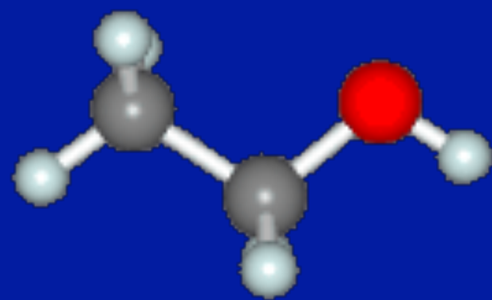
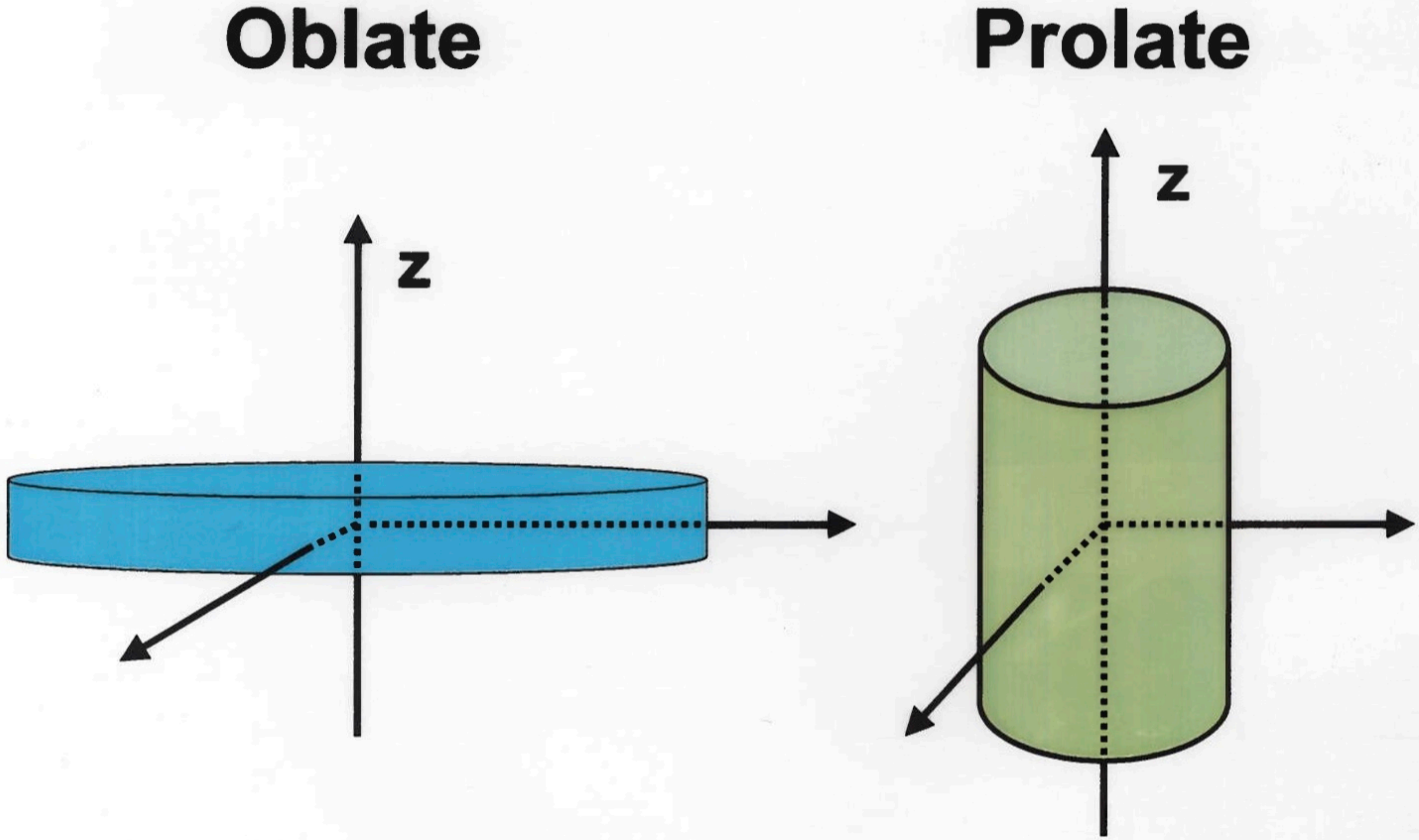
# AST 515
# Molecular Rotation Spectroscopy



September 30, 2013

# Symmetric Tops



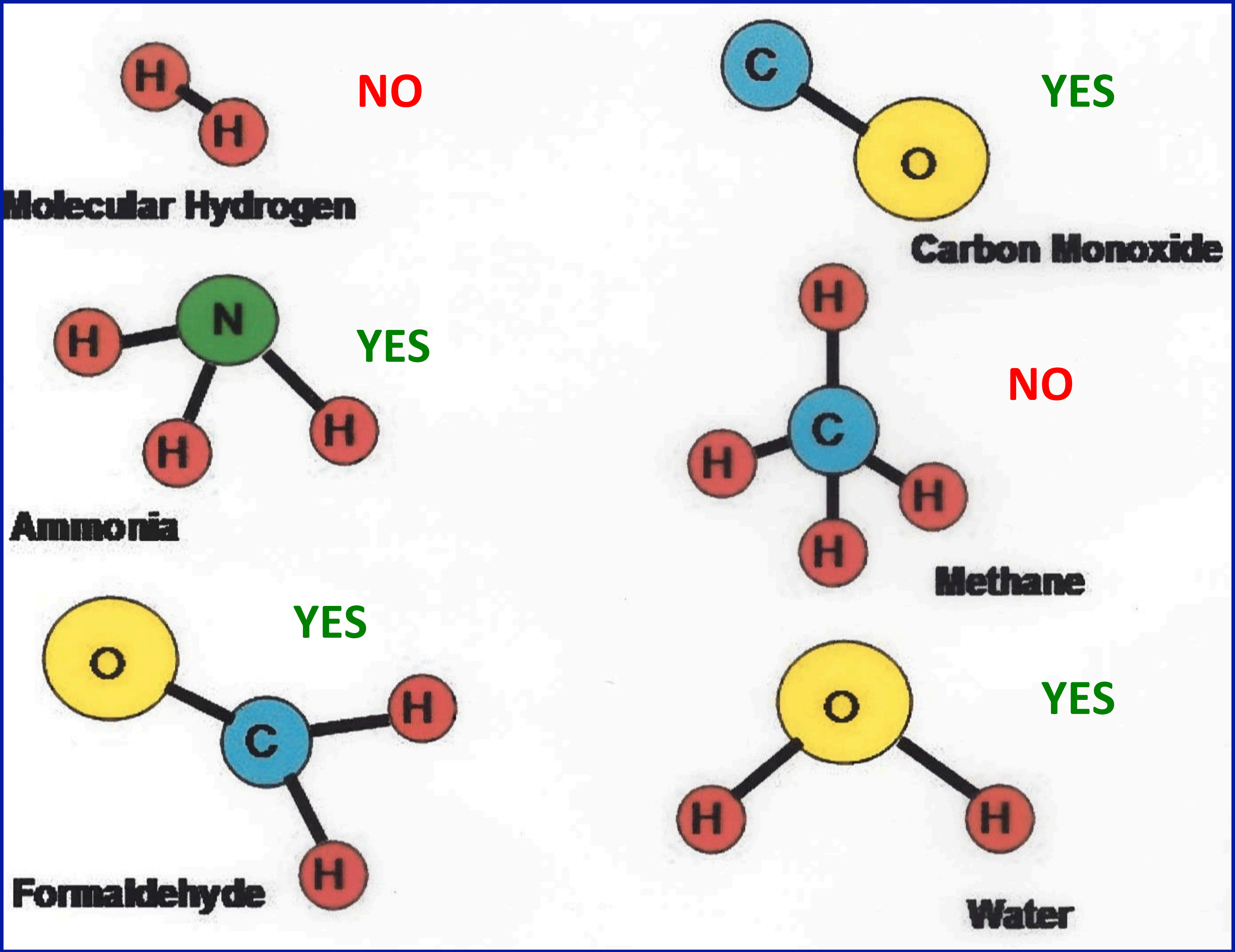

$I_A = I_B < I_C$ $\quad$ $I_A < I_B = I_C$

# Notation and Units

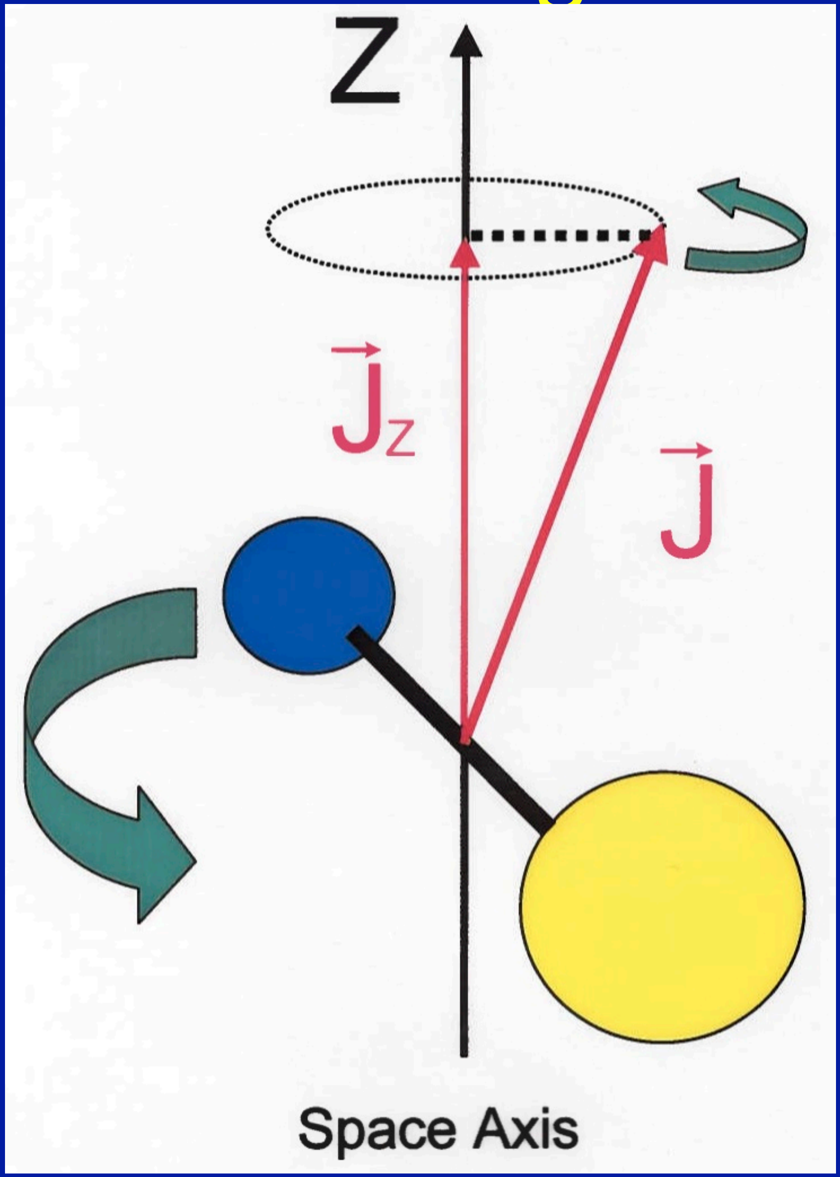
- Electric Dipole Moment
  - 1 Debye = 1 D = $10^{-18}$ cgs units (esu cm or statC cm)
  - CO $\mu_e$ = 0.11 D    HCN $\mu_e$ = 2.98 D

- Energy levels are expressed in many units:
  - $E = h\nu$     in units of ergs or eV
  - E/k has units of Temperature (K) [i.e. E = kT]
  - E/hc has units of $cm^{-1}$ or wavenumber
    - To convert from $cm^{-1}$ to K, multiply by hc/k = 1.439

