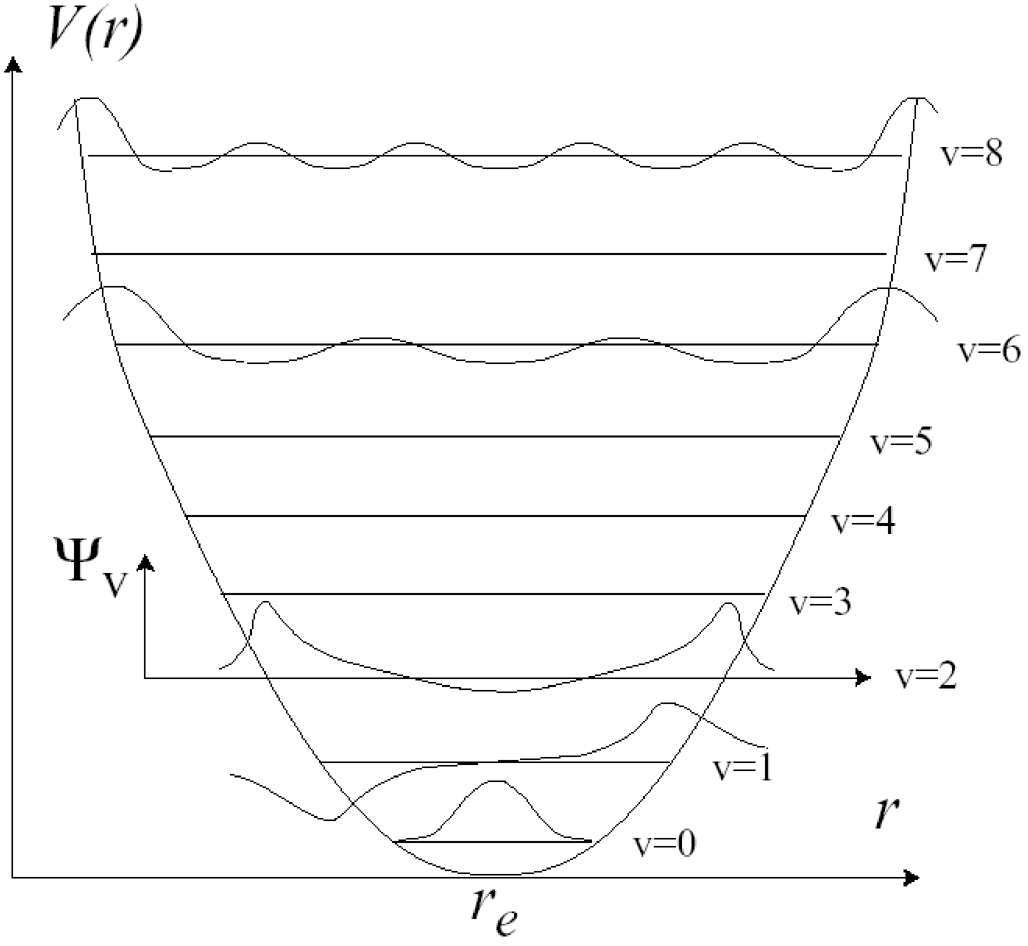
The spectral lines will therefore be given by

$$\begin{aligned}\nu &= \frac{E(\mathrm{v}')}{hc} - \frac{E(\mathrm{v}'')}{hc} = G(\mathrm{v}') - G(\mathrm{v}'') \\ &= G(\mathrm{v}''+1) - G(\mathrm{v}'') = \omega\left(\mathrm{v}''+\frac{3}{2}\right) - \omega\left(\mathrm{v}''+\frac{1}{2}\right) \\ &= \omega \quad \text{... all lines are coincident.}\end{aligned}$$

.... consequence of assuming S.H.O.

In reality, however, the system is not and the vibrational lines are not coincident.

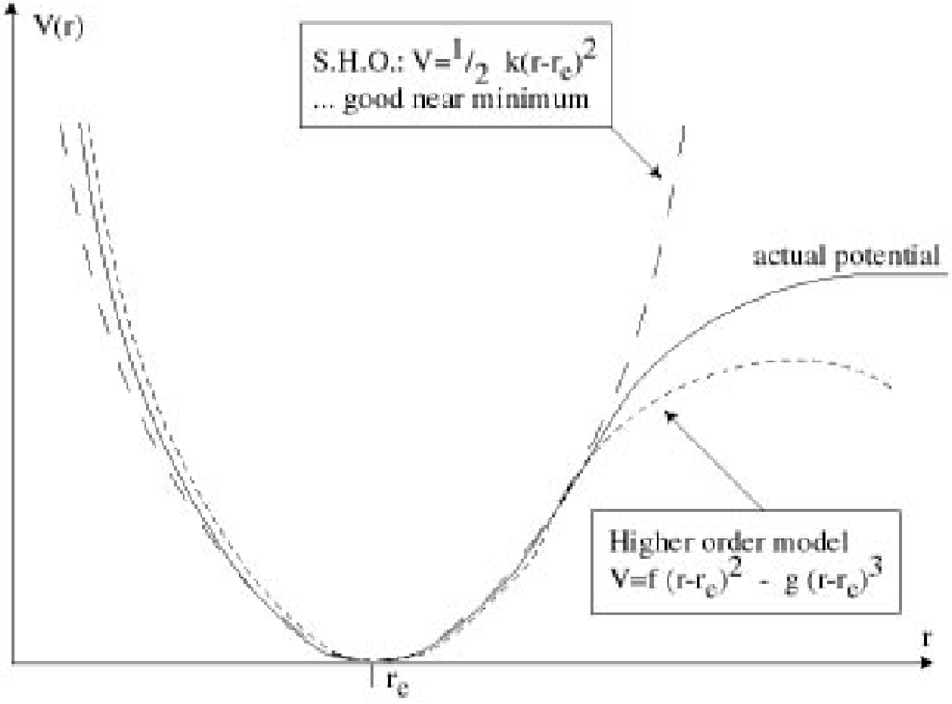
Continuing to discuss the S.H.O. we shall consider the form of the wavefunctions Ψ_v . Consider the following figure.



$$\mathrm{V}(r) = \frac{1}{2} k(r - r_e)^2$$

The Anharmonic Oscillator

The simple harmonic oscillator (S.H.O.) that we have been using up to now to describe the vibrational motion of a molecule is an approximation, which gives a good representation of the potential energy curve near its minimum. However to give a better description, which more closely follows the actual potential for more energetic vibrations, it is necessary to add higher order terms, In fact, it is found that a cubic potential is very good.



If we substitute this higher order model into the wave equation (Schrödinger's equation) and solve for the eigenvalues, we find that the vibrational energy is given by a high order polynomial

$$E(\mathrm{v}) = hc\omega_e\left(\mathrm{v}+\frac{1}{2}\right) - hc\omega_e x_e\left(\mathrm{v}+\frac{1}{2}\right)^2 + hc\omega_e y_e\left(\mathrm{v}+\frac{1}{2}\right)^3 + \ldots\ldots\ldots$$

In fact, because of this, a general polynomial is often simply assumed and the coefficients are found experimentally by fitting methods. More terms are included if higher accuracy is required. However, in most cases, it is sufficient to truncate the polynomial for $E(\mathrm{v})$ at the cubic or even the quadratic terms. To express the energy in wave numbers, we simply divide by hc to produce the vibrational energy term:

$$G(\mathrm{v}) = \frac{E(\mathrm{v})}{hc} = \omega_e\left(\mathrm{v}+\frac{1}{2}\right) - \omega_e x_e\left(\mathrm{v}+\frac{1}{2}\right)^2 + \omega_e y_e\left(\mathrm{v}+\frac{1}{2}\right)^3 + \ldots\ldots$$

where $\mathrm{v} = 0,1,2,\ldots\ldots$ and $\omega_e \gg \omega_e x_e \gg \omega_e y_e$.

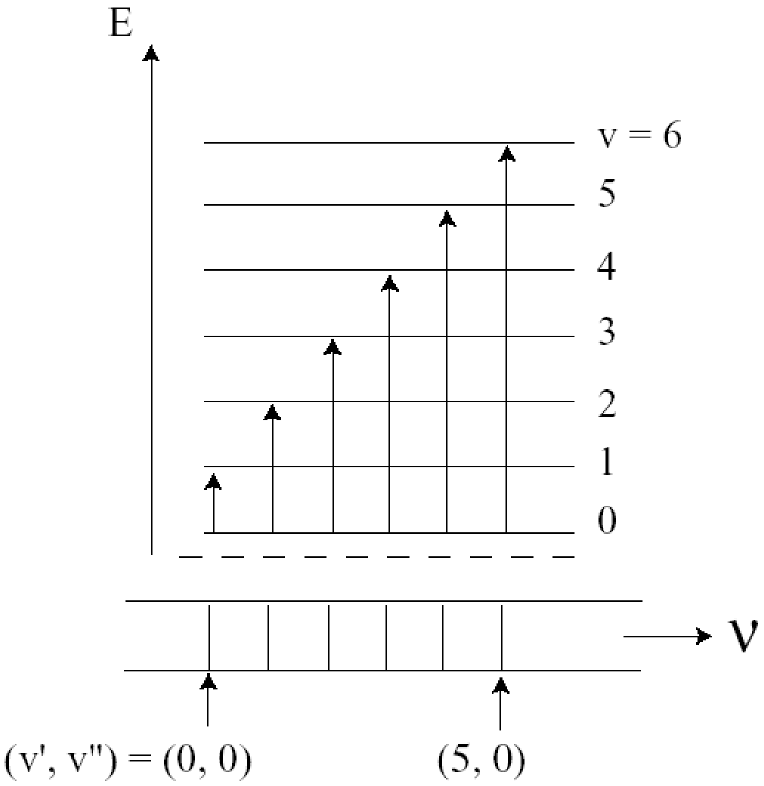
also, unlike the S.H.O. , $\omega_e c \neq \nu'_{osc}$.

Selection Rules for Vibrational Transitions allowed by the Anharmonic Oscillator Model

We will not go into the analysis for deriving the selection rules. However, the derivation will proceed along the same lines as for the S.H.O. model except that the wavefunctions of the anharmonic model will be used. Such a derivation will show that all vibrational transitions are allowed, with

$$\Delta v = \pm 1 , \quad \pm 2 , \quad \pm 3 , \quad \text{etc} \qquad \text{(selection rules for A.O.)}$$

However, examination of the transition probabilities shows that the $\underline{\Delta v = \pm 1}$ transition is <u>most intense.</u>

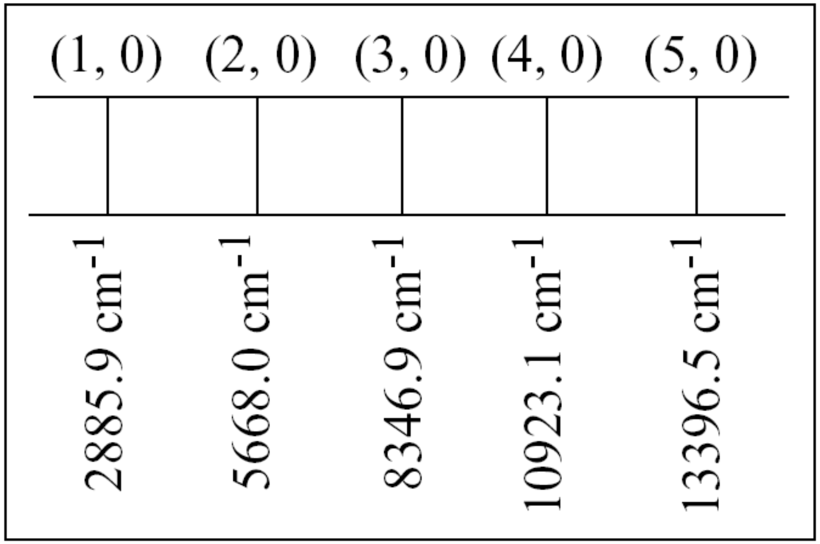


The values of the wavenumbers ν for the transitions with $\Delta v = 2, 3, 4, ...$ are approximately $2\times, 3\times, 4\times, ...$ the value of ν for the $\Delta v = 1$ transition. Because of this, the transitions are often termed:

$(1,0)$:"fundamental"; $(2,0)$:"second harmonic"; $(3,0)$:"third harmonic".

However, they are not true harmonics.

This will provide us with the following information:



We can use this information to construct the table below:

Infrared lines of cold HCl vapour

	Measured Values			Calculated*
v	ν (cm^{-1})	$\Delta G_{v+1/2}$	$\Delta^2 G_{v+1}$	ν (cm^{-1})
0	(0)			(0)
		2885.9		
1	2885.9		-103.7	2885.7
		2782.1		
2	5668.0		-103.2	5668.2
		2678.9		
3	8346.9		-102.8	8347.5
		2567.1		
4	10923.1		-102.6	10923.6
		2473.4		
5	13396.5			13396.5

*using values of ω_0 and $\omega_0 x_0$ determined from $\Delta G_{v+\frac{1}{2}}$ and $\Delta^2 G_{v+1}$ in table.

