Planck's formula

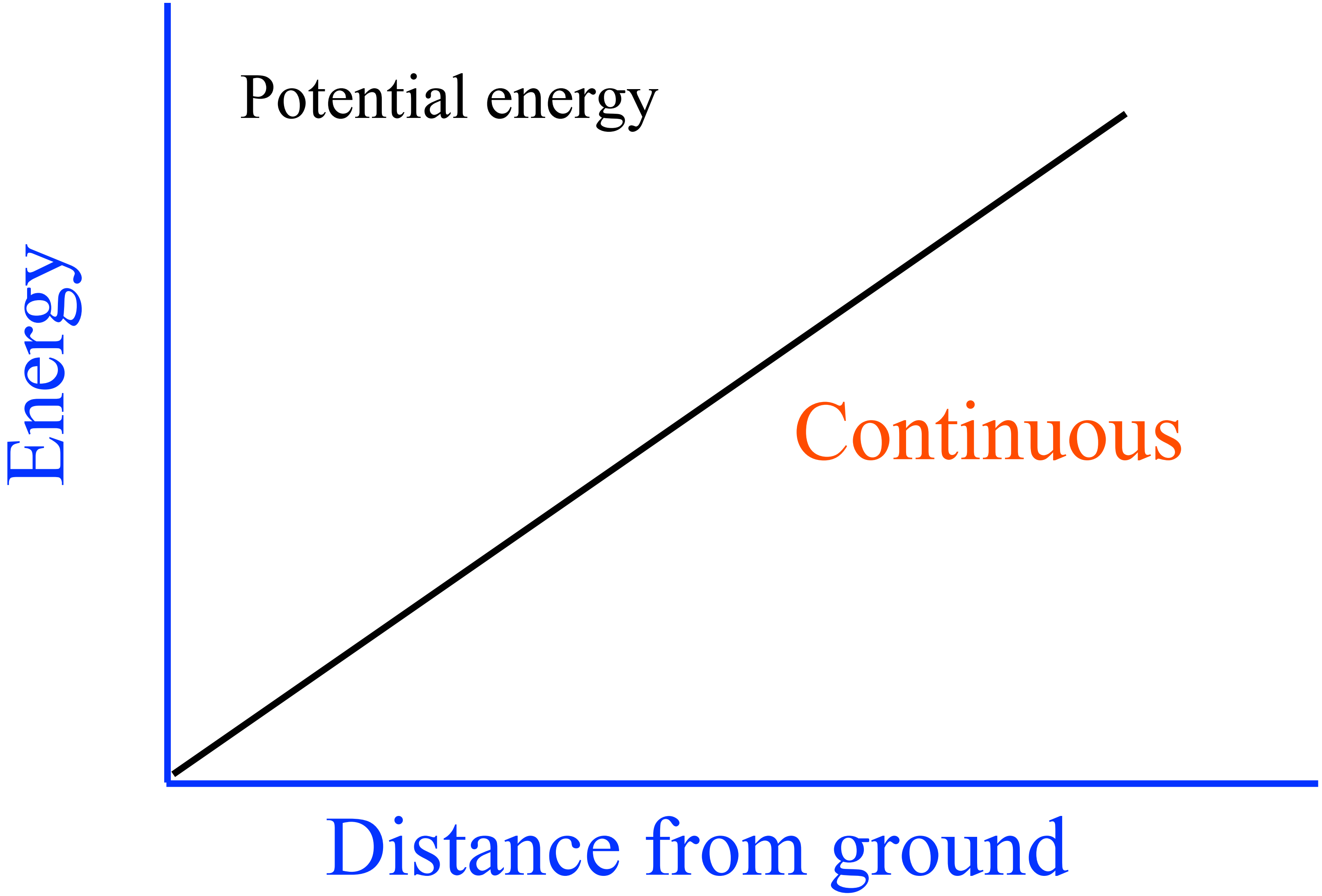
In 1900 Planck derived a formula that matched the measured curve exactly.

His derivation was based on the blackbody having energy states that are *quantized*.

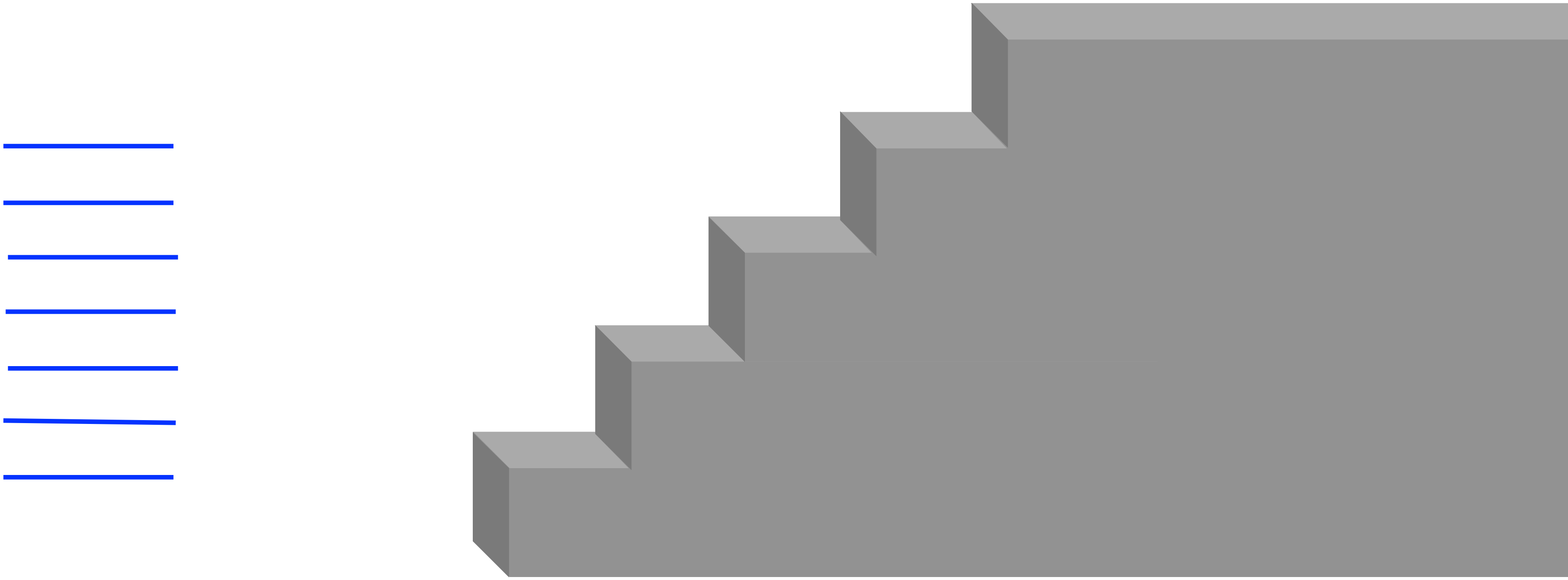
$$E = n h \nu$$

$n = 1, 2, 3, \ldots$

Energy in classical physics



Planck’s proposed energy



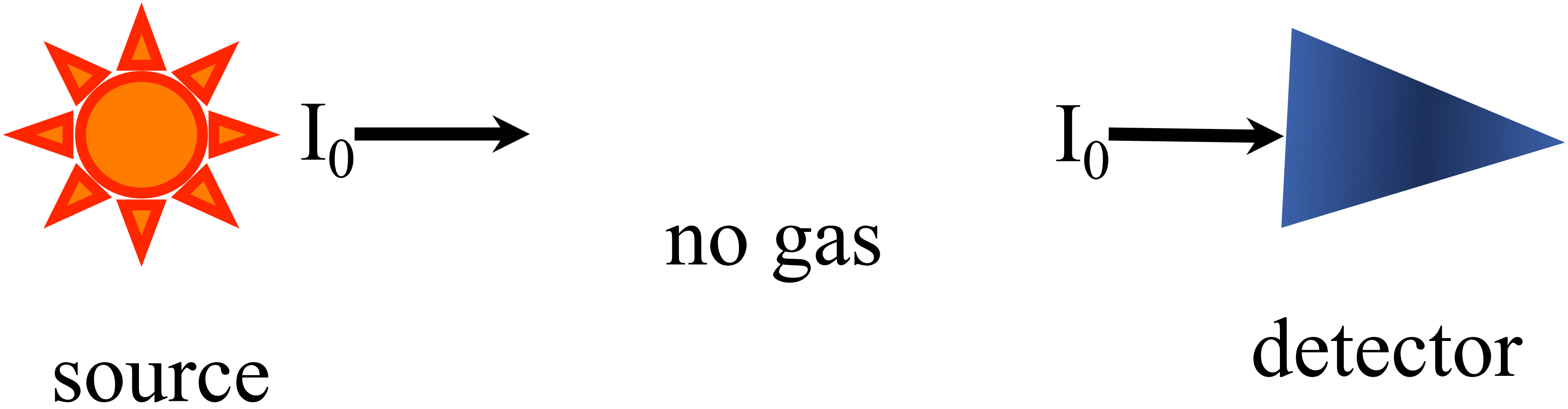
quantized

Spectra of atoms and molecules

Atoms and molecules interact with electromagnetic radiation.

Energy of the radiation at certain frequencies can be absorbed when it hits the atom or molecule