# Electric Dipole Moment

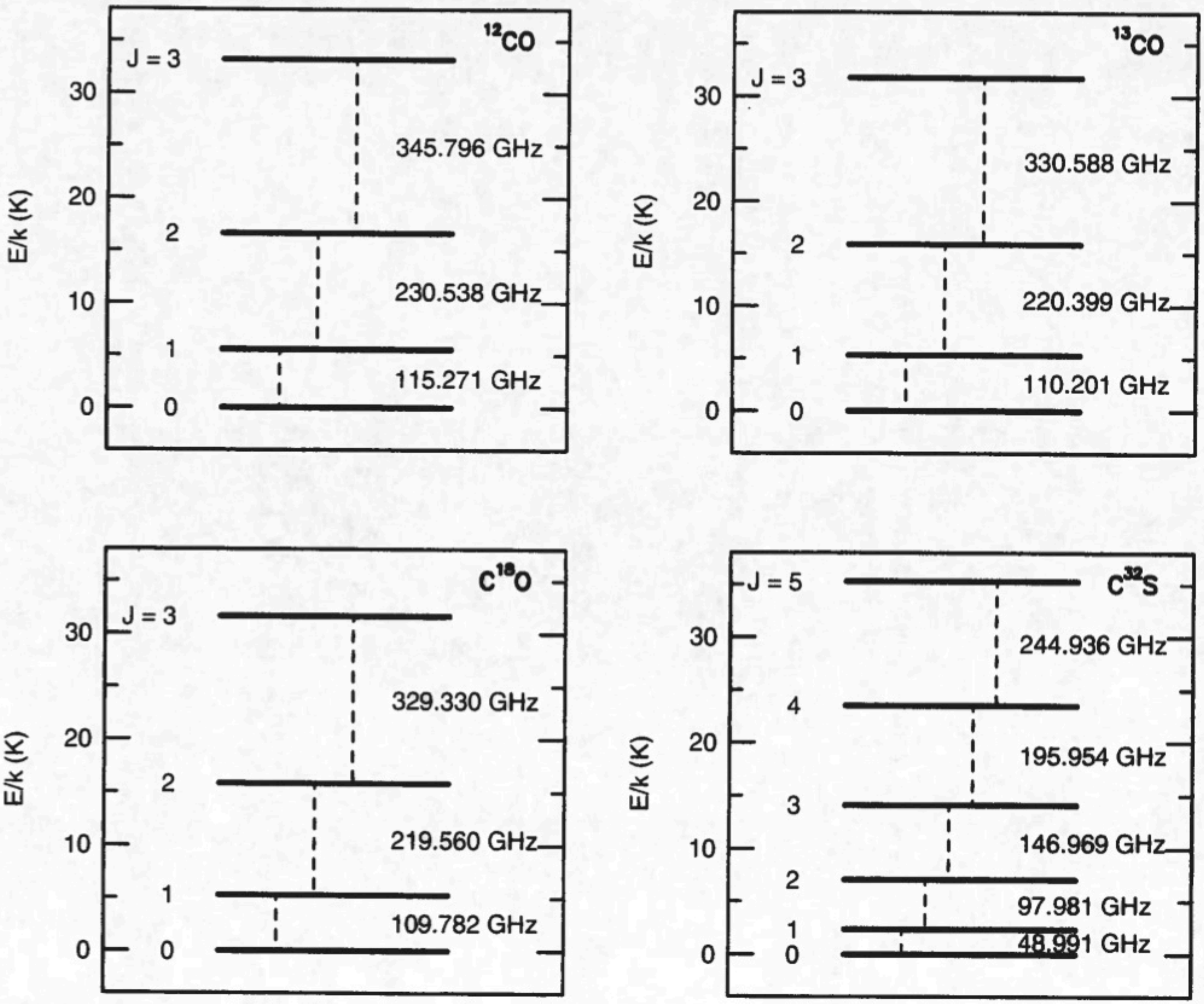


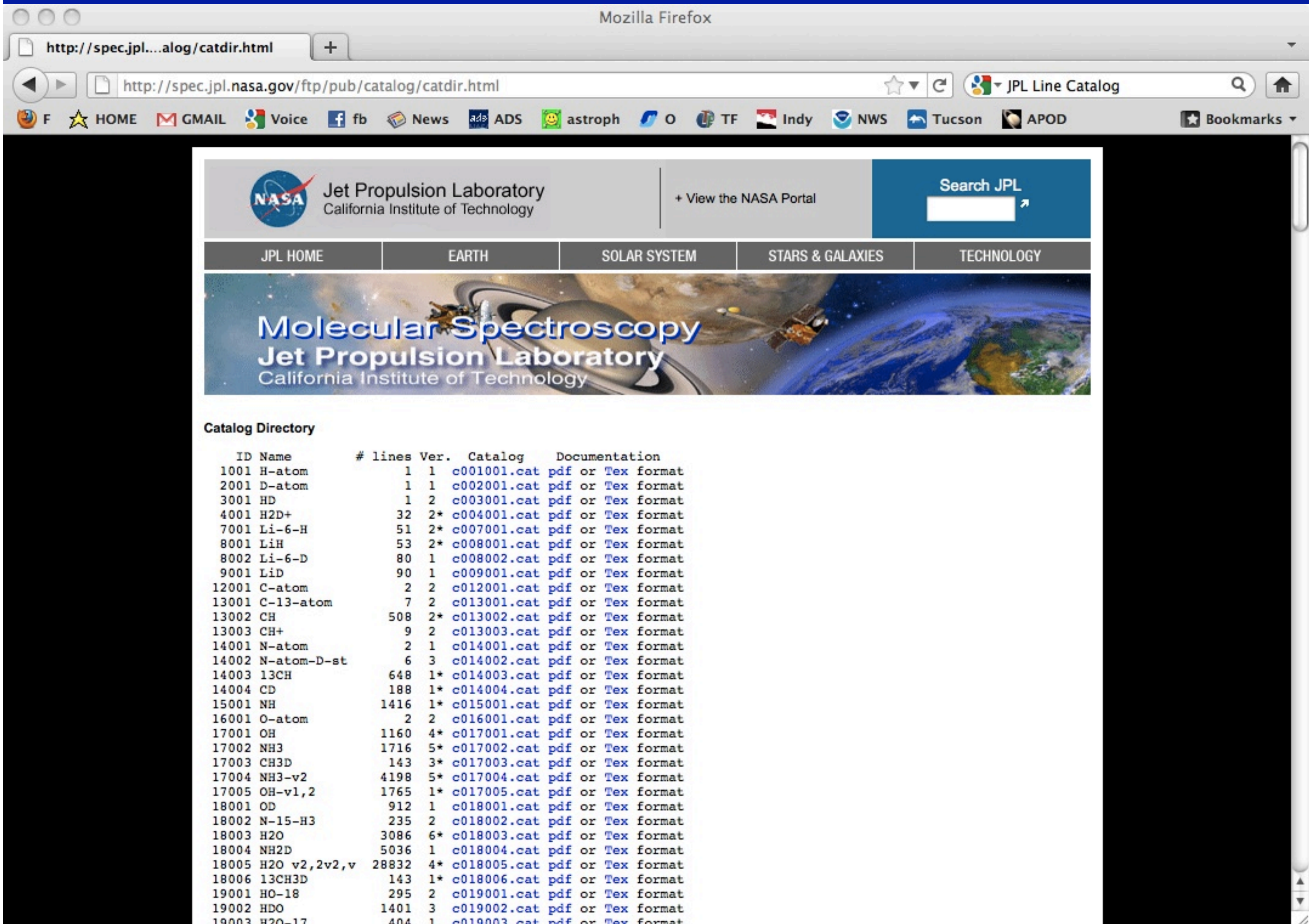
# Linear Molecule Angular Momenta




Molecule axis tipped w.r.t space axis

# Linear Molecule $^1\Sigma$ Example Rotational Spectra



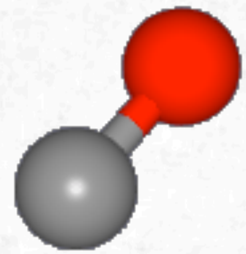



**Catalog Directory**

| ID | Name | # lines | Ver. | Catalog | Documentation |
|---|---|---|---|---|---|
| 1001 | H-atom | 1 | 1 | c001001.cat | pdf or Tex format |
| 2001 | D-atom | 1 | 1 | c002001.cat | pdf or Tex format |
| 3001 | HD | 1 | 2 | c003001.cat | pdf or Tex format |
| 4001 | H2D+ | 32 | 2* | c004001.cat | pdf or Tex format |
| 7001 | Li-6-H | 51 | 2* | c007001.cat | pdf or Tex format |
| 8001 | LiH | 53 | 2* | c008001.cat | pdf or Tex format |
| 8002 | Li-6-D | 80 | 1 | c008002.cat | pdf or Tex format |
| 9001 | LiD | 90 | 1 | c009001.cat | pdf or Tex format |
| 12001 | C-atom | 2 | 2 | c012001.cat | pdf or Tex format |
| 13001 | C-13-atom | 7 | 2 | c013001.cat | pdf or Tex format |
| 13002 | CH | 508 | 2* | c013002.cat | pdf or Tex format |
| 13003 | CH+ | 9 | 2 | c013003.cat | pdf or Tex format |
| 14001 | N-atom | 2 | 1 | c014001.cat | pdf or Tex format |
| 14002 | N-atom-D-st | 6 | 3 | c014002.cat | pdf or Tex format |
| 14003 | 13CH | 648 | 1* | c014003.cat | pdf or Tex format |
| 14004 | CD | 188 | 1* | c014004.cat | pdf or Tex format |
| 15001 | NH | 1416 | 1* | c015001.cat | pdf or Tex format |
| 16001 | O-atom | 2 | 2 | c016001.cat | pdf or Tex format |
| 17001 | OH | 1160 | 4* | c017001.cat | pdf or Tex format |
| 17002 | NH3 | 1716 | 5* | c017002.cat | pdf or Tex format |
| 17003 | CH3D | 143 | 3* | c017003.cat | pdf or Tex format |
| 17004 | NH3-v2 | 4198 | 5* | c017004.cat | pdf or Tex format |
| 17005 | OH-v1,2 | 1765 | 1* | c017005.cat | pdf or Tex format |
| 18001 | OD | 912 | 1 | c018001.cat | pdf or Tex format |
| 18002 | N-15-H3 | 235 | 2 | c018002.cat | pdf or Tex format |
| 18003 | H2O | 3086 | 6* | c018003.cat | pdf or Tex format |
| 18004 | NH2D | 5036 | 1 | c018004.cat | pdf or Tex format |
| 18005 | H2O v2,2v2,v | 28832 | 4* | c018005.cat | pdf or Tex format |
| 18006 | 13CH3D | 143 | 1* | c018006.cat | pdf or Tex format |
| 19001 | HO-18 | 295 | 2 | c019001.cat | pdf or Tex format |
| 19002 | HDO | 1401 | 3 | c019002.cat | pdf or Tex format |
| 19003 | H2O-17 | 404 | 1 | c019003.cat | pdf or Tex format |

# CO – JPL Line Catalog

| | | | |
|---|---|---|---|
| Species Tag: | 28001 | Species Name: | CO |
| Version: | 4 | | Carbon monoxide |
| Date: | Aug. 1997 | | |
| Contributor: | H. S. P. Müller | | |
| Lines Listed: | 91 | Q(300.0)= | 108.865 |
| Freq. (GHz) < | 9943 | Q(225.0)= | 81.718 |
| Max. J: | 91 | Q(150.0)= | 54.581 |
| LOGSTR0= | -36.5 | Q(75.00)= | 27.455 |
| LOGSTR1= | -36.5 | Q(37.50)= | 13.897 |
| Isotope Corr.: | 0.0 | Q(18.75)= | 7.122 |
| Egy. ($cm^{-1}$) > | 0.0 | Q(9.375)= | 3.744 |
| $\mu_a$ = | 0.11011 | A= | |
| $\mu_b$ = | | B= | 57635.968 |
| $\mu_c$ = | | C= | |



The experimental measurements were reported by (1) G. Winnewisser,S. P. Belov, Th. Klaus, and R. Schieder, 1997, J. Mol. Spect. **184**, . The dipole moment and dipole centrifugal corrections are taken from (2) D. Goorvitch, 1994, Astrophys. J. Suppl. **95**, 535.

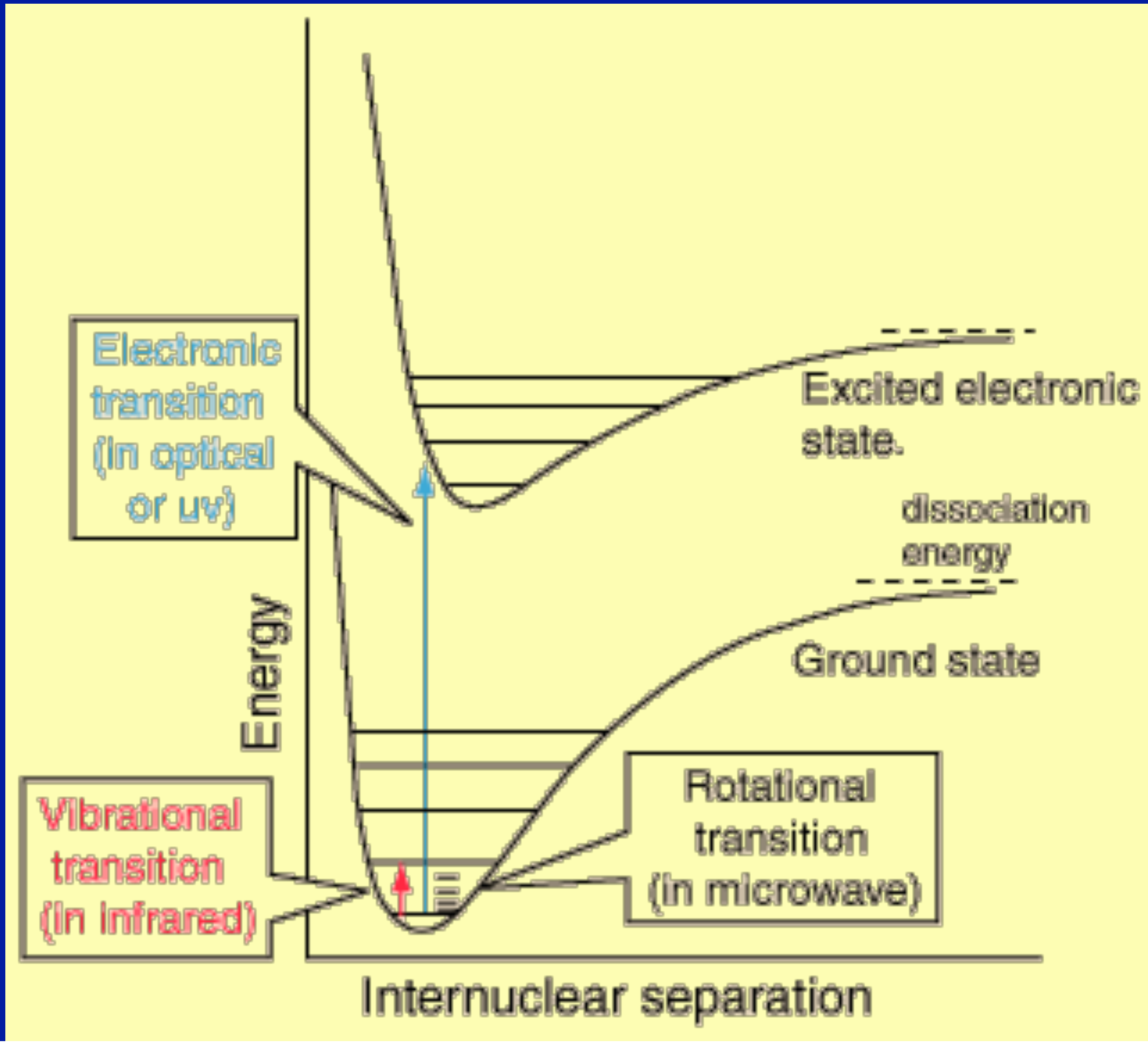
| Frequency | Unc. | Log(Int.) | | $E_l$ ($cm^{-1}$) | $g_u$ | Tag | | $J_u$ | $J_l$ |
|---|---|---|---|---|---|---|---|---|---|
| 115271.2018 | .0005 | -5.0105 | 2 | .0000 | 3 | -28001 | 101 | 1 | 0 |
| 230538.0000 | .0005 | -4.1197 | 2 | 3.8450 | 5 | -28001 | 101 | 2 | 1 |
| 345795.9899 | .0005 | -3.6118 | 2 | 11.5350 | 7 | -28001 | 101 | 3 | 2 |
| 461040.7682 | .0005 | -3.2657 | 2 | 23.0695 | 9 | -28001 | 101 | 4 | 3 |
| 576267.9305 | .0005 | -3.0118 | 2 | 38.4481 | 11 | -28001 | 101 | 5 | 4 |
| 691473.0763 | .0005 | -2.8193 | 2 | 57.6704 | 13 | -28001 | 101 | 6 | 5 |
| 806651.8060 | .0050 | -2.6716 | 2 | 80.7354 | 15 | -28001 | 101 | 7 | 6 |
| 921799.7000 | .0050 | -2.5590 | 2 | 107.6424 | 17 | -28001 | 101 | 8 | 7 |
| 1036912.3930 | .0050 | -2.4751 | 2 | 138.3904 | 19 | -28001 | 101 | 9 | 8 |
| 1151985.4520 | .0110 | -2.4156 | 2 | 172.9780 | 21 | -28001 | 10110 | | 9 |