$\Delta^2 G_{v+1} \Rightarrow \left.\begin{matrix}\omega_0 x_0 \\ \omega_e x_e\end{matrix}\right\} = 51.60\text{cm}^{-1}$

$\omega_0 x_0$, v and $\Delta G_{v+\frac{1}{2}} \Rightarrow$

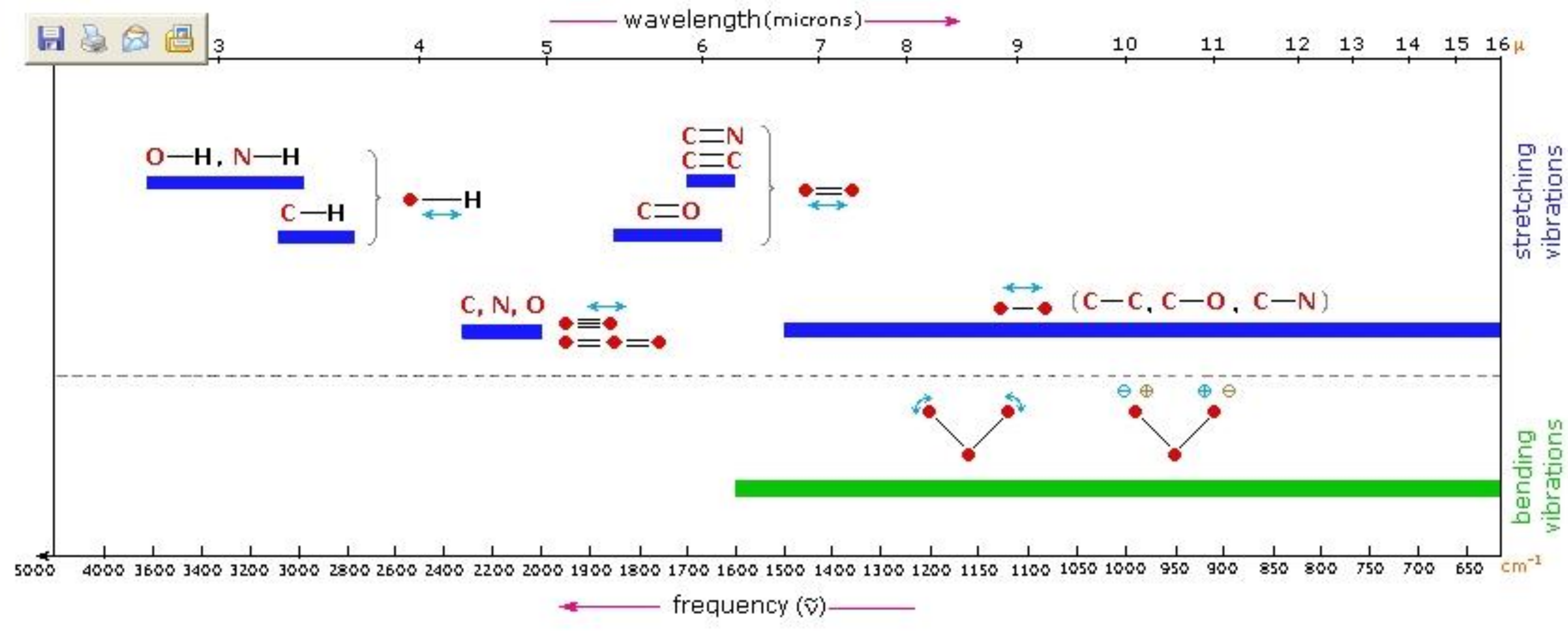
$\omega_0 = 2937.5\text{cm}^{-1}$ and

$\omega_e = 2989.1\text{cm}^{-1}$

Table 6.4. Characteristic bond stretching vibration frequencies of certain molecular groups

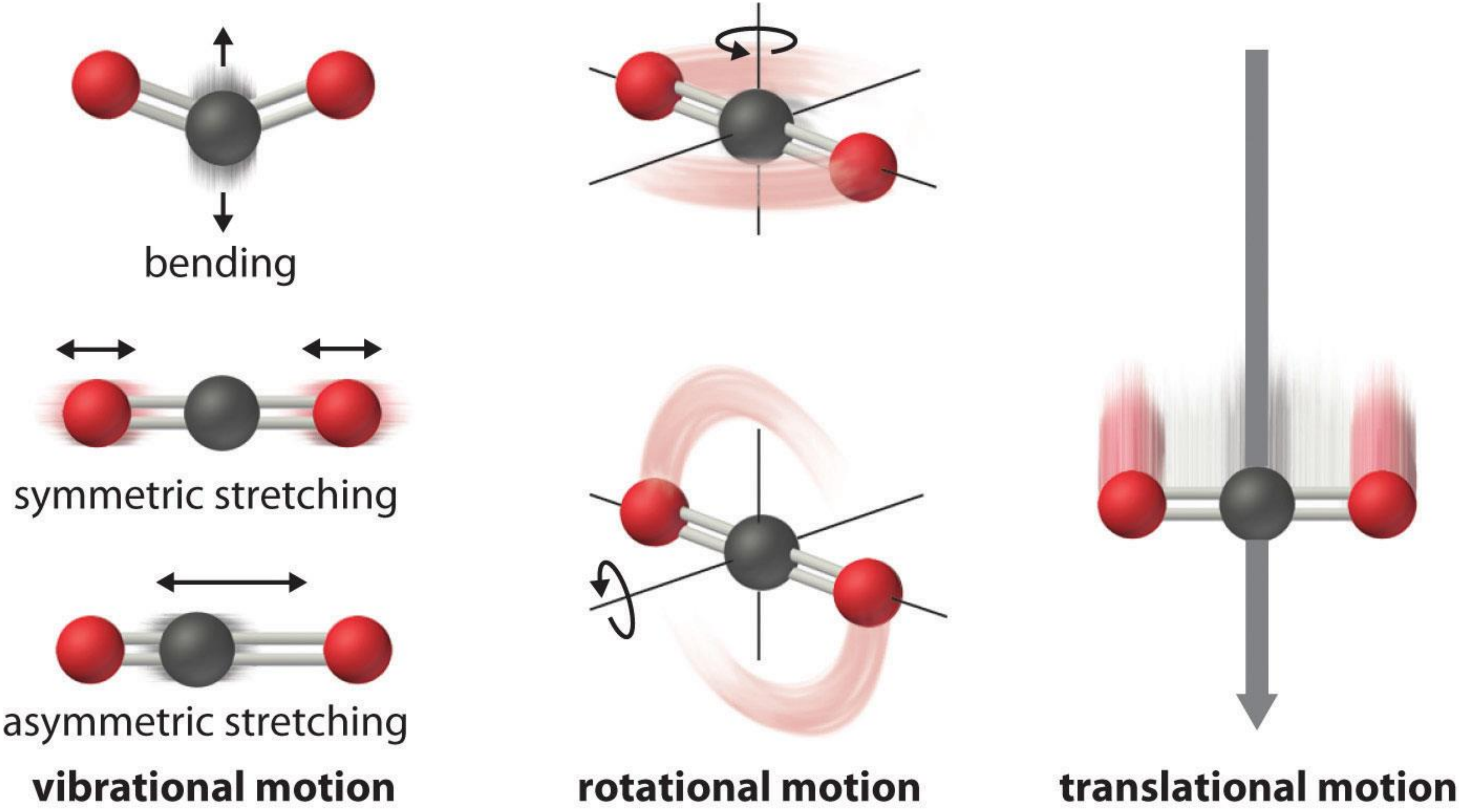
Group	Wave number [cm^{-1}]	Group	Wave number [cm^{-1}]	Group	Wave number [cm^{-1}]
$\equiv C-H$	3300	$>N-H$	3350	$\overset{\diagdown}{\underset{\diagup}{-}}C-C\overset{\diagup}{\underset{\diagdown}{-}}$	900
$\overset{\diagdown}{\underset{/\!/}{}}C-H$	3020	$>C=O$	1700	$\overset{\diagdown}{\underset{\diagup}{-}}C-F$	1100
		$-C\equiv N$	2100	$\overset{\diagdown}{\underset{\diagup}{-}}C-Cl$	650
$\overset{\diagdown}{\underset{\diagup}{-}}C-H$	2960	$-C\equiv C-$	2050	$\overset{\diagdown}{\underset{\diagup}{-}}C-Br$	560
$-O-H$	3680 (gas) 3400 (liquid)	$>C=C<$	1650	$\overset{\diagdown}{\underset{\diagup}{-}}C-I$	500

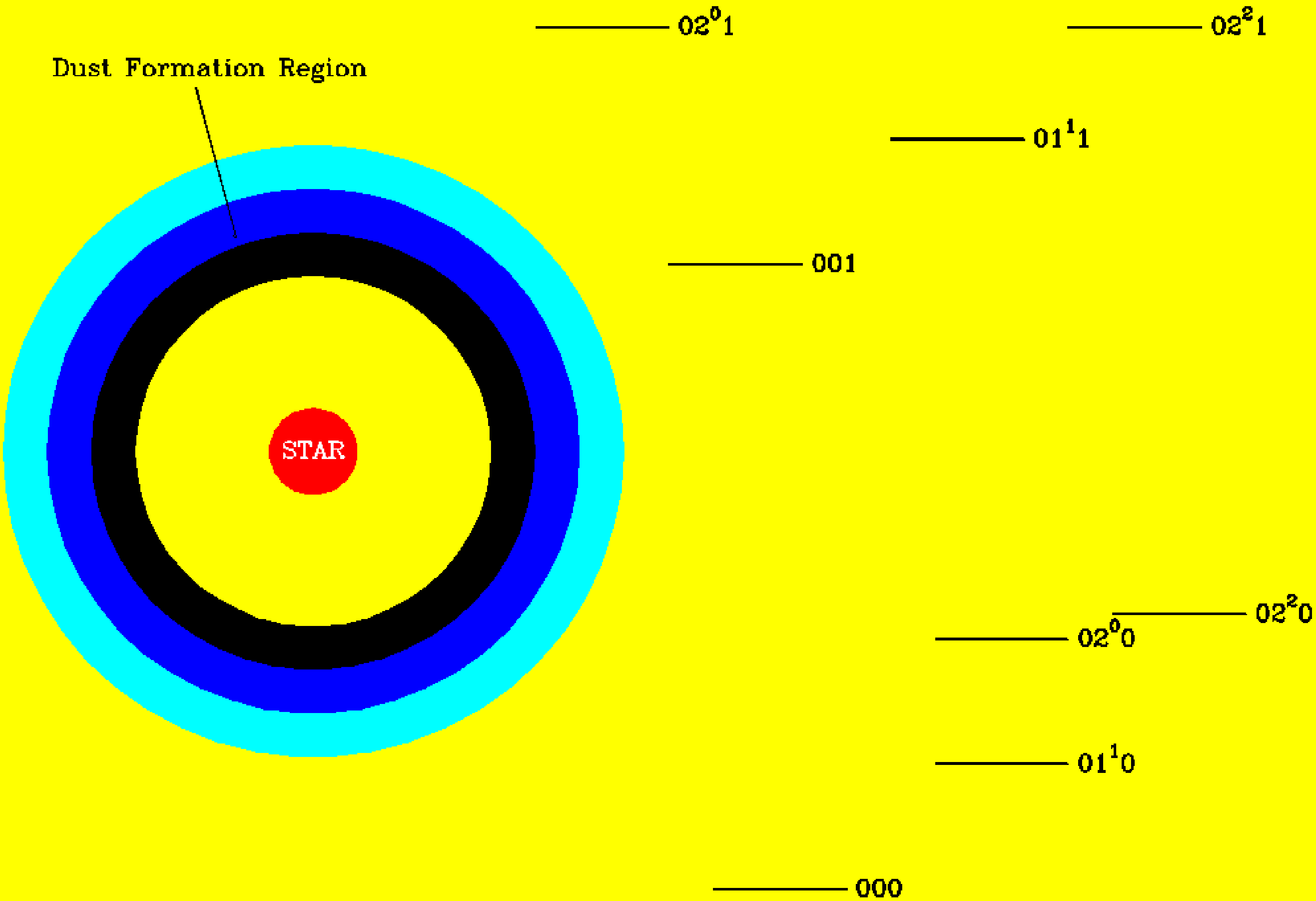
www.cem.msu.edu/~reusch/OrgPage/VirtualText/Spectrpy/InfraRed/irspec1.htm#ir2