Energy is conserved so it has to go somewhere



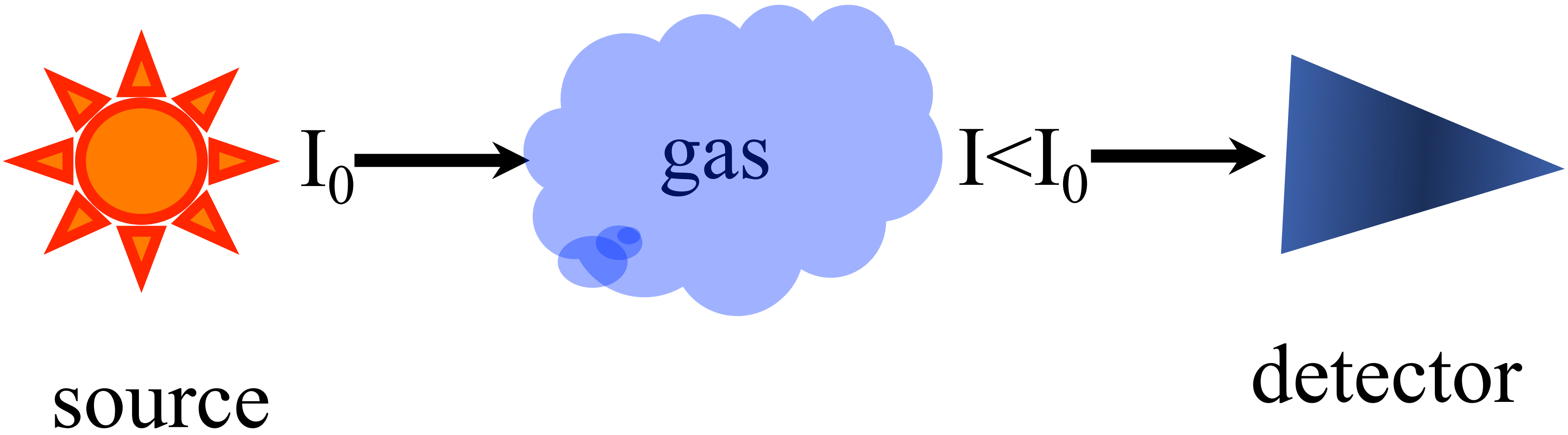
source

I_0

no gas

I_0

detector



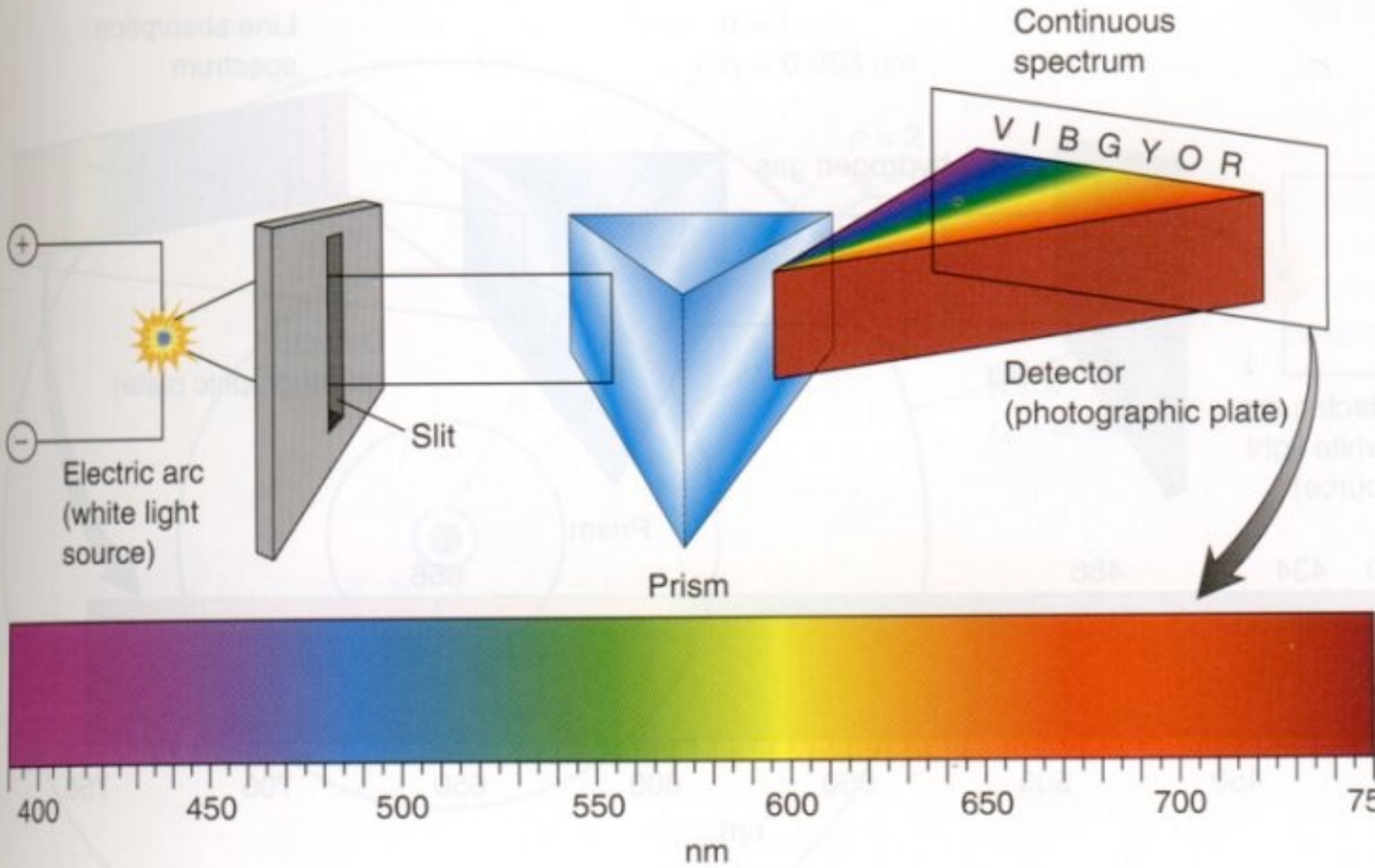
I_0

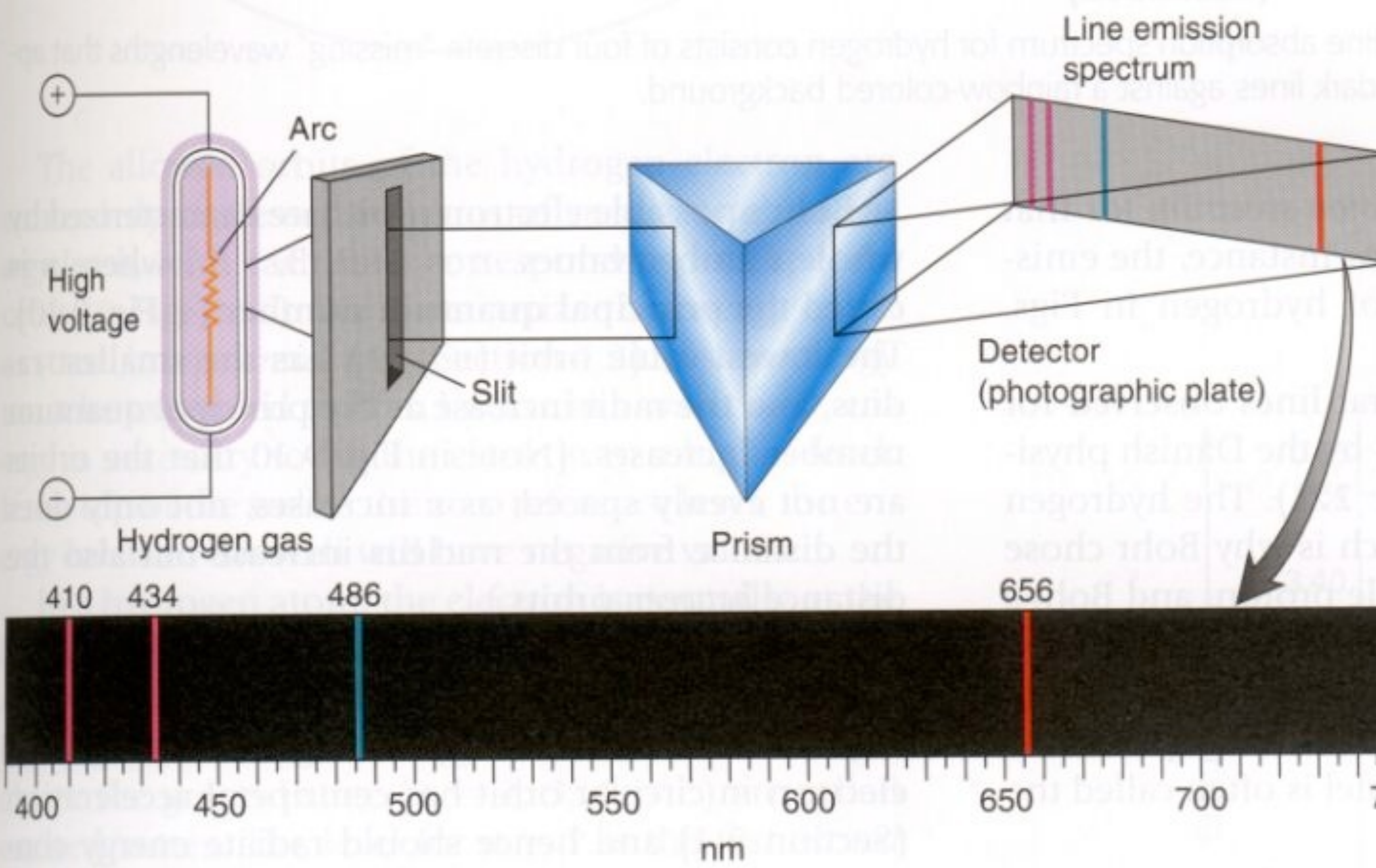
gas

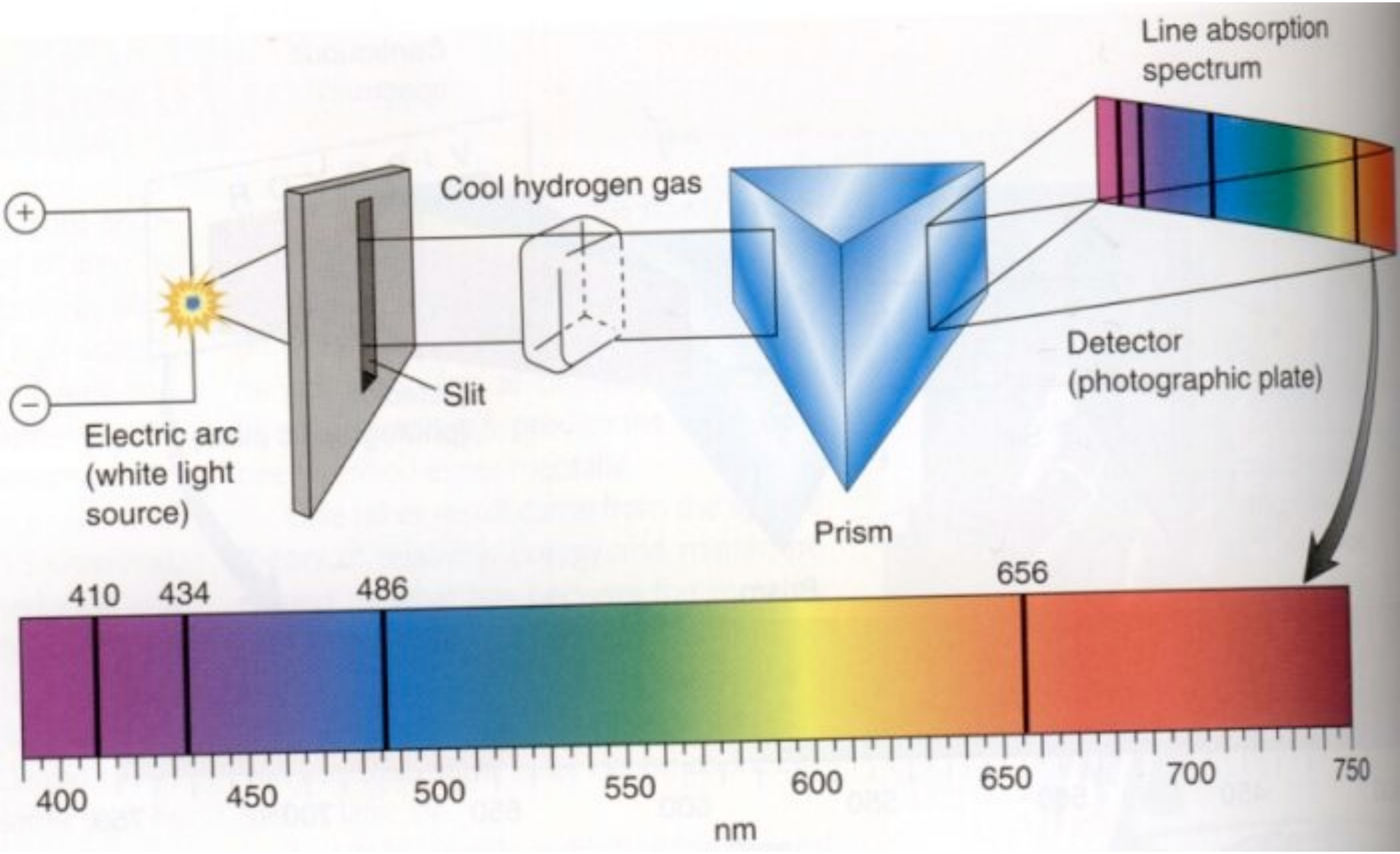
$I<I_0$

source

detector


Continuous
spectrum
V I B G Y O R
Electric arc
(white light
source)
Slit
Prism
Detector
(photographic plate)
400
450
500
550
600
650
700
75
nm

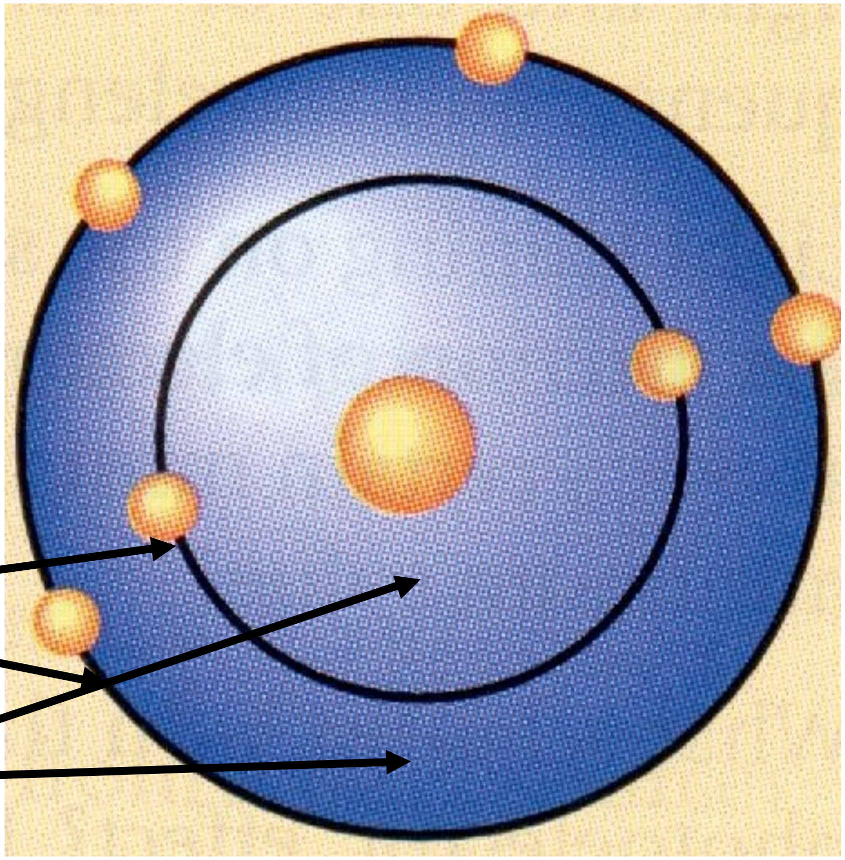

Line emission spectrum
Arc
High voltage
Slit
Hydrogen gas
Prism
Detector (photographic plate)
410
434
486
656
400
450
500
550
600
650
700
nm



Line absorption spectrum
Cool hydrogen gas
Electric arc (white light source)
Slit
Prism
Detector (photographic plate)
410
434
486
656
400
450
500
550
600
650
700
750
nm

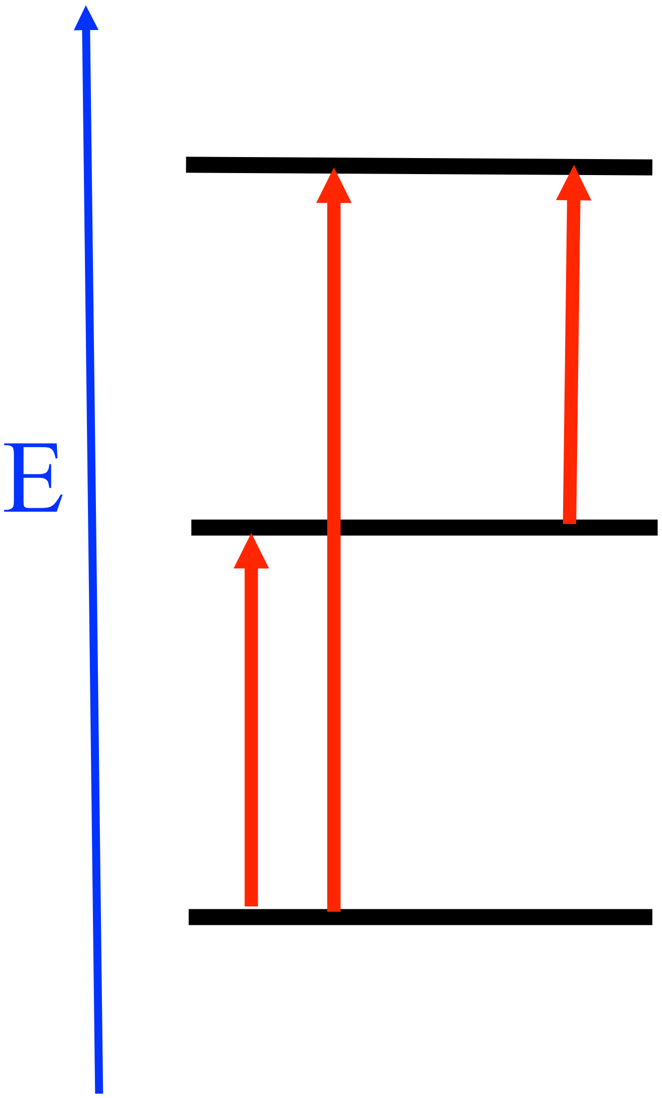
Explanation: quantization of energy of atoms and molecules