# Linear Molecules

Table 1. Parameters of Linear Molecules in $^1\Sigma$ States

| Molecule | Name | B (GHz) | $\mu$ (D)[a] | Molecule | Name | B (GHz) | $\mu$ (D)[a] |
|---|---|---|---|---|---|---|---|
| $CO$ | Carbon Monoxide | 57.635968 | 0.11011 | $CS$ | Carbon Monosulfide | 24.495562 | 1.957 |
| $^{13}CO$ | | 55.101011 | 0.11046 | $C^{34}S$ | | 24.103541 | 1.957 |
| $C^{17}O$ | | 56.179990 | 0.11034 | $^{13}CS$ | | 23.123856 | 1.957 |
| $C^{18}O$ | | 54.891420 | 0.11079 | $HCN$ | Hydrogen Cyanide | 44.315975 | 2.984 |
| $HCO^+$ | Oxomethylium | 44.5944 | 3.30 | $H^{13}CN$ | | 43.170137 | 2.984 |
| $H^{13}CO^+$ | | 43.37722 | 3.3 | $HC^{15}N$ | | 43.02769 | 2.984 |
| $HC^{18}O^+$ | | 42.58121 | 3.30 | $DCN$ | | 36.20746 | 2.984 |
| $DCO^+$ | | 36.01976 | 3.3 | $HNC$ | Hydrogen Isocyanide | 45.33199 | 3.05 |
| $HOC^+$ | Hydroxymethylidynium | 44.7349 | 4.0 | $HN^{13}C$ | | 43.54561 | 2.699 |
| $N_2H^+$ | Diazenylium | 46.586867 | 3.40 | $H^{15}NC$ | | 43.02769 | 2.984 |
| $N_2D^+$ | | 38.554719 | 3.40 | $DNC$ | | 38.152998 | 3.050 |
| $SiO$ | Silicon Monoxide | 21.711967 | 3.098 | $HC_3N$ | Cyanoacetylene | 4.549058 | 3.724 |

# Molecular Potential Energy



# Energy Levels – Angular Momentum Expansion

$$E = B\,[J(J+1)]^1 - D\,[J(J+1)]^2 + H\,[J(J+1)]^3 + \ldots$$

**Table 2**
Molecular constants for $C_3N^-$.

| | This work[a] | Ref. [16] |
|---|---|---|
| $B$/MHz | 4851.62155(27) | 4851.62153(17) |
| $D$/Hz | 686.06(16) | 685.78(9) |
| $H$/μHz | 98.(30) | |
| $eQq$/MHz | −3.2483(72) | −3.248(5) |

[a] The numbers in parentheses indicate one standard deviation to the last significant digits.

Amano 2010, Journal of Molecular Spectroscopy 259, 16

# $H_2$

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

**2 H nuclei (I = ½) ⇒ F-D Statistics ⇒ Total ⇒ −**

**Electronic** $^1\Sigma_g^+$ ⇒ **+**

**Vibrational** **v = 0** ⇒ **+**

**Nuclear** ⇒ **3 sym. (ortho)** **+** **OR**

**1 antisym. (para)** **−**

**Rotational** ⇒ **EVEN J** ⇒ **+** ⇒ **PARA**

⇒ **ODD J** ⇒ **−** ⇒ **ORTHO**

# $N_2$

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

**2 N nuclei (I = 1) ⇒ B-E Statistics ⇒ Total ⇒ +**

**Electronic** $^1\Sigma_g^+$ ⇒ **+**

**Vibrational** **v = 0** ⇒ **+**

**Nuclear** ⇒ **6 sym. (ortho)** **+** **OR**

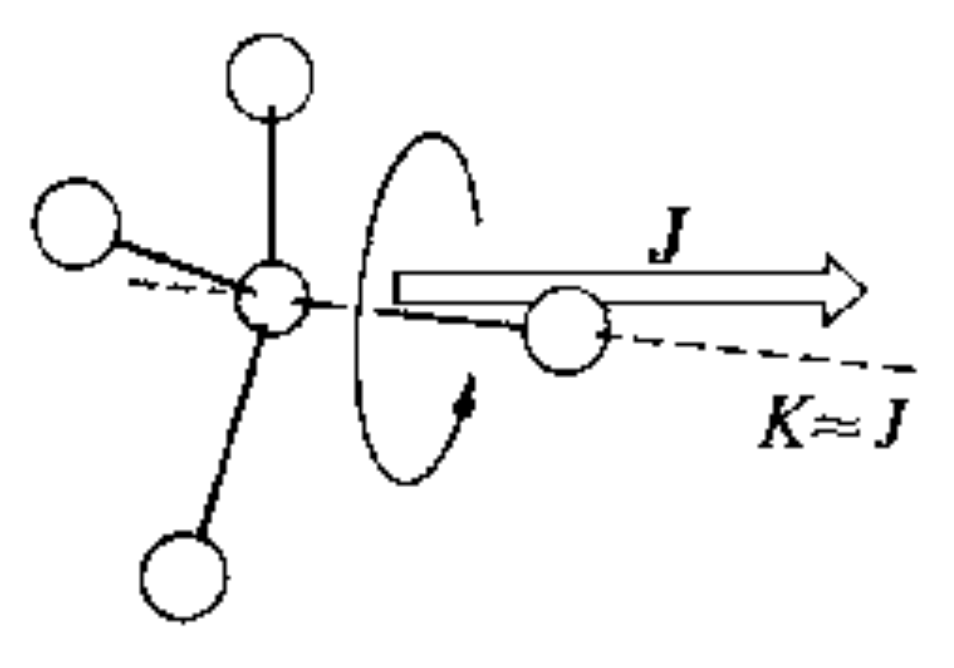
**3 antisym. (para)** **-**

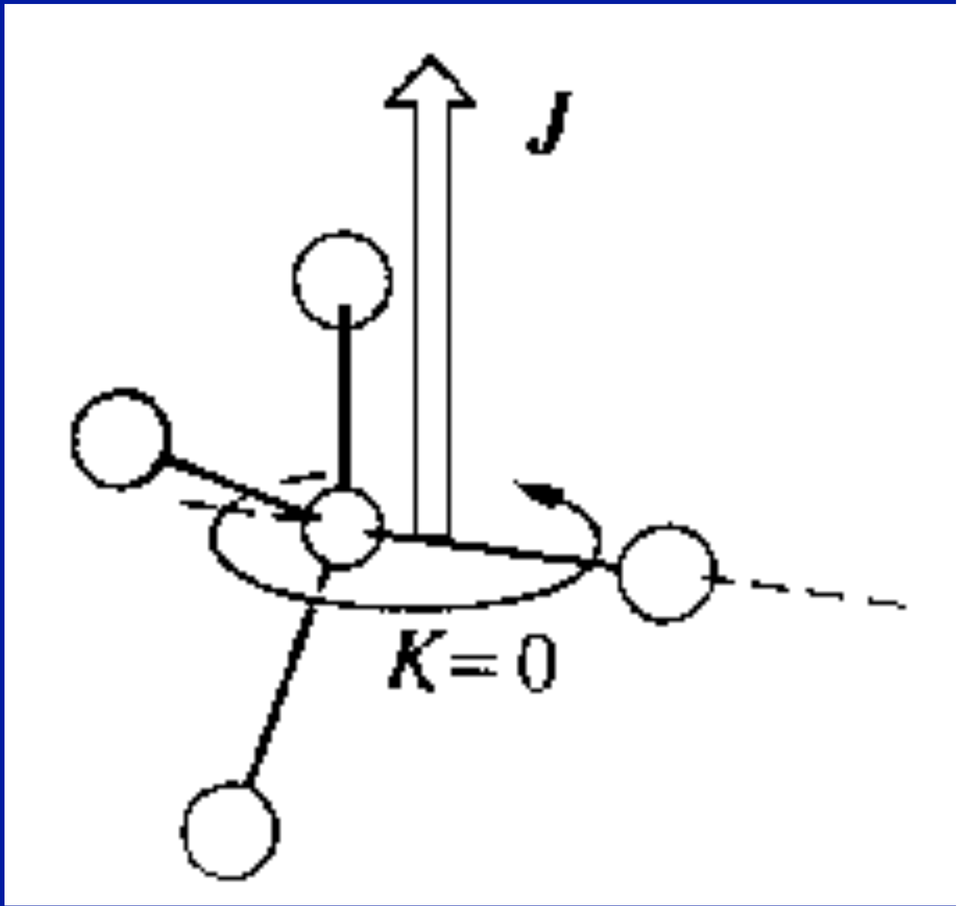
**Rotational** ⇒ **EVEN J** ⇒ **+** ⇒ **ORTHO**

⇒ **ODD J** ⇒ **-** ⇒ **PARA**

# Symmetric Tops

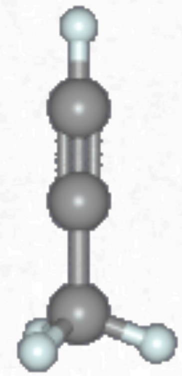
K = Projection of total angular momentum J on symmetry axis




K = 0, +/- 1, +/- 2, … +/- J      +/- levels degenerate

| | | | |
|---|---|---|---|
| Species Tag: | 40001 | Species Name: | CH3CCH |
| Version: | 1 | | Propyne |
| Date: | Dec. 1979 | | |
| Contributor: | R. L. Poynter | | |