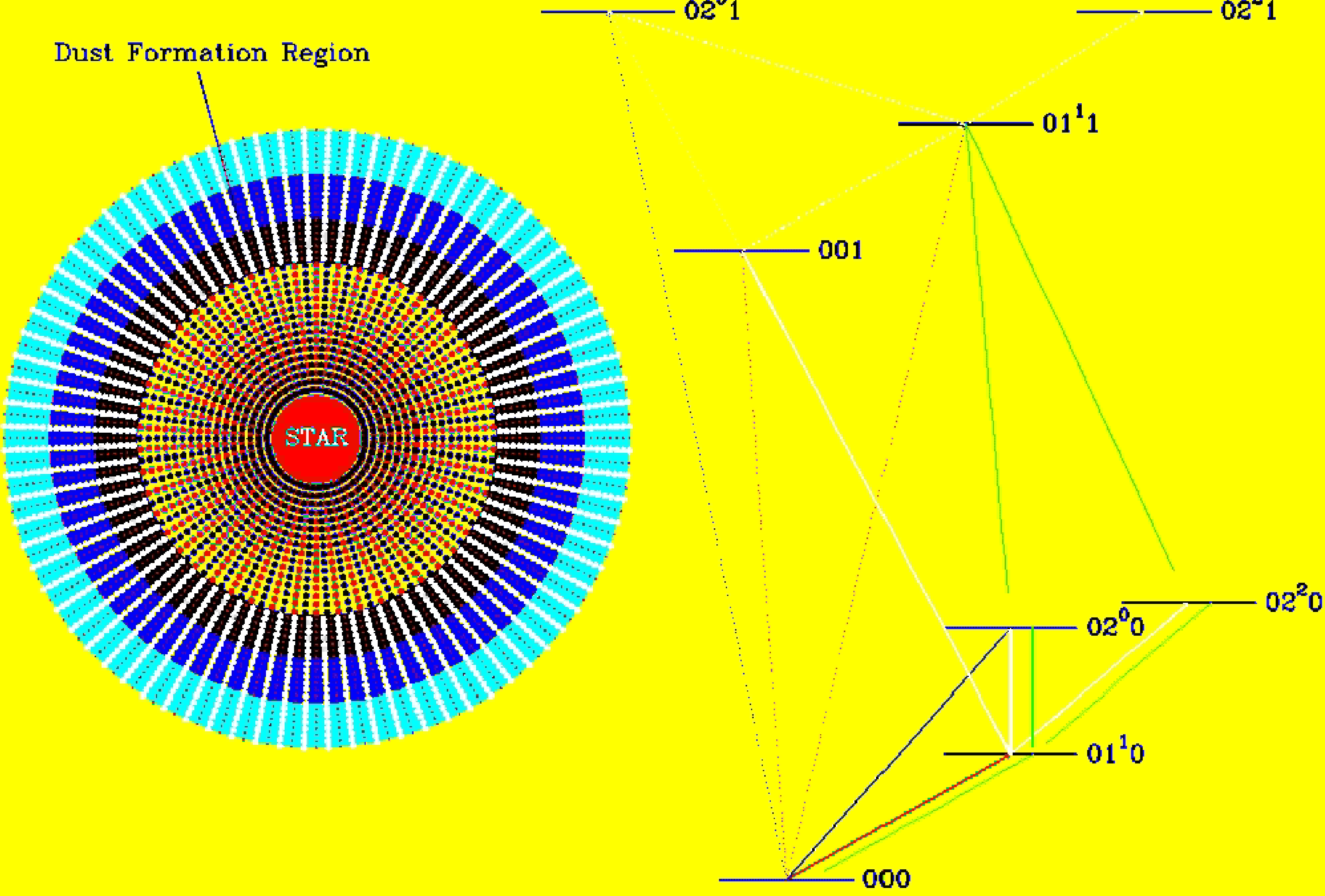


In polyatomic molecules the number of vibrational modes can be large (HCN : three modes, antisymmetrical stretching, symmetrical stretching and bending

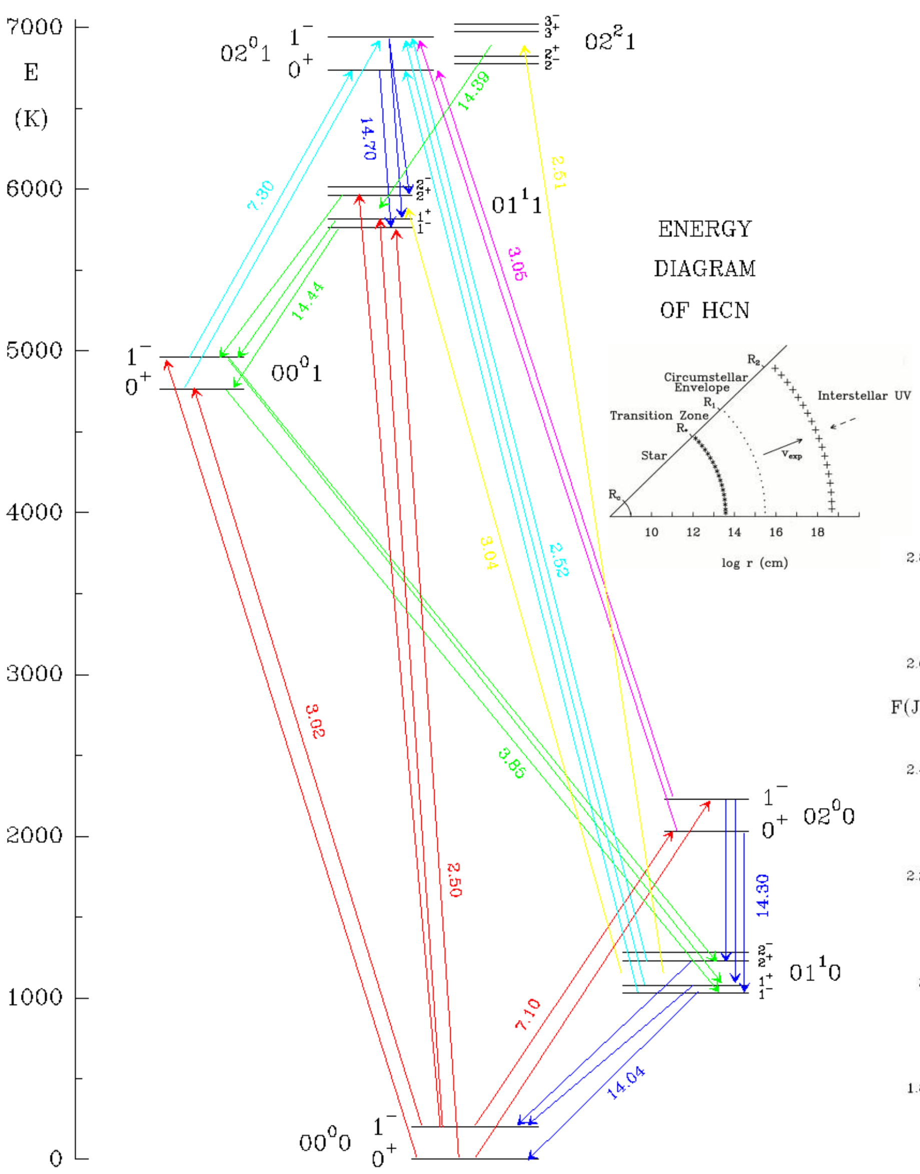
The role of vibrational states in the pumping of the molecular energy levels

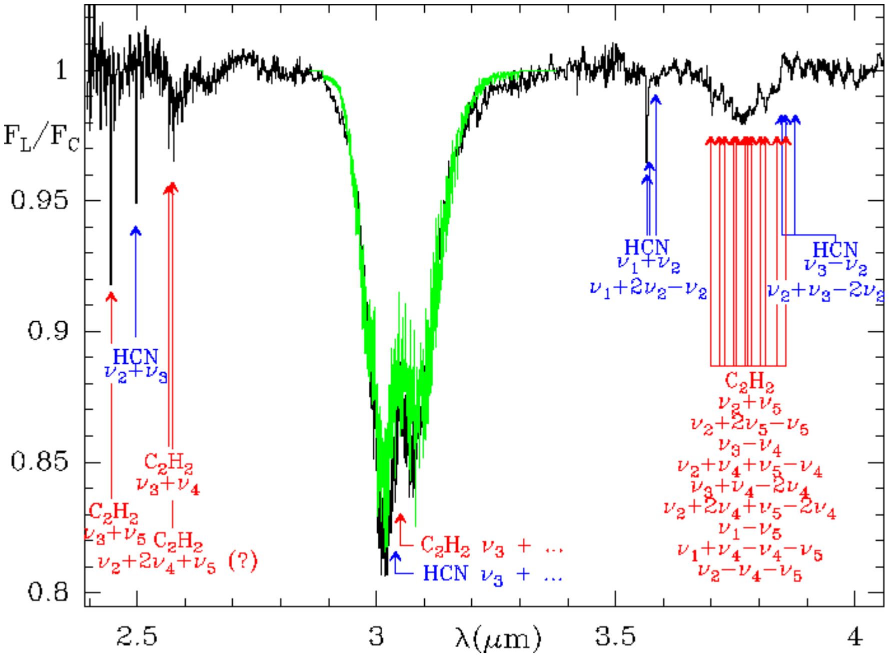

bending
symmetric stretching
asymmetric stretching
vibrational motion
rotational motion
translational motion

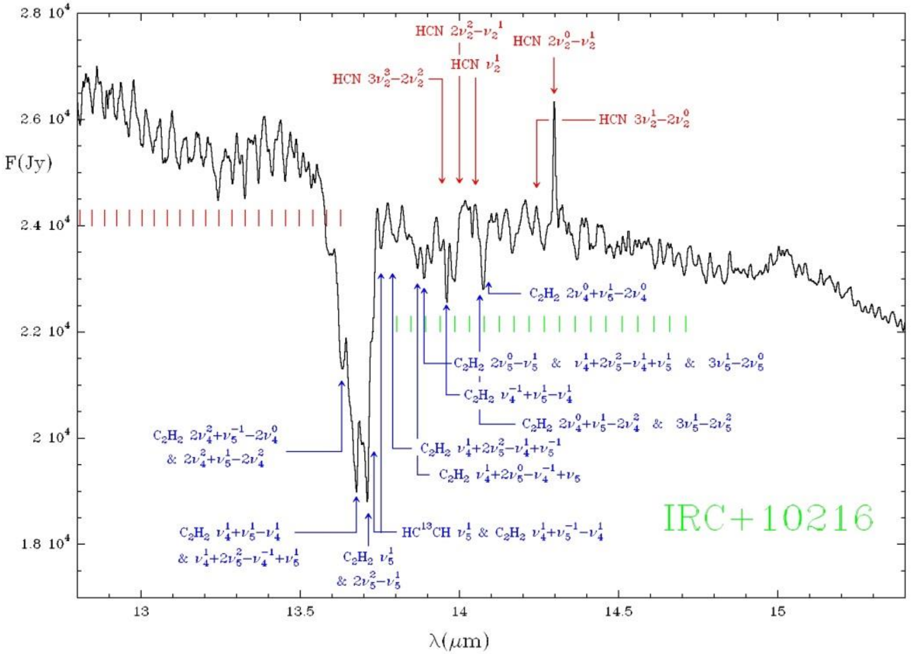

02^0 1
02^2 1
Dust Formation Region
01^1 1
001
STAR
02^2 0
02^0 0
01^1 0
000

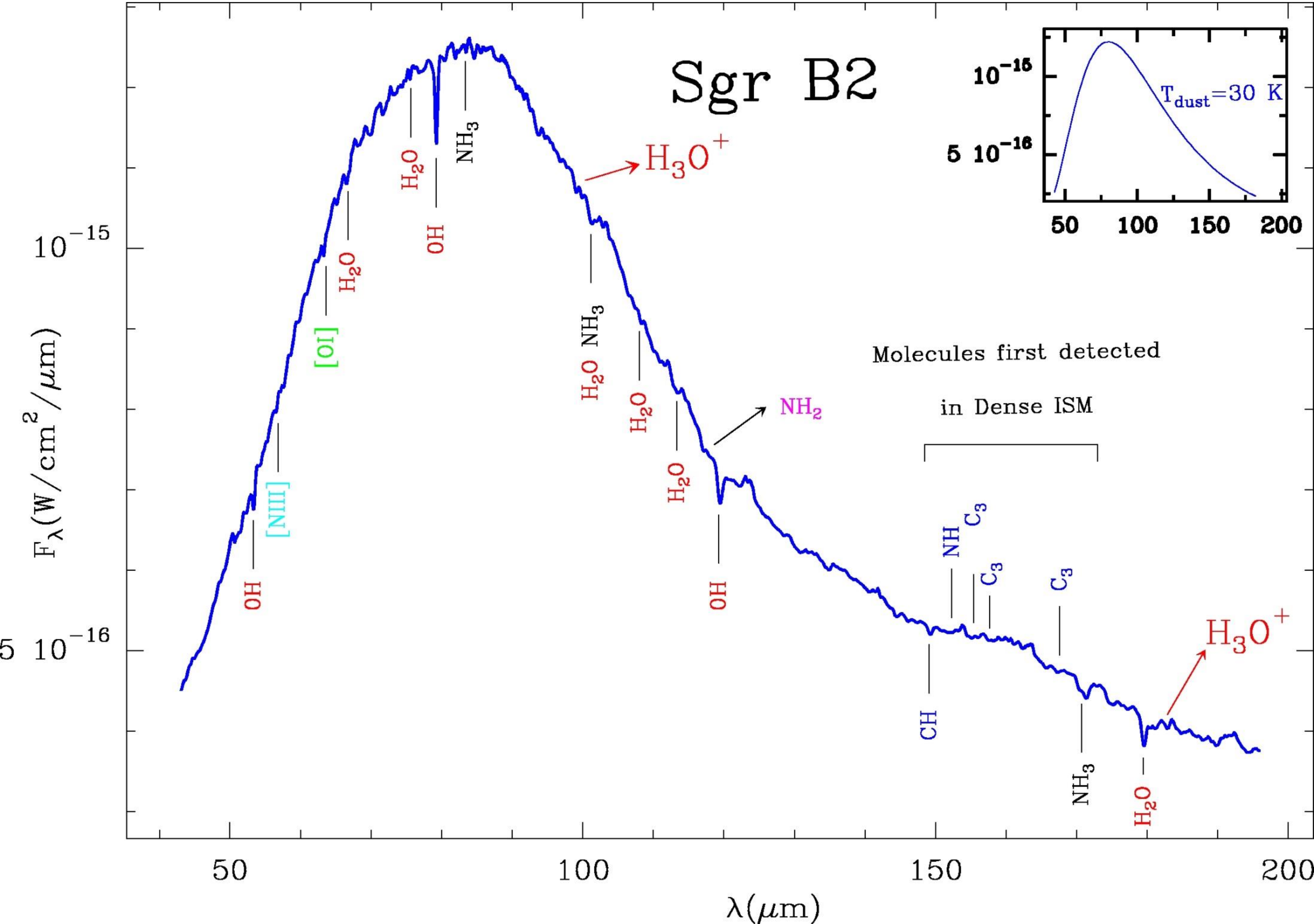

Dust Formation Region
STAR
$02^{0}1$
$02^{2}1$
$01^{1}1$
001
$02^{0}0$
$02^{2}0$
$01^{1}0$
000