First model was Bohr’s planetary model of the atom



Allowed energy state

Disallowed energy state

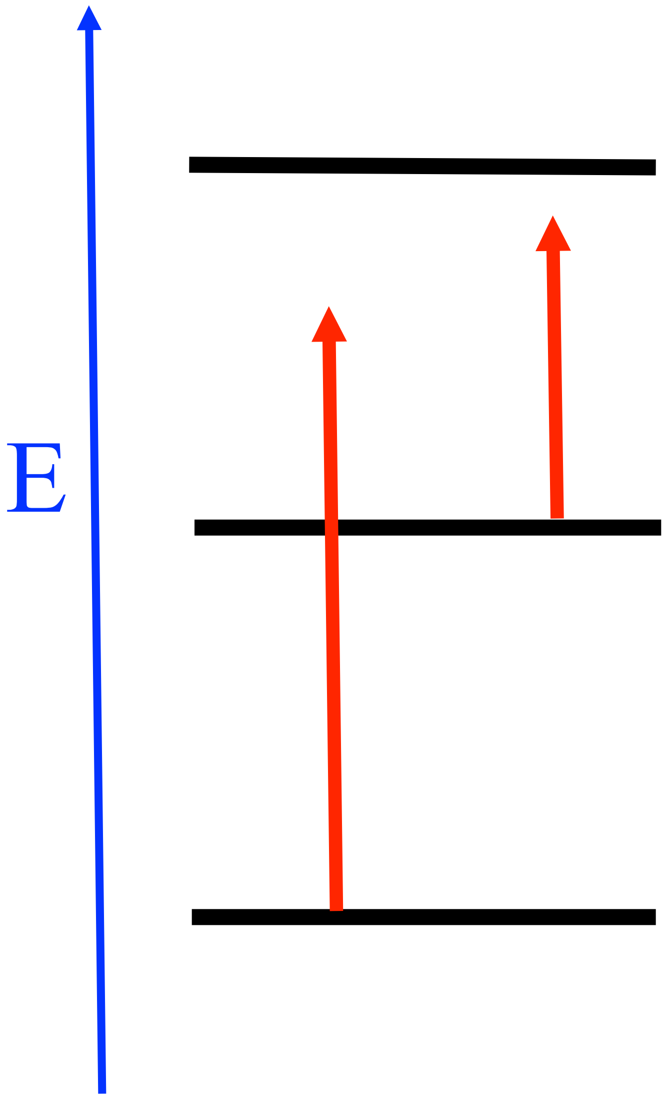


line 1 in spectrum

line 3 in spectrum

line 2 in spectrum

Allowed states



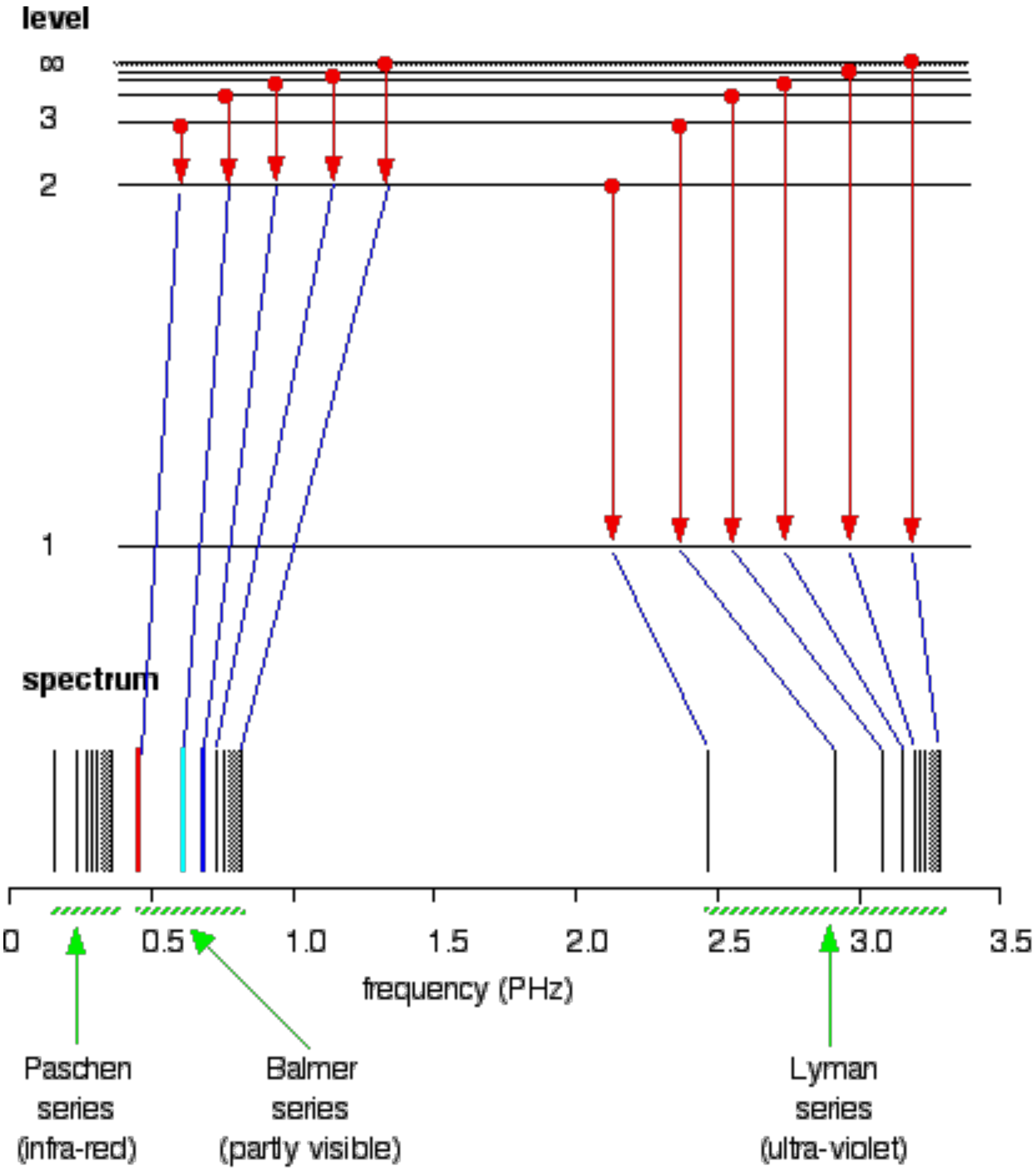
Allowed states

line 1 not observed

hν of the photon must be very close to the energy of separation of the levels for a transition to occur.

What was observed - Electronic Spectra

Electronic Spextra



Electronic Spectra

$$\frac{1}{\lambda} = R\left(\frac{1}{(n'')^2} - \frac{1}{(n')^2}\right)$$

where is the Rydberg constant:

$R = 1.097373 \times 10^7\ \mathrm{m}^{-1}$

Microwave – molecular rotation

Electronic Spectra

when n”=1 ⇒ Lyman series

when n”=2 ⇒ Balmer series

when n”=3 ⇒ Paschen series

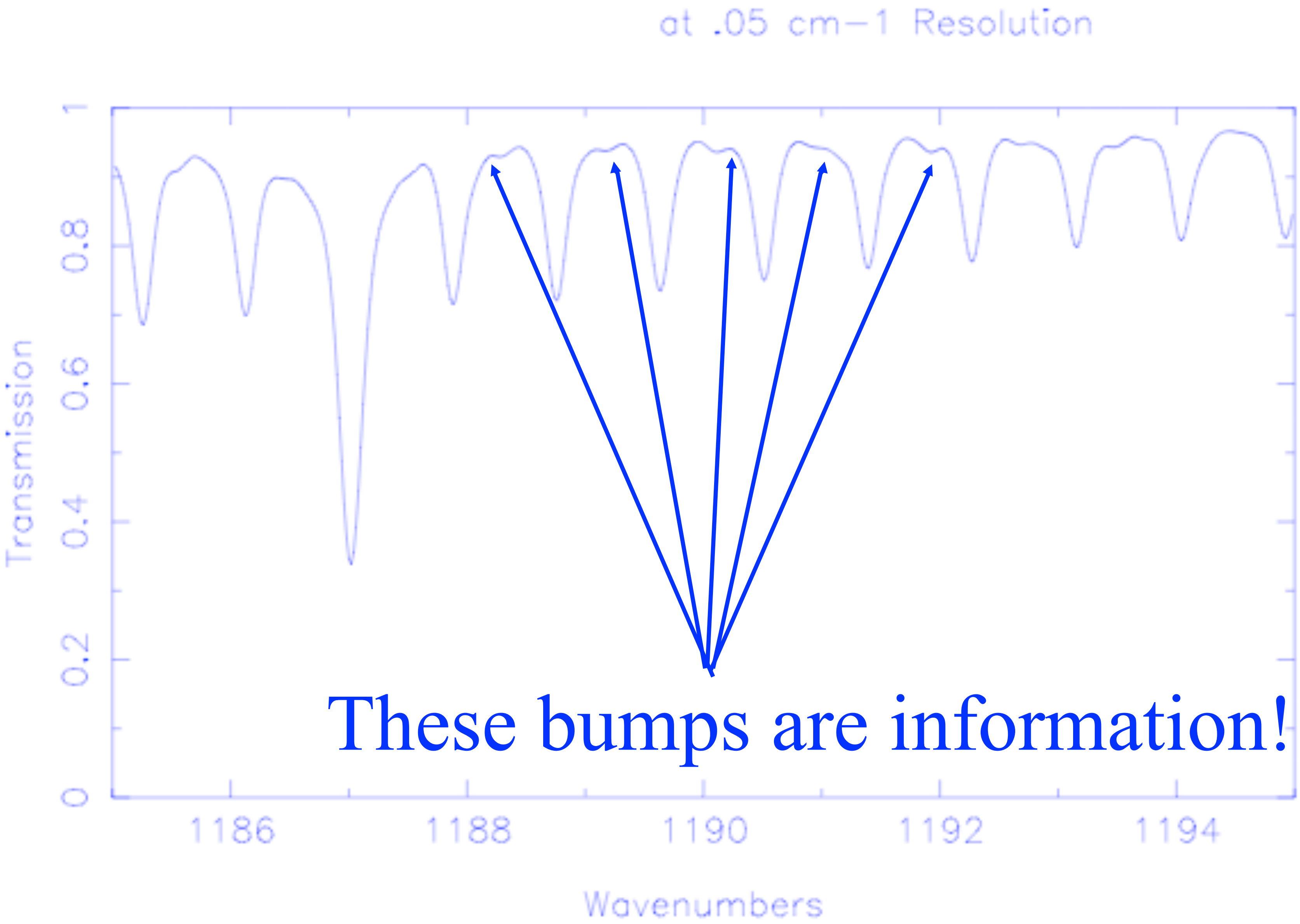
when n”=4 ⇒ Brackett series

Visible region – electronic spectra

Infrared – molecular vibration and rotation

Microwave – molecular rotation

What do we see?



These bumps are information!

Carbon Dioxide

Isotopically enriched sample ^{17}O

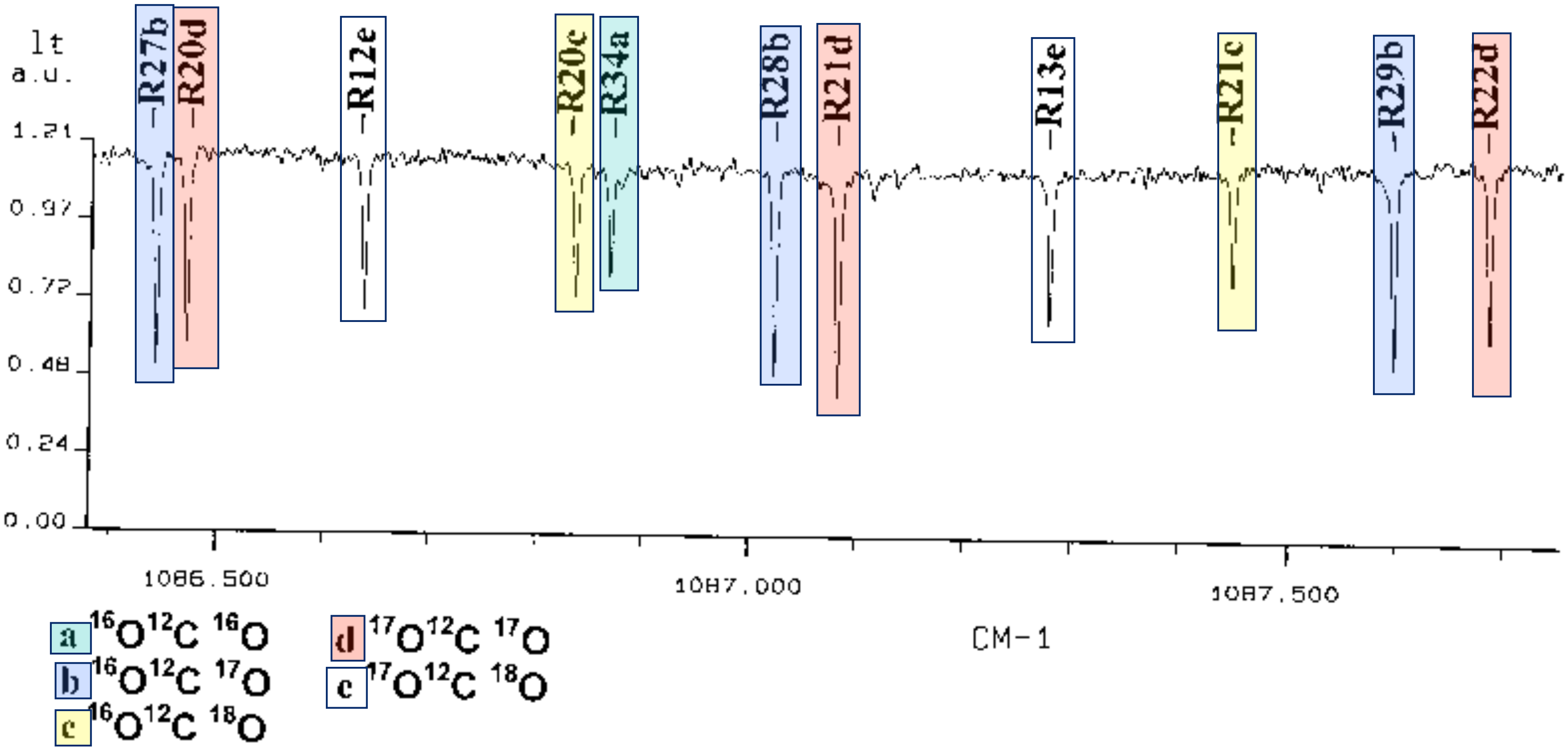
$^{16}O^{12}C^{16}O$ m = 44 g/mol

$^{16}O^{12}C^{17}O$ m = 45 g/mol

$^{16}O^{12}C^{18}O$ m = 46 g/mol

$^{17}O^{12}C^{17}O$ m = 46 g/mol

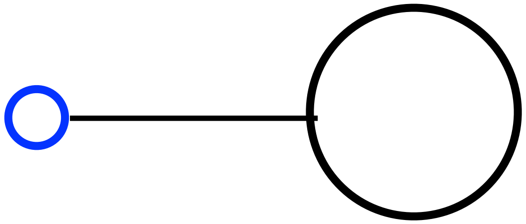
$^{17}O^{12}C^{18}O$ m = 47 g/mol



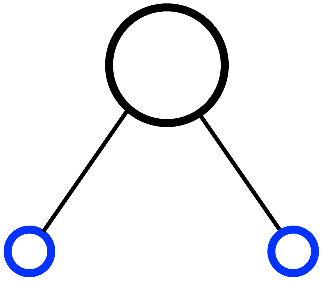
lt
a.u.
1.21
0.97
0.72
0.48
0.24
0.00
R27b
R20d
R12e
R20c
R34a
R28b
R21d
R13e
R21c
R29b
R22d
1086.500
1087.000
1087.500
CM-1
a 16O12C 16O
b 16O12C 17O
c 16O12C 18O
d 17O12C 17O
e 17O12C 18O