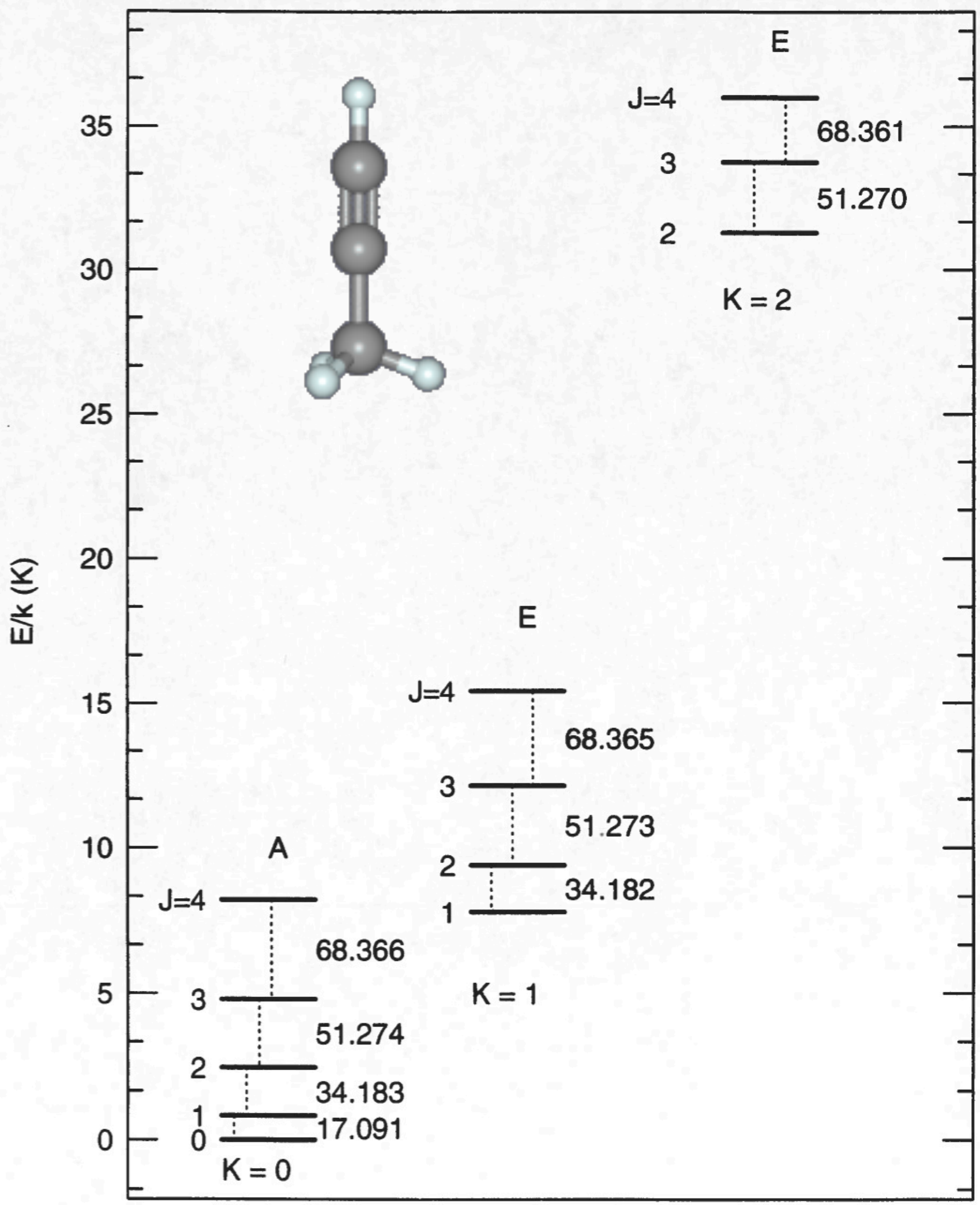


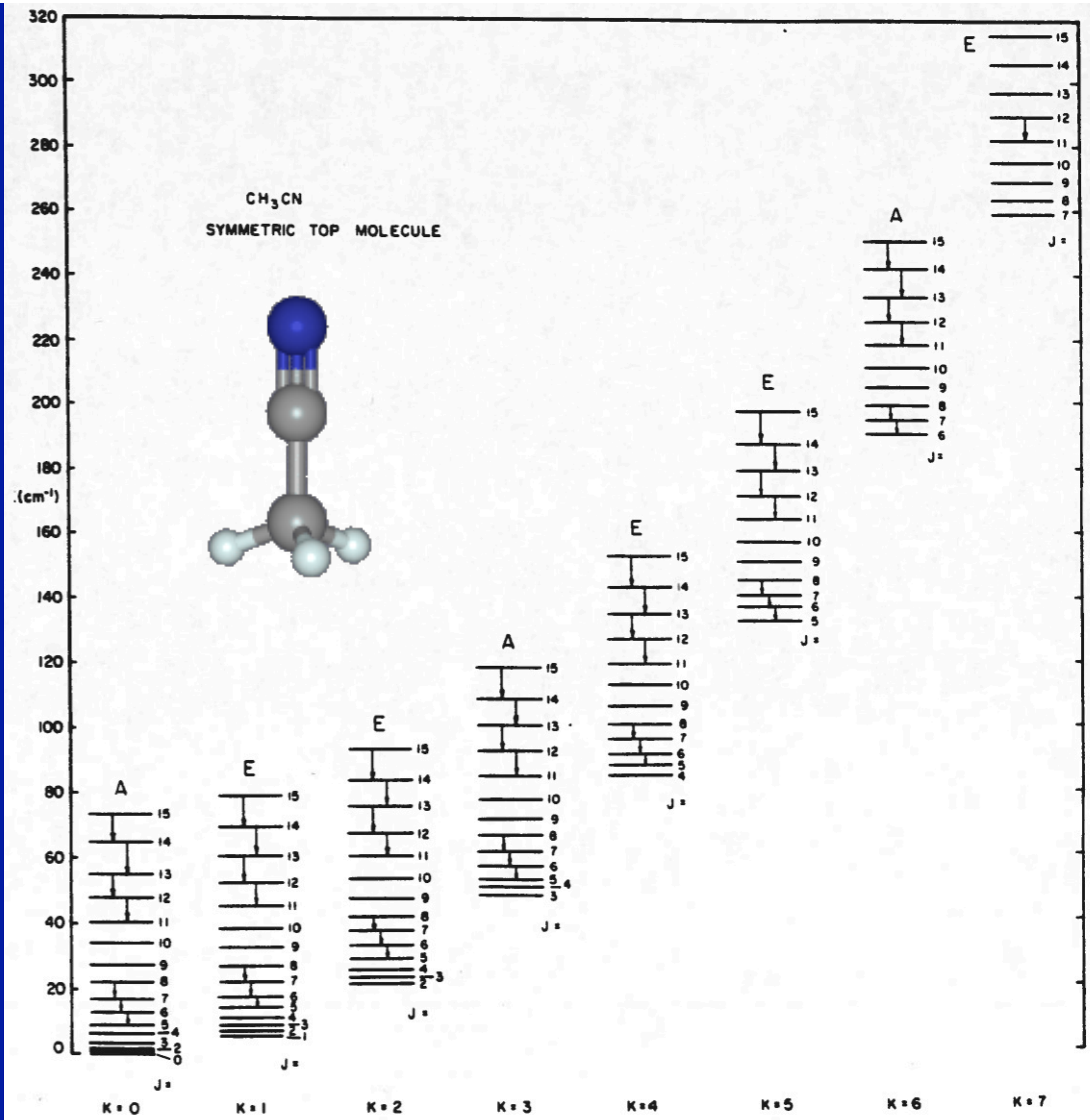
| | | | |
|---|---|---|---|
| Lines Listed: | 813 | Q(300.0)= | 5428.751 |
| Freq. (GHz) < | 1345 | Q(225.0)= | 3524.521 |
| Max. J: | 79 | Q(150.0)= | 1920.879 |
| LOGSTR0= | -6.7 | Q(75.00)= | 679.673 |
| LOGSTR1= | -5.8 | Q(37.50)= | 241.268 |
| Isotope Corr.: | 0. | Q(18.75)= | 88.267 |
| Egy. ($cm^{-1}$) > | 0.0 | Q(9.375)= | 34.419 |
| $\mu_a$ = | 0.75 | A= | 158590. |
| $\mu_b$ = | | B= | 8545.86 |
| $\mu_c$ = | | C= | B |

The experimental measurements were obtained from A. Dubrulle, D. Boucher, J. Burie, and J. Demaison, 1978, J. Mol. Spect. **72**, 158. The *A* rotational constant was estimated from the structure. The dipole moment was measured by J. S. Muenter and V. W. Laurie. 1966. J. Chem. Phys. **45**, 855.

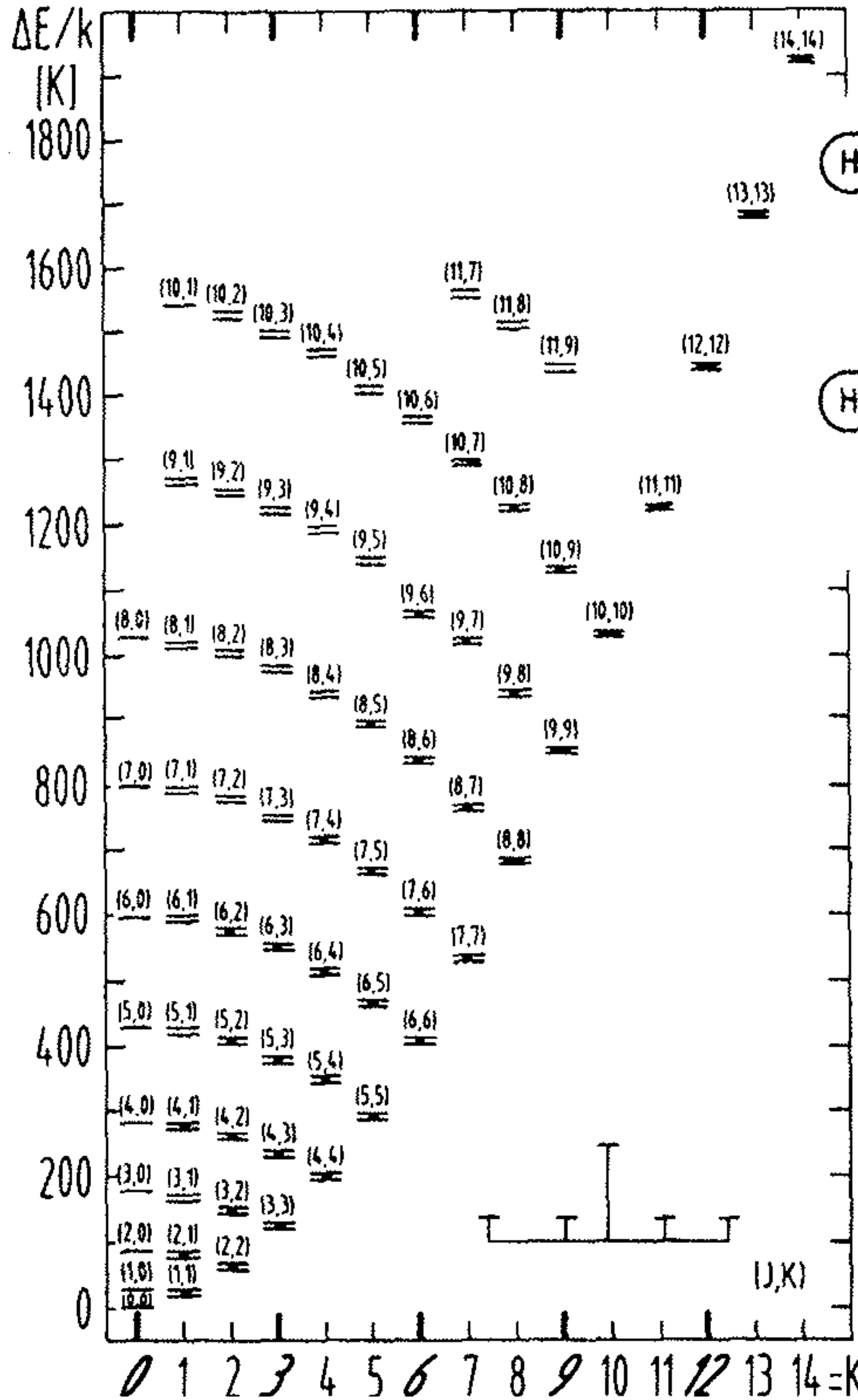
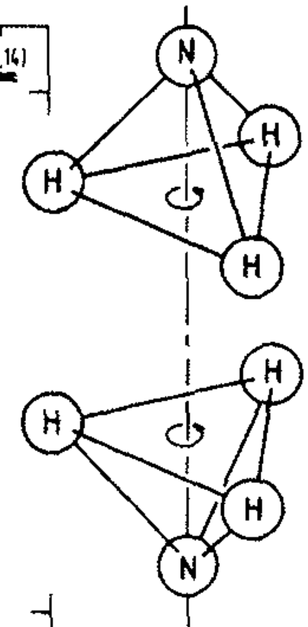
| Frequency | Unc. | Log(Int.) | | $E_l$ ($cm^{-1}$) | $g_u$ | Tag | $J_u$ $K_u$ | $J_l$ $K_l$ |
|---|---|---|---|---|---|---|---|---|
| 221559.1127 | .0304 | -5.4864 | 3 | 765.0554 | 54 | 40001 | 2021312 | 1212 |
| 221655.8226 | .0187 | -5.2640 | 3 | 649.9614 | 27 | 40001 | 2021311 | 1211 |
| 221744.2486 | .0134 | -4.8872 | 3 | 544.8755 | 27 | 40001 | 2021310 | 1210 |
| 221824.3680 | .0600 | -4.2822 | 3 | 449.7978 | 54 | -40001 | 20213 9 | 12 9 |
| 221896.1150 | .0122 | -4.3290 | 3 | 364.7283 | 27 | 40001 | 20213 8 | 12 8 |
| 221959.4966 | .0114 | -4.1144 | 3 | 289.6671 | 27 | 40001 | 20213 7 | 12 7 |
| 222014.4480 | .0600 | -3.6330 | 3 | 224.6139 | 54 | -40001 | 20213 6 | 12 6 |
| 222061.0344 | .0077 | -3.7847 | 3 | 169.5690 | 27 | 40001 | 20213 5 | 12 5 |
| 222099.1514 | .0054 | -3.6644 | 3 | 124.5323 | 27 | 40001 | 20213 4 | 12 4 |
| 222128.8080 | .0600 | -3.2709 | 3 | 89.5037 | 54 | -40001 | 20213 3 | 12 3 |
| 222150.0084 | .0017 | -3.5063 | 3 | 64.4833 | 27 | 40001 | 20213 2 | 12 2 |
| 222162.7287 | .0011 | -3.4672 | 3 | 49.4710 | 27 | 40001 | 20213 1 | 12 1 |
| 222166.9700 | .0050 | -3.4541 | 3 | 44.4669 | 27 | -40001 | 20213 0 | 12 0 |