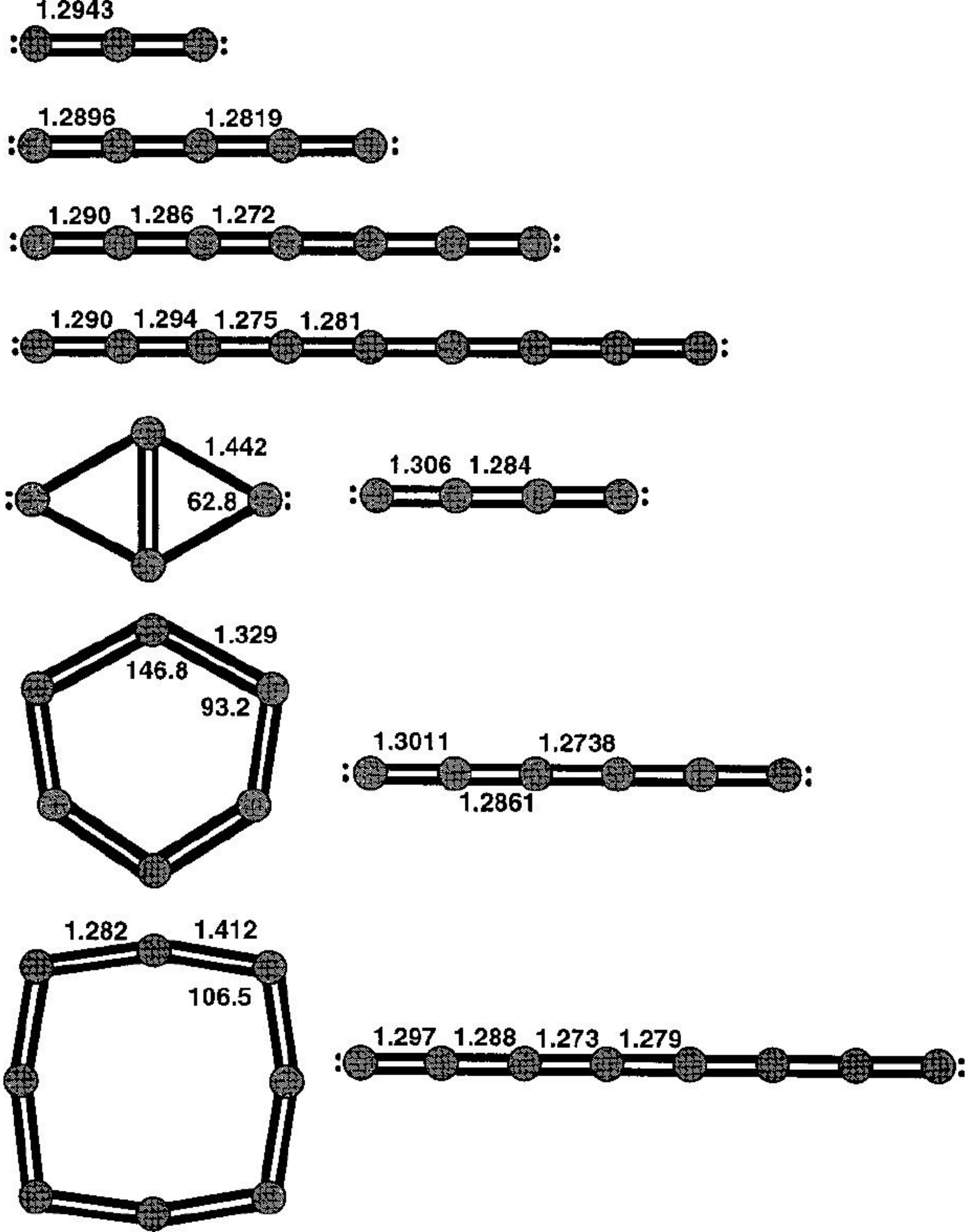
González-Alfonso & Cernicharo 1998








Sgr B2
T_{dust}=30 K
10^{-15}
5 10^{-16}
50
100
150
200
$F_\lambda(W/cm^2/\mu m)$
$\lambda(\mu m)$
10^{-15}
5 10^{-16}
50
100
150
200
OH
[NIII]
[OI]
H_2O
H_2O
OH
NH_3
H_3O^+
NH_3
H_2O
H_2O
H_2O
NH_2
OH
Molecules first detected
in Dense ISM
CH
NH
C_3
C_3
C_3
NH_3
H_2O
H_3O^+



Cumulenic Carbon Clusters

bending modes (far-IR)

C_3 ν_2=63.4 cm^{-1} (158 μm)

C_4 ν_5= 160±4 cm^{-1} (61-64 μm)

C_5 ν_7= 107±5 cm^{-1} (89-98 μm)

C_6 ν_9= 90±50 cm^{-1} (71-250 μm)

C_7 ν_{11}= 80 cm^{-1} (125 μm)

C_8 ??

C_9 ν_{15}= 51 cm^{-1} (196 μm)

C_{10} ? (linear isomer observed)

Orden & Saykally 1998
Chem. Rev. 98, 2313

FAR-INFRARED DETECTION OF C_3 IN SAGITTARIUS B2 AND IRC +10216[1]

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ABSTRACT

We report on the detection of nine lines of the ν_2 bending mode of triatomic carbon, C_3, in the direction of Sagittarius B2. The $R(4)$ and $R(2)$ lines of C_3 have been also detected in the carbon-rich star IRC +10216. The abundances of C_3 in the direction of Sgr B2 and IRC +10216 are $\simeq 3 \times 10^{-8}$ and $\simeq 10^{-6}$, respectively. In Sgr B2 we have also detected the 2_3–1_2 line of NH with an abundance of a few times 10^{-9}. Polyatomic molecules will have a weak contribution from their pure rotational spectrum to the emission/absorption in the far-infrared. We suggest, however, that they could be, through their low-lying vibrational bending modes, the dominant carriers of emission/absorption in the spectrum of bright far-infrared sources.

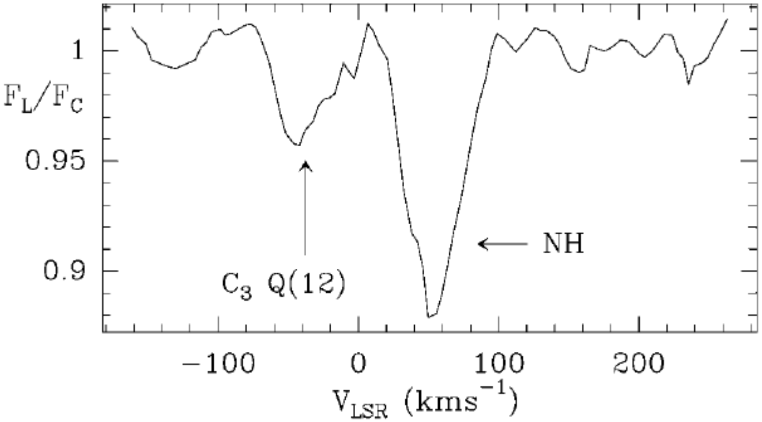
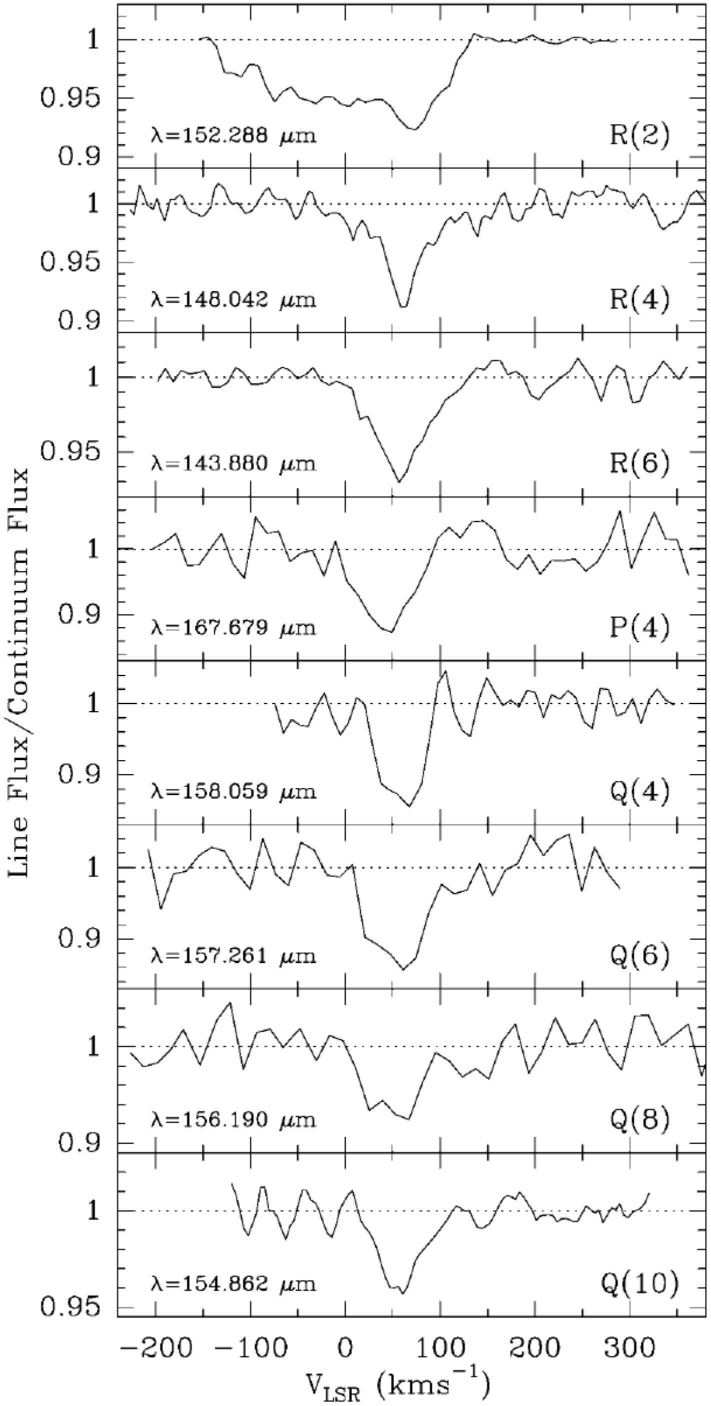


Fig. 3.—The 2_3–1_2 line of NH in Sgr B2. In the same spectrum, the C_3 $Q(12)$ is also detected with an absorption of 3.5%.



More on rotational spectroscopy…

- Diatomic or linear molecules are just a simple case (J)

- In general a molecule will have three principal axis with moment of inertia I_A, I_B, I_C. Here we can distinguish:

Spherical tops: $I_A=I_B=I_C$ Example: Amonium ion NH_4^+

Symmetric tops: $I_A=I_B<I_C$ (prolate) $I_A<I_B=I_C$ (oblate) (J,K)

Asymmetric tops: I_A,I_B,I_C all different (Ex: H_2O) (J,K_+,K_-)

Unperturbed Hamiltonian

$$A\hat{J}_a^2 + B\hat{J}_b^2 + C\hat{J}_c^2$$

Centrifugal Distortion

$$-\Delta_J\hat{\mathbf{J}}^4 - \Delta_{JK}\hat{\mathbf{J}}^2\hat{J}_z^2 - \Delta_K\hat{J}_z^4$$
$$-\tfrac{1}{2}\left[\delta_J\hat{\mathbf{J}}^2 + \delta_K\hat{J}_z^2, \hat{J}_+^2 + \hat{J}_-^2\right]_+$$

Quartic

$$+H_J\hat{\mathbf{J}}^6 + H_{JK}\hat{\mathbf{J}}^4\hat{J}_z^2 + H_{KJ}\hat{\mathbf{J}}^2\hat{J}_z^4 + H_K\hat{J}_z^6$$
$$+\tfrac{1}{2}\left[\phi_J\hat{\mathbf{J}}^4 + \phi_{JK}\hat{\mathbf{J}}^2\hat{J}_z^2 + \phi_K\hat{J}_z^4, \hat{J}_+^2 + \hat{J}_-^2\right]_+$$

Sextic

The description of energy levels needs 3 rotational quantum numbers: J (main rotation quantum number), K_+ (projection of J on the symmetry axis of the limiting oblate symmetric top), K_- (same projection but for the limiting prolate symmetric top)

More on rotational spectroscopy…

Additional quantum numbers are needed or levels can be missing if:

- **Electric dipole moment does not follow a principal axis of inertia (example HDO, μ_a=0.65 μ_b=1.73; for H2O μ_b=1.85).**
- **There is an internal specular symmetry (Ex: NH_3)**
- **There is an internal symmetry by rotation (CH_3CCH)**
- **There is a nuclear spin (small degeneracy breakdown)**
- **There is a magnetic dipole moment and an external magnetic field.**
- **There are degenerate vibrational modes (ℓ-type doubling)**

Generalizing the moment of inertia from Rigid Rotator to Polyatomic Molecules

It is helpful to consider the molecular moment of inertia projected on each of the three Cartesian (xyz) axes. Written in this way, we see that the moment of inertia is actually a two-dimensional vector, called a *tensor*, or the ***inertia tensor***

$$\mathbf{I} = \begin{pmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{yx} & I_{yy} & I_{yz} \\ I_{zx} & I_{zy} & I_{zz} \end{pmatrix}$$

where the individual elements are defined as

$$I_{xx} = \sum_{j=1}^{N} m_j[(y_j - y_{cm})^2 + (z_j - z_{cm})^2]$$

$$I_{yy} = \sum_{j=1}^{N} m_j[(x_j - x_{cm})^2 + (z_j - z_{cm})^2]$$

$$I_{zz} = \sum_{j=1}^{N} m_j[(y_j - y_{cm})^2 + (x_j - x_{cm})^2], \ \ and$$

$$I_{xy} = -\sum_{j=1}^{N} m_j[(x_j - x_{cm})\,(y_j - y_{cm})], \ldots \ \ with$$

$$I_{xy} = I_{yx}, \ \ \ldots$$

with the subscript $_{cm}$ representing the center of mass positions for the molecule.