molecules with dipole moments

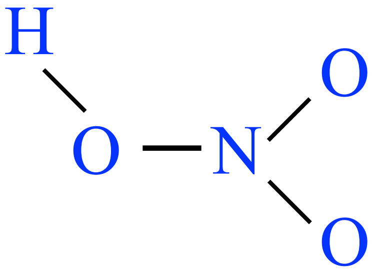
HCl



H_2O



HNO_3

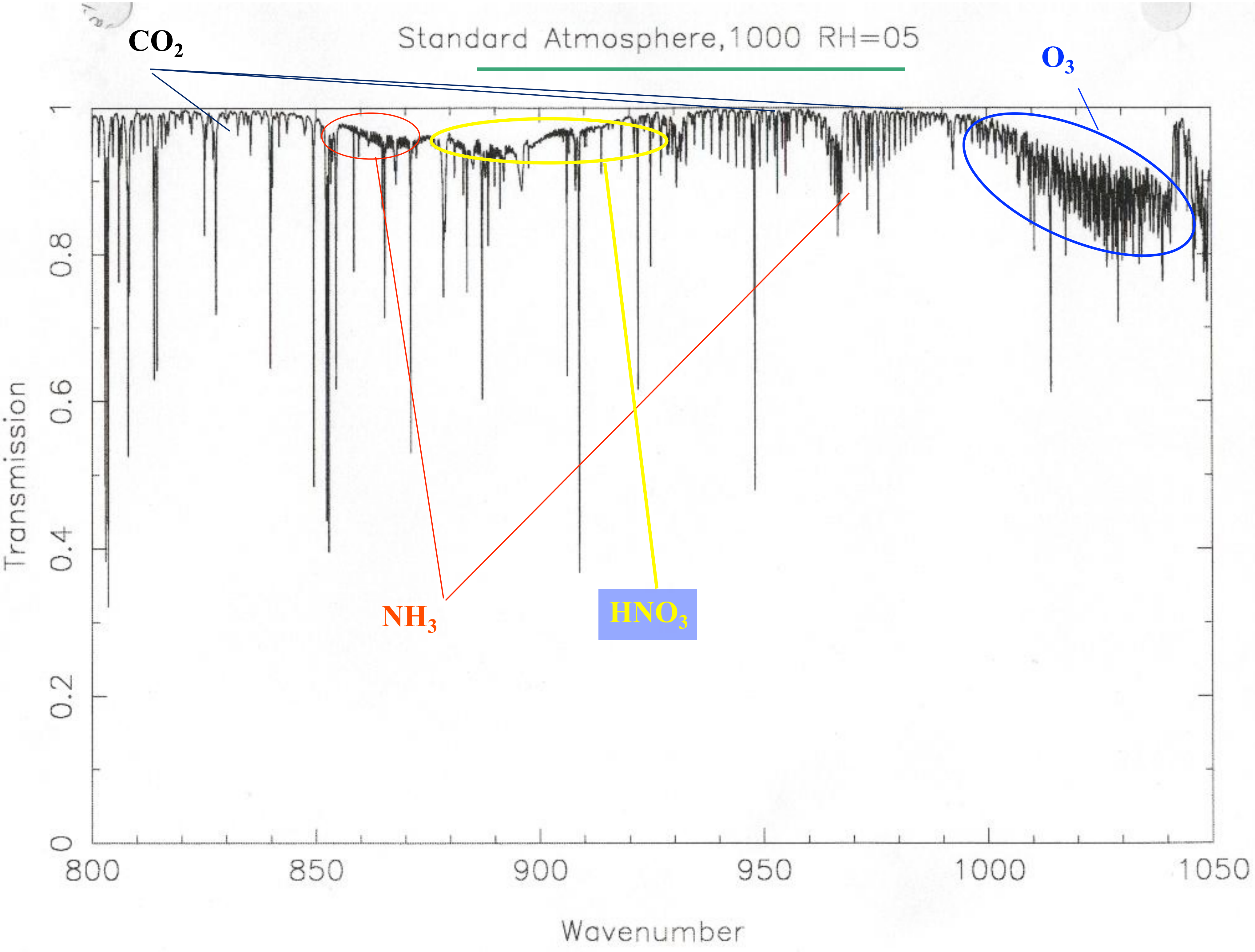


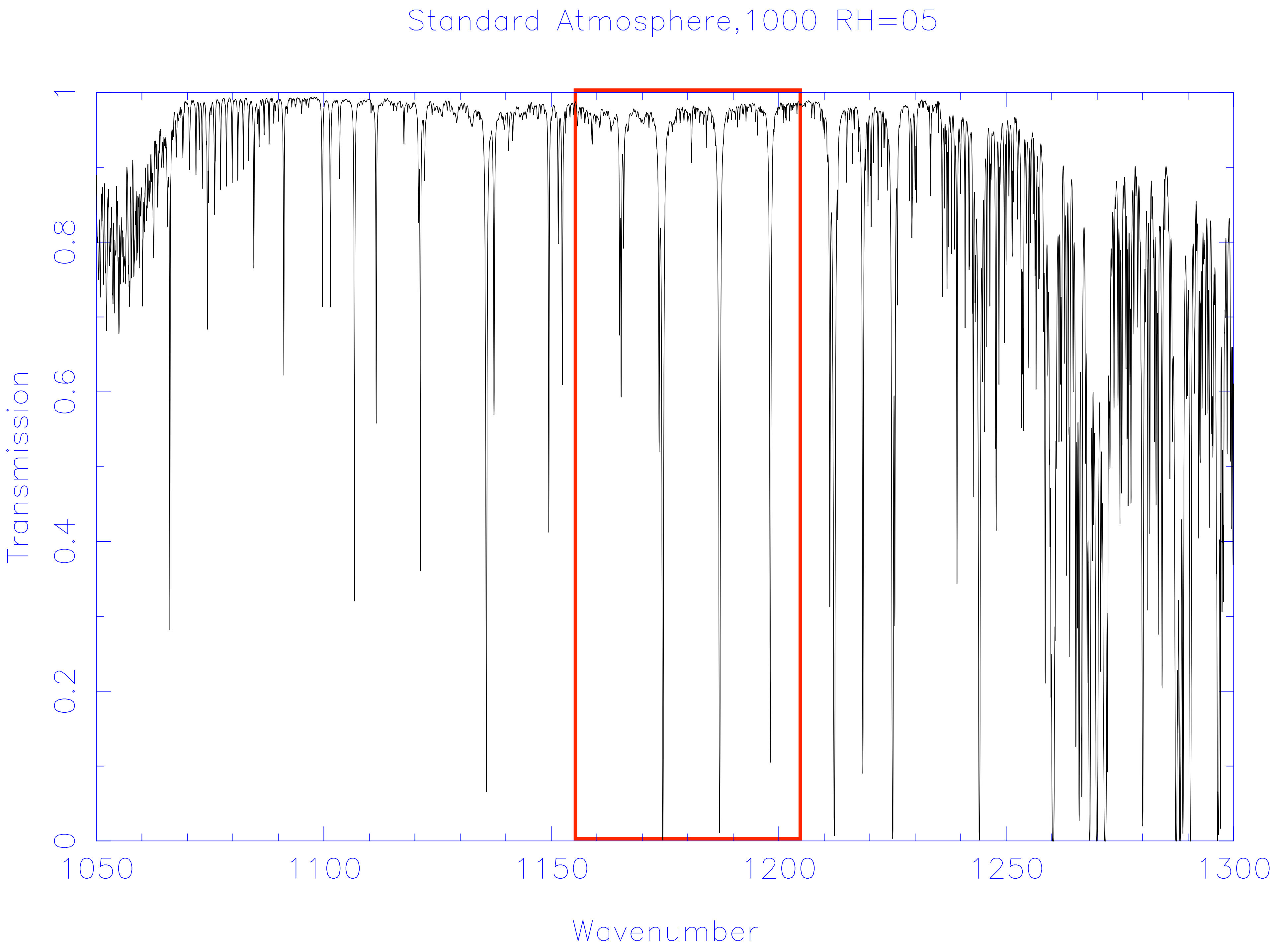
molecules with quadrupole moment

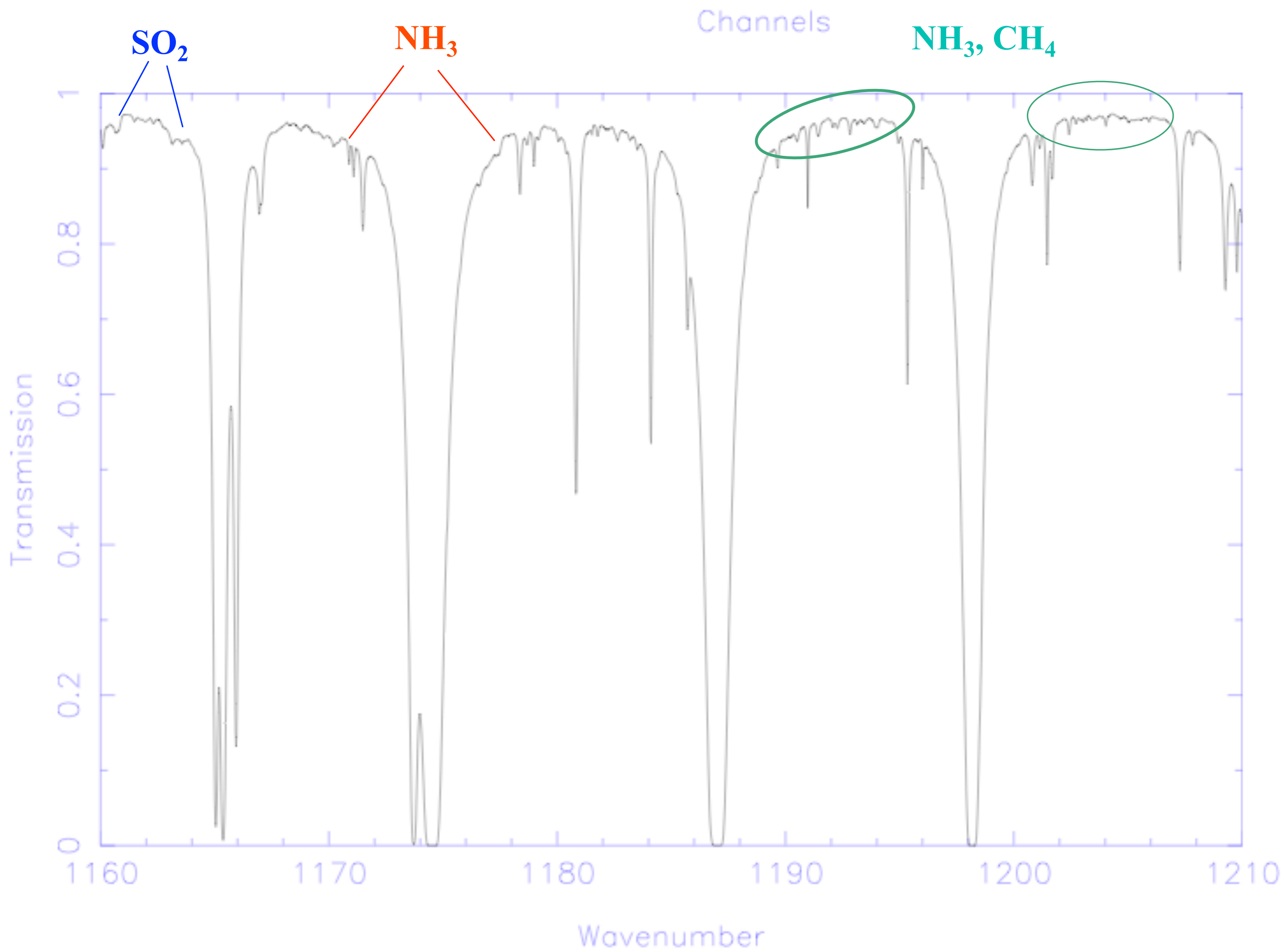
more symmetric, cylindrical distribution

examples:

N_2

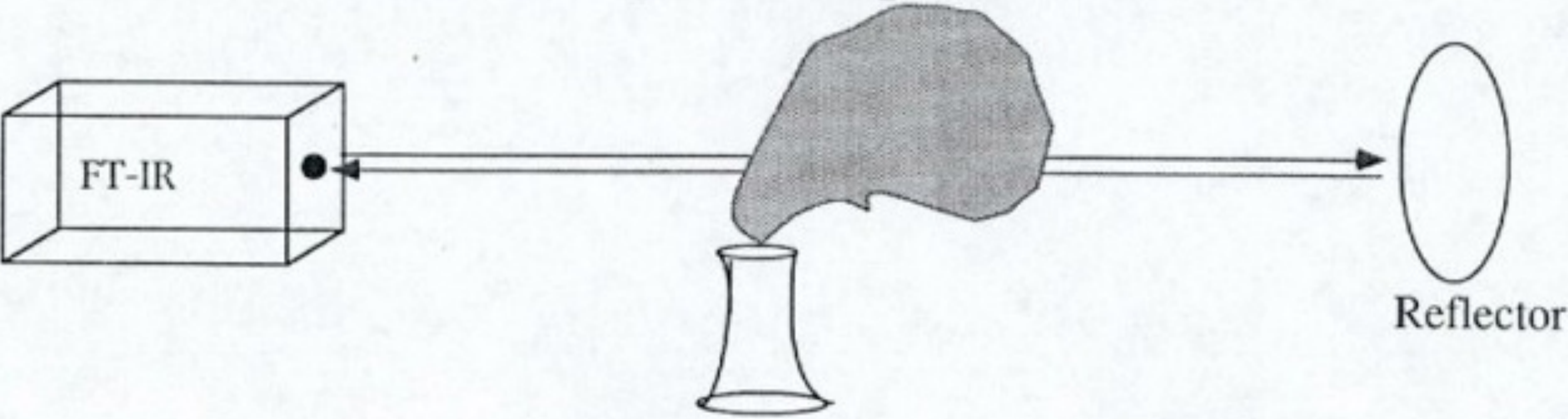

CO$_2$
Standard Atmosphere,1000 RH=05
O$_3$
NH$_3$
HNO$_3$
Transmission
0
0.2
0.4
0.6
0.8
1
800
850
900
950
1000
1050
Wavenumber

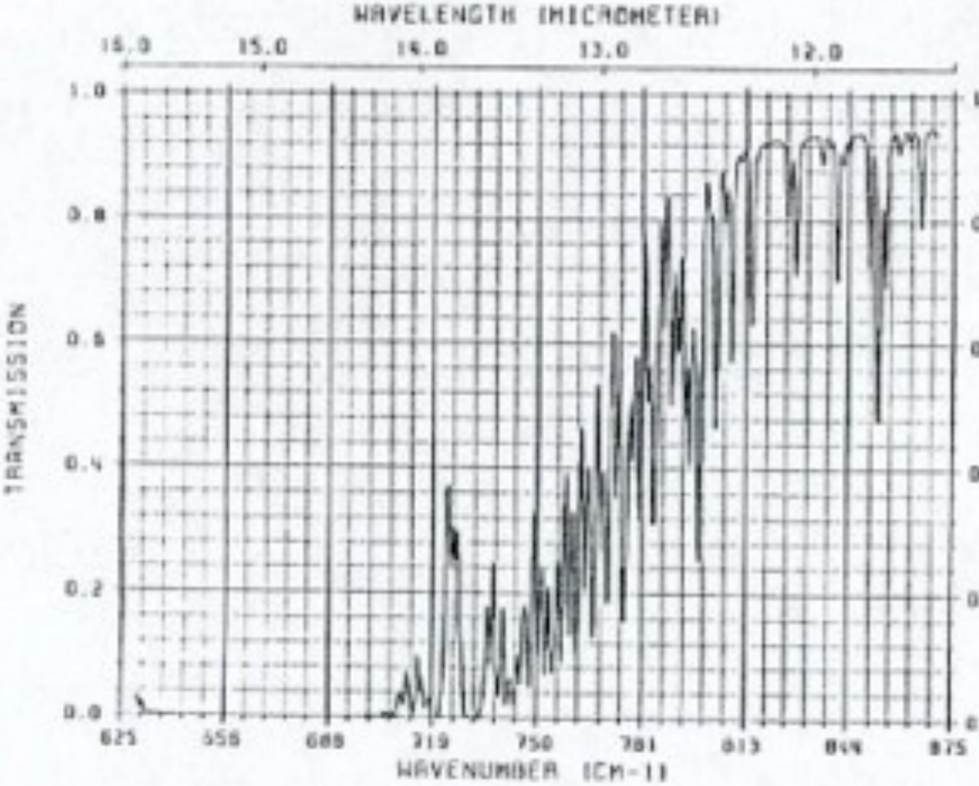

Standard Atmosphere,1000 RH=05
Transmission
0
0.2
0.4
0.6
0.8
1
1050
1100
1150
1200
1250
1300
Wavenumber