$CH_3CCH$ Rotational Levels

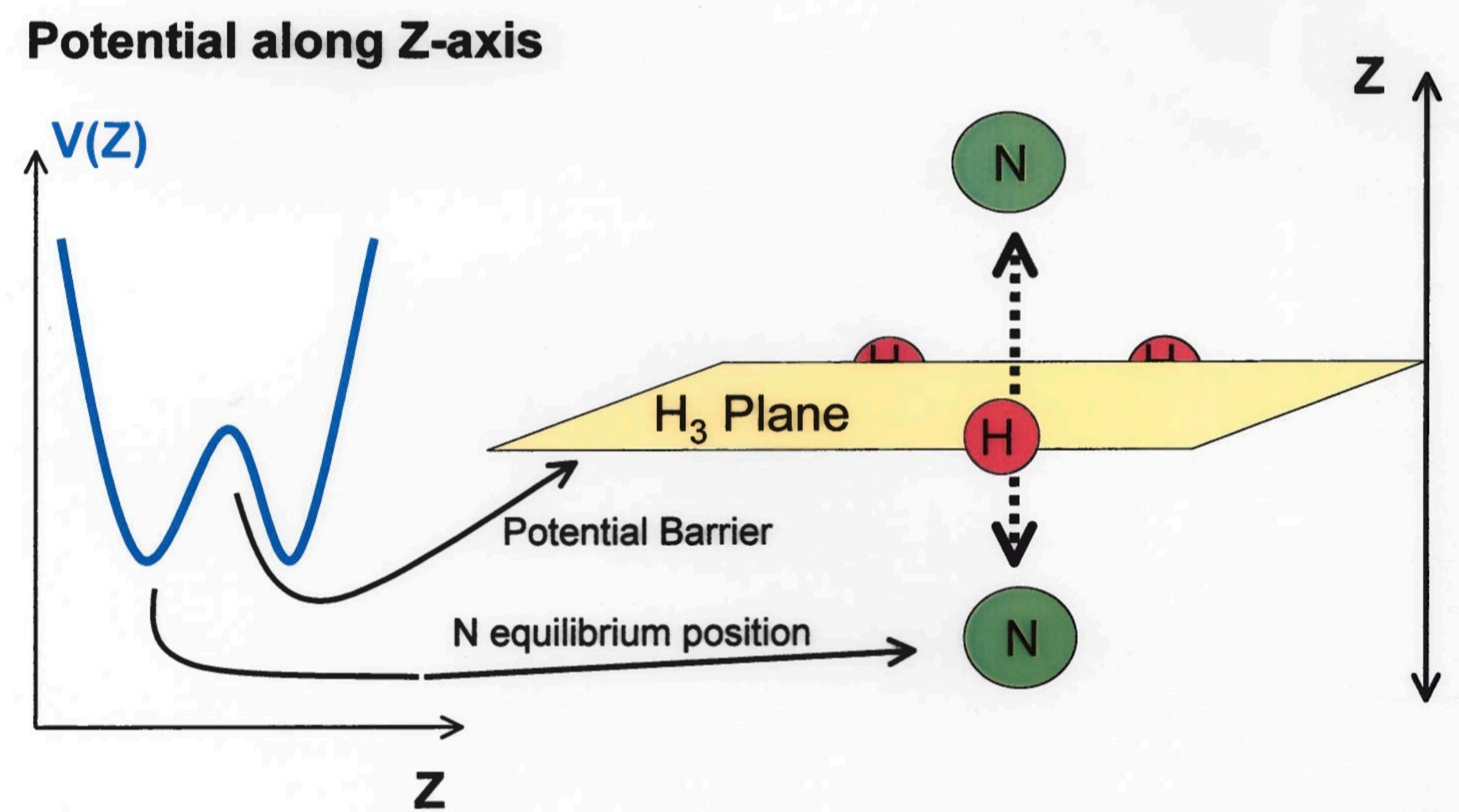


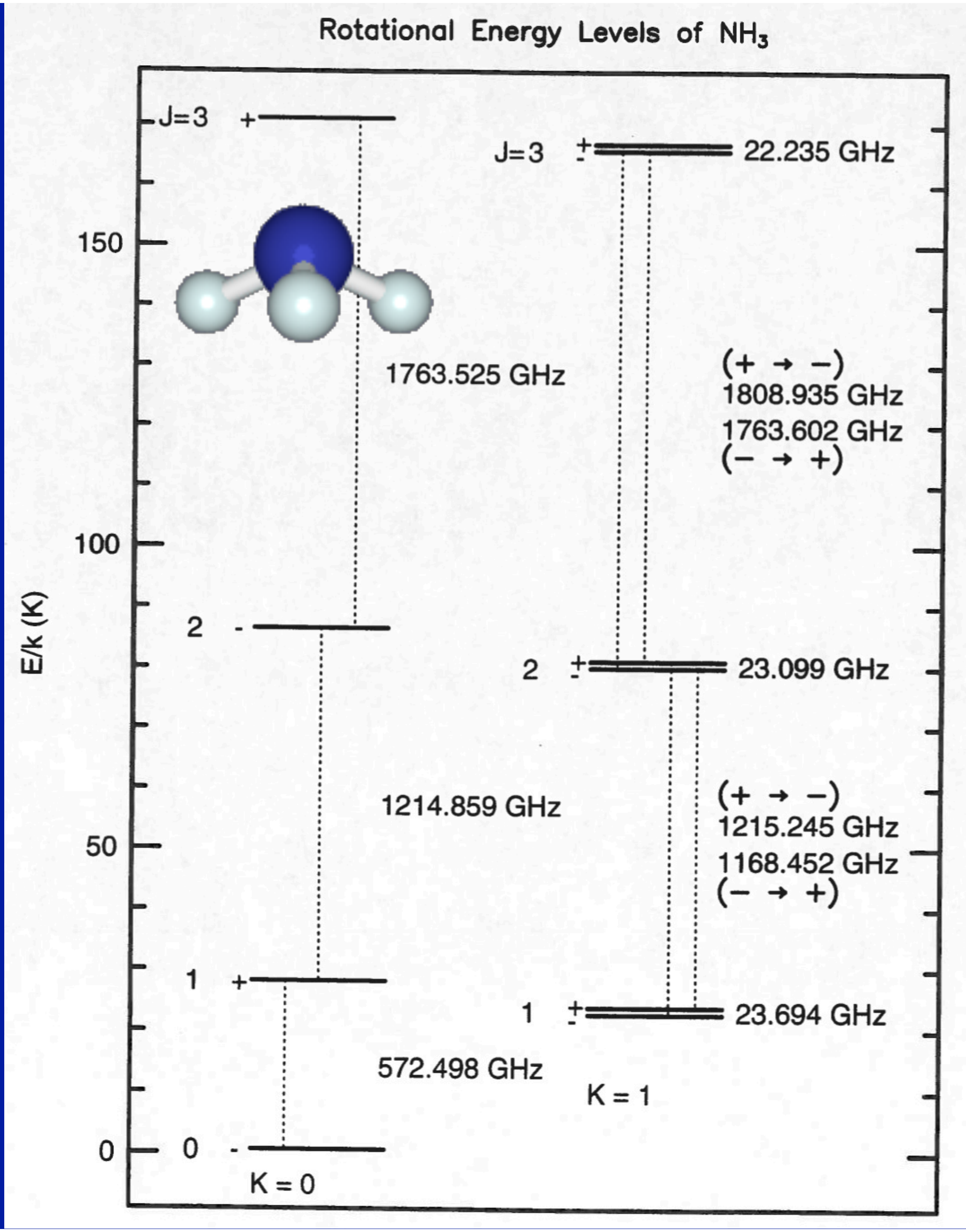


CH3CN
SYMMETRIC TOP MOLECULE
(cm-1)
K = 0
K = 1
K = 2
K = 3
K = 4
K = 5
K = 6
K = 7
A
E
J =


ΔE/k
[K]
1800
1600
1400
1200
1000
800
600
400
200
0
(0,0) (1,0) (2,0) (3,0) (4,0) (5,0) (6,0) (7,0) (8,0)
(1,1) (2,1) (3,1) (4,1) (5,1) (6,1) (7,1) (8,1) (9,1) (10,1)
(2,2) (3,2) (4,2) (5,2) (6,2) (7,2) (8,2) (9,2) (10,2)
(3,3) (4,3) (5,3) (6,3) (7,3) (8,3) (9,3) (10,3)
(4,4) (5,4) (6,4) (7,4) (8,4) (9,4) (10,4)
(5,5) (6,5) (7,5) (8,5) (9,5) (10,5)
(6,6) (7,6) (8,6) (9,6) (10,6)
(7,7) (8,7) (9,7) (10,7) (11,7)
(8,8) (9,8) (10,8) (11,8)
(9,9) (10,9) (11,9)
(10,10)
(11,11)
(12,12)
(13,13)
(14,14)
(J,K)
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 =K

N
H
H
H
H
H
H
N

# Ammonia Inversion





Rotational Energy Levels of NH3
E/k (K)
0
50
100
150
J=3
2
1
0
+
-
+
-
1763.525 GHz
1214.859 GHz
572.498 GHz
K = 0
J=3
2
1
22.235 GHz
23.099 GHz
23.694 GHz
(+ → −)
1808.935 GHz
1763.602 GHz
(− → +)
(+ → −)
1215.245 GHz
1168.452 GHz
(− → +)
K = 1

# $H_3O^+$ Rotation-Inversion

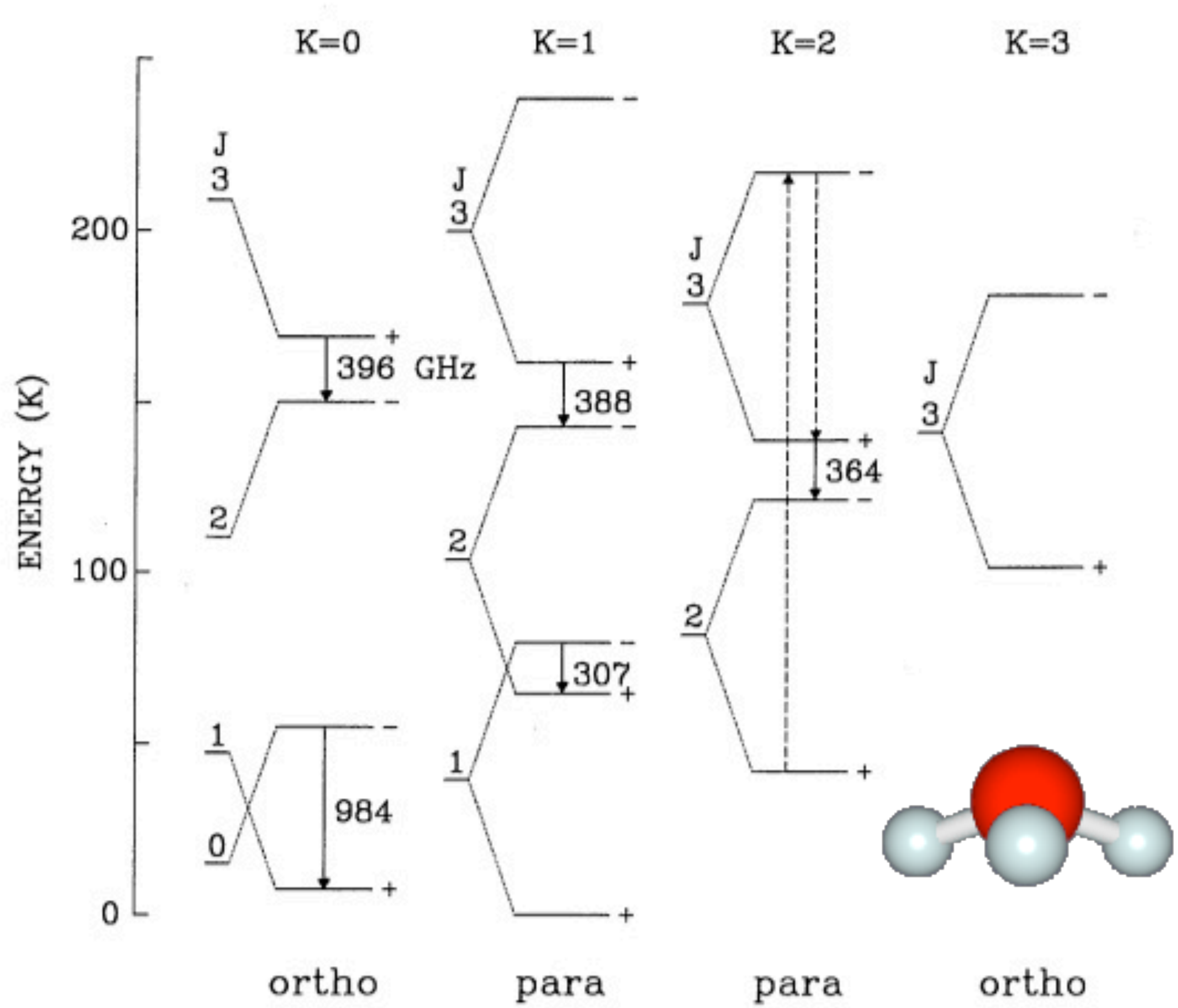
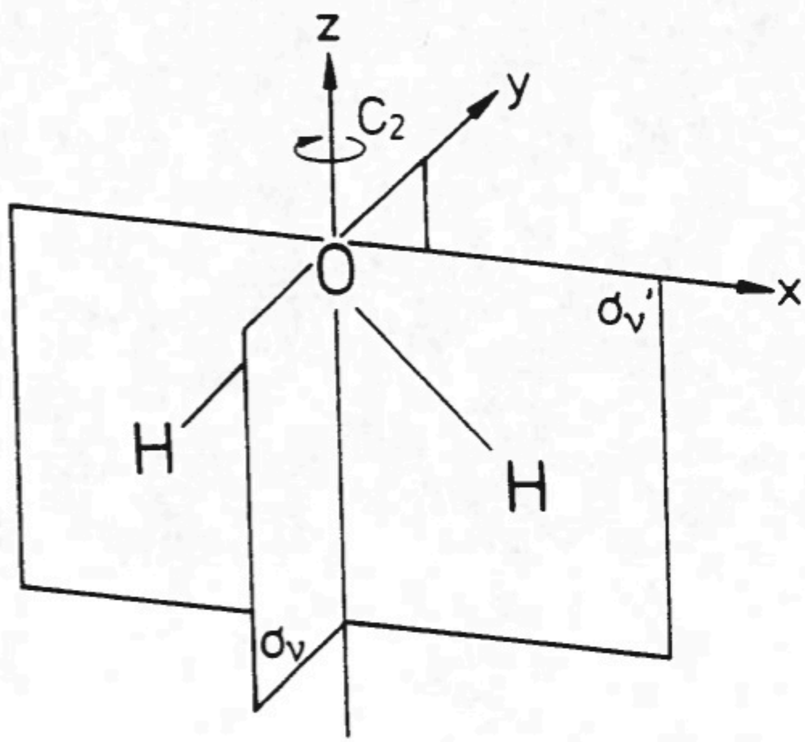



FIG. 1.—Energy level diagram of $H_3O^+$, illustrating the submillimeter transitions (*full lines*) and the possible radiative pumping of the 364 GHz line (*dashed lines*).

# Symmetry Point Groups: $C_{2v}$ & $C_{3v}$



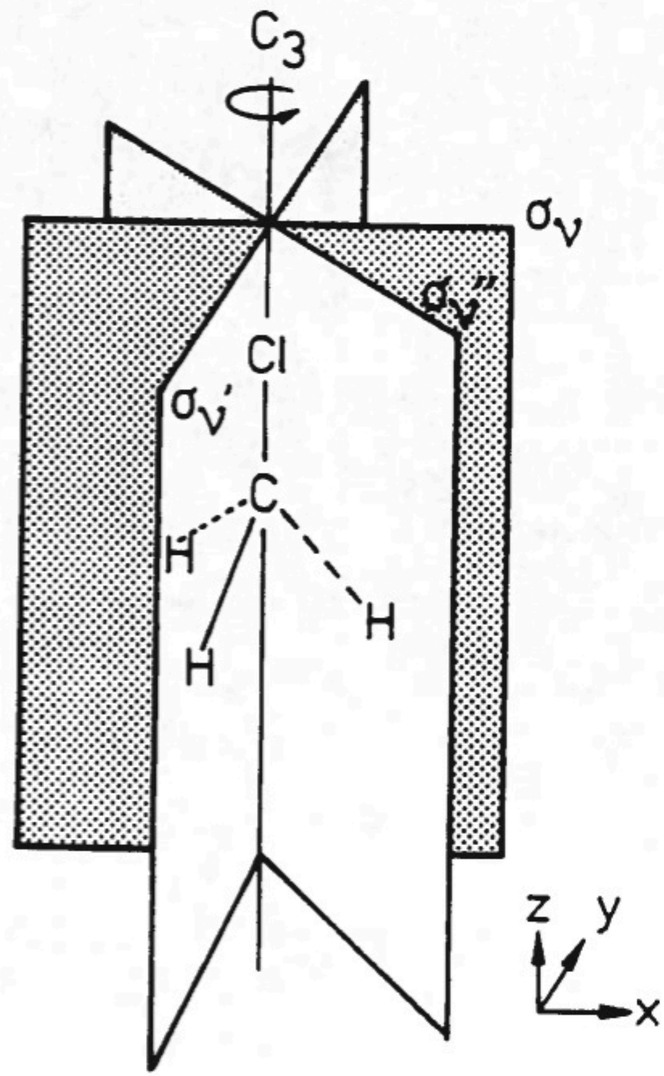



**Table 3.3** Nuclear Statistical Weights[a] for Symmetric-top Molecules Having $C_{3v}$ Symmetry

| *Statistics* | *J* | *K* | *Inversion Level* | *Statistical Weight g(nuclear)* |
|---|---|---|---|---|
| | | *When Inversion Levels Are Separated*[b] | | |
| Either | Even or odd | Not 0 and multiple of 3 | Either | $\frac{1}{3}(2I+1)(4I^2+4I+3)$ |
| Either | Even or odd | Not 0 and not multiple of 3 | Either | $\frac{1}{3}(2I+1)(4I^2+4I)$ |
| Fermi-Dirac<br>Bose-Einstein | Even<br>Odd | 0 | Lower | $\frac{1}{3}(2I+1)(2I-1)I$ |
| Fermi-Dirac<br>Bose-Einstein | Even<br>Odd | 0 | Upper | $\frac{1}{3}(2I+1)(2I+3)(I+1)$ |
| Fermi-Dirac<br>Bose-Einstein | Odd<br>Even | 0 | Lower | $\frac{1}{3}(2I+1)(2I+3)(I+1)$ |
| Fermi-Dirac<br>Bose-Einstein | Odd<br>Even | 0 | Upper | $\frac{1}{3}(2I+1)(2I-1)I$ |
| | | *When Inversion Levels Are Not Separated*[c] | | |
| Either | Even | 0 or multiple of 3 | | $\frac{1}{3}(2I+1)(4I^2+4I+3)$ |
| Either | Even or odd | Not multiple of 3 | | $\frac{1}{3}(2I+1)(4I^2+4I)$ |