The mathematics of classical rigid bodies tells us that the ***inertia tensor*** for molecules can always be diagonalized so that the off-diagonal elements (*e.g.*, I_{xy}) are zero. The convention is that the resulting ***diagonalized inertia tensor*** has the diagonal elements relabeled as $I_{xx} = I_A$, $I_{yy} = I_B$, and $I_{zz} = I_C$, or

$$\mathbf{I} = \begin{pmatrix} I_A & & \\ & I_B & \\ & & I_C \end{pmatrix}$$

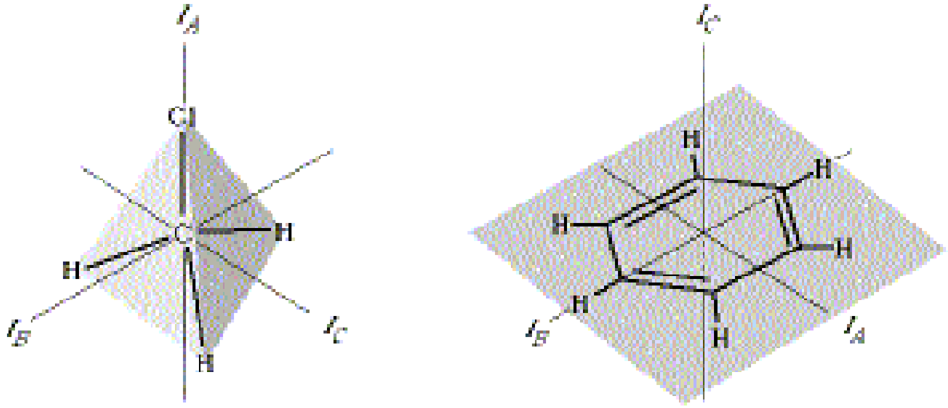
Thus, to represent molecular rotations for even the most asymmetric molecules, we need consider only the three axes *A, B,* and *C* that are mutually orthogonal along the x, y, and z directions. Another convention is that for molecules, we always define the A axis to have the smallest moment of inertia, and hence the highest rotation frequency, as $I_A \leq I_B \leq I_C$.

Spherical rotors, (or ***spherical tops***) are molecules for which $I_A = I_B = I_C$. Examples of ***spherical top*** molecules are methane (CH_4), sulfur hexafluoride (SF_6), and carbon tetrachloride (CCl_4).

Linear molecules have $I_A = I_B$, and $I_C = 0$. Examples of linear rotors are all of the diatomic molecules, plus carbon dioxide (CO_2).

When the molecule has some high degree of symmetry, often two of the moments of inertia are the same, where $I_A = I_B \neq I_C$ or $I_A \neq I_B = I_C$. These cases are referred to a ***symmetric rotors***, *a.k.a.* in the spectroscopic literature as ***symmetric tops***.

A ***symmetric top*** with $I_A < I_B = I_C$ is called a *prolate symmetric top;* when $I_C > I_A = I_B$, then the molecule is classified an *oblate symmetric top*. Examples of *symmetric top* molecules are chloroform ($CHCl_3$, prolate), and benzene (C_6H_6, oblate).



Prolate symmetric top

$I_A < I_B = I_C$

(a)

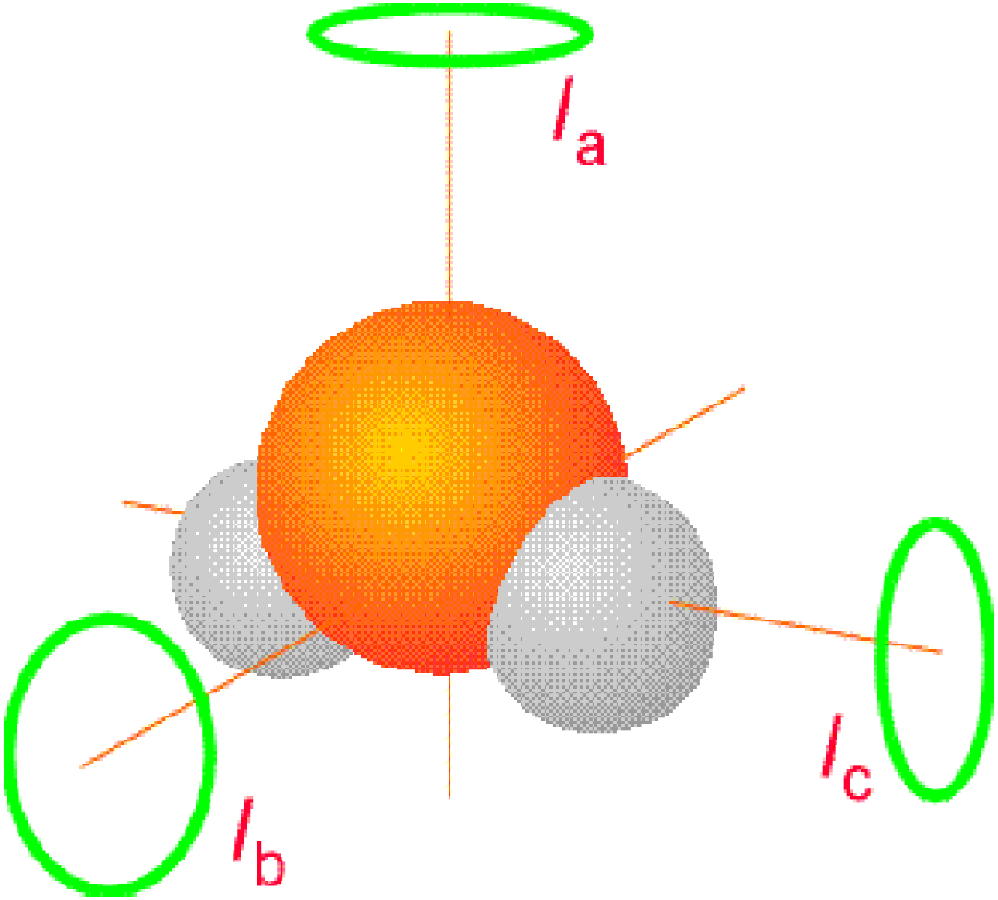
Oblate symmetric top

$I_C > I_A = I_B$

(b)

The general case where $I_A \neq I_B \neq I_C$ is called the ***asymmetric rotor***. Most all larger molecules are asymmetric rotors, even when they have a high degree of molecular symmetry.

As shown below, water is also an *asymmetric rotor*.



The generalization of the ***rigid rotor*** to the three-dimensional case for an ***asymmetric rotor*** requires that we consider the fact that the angular momentum squared operator ***J*** is now represented as

$$J^2 = J_A^2 + J_B^2 + J_C^2$$

and consequently, the Hamiltonian operator for the ***asymmetric rotor*** is given by

$$\hat{H} = \frac{J_A^2}{2I_A} + \frac{J_B^2}{2I_B} + \frac{J_C^2}{2I_C}$$

There are in general three rotational energies, one for rotation about each of the three orthogonal axes A, B, and C. Because of orthogonality, the rotational axes have separable rigid rotor solutions, leading to energy eigenvalues

$E_A(J) = h^2/(8\pi^2 I_A) \times J(J+1)$, $E_B(J) = h^2/(8\pi^2 I_B) \times J(J+1)$, and $E_C(J) = h^2/(8\pi^2 I_C) \times J(J+1)$.

It is *very important* to keep track of units in spectroscopy. In rotational spectroscopy, the energies may be reported in GHz (10^9 s^{-1}), or cm^{-1} (1 cm^{-1} = 30 GHz). It is quite common to find the rotational energies written in terms of the three ***rotational constants*** A, B, and C, given by

$$\widetilde{A} = \frac{h}{8\pi^2 c I_A}\,;\ \widetilde{B} = \frac{h}{8\pi^2 c I_B}\,;\ and\ \widetilde{C} = \frac{h}{8\pi^2 c I_C}\,;$$

where the units are wavenumbers (cm^{-1}).

SYMMETRIC MOLECULES

A molecule in which two of the principal moments of inertia are equal is a symmetric-top rotor. This condition is generally met when the molecule has an axis of symmetry which is trigonal or greater. The molecules PH_3, CH_3F, CH_3CCH, CH_3SiH_3, and CF_3SF_5 are examples of symmetric-top molecules. A linear molecule can be treated as a special case of a symmetric top in which the angular momentum about the symmetry axis is zero.

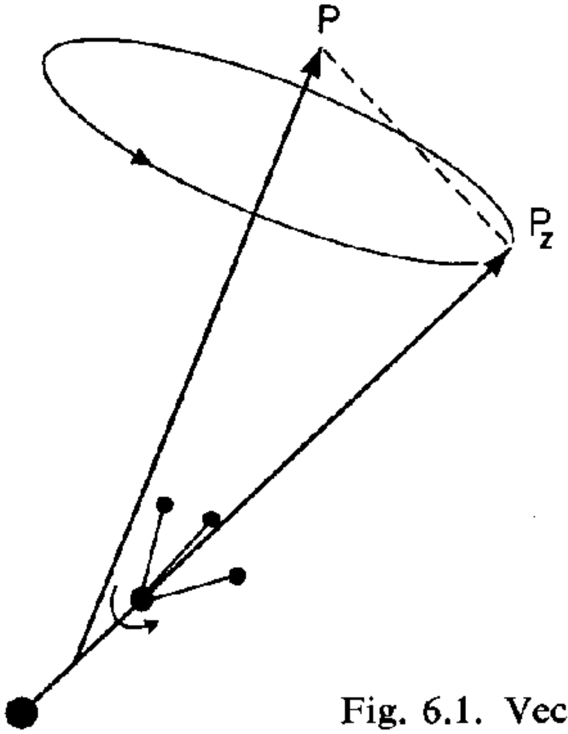


Fig. 6.1. Vector diagram of a symmetric rotor.

Gordy and Cook
"Microwave Spectroscopy"
Chapter 6

In a symmetric top, one of the principal axes of inertia must lie along the molecular axis of symmetry. The principal moments of inertia which have their axes perpendicular to this axis are equal. If a, the axis of least moment of inertia ($I_a < I_b = I_c$), lies along the symmetry axis, the molecule is a prolate symmetric top (CH_3CCH, for example). If c, the axis of the greatest moment of inertia ($I_a = I_b < I_c$), lies along the symmetry axis, the molecule is an oblate symmetric top (BCl_3, for example). Most of the symmetric-top molecules observed in the microwave region are prolate. With the a axis chosen along the symmetry axis ($I_c = I_b$) and with $P^2 = P_a{}^2 + P_b{}^2 + P_c{}^2$, the Hamiltonian operator may be expressed as

$$\mathscr{H}_r = \frac{P^2}{2I_b} + \frac{1}{2}\left(\frac{1}{I_a} - \frac{1}{I_b}\right)P_a{}^2$$

Eigenvalues for the angular momentum operators P^2, P_z, and P_Z for the symmetric-top rotor

$$(J,K,M|P^2|J,K,M) = \hbar^2 J(J+1)$$

$$(J,K,M|P_z|J,K,M) = \hbar K$$

$$(J,K,M|P_Z|J,K,M) = \hbar M$$

where

$$J = 0, 1, 2, 3, \ldots$$

$$K = 0, \pm 1, \pm 2, \pm 3, \ldots, \pm J$$

$$M = 0, \pm 1, \pm 2, \pm 3, \ldots, \pm J$$

In the x, y, z system, z is chosen as the symmetry axis of the top. In the a, b, c system used here for designation of the principal axes of inertia, z becomes a for the prolate top, and z becomes c for the oblate top. In the field-free rotor, the rotational energies do not depend on M. It is evident that the Hamiltonian of Eq. (6.1) commutes with P^2 and P_a and is therefore diagonal in the J,K representation. Its eigenvalues, which are the quantized rotational energies of the rigid prolate symmetric top, are therefore

$$E_{J,K} = (J,K|\mathscr{H}_r|J,K) = \frac{1}{2I_b}(J,K|P^2|J,K) + \frac{1}{2}\left(\frac{1}{I_a} - \frac{1}{I_b}\right)(J,K|P_a{}^2|J,K)$$

$$= \left(\frac{h^2}{8\pi^2 I_b}\right)J(J+1) + \left(\frac{h^2}{8\pi^2}\right)\left(\frac{1}{I_a} - \frac{1}{I_b}\right)K^2$$

With the designation $A = h/(8\pi^2 I_a)$ and $B = h/(8\pi^2 I_b)$, $E_{J,K}$ can be written

$$E_{J,K} = h[BJ(J+1) - (A - B)K^2]$$

Since P_a is a component of P, the values of K cannot exceed those of J in magnitude. Although K can have both negative and positive values, the + and − values do not lead to separate sets of energy levels because K appears only as a squared term . Thus all K levels except those for $K = 0$ are doubly degenerate. This K degeneracy cannot be removed by either external or internal fields. In addition to the K degeneracy, there is a $(2J + 1)$, M-degeneracy in the field-free symmetric rotor as in the linear molecule. Unlike the K degeneracy, the M degeneracy can be lifted completely by the application of an external electric or magnetic field (see Chapters 10 and 11).