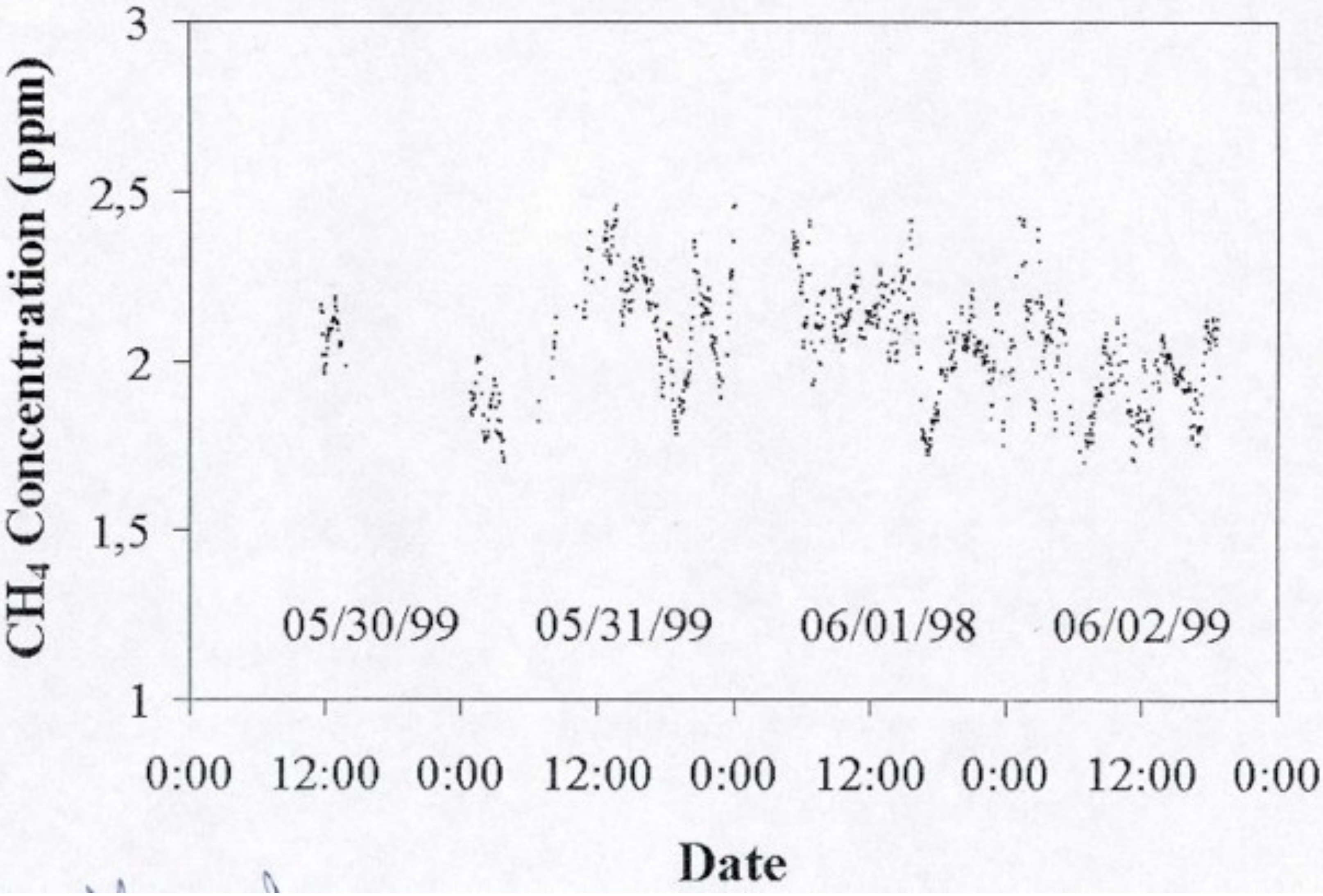
SO_2
NH_3
Channels
NH_3, CH_4
1
0.8
0.6
0.4
0.2
0
Transmission
1160
1170
1180
1190
1200
1210
Wavenumber

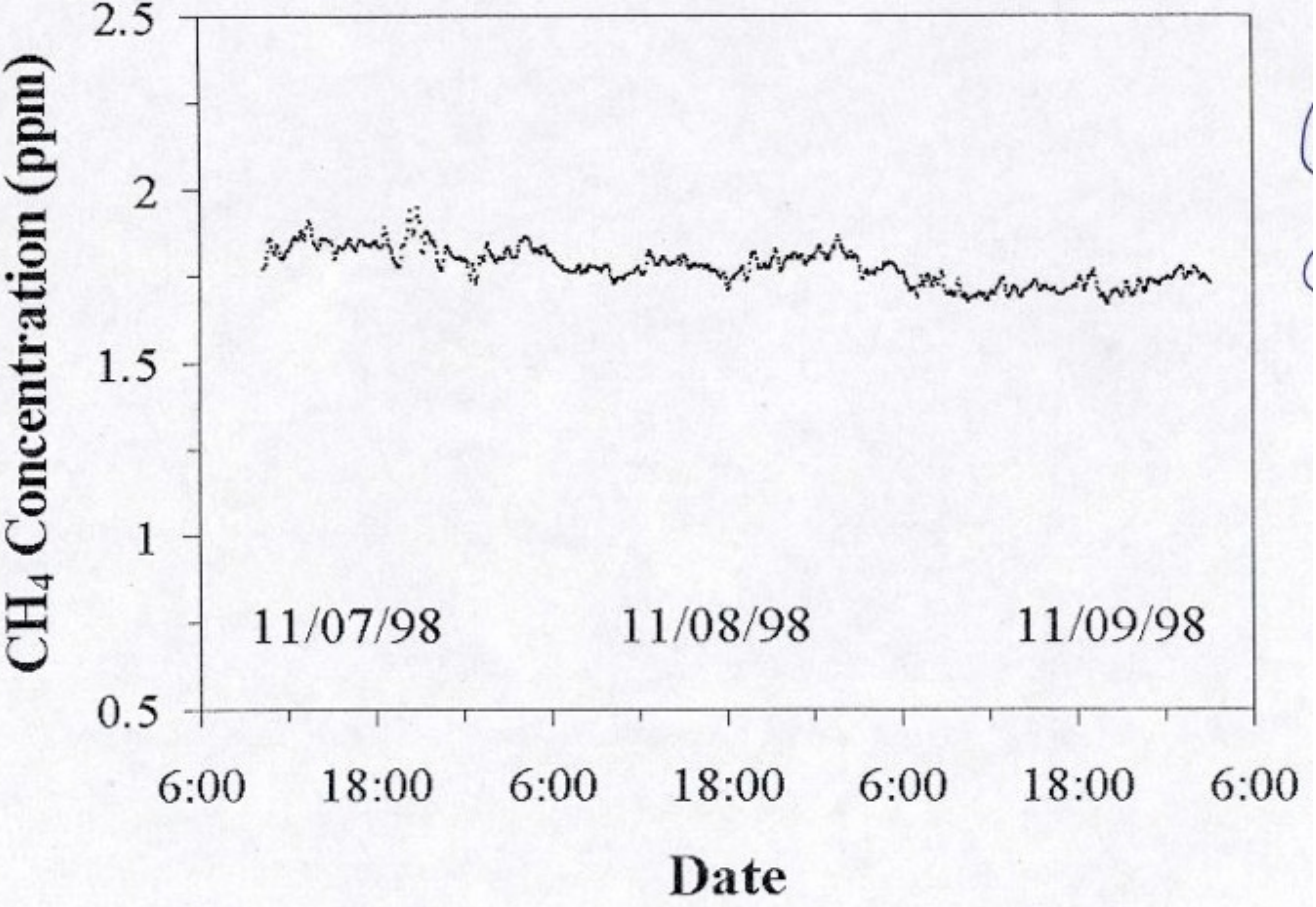
Remote Sensing of Atmospheric Pollutants





Monitoring of CH_4 above the "Lac Piché" (June 99)




2.5
2
1.5
1
0.5
CH$_4$ Concentration (ppm)
11/07/98
11/08/98
11/09/98
6:00
18:00
6:00
18:00
6:00
18:00
6:00
Date

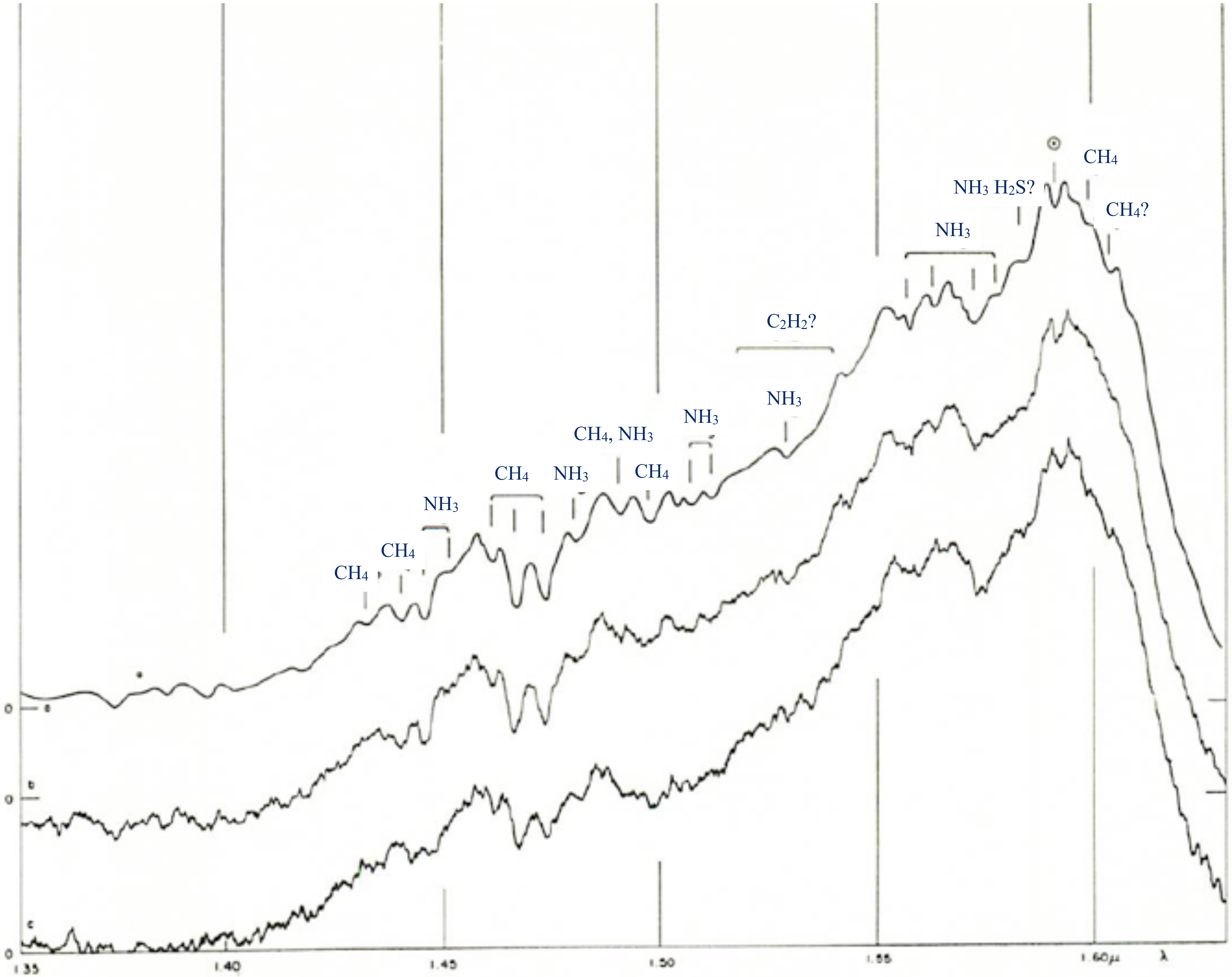
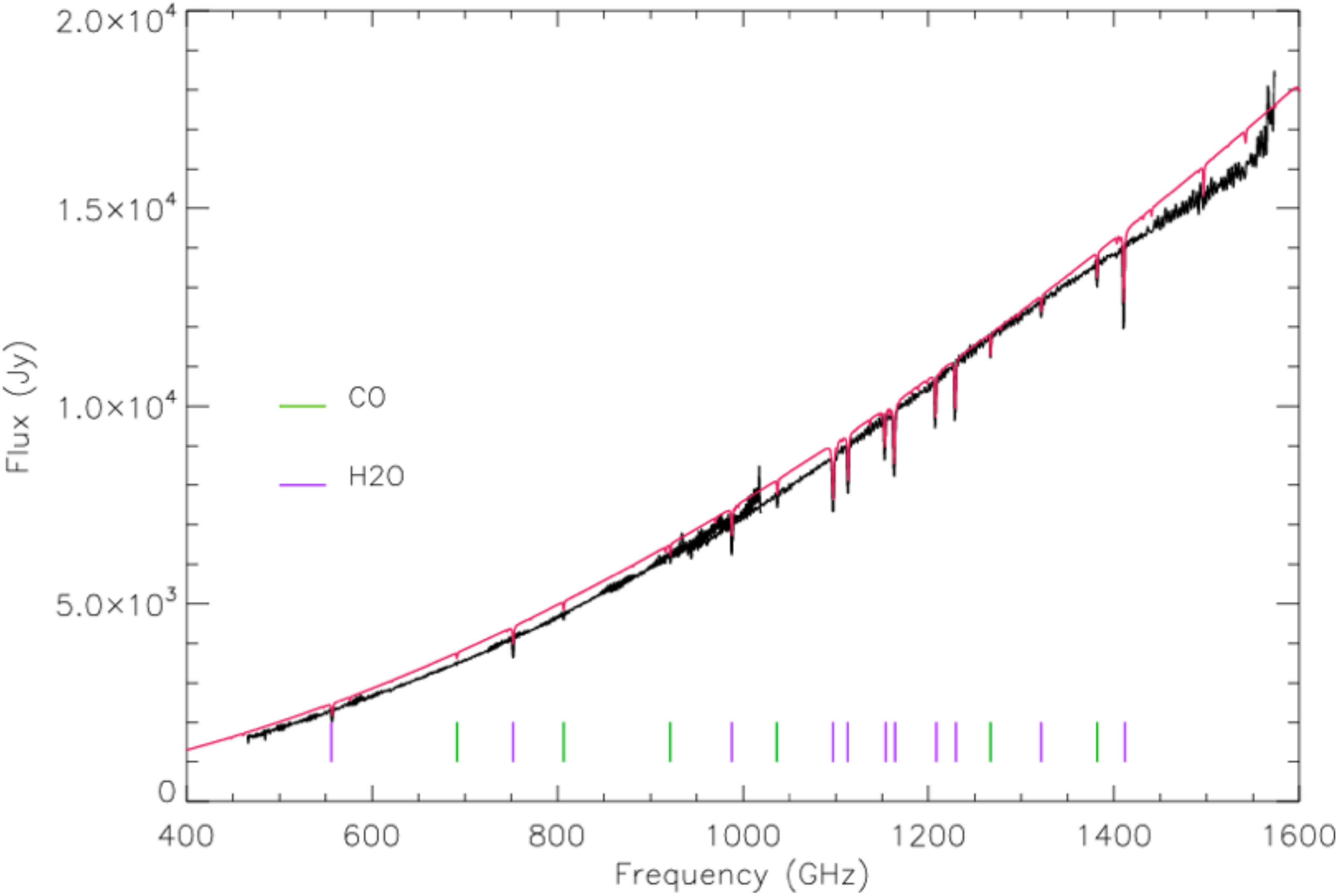