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

# Ray's Asymmetry Parameter

$\kappa = -1$
Prolate

$\kappa = 1$
Oblate

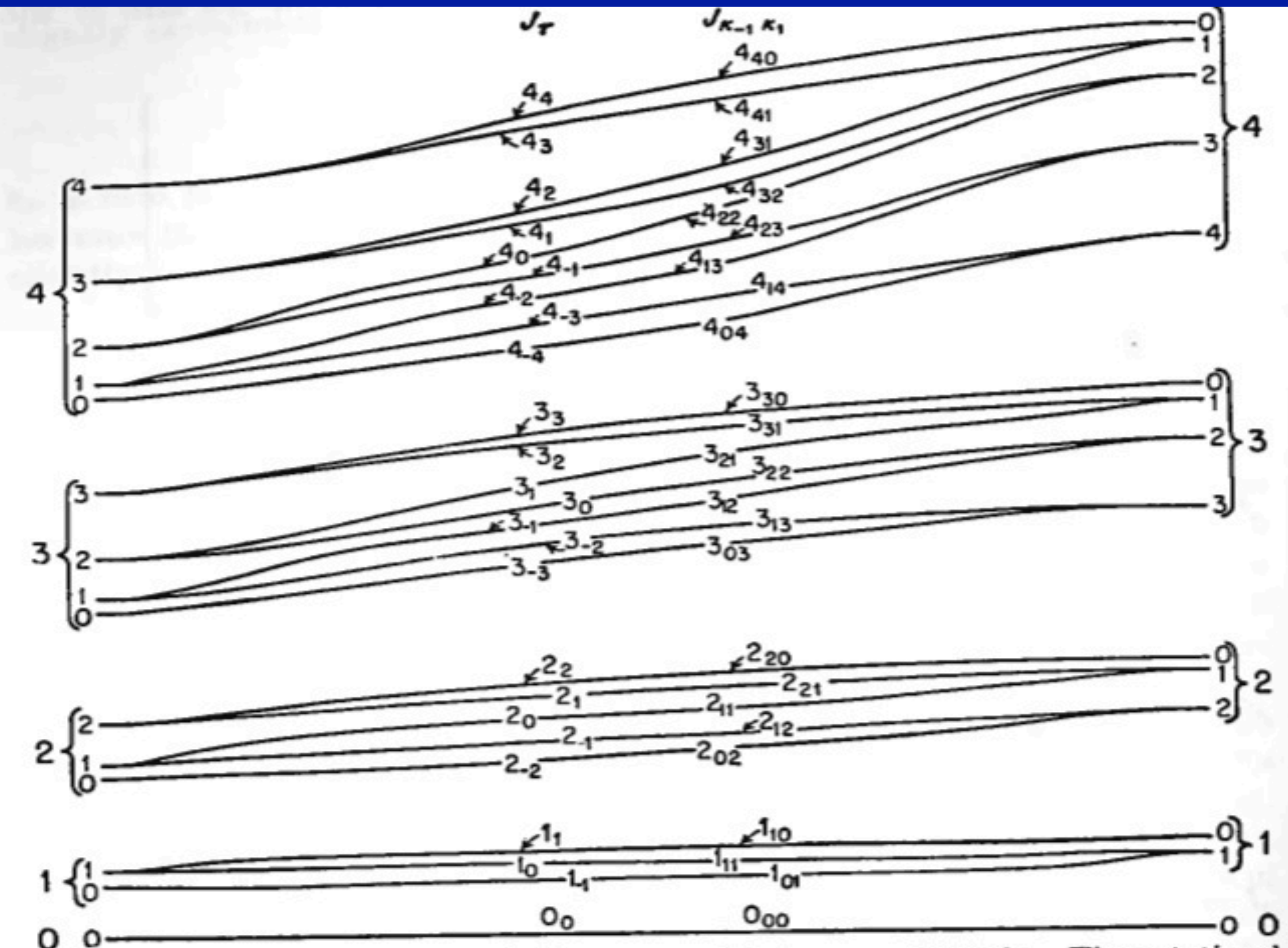



FIG. 4-1. Qualitative behavior of the asymmetric-top energy levels. The rotational constant $B$ varies from left to right, equaling $C$ and giving a prolate symmetric top on the left, and equaling $A$ to give an oblate symmetric top on the right.

# Asymmetric Top Selection Rules

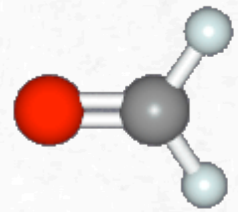
Table 6. Selection Rules for Asymmetric Top Molecules

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

[a] e = even and o = odd

| | | | |
|---|---|---|---|
| Species Tag: | 30004 | Species Name: | H2CO |
| Version: | 2 | | Formaldehyde |
| Date: | Nov. 1997 | | |
| Contributor: | H. S. P. Müller | | |

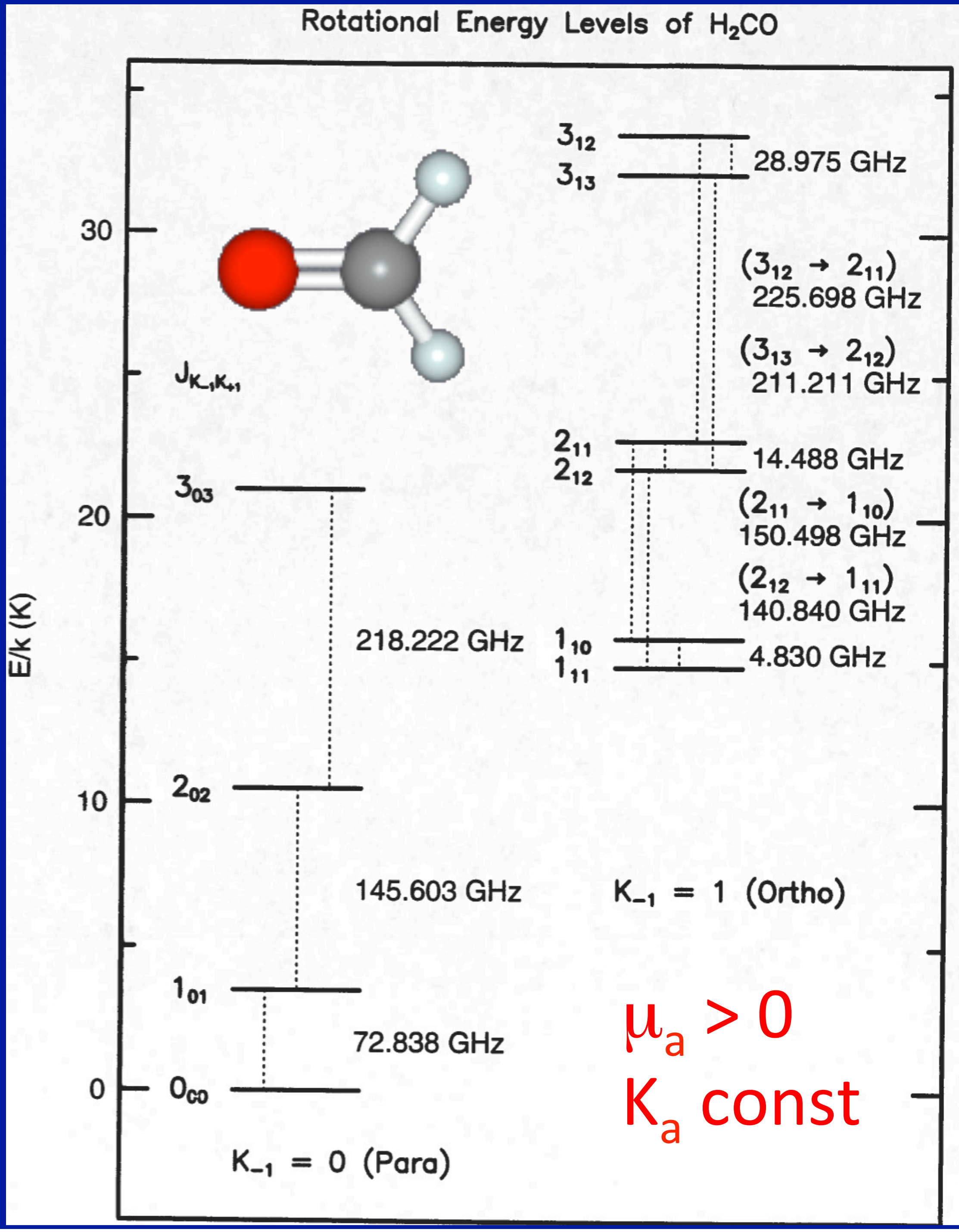
| | | | |
|---|---|---|---|
| Lines Listed: | 3506 | Q(300.0)= | 2883.014 |
| Freq. (GHz) < | 9999 | Q(225.0)= | 1872.622 |
| Max. J: | 57 | Q(150.0)= | 1019.971 |
| LOGSTR0= | -20.0 | Q(75.00)= | 361.720 |
| LOGSTR1= | -9.0 | Q(37.50)= | 128.649 |
| Isotope Corr.: | 0. | Q(18.75)= | 44.681 |
| Egy. ($cm^{-1}$) > | 0.0 | Q(9.375)= | 13.801 |
| $\mu_a$ = | 2.331 | A= | 281970.58 |
| $\mu_b$ = | | B= | 38833.987 |
| $\mu_c$ = | | 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 | 2 | 1 | 2 |
| 218222.1920 | .0100 | -2.7693 | 3 | 7.2864 | 7 | -30004 | 303 | 3 | 0 | 3 | 2 | 0 | 2 |
| 218475.6320 | .0100 | -3.0917 | 3 | 40.0402 | 7 | -30004 | 303 | 3 | 2 | 2 | 2 | 2 | 1 |
| 218760.0660 | .0100 | -3.0906 | 3 | 40.0426 | 7 | -30004 | 303 | 3 | 2 | 1 | 2 | 2 | 0 |
| 225697.7750 | .0100 | -2.3318 | 3 | 15.7202 | 21 | -30004 | 303 | 3 | 1 | 2 | 2 | 1 | 1 |
| 281526.9290 | .0100 | -2.0074 | 3 | 22.2822 | 27 | -30004 | 303 | 4 | 1 | 4 | 3 | 1 | 3 |
| 290623.4050 | .0100 | -2.4132 | 3 | 14.5655 | 9 | -30004 | 303 | 4 | 0 | 4 | 3 | 0 | 3 |
| 291237.7800 | .2000 | -2.6044 | 3 | 47.3278 | 9 | -30004 | 303 | 4 | 2 | 3 | 3 | 2 | 2 |
| 291380.4880 | .1000 | -2.4462 | 3 | 88.2382 | 27 | -30004 | 303 | 4 | 3 | 2 | 3 | 3 | 1 |
| 291384.2640 | .1000 | -2.4461 | 3 | 88.2383 | 27 | -30004 | 303 | 4 | 3 | 1 | 3 | 3 | 0 |
| 291948.0600 | .2000 | -2.6024 | 3 | 47.3397 | 9 | -30004 | 303 | 4 | 2 | 2 | 3 | 2 | 1 |
| 300836.6350 | .0100 | -1.9524 | 3 | 23.2487 | 27 | -30004 | 303 | 4 | 1 | 3 | 3 | 1 | 2 |
| 351768.6450 | .0300 | -1.7287 | 3 | 31.6729 | 33 | -30004 | 303 | 5 | 1 | 5 | 4 | 1 | 4 |
| 362736.0480 | .0300 | -2.1465 | 3 | 24.2597 | 11 | -30004 | 303 | 5 | 0 | 5 | 4 | 0 | 4 |
| 363945.8940 | .0300 | -2.2875 | 3 | 57.0425 | 11 | -30004 | 303 | 5 | 2 | 4 | 4 | 2 | 3 |
| 364103.2490 | .0300 | -2.8594 | 3 | 155.1694 | 11 | -30004 | 303 | 5 | 4 | 2 | 4 | 4 | 1 |
| 364103.2490 | .0300 | -2.8594 | 3 | 155.1694 | 11 | -30004 | 303 | 5 | 4 | 1 | 4 | 4 | 0 |
| 364275.1410 | .1000 | -2.0129 | 3 | 97.9576 | 33 | -30004 | 303 | 5 | 3 | 3 | 4 | 3 | 2 |
| 364288.8840 | .1000 | -2.0128 | 3 | 97.9578 | 33 | -30004 | 303 | 5 | 3 | 2 | 4 | 3 | 1 |
| 365363.4280 | .0300 | -2.2842 | 3 | 57.0780 | 11 | -30004 | 303 | 5 | 2 | 3 | 4 | 2 | 2 |
| 375893.2160 | .0300 | -1.6752 | 3 | 33.2835 | 33 | -30004 | 303 | 5 | 1 | 4 | 4 | 1 | 3 |




$\mu_a > 0$

$K_a$ const

# $H_2CO$

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

2 H nuclei (I = ½) ⇒ F-D Statistics ⇒ Total ⇒ -

Electronic $^1\Sigma_g^+$ ⇒ +

Vibrational v = 0 ⇒ +

Nuclear ⇒ 3 sym. (ortho) + OR

1 antisym. (para) -

Rotational ⇒ ee & eo ⇒ + ⇒ PARA

⇒ oo & oe ⇒ - ⇒ ORTHO

# Asymmetric Top Rotation Symmetry

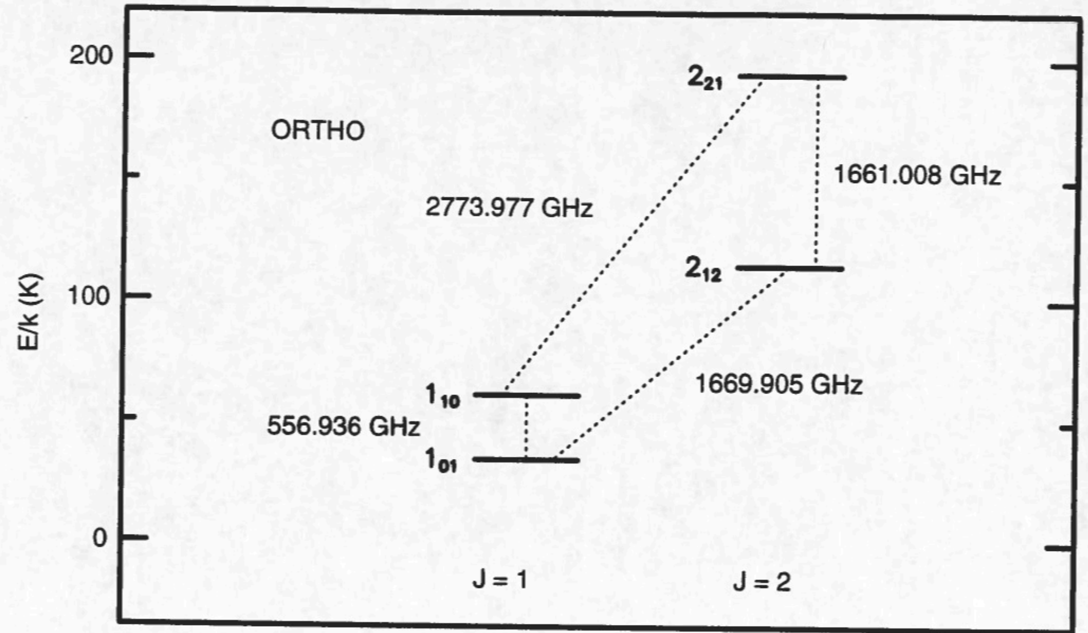
Table 7. Behavior of Rotational Wavefunction with $\pi$ rotation about the Principle Axes

| $K_{-1}K_{+1}$ [a] | $J_{K_{-1}K_{+1}}$ Symmetry [b] | | |
|---|---|---|---|
| | A | B | C |
| ee | + | + | + |
| eo | + | − | − |
| oo | − | + | − |
| oe | − | − | + |