In a true symmetric top, any permanent dipole moment must of necessity lie along the symmetry axis. All matrix elements of this dipole moment resolved along a space-fixed axis vanish except those between states corresponding to $J \rightarrow J$ or $J \pm 1$, $K \rightarrow K$. The selection rules for the field-free rotor are therefore

$$\Delta J = 0, \ \pm 1 \qquad \Delta K = 0$$

$$(J,K,M|P_z^2|J,K,M) = K^2\hbar^2$$

$$(J,K,M|P_y^2|J,K,M) = (\hbar^2/2)[J(J+1) - K^2]$$

$$(J,K,M|P_x^2|J,K,M) = \frac{\hbar^2}{2}[J(J+1) - K^2]$$

$$(J,K,M|P_x^2|J,K\pm 2,M) = -\frac{\hbar^2}{4}[J(J+1) - K(K\pm 1)]^{1/2} \times [J(J+1) - (K\pm 1)(K\pm 2)]^{1/2}$$

$$|(J,K|\mu|J+1,K)|^2 = \sum_{F=X,Y,Z}\sum_{M'}|(J,K,M|\mu_F|J+1,K,M')|^2 = \mu^2\frac{(J+1)^2 - K^2}{(J+1)(2J+1)}$$

For the $J \rightarrow J$ or the inversion type of transition the result is

$$|(J,K^-|\mu|J,K^+)|^2 = \sum_{F=X,Y,Z}\sum_{M'}|(J,K^-,M|\mu_F|J,K^+,M')|^2 = \mu^2\frac{K^2}{J(J+1)}$$

The rule corresponding to absorption of radiation is $J \rightarrow J + 1$ and $K \rightarrow K$. Application of these rules gives the formula for the absorption frequencies for the rigid symmetric top

$$\nu = 2B(J + 1) \tag{6.8}$$

which is exactly that for the linear molecule. However, as we shall see below, centrifugal stretching separates the lines corresponding to different $|K|$ by small frequency differences which are usually sufficient to make these lines resolvable in the microwave region.

Factors of Direction Cosine Matrix Elements[a] of Symmetric-Top Rotors[b]

Matrix element factor	Value of J' $J + 1$	J	$J - 1$
$(J\|\Phi_{Fg}\|J')$	$\{4(J+1)[(2J+1)(2J+3)]^{1/2}\}^{-1}$	$[4J(J+1)]^{-1}$	$[4J(4J^2-1)^{1/2}]^{-1}$
$(J,K\|\Phi_{Fz}\|J',K)$	$2[(J+1)^2-K^2]^{1/2}$	$2K$	$-2(J^2-K^2)^{1/2}$
$(J,K\|\Phi_{Fy}\|J',K\pm 1)$ $= \mp i(J,K\|\Phi_{Fx}\|J',K\pm 1)$	$\mp[(J\pm K+1)(J\pm K+2)]^{1/2}$	$[J(J+1)-K(K\pm 1)]^{1/2}$	$\mp[(J\mp K)(J\mp K-1)]^{1/2}$
$(J,M\|\Phi_{Zg}\|J',M)$	$2[(J+1)^2-M^2]^{1/2}$	$2M$	$-2(J^2-M^2)^{1/2}$
$(J,M\|\Phi_{Yg}\|J',M\pm 1)$ $= \pm i(J,M\|\Phi_{Xg}\|J',M\pm 1)$	$\mp[(J\pm M+1)(J\pm M+2)]^{1/2}$	$[J(J+1)-M(M\pm 1)]^{1/2}$	$\mp[(J\mp M)(J\mp M-1)]^{1/2}$

[a] Cross, Hainer, and King.[5]

[b] The matrix elements are obtained from the factors with the relation: $(J,K,M|\Phi_{Fg}|J',K',M') = (J|\Phi_{Fg}|J')(J,K|\Phi_{Fg}|J',K')(J,M|\Phi_{Fg}|J',M')$, $F = X,Y,Z$ and $g = x,y,z$.

Centrifugal Distorsion

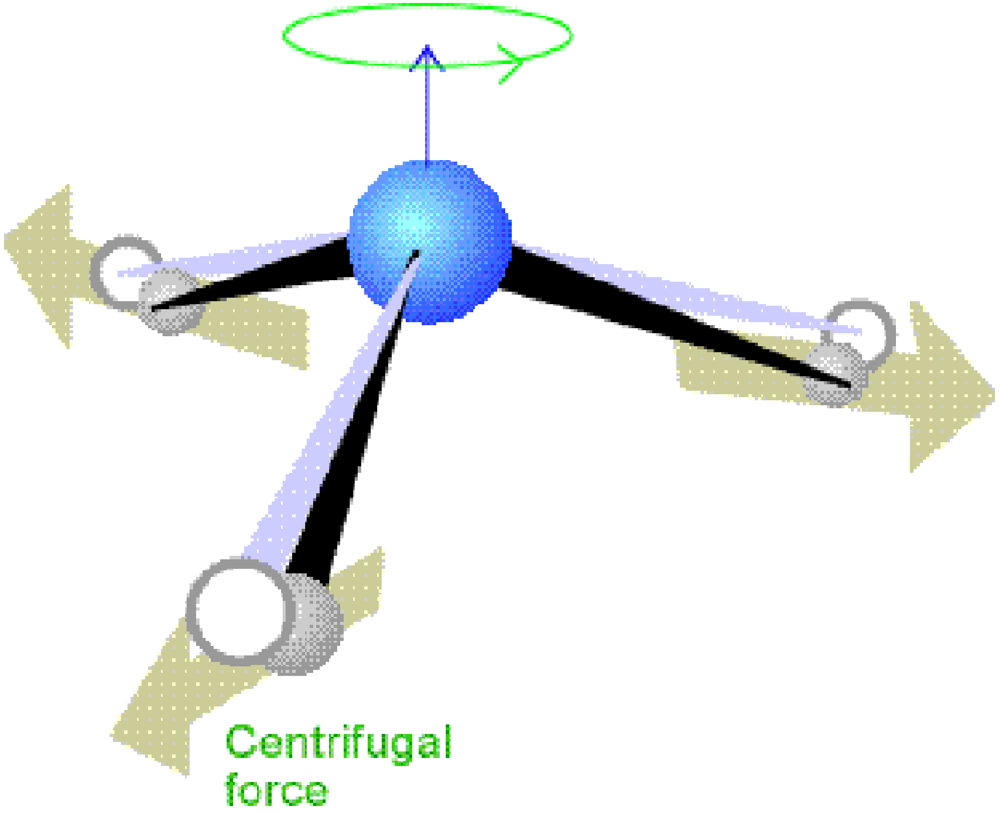
Centrifugal stretching is treated as a perturbation on the eigenstates of the rigid rotor. If $\mathscr{H}_r$ represents the Hamiltonian of the rigid rotor and $\mathscr{H}_d$ represents that of the distortional energy, the rotational Hamiltonian is

$$\mathscr{H} = \mathscr{H}_r + \mathscr{H}_d \tag{6.9}$$

In Chapter 8 it is shown that the centrifugal distortional Hamiltonian has the form

$$\mathscr{H}_d = \frac{\hbar^4}{4} \sum_{\alpha\beta\gamma\delta} \tau_{\alpha\beta\gamma\delta} P_\alpha P_\beta P_\gamma P_\delta \tag{6.10}$$

where $\alpha, \beta, \gamma, \delta$ represent the principal coordinate axes of the moments of inertia and where each must be summed over all three coordinate axes. However, in the first-order perturbation treatment, the terms with odd powers in any angular momentum which occur in the sum average to zero. Furthermore, by use of the angular momenta commutation rules and the fact that many of the τ's are equal, the Hamiltonian can be further simplified.



$$\mathscr{H}_d^{(1)} = \frac{1}{4}\sum \tau'_{\alpha\alpha\beta\beta} {P_\alpha}^2 {P_\beta}^2$$

$$= \frac{1}{4}\left[\tau'_{xxxx}{P_x}^4 + \tau'_{yyyy}{P_y}^4 + \tau'_{zzzz}{P_z}^4 + \tau'_{xxyy} \times ({P_x}^2{P_y}^2 + {P_y}^2{P_x}^2) + \tau'_{xxzz}({P_x}^2{P_z}^2 + {P_z}^2{P_x}^2) + \tau'_{yyzz}({P_y}^2{P_z}^2 + {P_z}^2{P_y}^2)\right]$$

$$E_d^{(1)} = (J,K|\mathscr{H}_d^{(1)}|J,K)$$

Matrix Elements of $P_\alpha{}^2 P_\beta{}^2$ in a Symmetric Rotor Representation[a]

$$(K|P_z{}^4|K) = K^4$$
$$(K|P_y{}^4|K) = \tfrac{1}{4}[(P^2 - K^2)^2 + \tfrac{1}{4}\{f_+(0)f_+(1) + f_-(0)f_-(1)\}]$$
$$(K|P_x{}^4|K) = (K|P_y{}^4|K)$$
$$(K|P_x{}^2P_y{}^2 + P_y{}^2P_x{}^2|K) = \tfrac{1}{2}[(P^2 - K^2)^2 - \tfrac{1}{4}\{f_+(0)f_+(1) + f_-(0)f_-(1)\}$$
$$(K|P_y{}^2P_z{}^2 + P_z{}^2P_y{}^2|K) = K^2[P^2 - K^2]$$
$$(K|P_x{}^2P_z{}^2 + P_z{}^2P_x{}^2|K) = (K|P_y{}^2P_z{}^2 + P_z{}^2P_y{}^2|K)$$

$$(K|P_y{}^4|K \pm 2) = \tfrac{1}{8}\{2P^2 - K^2 - (K \pm 2)^2\}\{f_\pm(0)f_\pm(1)\}^{1/2}$$
$$(K|P_x{}^4|K \pm 2) = -(K|P_y{}^4|K \pm 2)$$
$$(K|P_y{}^2P_z{}^2 + P_z{}^2P_y{}^2|K \pm 2) = \tfrac{1}{4}\{K^2 + (K \pm 2)^2\}\{f_\pm(0)f_\pm(1)\}^{1/2}$$
$$(K|P_x{}^2P_z{}^2 + P_z{}^2P_x{}^2|K \pm 2) = -(K|P_y{}^2P_z{}^2 + P_z{}^2P_y{}^2|K \pm 2)$$

$$(K|P_y{}^4|K \pm 4) = \tfrac{1}{16}\{f_\pm(0)f_\pm(1)f_\pm(2)f_\pm(3)\}^{1/2}$$
$$(K|P_x{}^4|K \pm 4) = (K|P_y{}^4|K \pm 4)$$
$$(K|P_x{}^2P_y{}^2 + P_y{}^2P_x{}^2|K \pm 4) = -2(K|P_y{}^4|K \pm 4)$$
$$P^2 = J(J+1); \qquad f_\pm(l) = \{P^2 - (K \pm l)(K \pm l \pm 1)\}$$

$$E_d^{(1)} = -h[D_J J^2(J+1)^2 + D_{JK} J(J+1)K^2 + D_K K^4]$$

The energies of symmetric rotor are :

$$E_{J,K} = h[BJ(J+1) + (A-B)K^2 - D_J J^2(J+1)^2 - D_{JK} J(J+1)K^2 - D_K K^4]$$

and the frequencies for a transition J=>J+1 :

$$\nu = 2B(J+1) - 4D_J(J+1)^3 - 2D_{JK}(J+1)K^2$$

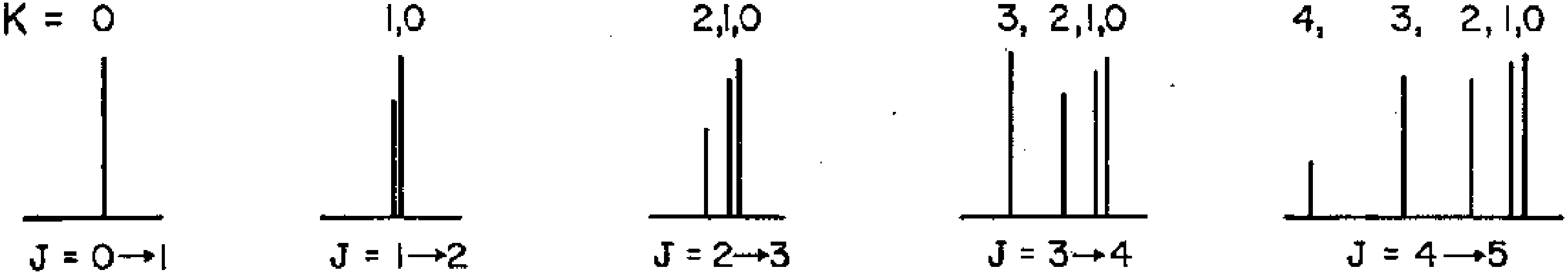


Fig. 6.2. Diagram indicating the general appearance of the rotational spectrum of a symmetric-top molecule. The lines of different *K* for the same *J* transition are separated by centrifugal distortion. This separation is extremely small compared with the separation of the different *J* transitions.