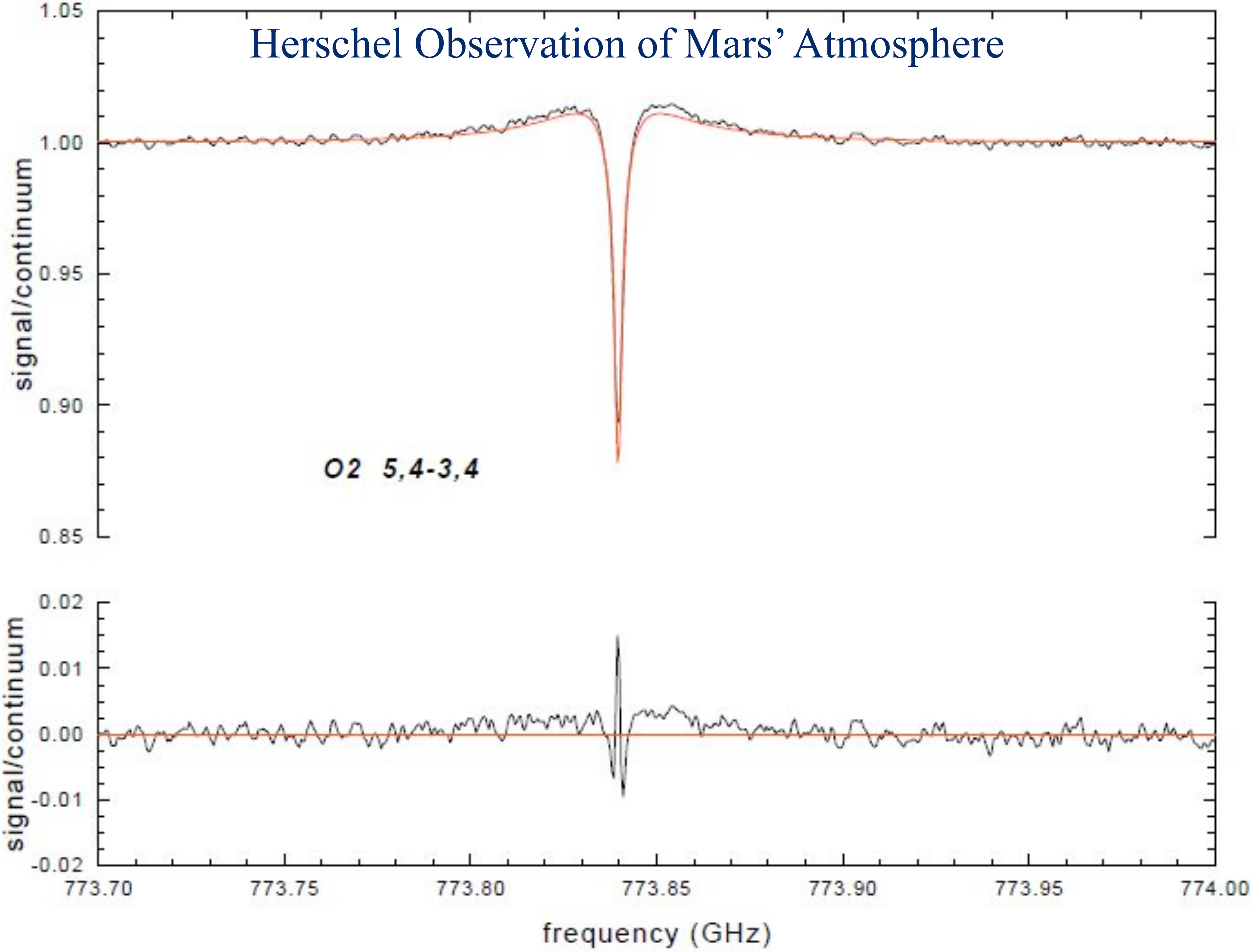
Fig. 3 Spectrum of Jupiter, Part 3, 1.35–1.63 μ; as Fig. 1.

DALE **P. CRUIKSHANK** and ALAN **B. BINDER,** *Astrophysics and Space Science* 3 (1969) 347-356

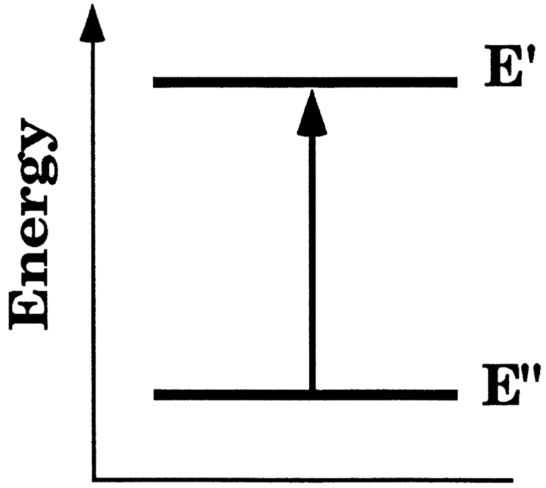
Herschel Observation of Mars' Atmosphere

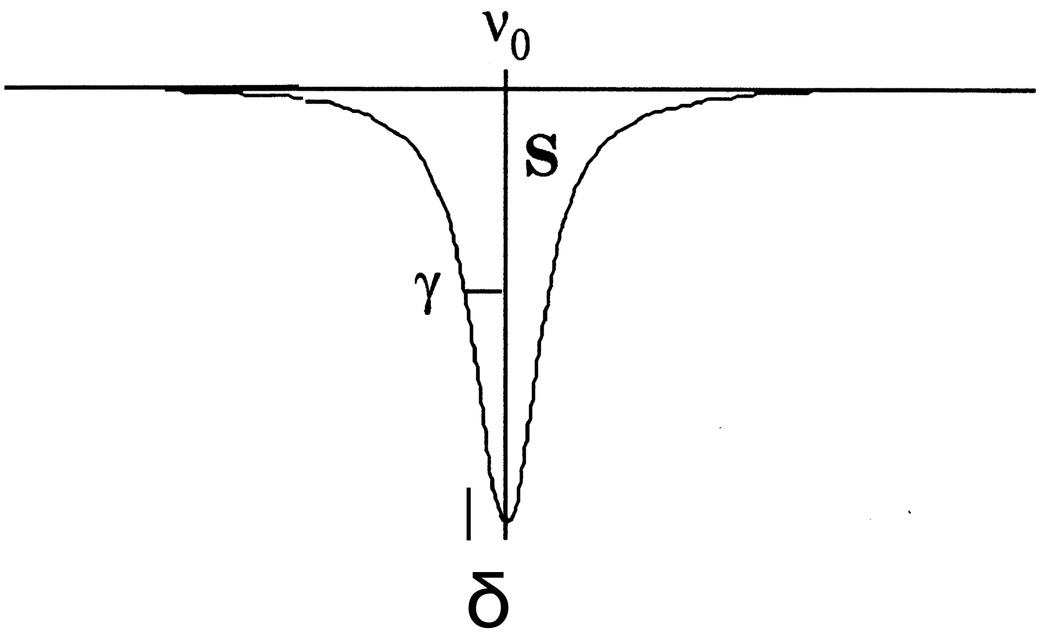


Herschel Observation of Mars' Atmosphere

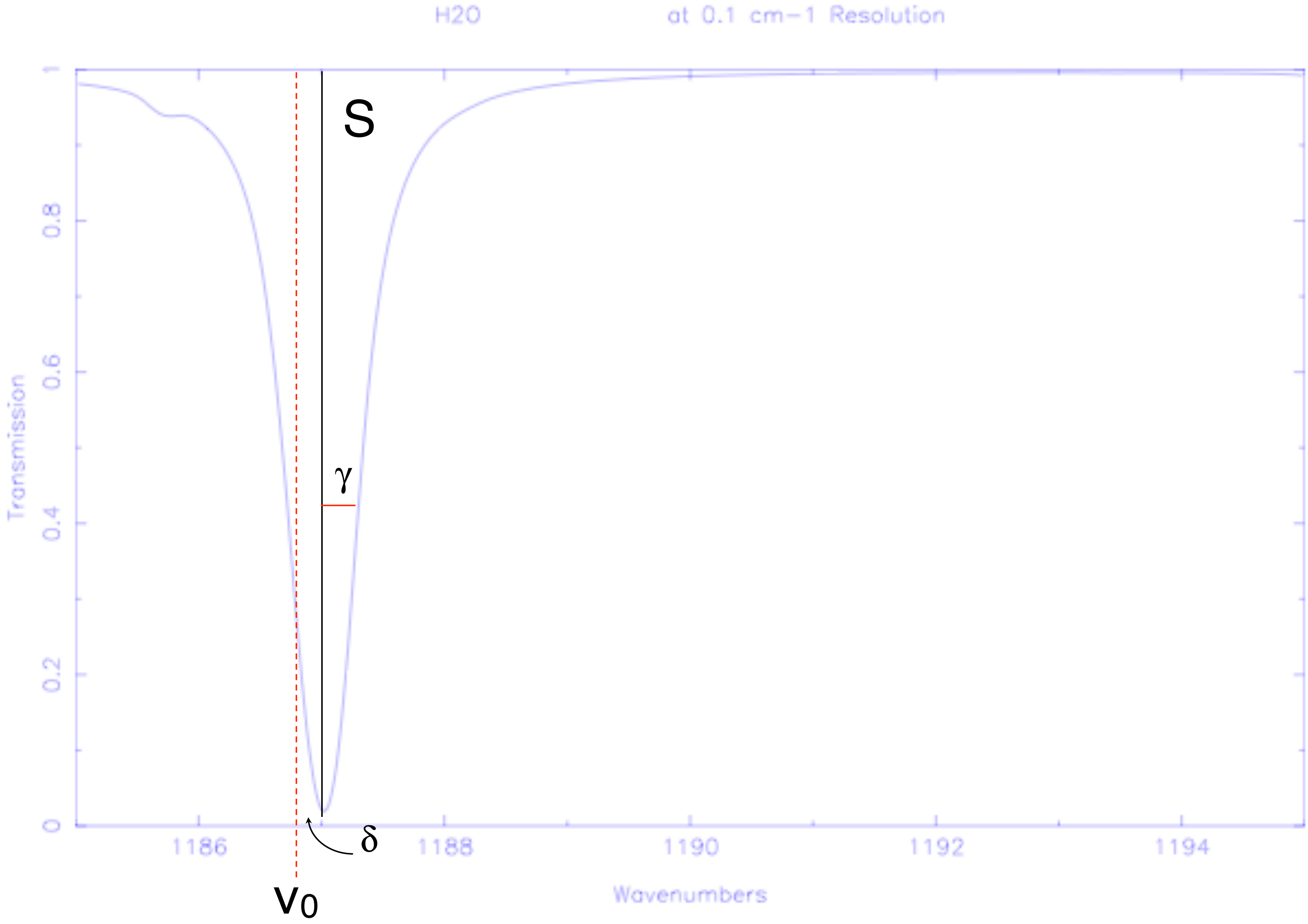


Important Line Parameters





Quantized Energy Transition ⇨ Broadened Lorentzian Line Shape


H2O
at 0.1 cm-1 Resolution
Transmission
Wavenumbers
0
0.2
0.4
0.6
0.8
1
1186
1188
1190
1192
1194
S
γ
δ
v_0

Spectral Parameters

ν_0 - vacuum wavenumber (cm^{-1})

S - line intensity ($cm^{-1}/(molecule\ cm^{-2})$)

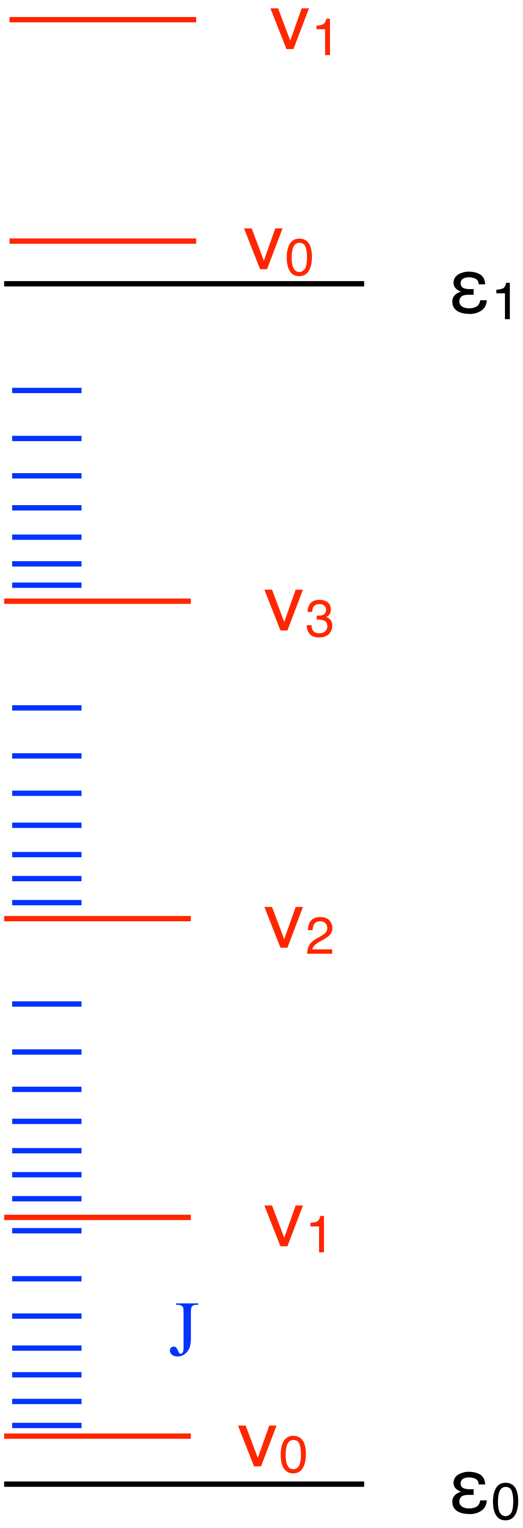
γ - half-width at half-maximum (cm^{-1}/atm)

δ - line shift (cm^{-1}/atm)