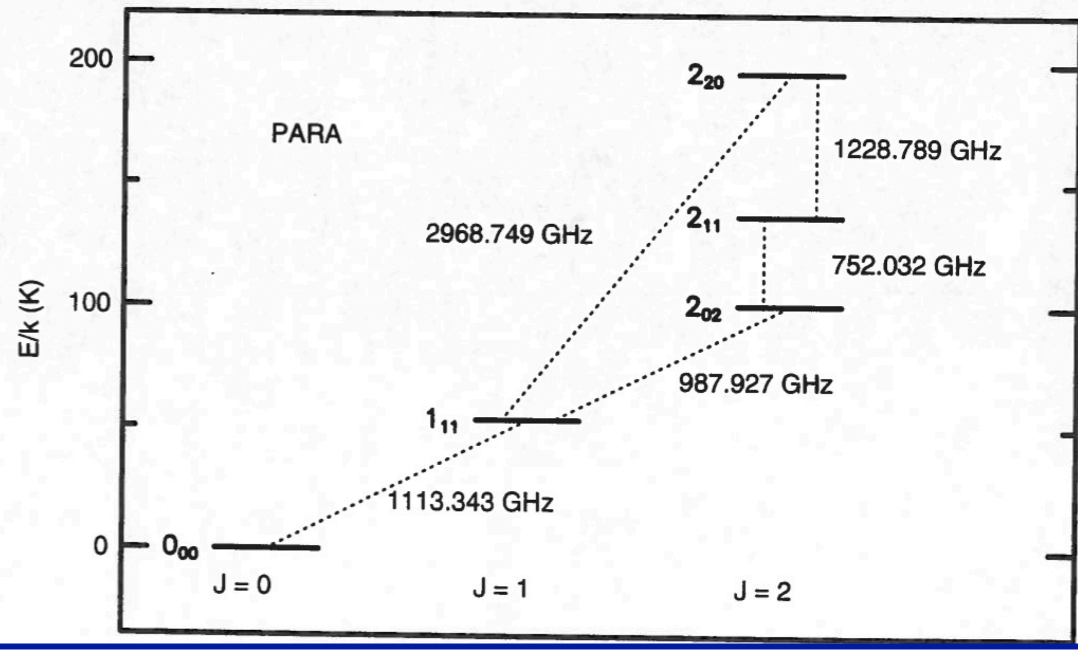
[a] e = even and o = odd

[b] + = symmetric and − = antisymmetric for rotational of $\pi$ about the principle axes A, B, or C.

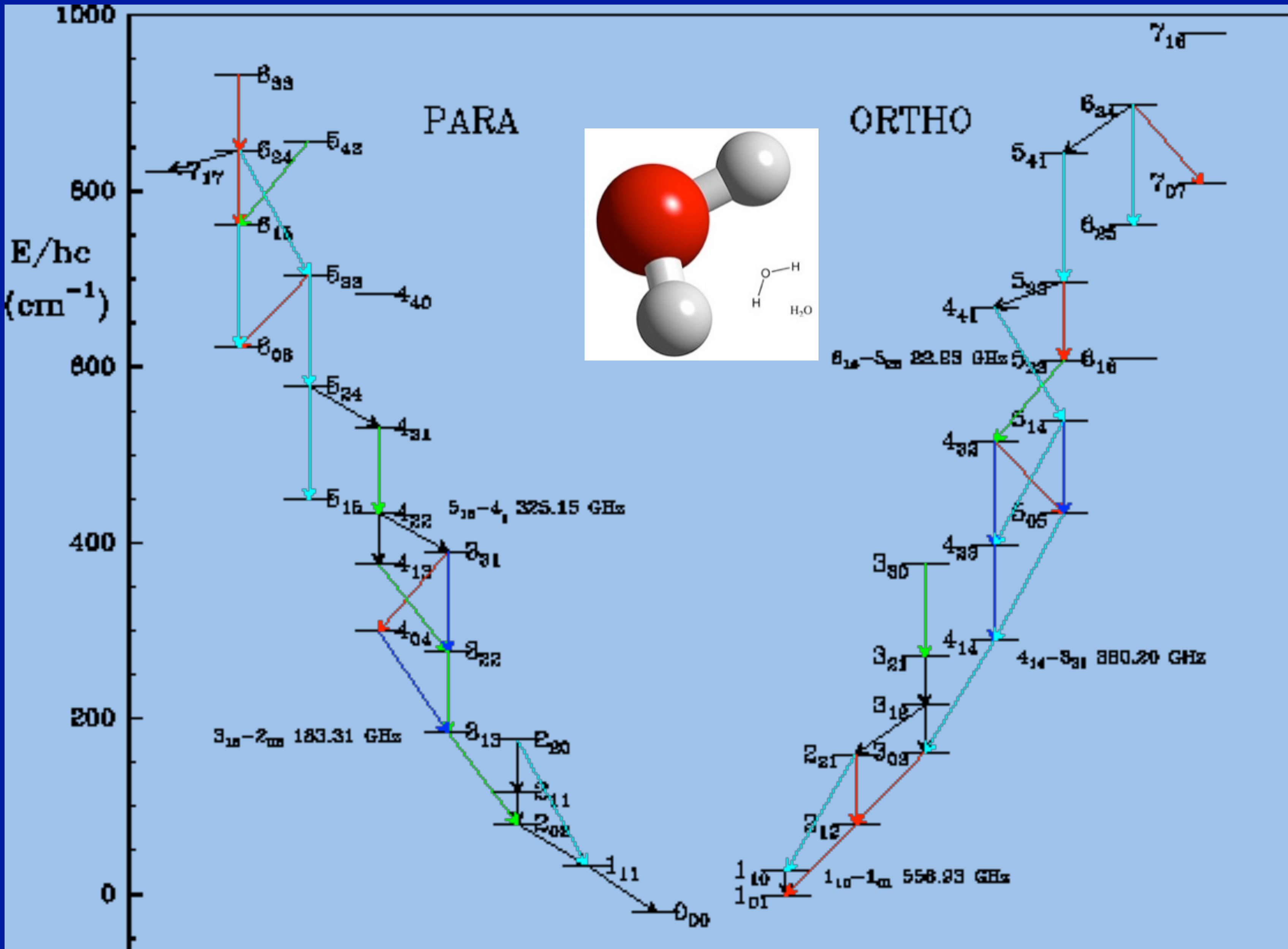
Rotational Energy Levels of $H_2O$

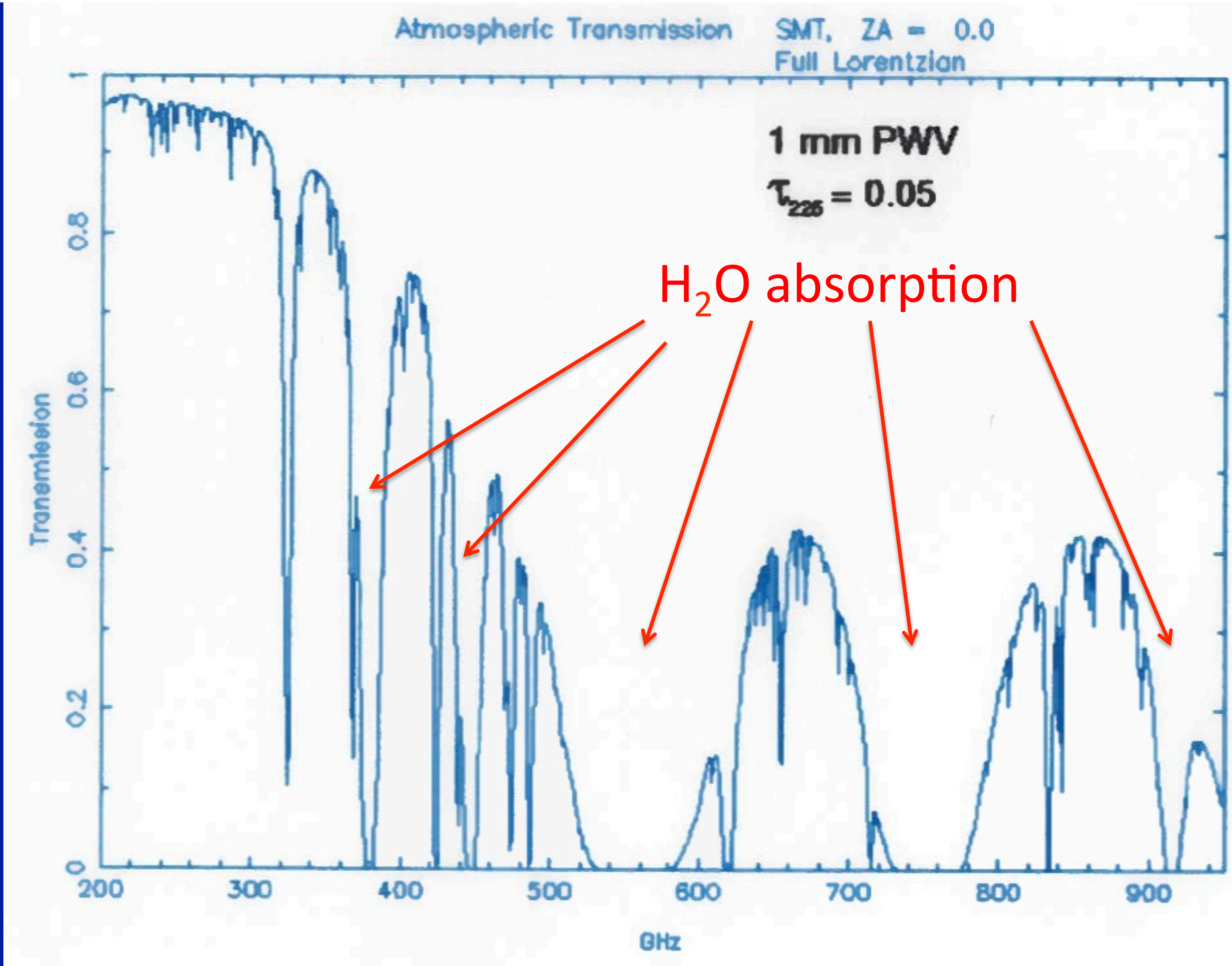



$\mu_b > 0$ ----> $K_a$ ***and*** $K_c$ change



# More $H_2O$ Energy Levels




Atmospheric Transmission SMT, ZA = 0.0
Full Lorentzian
1 mm PWV
$\tau_{225} = 0.05$
$H_2O$ absorption
Transmission
0
0.2
0.4
0.6
0.8
1
200
300
400
500
600
700
800
900
GHz

# $H_2O$

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

**2 H nuclei (I = ½) ⇒ F-D Statistics ⇒ Total ⇒ −**

**Electronic** $^1\Sigma_g^+$ ⇒ **+**

**Vibrational** **v = 0** ⇒ **+**

**Nuclear** ⇒ **3 sym. (ortho)** **+** **OR**

**1 antisym. (para)** **−**

**Rotational** ⇒ **ee & oo** ⇒ **+** ⇒ **PARA**

⇒ **eo & oe** ⇒ **−** ⇒ **ORTHO**

# Asymmetric Top Rotation Symmetry

Table 7. Behavior of Rotational Wavefunction with $\pi$ rotation about the Principle Axes

| $K_{-1}K_{+1}$[a] | $J_{K_{-1}K_{+1}}$ Symmetry[b] A | B | C |
|---|---|---|---|
| ee | + | + | + |
| eo | + | − | − |
| oo | − | + | − |
| oe | − | − | + |

[a] e = even and o = odd

[b] + = symmetric and − = antisymmetric for rotational of $\pi$ about the principle axes A, B, or C.

# $SO_2$

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

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

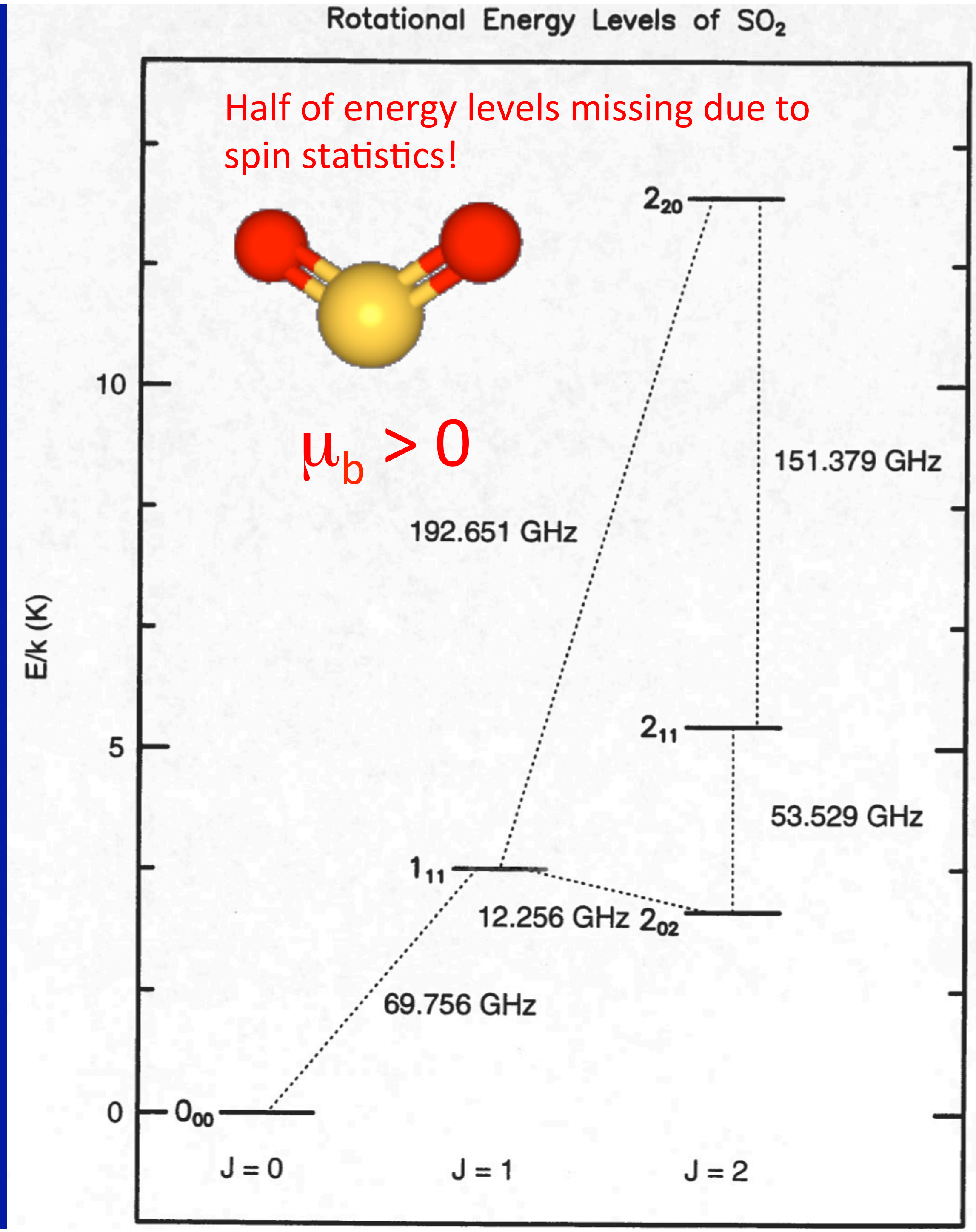
Electronic $^1\Sigma_g^+$ $\Rightarrow$ +