Spectral Constants for the Ground Vibrational State of Some Organic Symmetric-Top Molecules[a]

Molecule	B_0 (Mc)	D_J (kc)	D_{JK} (kc)	Ref.
CH_3F	25 536.148	60.4	439.26	b
$CH_3{}^{35}Cl$	13 292.86	18.1	198	b
$CH_3{}^{79}Br$	9 568.20	9.9	128.3	b
CH_3I	7 501.30	6.28	98.5	b
CHF_3	10 348.862	11.3	−18.0	c
$CH^{35}Cl_3$	3 302.083	1.52	−2.5	d
CH_3CN	9 198.899	3.81	176.9	e
CF_3CN	2 945.528	0.306	5.81	c
CH_3CCH	8 545.877	2.96	162.9	c
CF_3CCH	2 877.948	0.24	6.3	f
$CH_3CC^{35}Cl$	2 232.271		21.5	g
CH_3CCCN	2 065.73	0.1	19.8	h
CH_3CCCCH	2 035.74	0.07	19.8	i
$CH_3{}^{198}Hg^{35}Cl$	2 077.48	0.241	21.0	j
$(CH_3)_3CH$	7 789.45	11		k
$(CH_3)_3CC\equiv CH$	2 683.18			l
$(CH_3)_3C—C\equiv C^{35}Cl$	890.482	0.03		m
$^{28}SiH_3CCH$	4 828.687	2.1	63	n
$^{28}SiH_3CCCH_3$	2 068.280	0.127	5.54	o
$^{28}SiH_3NCS$	1 516.018	<0.3	41.9	p
$C_7H_{13}N$	2 431.4	4	<15	q
$C_5H_5{}^{58}NiNO$	1 259.25	~0.05		r
$C_5H_5Mn(CO)_3$	826.5			s
$C_6H_6{}^{52}Cr(CO)_3$	729.8			s

ROTATION-INVERSION

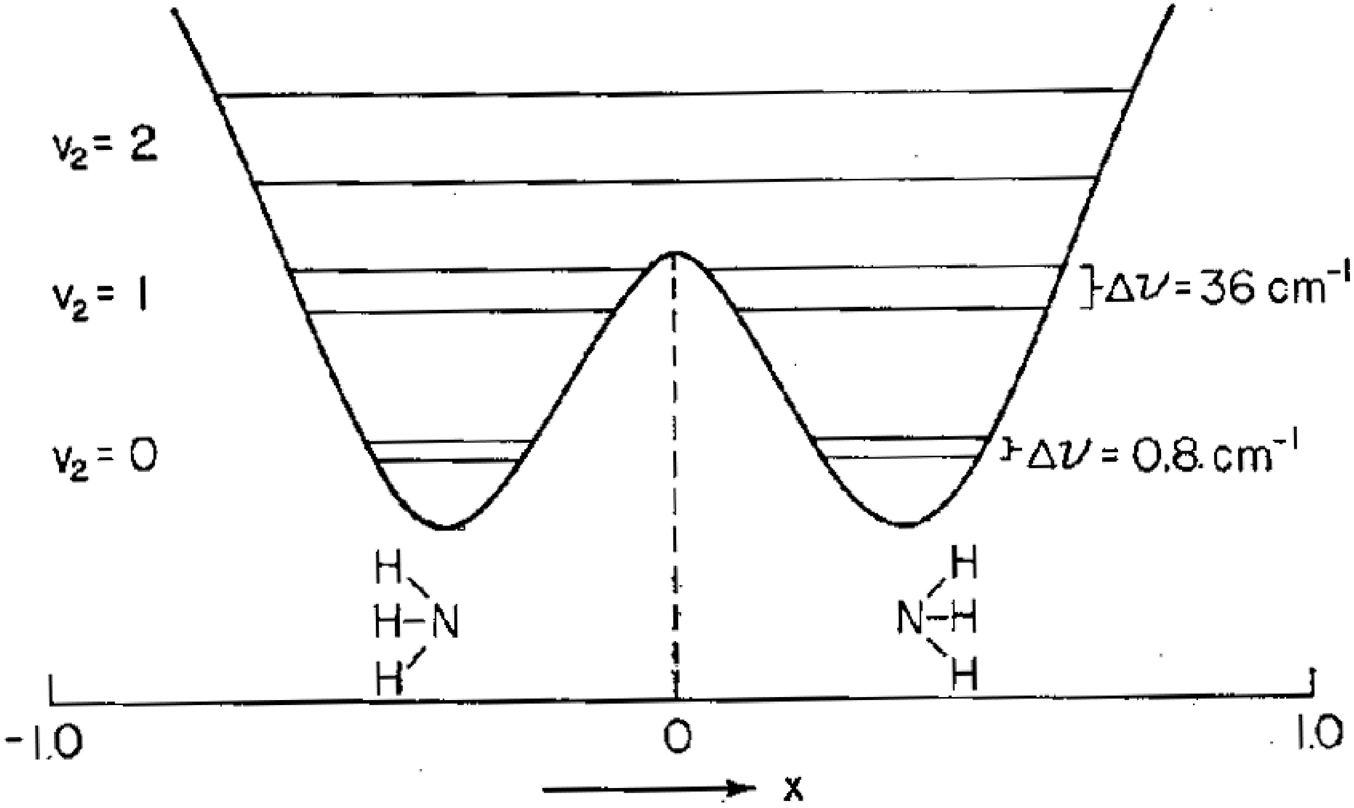
According to quantum mechanics, pyramidal XY_3 symmetric-top molecules can execute inversion motion in which the X atom moves through the Y_3 plane to achieve an identical but inverted pyramidal configuration. The inverted configuration is obtained mathematically by a change of sign of the coordinates of all the particles measured from the center of mass. Theoretically, such inversion is possible in any nonplanar molecule
but, practically, it is of significance for only a very few. The inversion potential curve of the NH_3 molecule is illustrated by Figure 6.6. The potential energy of the molecule plotted as a function of the distance between the N atom and the H_3 plane has double minima corresponding to the two equivalent equilibrium configurations.

The wave functions of the molecule can be expressed as linear combinations of ϕ_L and ϕ_R of those of the molecule in the equivalent right and left configurations. These functions,

$$\psi_+ = \frac{1}{\sqrt{2}}(\phi_L + \phi_R)$$

$$\psi_- = \frac{1}{\sqrt{2}}(\phi_L - \phi_R)$$

have opposite symmetry. For an infinitely high barrier they represent



Potential curve of the NH_3 inversion.

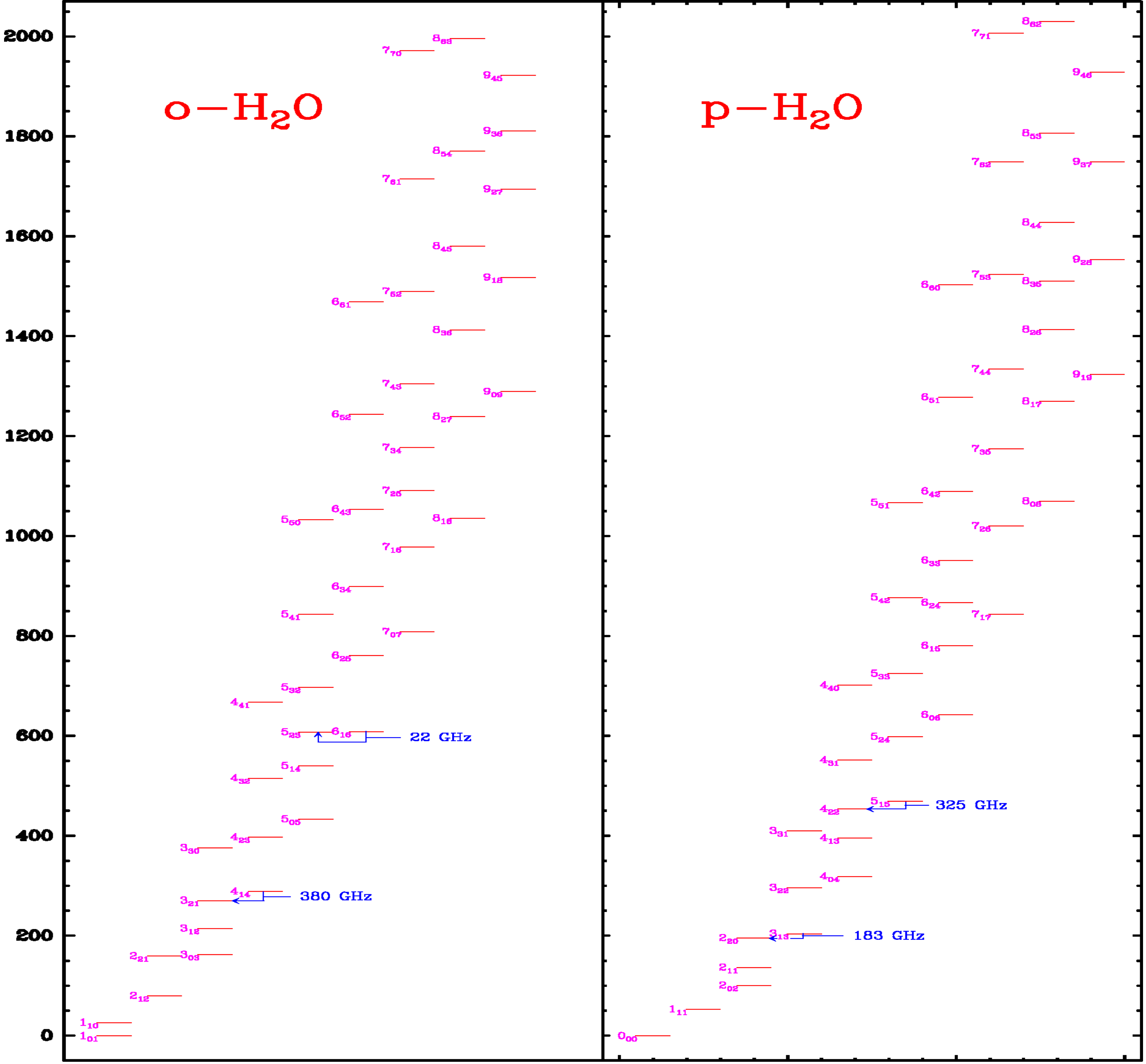
degenerate states; but when the barrier is sufficiently low, as in NH_3, the two states are separated by a measurable interaction energy. Selection rules allow transitions + ↔ – between the states giving rise to inversion spectra.

So far we have considered only the rotational spectrum of the linear molecules. What happens when the molecule is not linear, like water vapor H_2O ? or when it is only symmetric but not lineal as ammonia, NH_3 ?

The energy of symmetric molecules can be easily calculated, at least the rotational part. The structure of the rotational levels is, however, very different from that of linear species. In this case, two principal moments of inertia are identical.

When the molecule is asymmetric, like water vapor, the hamiltonian describing the energy of the system is very complex. No simple formula can be given. Selection rules allow much more rotational transitions. If the molecule is heavy then the three rotational constants (A, B, C) and a few distortion constants are enough to reproduce the spectrum. If the molecule is very light like H_2O high order corrections have to be applied (terms in J^{12} for example).