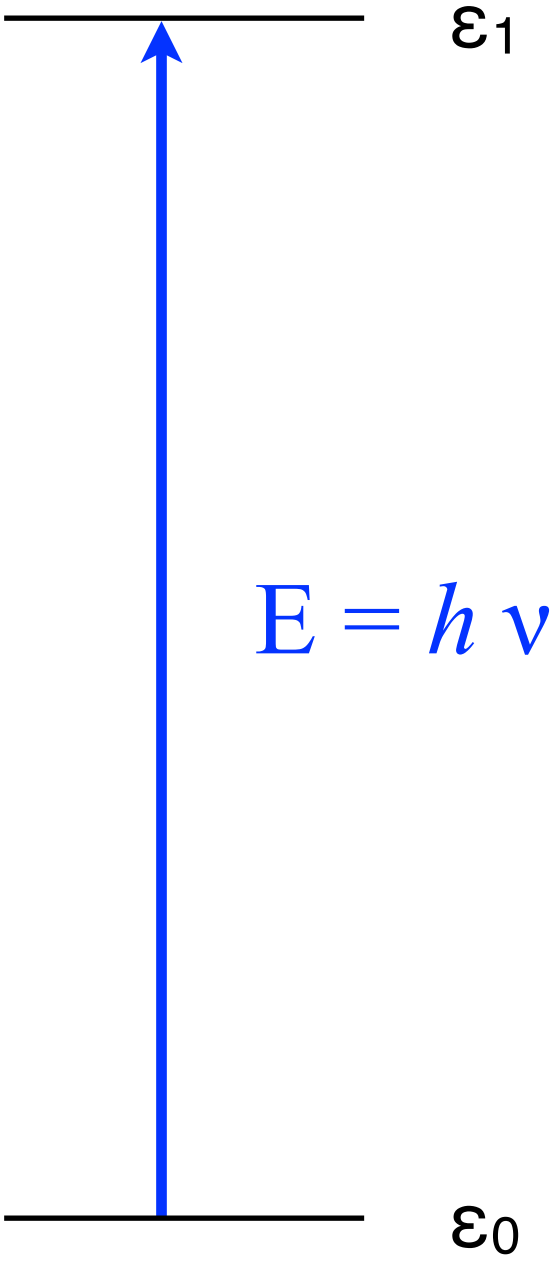
E” - lower state energy (cm^{-1})

n - temperature dependence of γ

Energy Structure



Visible - UV region

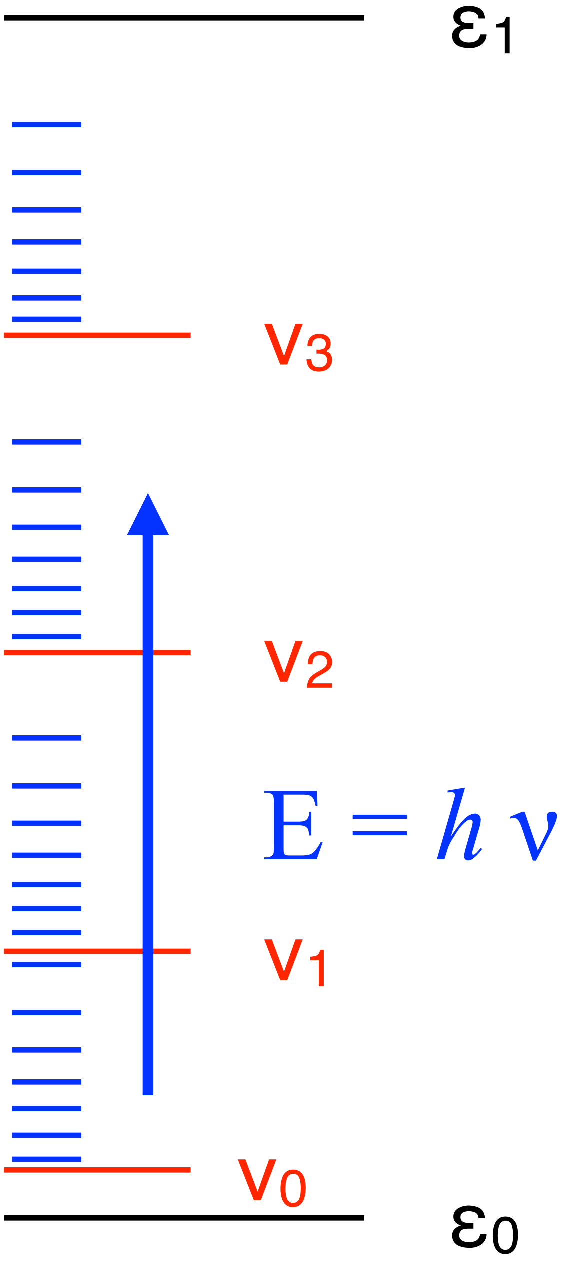


change in the electronic state

high energy

>14,000 wavenumbers

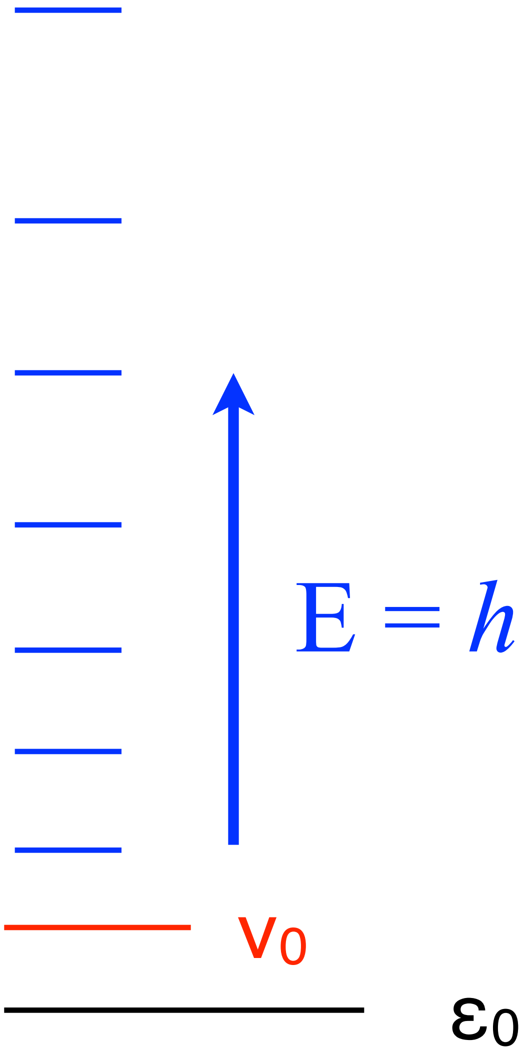
Infrared region



transitions are between rovibrational states

1000 to 14,000 wavenumbers

microwave region

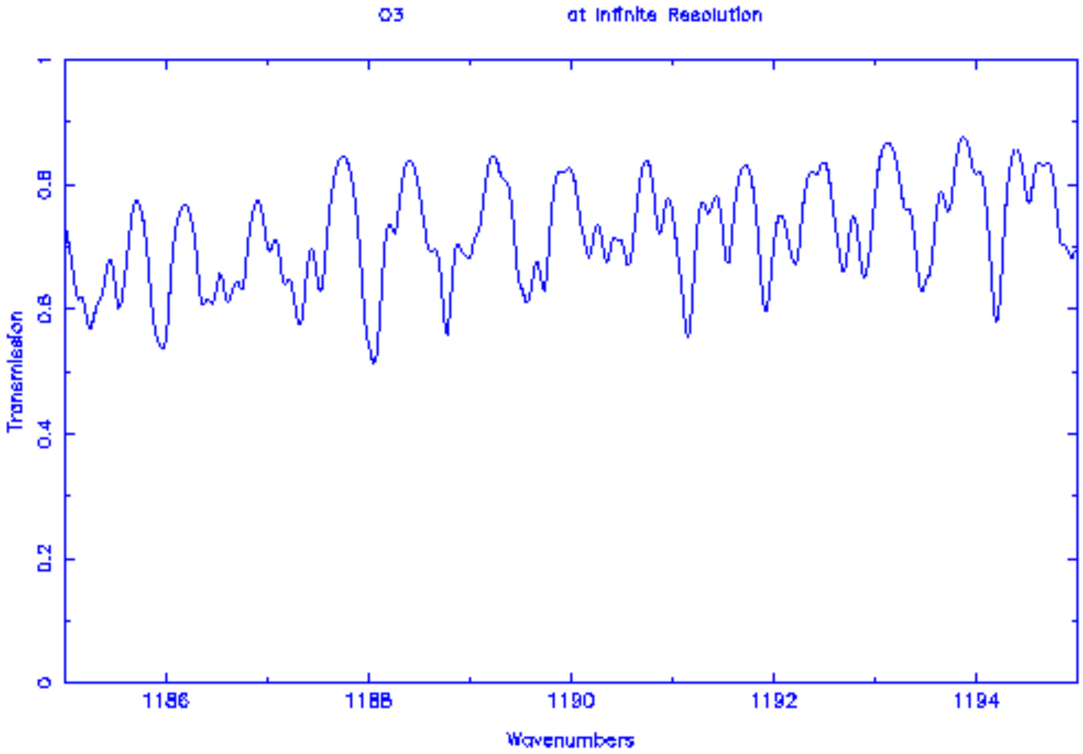


transitions are between rotational levels

0 to 1000 wavenumbers

Parameters ←→ Spectrum

Spectral Parameters

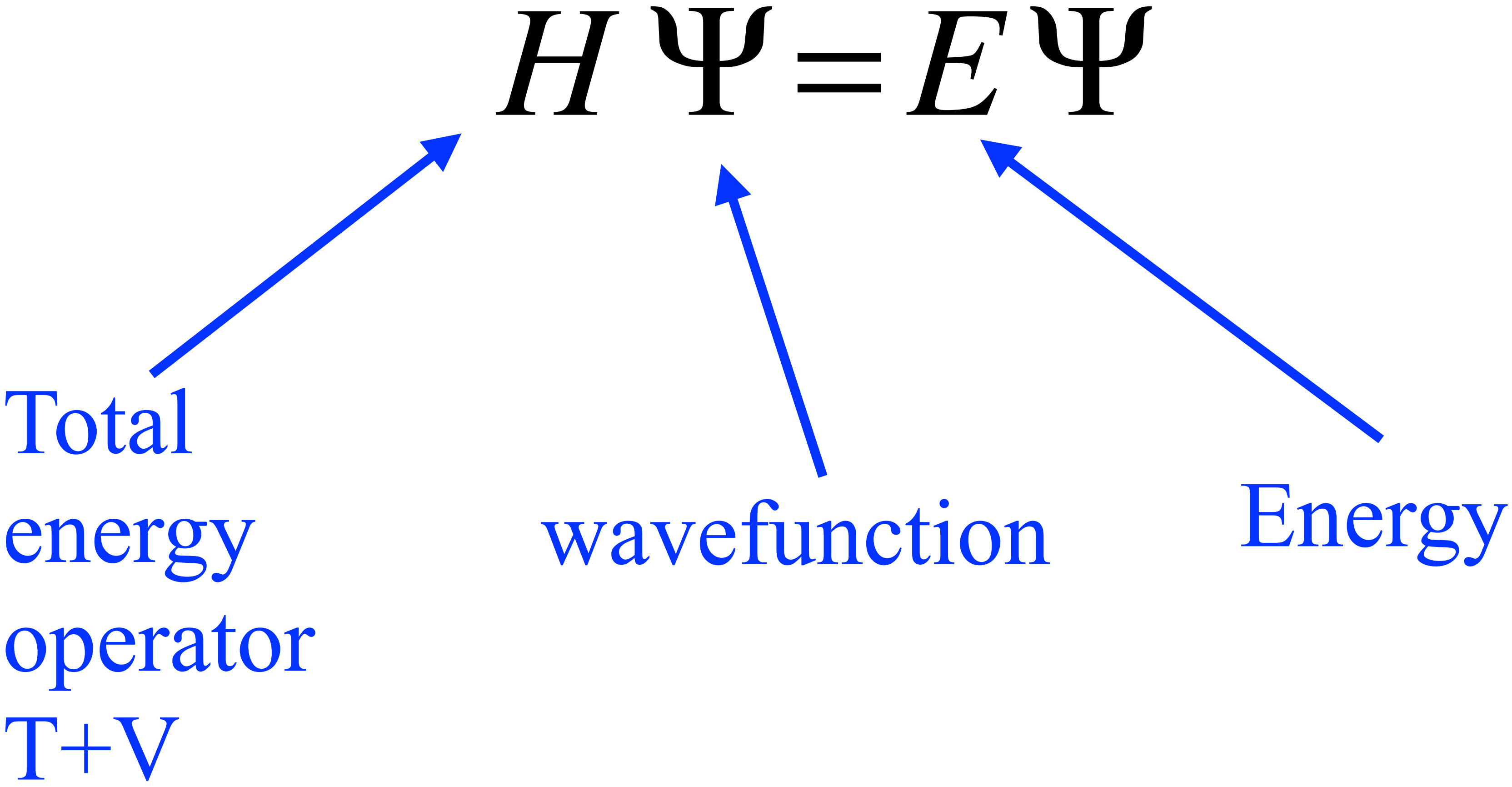


Spectral parameters come from:

- HITRAN Database
- GEISA Database

But data is incomplete and only approximate

Energy Structure
The Schrodinger Equation



$$H\Psi = E\Psi$$

Total
energy
operator
T+V

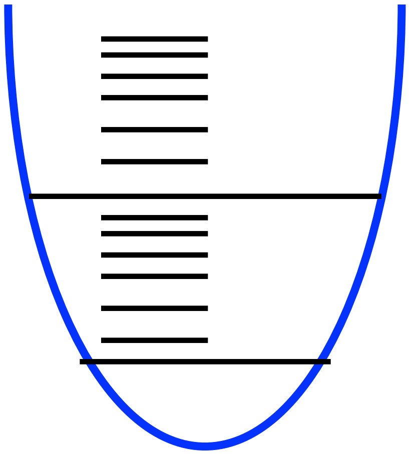
wavefunction

Energy

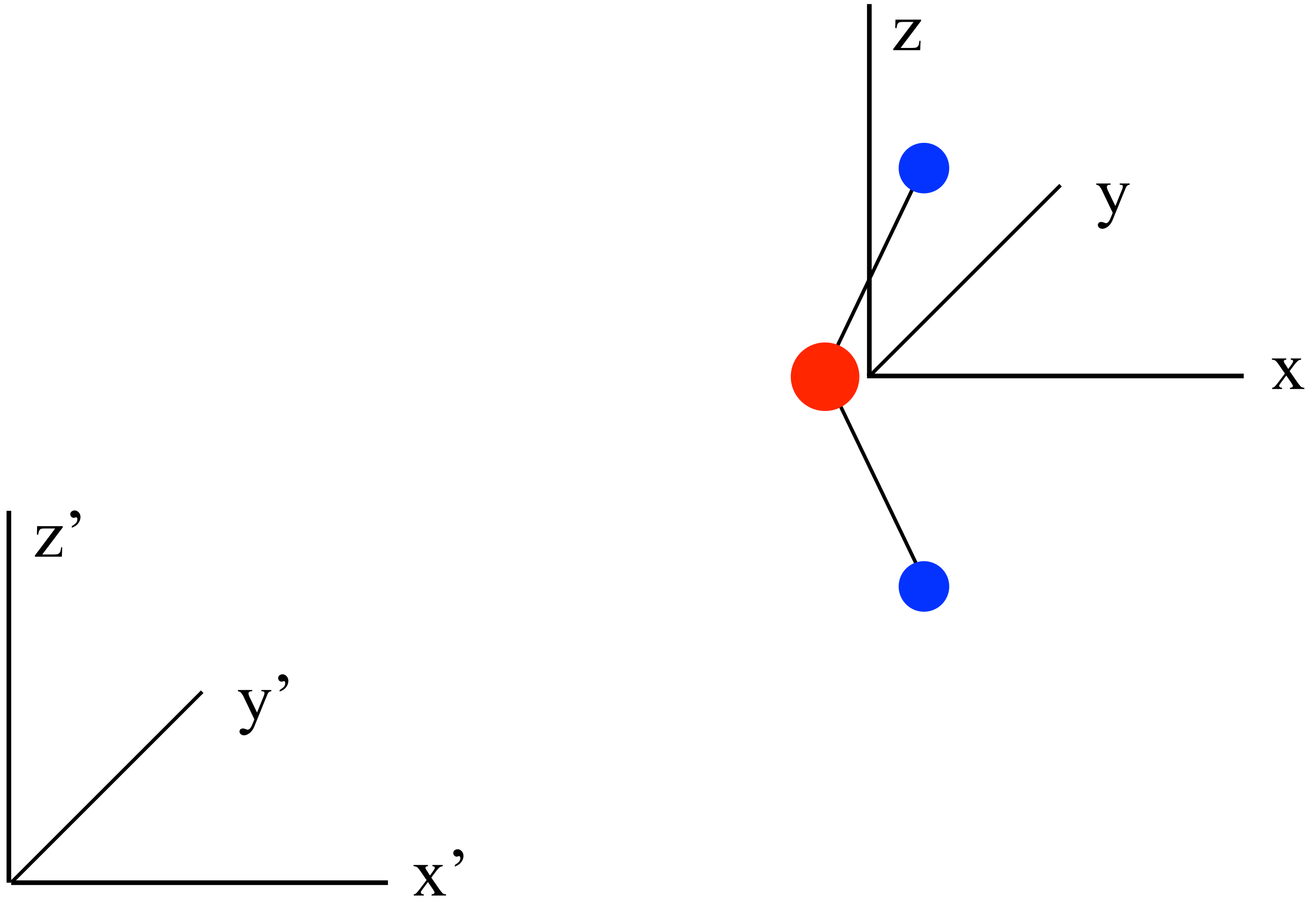
Rotational Energy Structure

$$H\Psi = E\Psi$$

Here the kinetic energy is that of the molecule rotating and potential energy of the vibrational state.