Vibrational v = 0 $\Rightarrow$ +

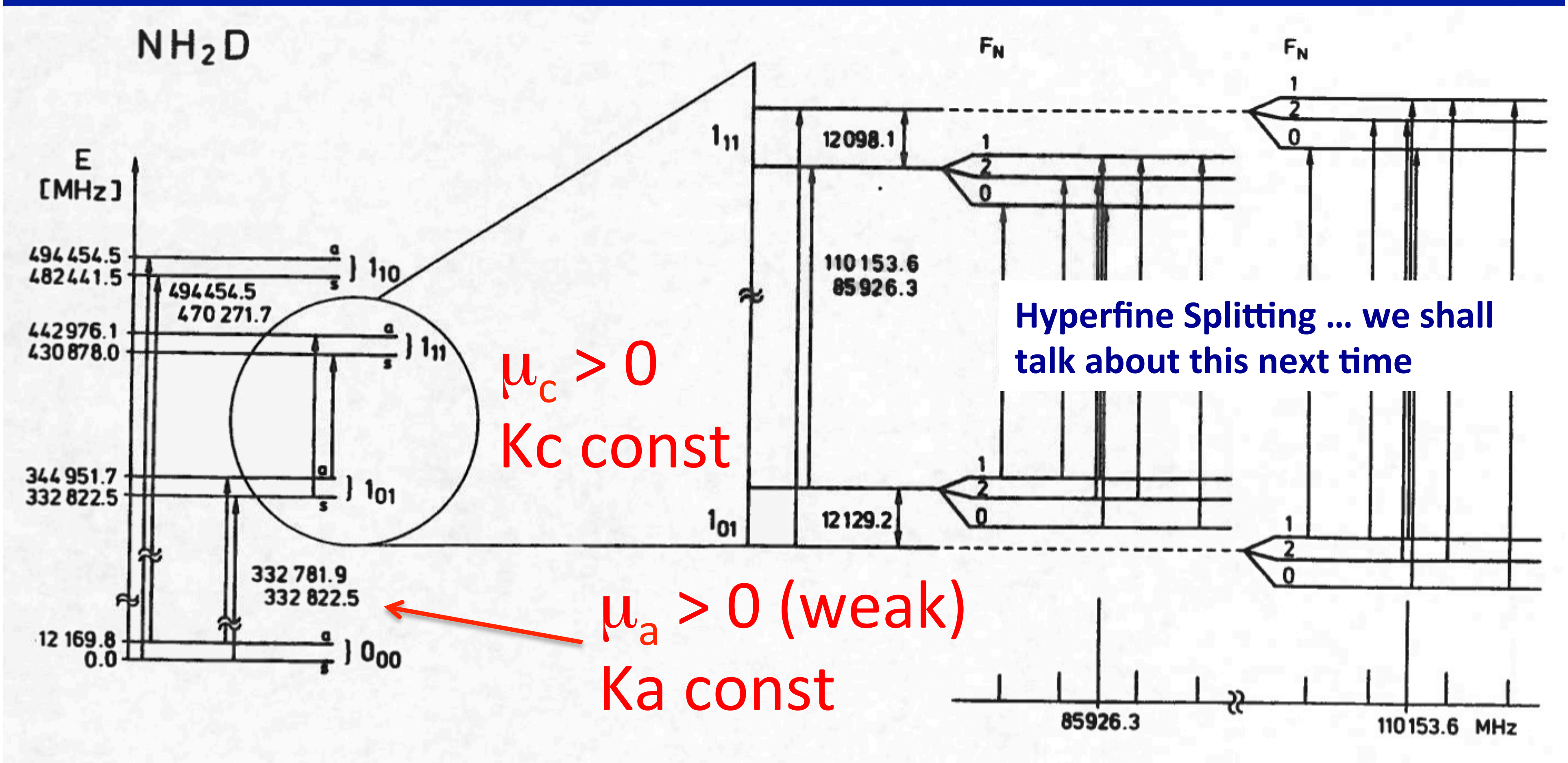
Nuclear $\Rightarrow$ ONLY sym. +

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

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

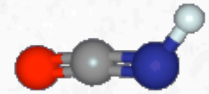

Rotational Energy Levels of $SO_2$
Half of energy levels missing due to spin statistics!
$\mu_b > 0$
E/k (K)
0
5
10
$0_{00}$
$1_{11}$
$2_{02}$
$2_{11}$
$2_{20}$
69.756 GHz
12.256 GHz
53.529 GHz
151.379 GHz
192.651 GHz
J = 0
J = 1
J = 2

# Asymmetric Tops w/ Inversion



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

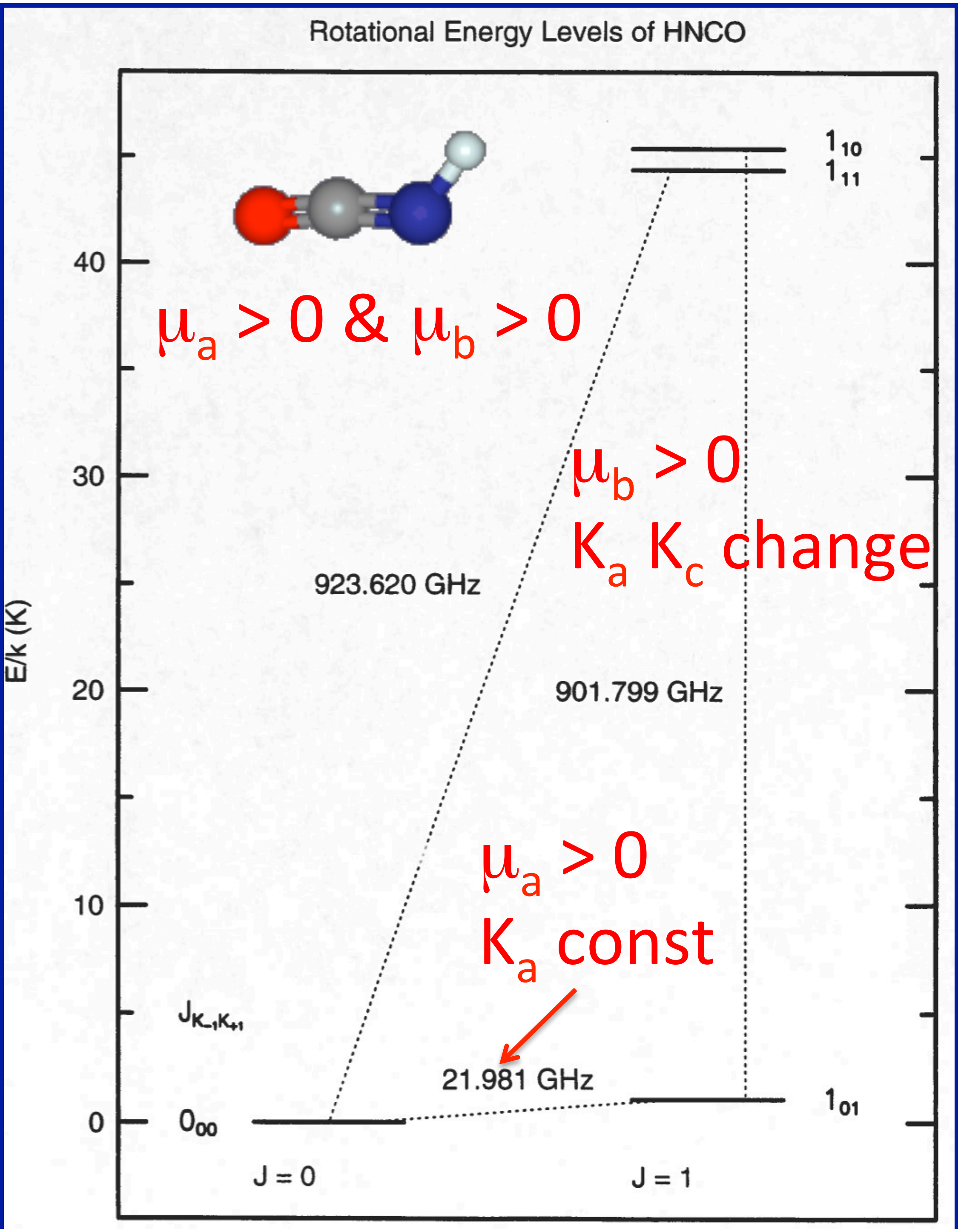
| | |
|---|---|
| Species Name: | HNCO |
| | Isocyanic acid |



| | |
|---|---|
| Lines Listed: | 6078 |
| Freq. (GHz) < | 2997 |
| Max. J: | 47 |
| LOGSTR0= | -10.0 |
| LOGSTR1= | -10.0 |
| Isotope Corr.: | 0.0 |
| Egy. ($cm^{-1}$) > | 0.0 |
| $\mu_a$ = | 1.6020 |
| $\mu_b$ = | 1.3500 |
| $\mu_c$ = | |

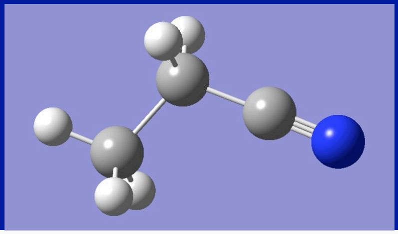
| | |
|---|---|
| Q(300.0)= | 7785.741 |
| Q(225.0)= | 5123.892 |
| Q(150.0)= | 2802.206 |
| Q(75.00)= | 992.888 |
| Q(37.50)= | 352.614 |
| Q(18.75)= | 129.479 |
| Q(9.375)= | 56.351 |
| A= | 912711.435(197) |
| B= | 11071.0098(9) |
| C= | 10910.5763(10) |

| Frequency | Unc. | Log(Int.) | | $E_l$ ($cm^{-1}$) | $g_u$ | | | $J_u$ | $K_a$ | $K_c$ | 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 | 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 |



Rotational Energy Levels of HNCO
E/k (K)
0
10
20
30
40
$1_{10}$
$1_{11}$
$1_{01}$
$0_{00}$
$J_{K_{-1}K_{+1}}$
923.620 GHz
901.799 GHz
21.981 GHz
J = 0
J = 1
$\mu_a > 0$ & $\mu_b > 0$
$\mu_b > 0$
$K_a$ $K_c$ change
$\mu_a > 0$
$K_a$ const

# Ethyl Cyanide – $CH_3CH_2CN$ – "Weed"



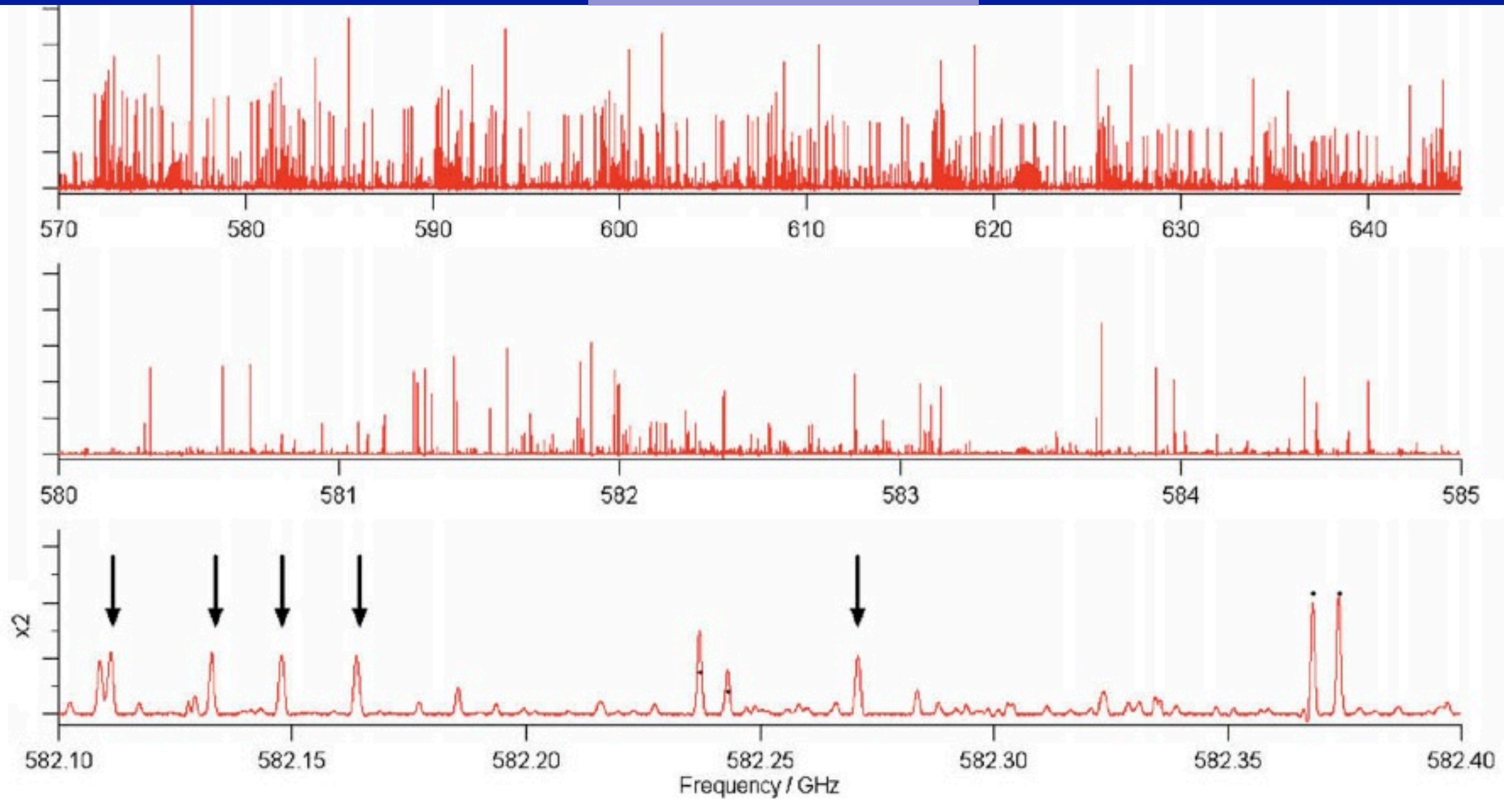



**Fig. 19.** Spectrum of ethyl cyanide at 300 K, shown as a series of spectral expansions. In the lower panel (expanded 2× vertically) a comparison is made with a catalog based on a quantum mechanical model (the dots indicate frequency and intensity of the catalog lines). The arrows show lines that are 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