Pcm2l.exe


$o-H_2O$
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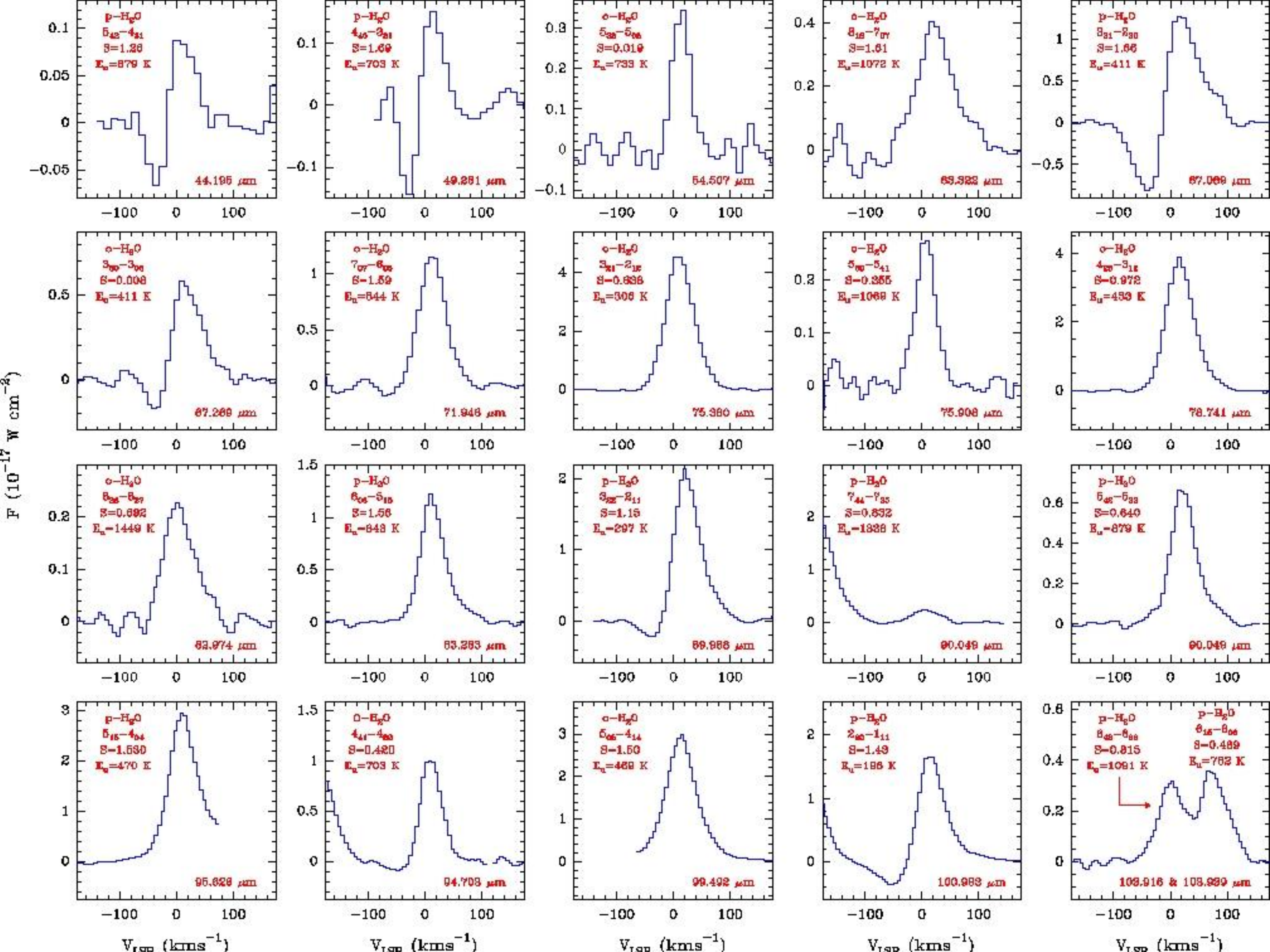
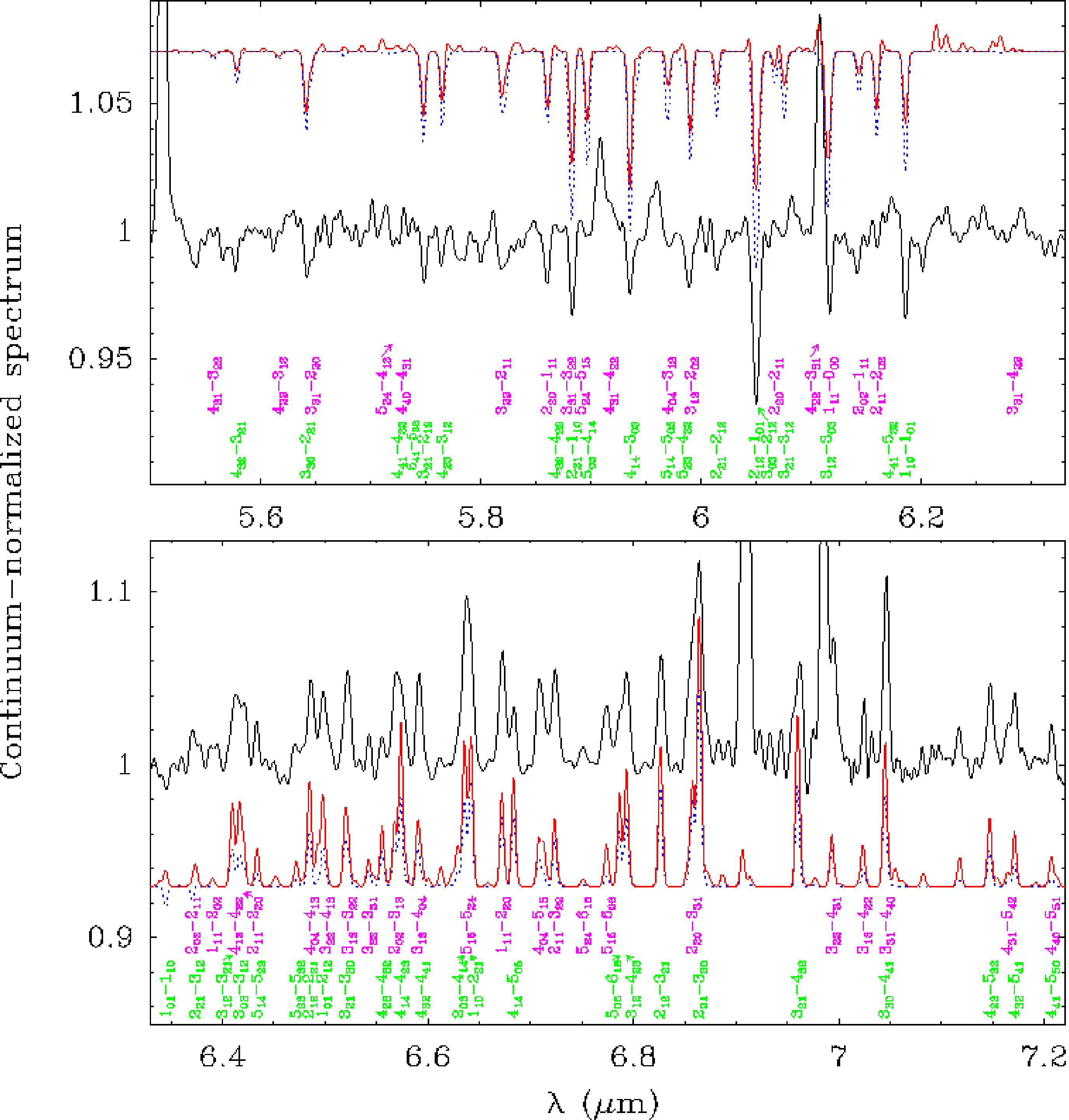
9_{46}
183 GHz
325 GHz



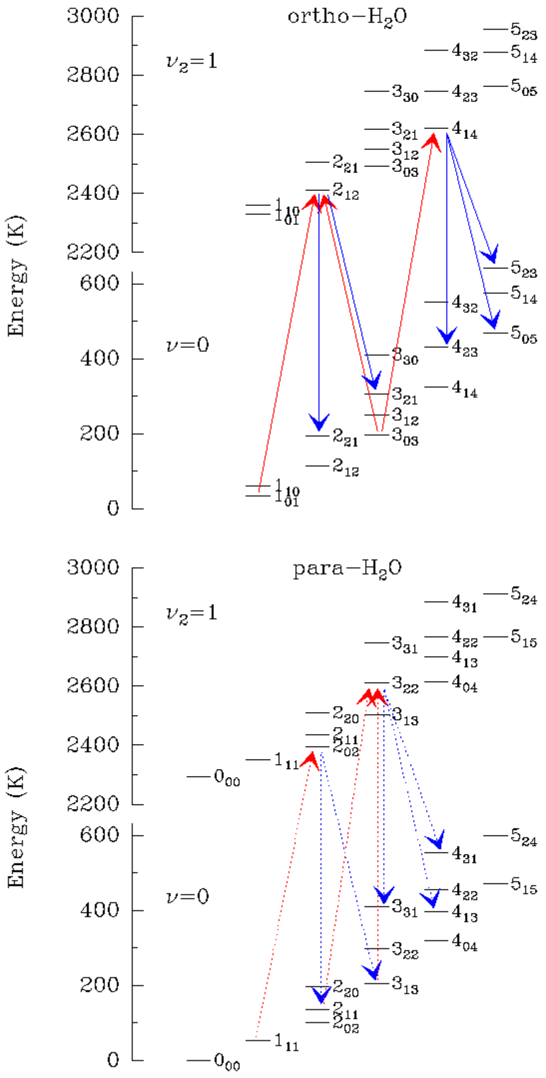
p-H$_2$O $5_{42}-4_{31}$ S=1.26 E$_u$=879 K 44.195 μm
p-H$_2$O $4_{40}-3_{31}$ S=1.69 E$_u$=703 K 49.281 μm
o-H$_2$O $5_{32}-4_{05}$ S=0.019 E$_u$=733 K 54.507 μm
o-H$_2$O $8_{18}-7_{07}$ S=1.61 E$_u$=1072 K 63.322 μm
p-H$_2$O $3_{31}-2_{20}$ S=1.66 E$_u$=411 K 67.089 μm
o-H$_2$O $3_{30}-2_{21}$ S=0.008 E$_u$=411 K 67.269 μm
o-H$_2$O $7_{07}-6_{16}$ S=1.59 E$_u$=844 K 71.946 μm
o-H$_2$O $3_{21}-2_{12}$ S=0.698 E$_u$=306 K 75.380 μm
o-H$_2$O $5_{50}-5_{41}$ S=0.355 E$_u$=1068 K 75.908 μm
o-H$_2$O $4_{23}-3_{12}$ S=0.972 E$_u$=433 K 78.741 μm
o-H$_2$O $8_{36}-8_{27}$ S=0.692 E$_u$=1449 K 82.974 μm
p-H$_2$O $6_{06}-5_{15}$ S=1.56 E$_u$=643 K 83.283 μm
p-H$_2$O $3_{22}-2_{11}$ S=1.15 E$_u$=297 K 89.988 μm
p-H$_2$O $7_{44}-7_{35}$ S=0.832 E$_u$=1336 K 90.049 μm
p-H$_2$O $5_{42}-5_{33}$ S=0.640 E$_u$=879 K 90.049 μm
p-H$_2$O $5_{15}-4_{04}$ S=1.530 E$_u$=470 K 95.626 μm
o-H$_2$O $4_{41}-4_{32}$ S=0.420 E$_u$=703 K 94.703 μm
o-H$_2$O $5_{05}-4_{14}$ S=1.50 E$_u$=468 K 99.492 μm
p-H$_2$O $2_{20}-1_{11}$ S=1.43 E$_u$=196 K 100.983 μm
p-H$_2$O $6_{43}-6_{34}$ S=0.815 E$_u$=1091 K
p-H$_2$O $6_{15}-6_{06}$ S=0.489 E$_u$=782 K
103.916 & 103.939 μm
F (10^{-17} W cm^{-2})
V$_{LSR}$ (kms^{-1})
−100
0
100

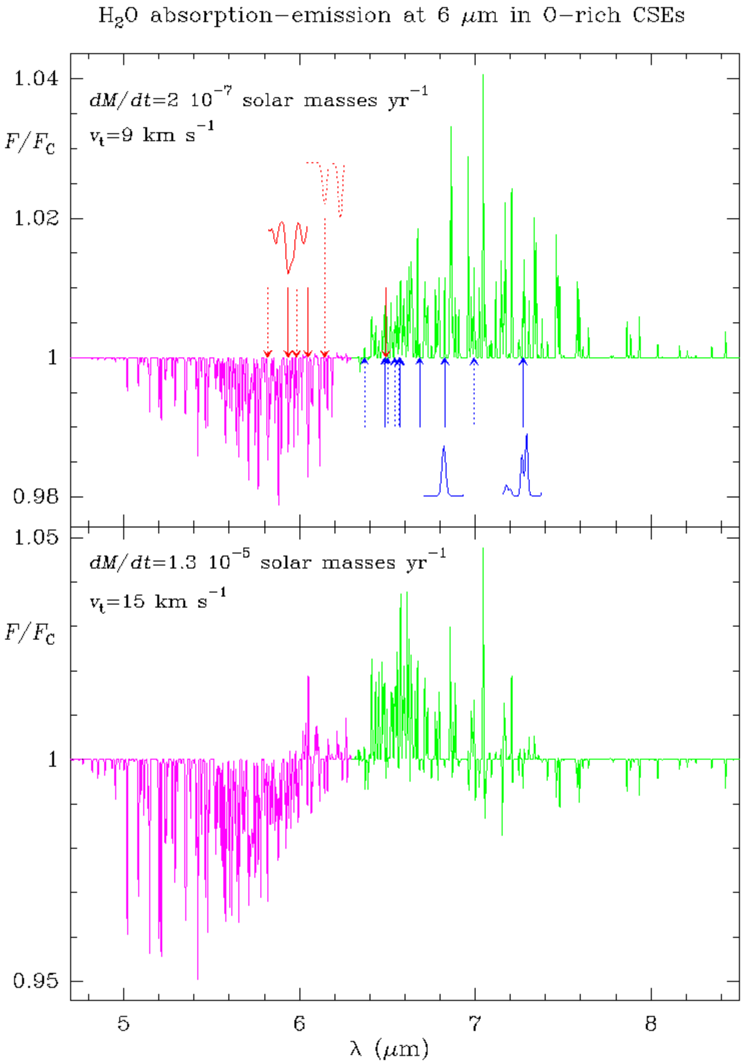


The pumping of H_2O is strongly affected by the dust grains absorption/ emission.

Radiative transfer models have to include these effects as they become crucial as soon as the dust opacity is ≈ 1.

González-Alfonso et. al. 1998, ApJ Letters, 502,L169





González-Alfonso et al., 1999

Each molecule will have different excitation mechanisms depending on:

Its frequencies and rotational dipole(s) moment(s)

Its collisional rates with H_2, He, H, e- (depending on the media)

Infrared pumping (depends on the media and the source structure and on the dust effect on the IR photons). It depends also on the vibrational dipole moments

Its molecular abundance (opacity effects, radiative trapping)

The spatial structure of the source

Chemical pumping (NH_3, CH_3CN, ….)