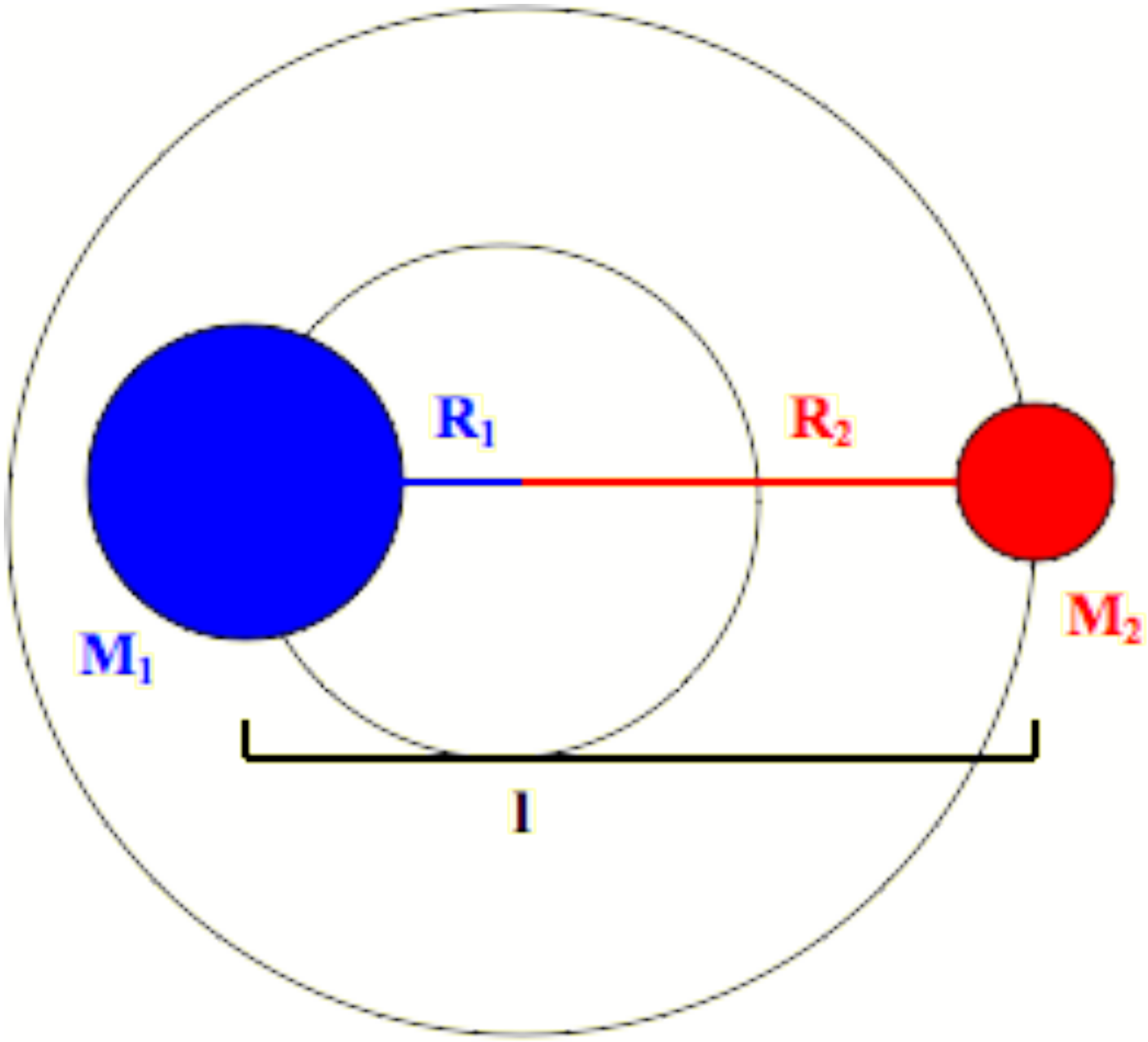


Lab vs. molecule fixed frames

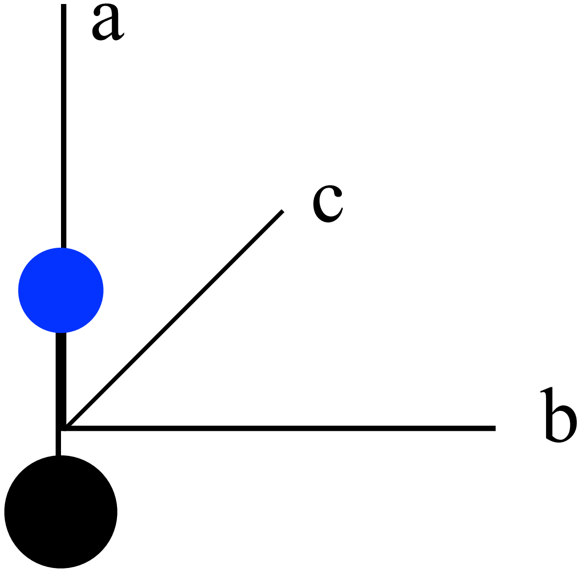


Lab frame

where $I = \sum m_i r_i^2$, I is a tensor



Linear Molecule



$I_A = 0$ and $I_B = I_C$

moment of inertia

The energy of a rotation molecule is given in terms of the moment of inertia

$$E(cm^{-1}) = \frac{1}{2hc} I_B \omega^2$$

$$E\left(cm^{-1}\right) = \frac{h}{8\pi^2 c I_B} J\left(J+1\right)$$

Linear Molecules

$$E = \frac{h}{8\pi^2 c I_B} J(J+1)$$

we define the rotational constant B

$$B = \frac{h}{8\pi^2 c I_B}$$

which gives

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

Determining the Rotational Constants

Consider the transitions J → J + 1 and J + 1 → J + 2.

The frequencies are given by

$\nu_1 = E_{J+1} - E_J$ and $\nu_2 = E_{J+2} - E_{J+1}$.

The separation between the lines is

$$\Delta\nu = \nu_2 - \nu_1$$

$$E = BJ\left(J+1\right)$$

Determining the Rotational Constants

Consider the transitions from a level J to J + 1

$$\nu = E_{J+1} - E_J$$

$$\Delta\nu = B(J+1)(J+2) - BJ(J+1)$$

Determining the Rotational Constants

$$\Delta \nu = B(J^2 + 3J + 2 - J^2 - J)$$

$$\Delta \nu = 2B\left(J + 1\right)$$

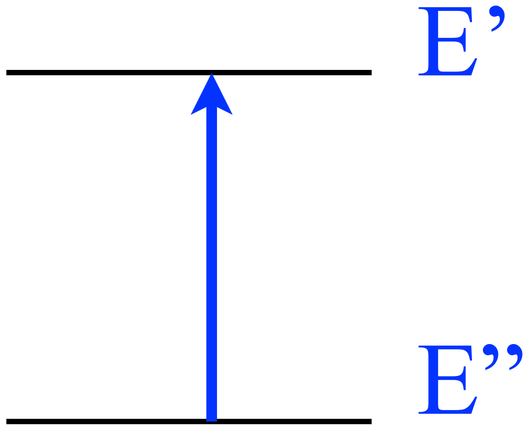
The spacing between adjacent lines is

Get the separation between lines (Δν) from the spectra

$$\Delta\nu(J+1)-\Delta\nu(J)=2B$$

Spectroscopic Convention

Consider a transition from some lower state to an upper state.



The frequency is given by ν = E’-E”

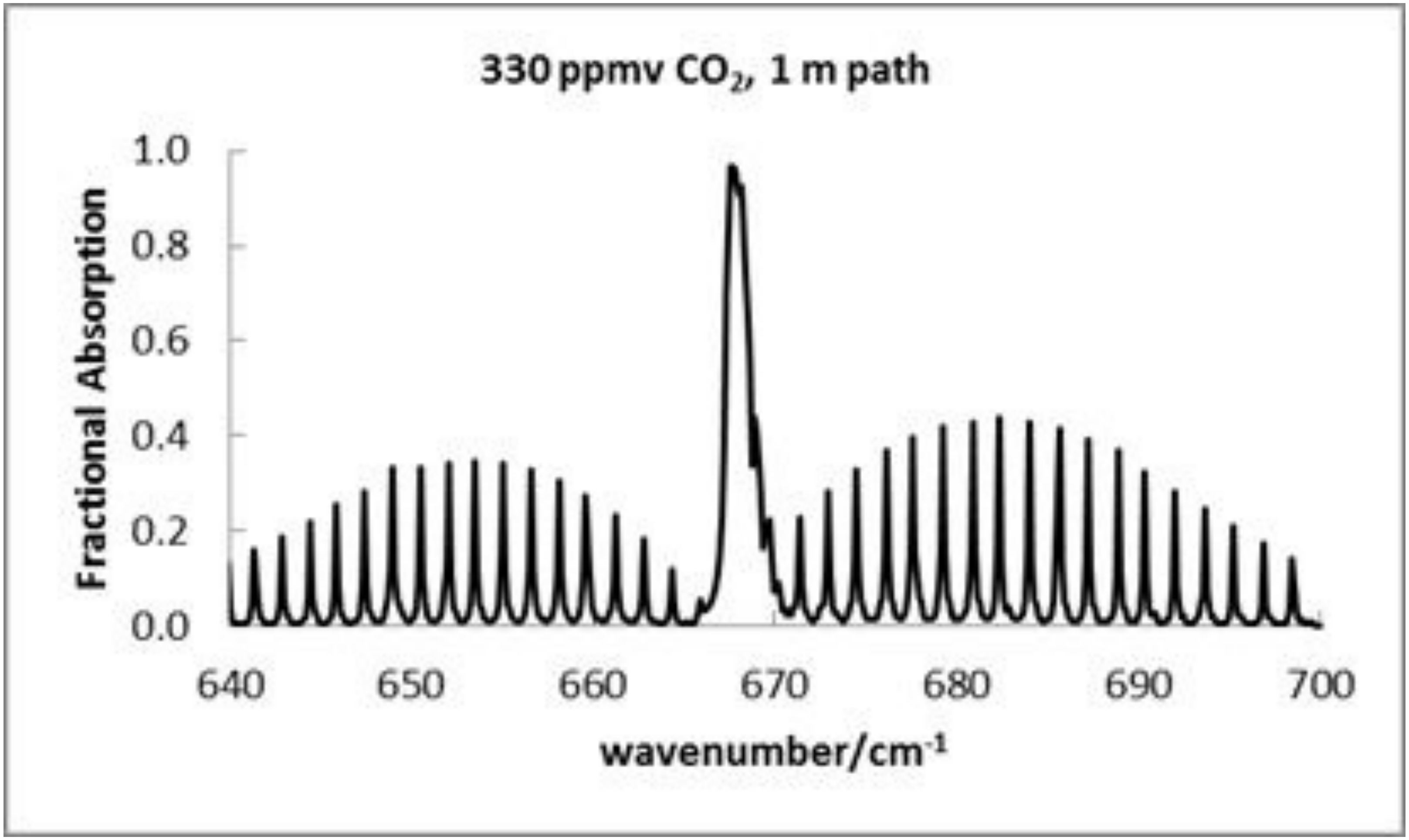
The spectroscopic convention is

‘ labels the upper state and

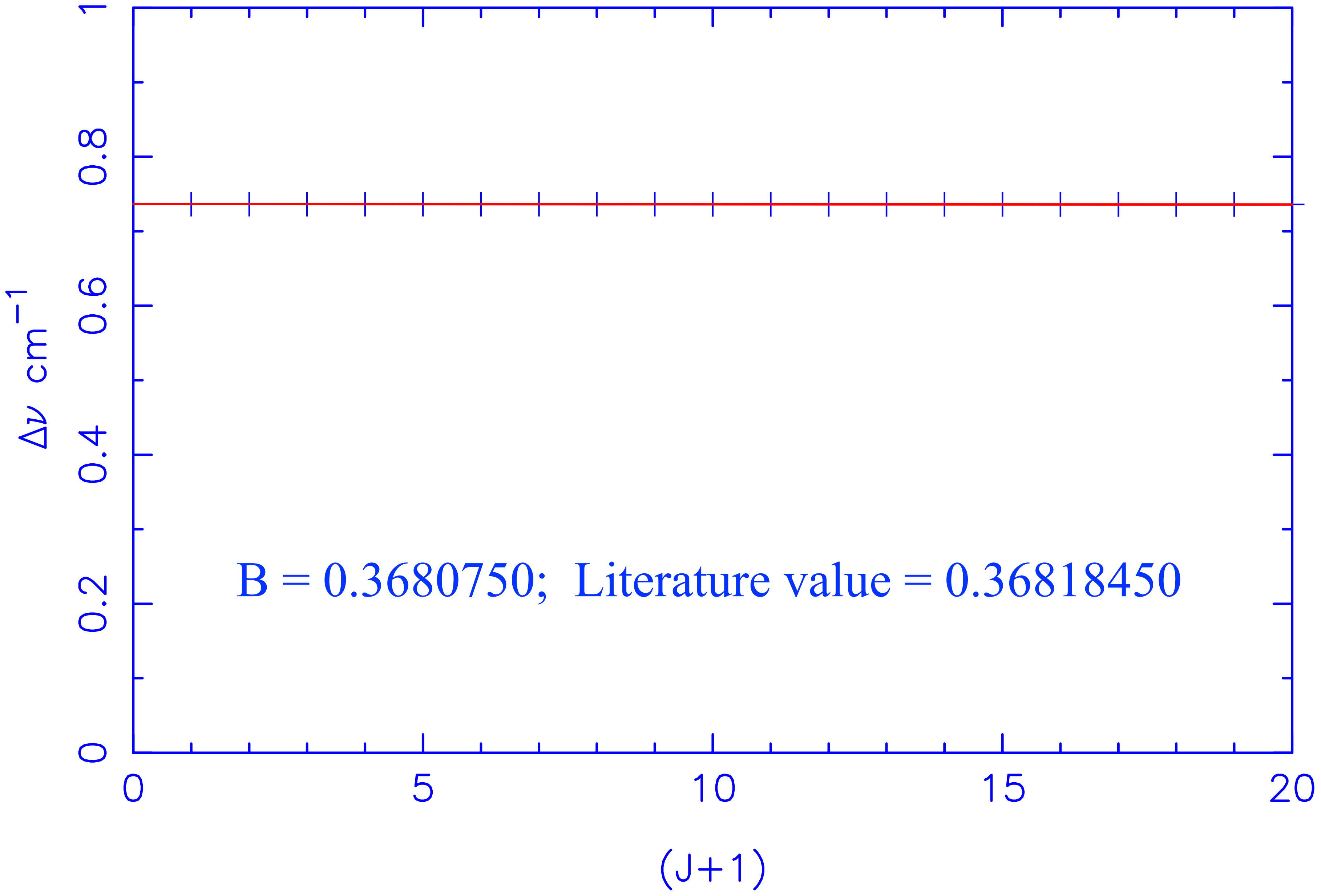
“ labels the lower state.

CO_2

Get the separation between lines ($\Delta\nu$) from the spectra

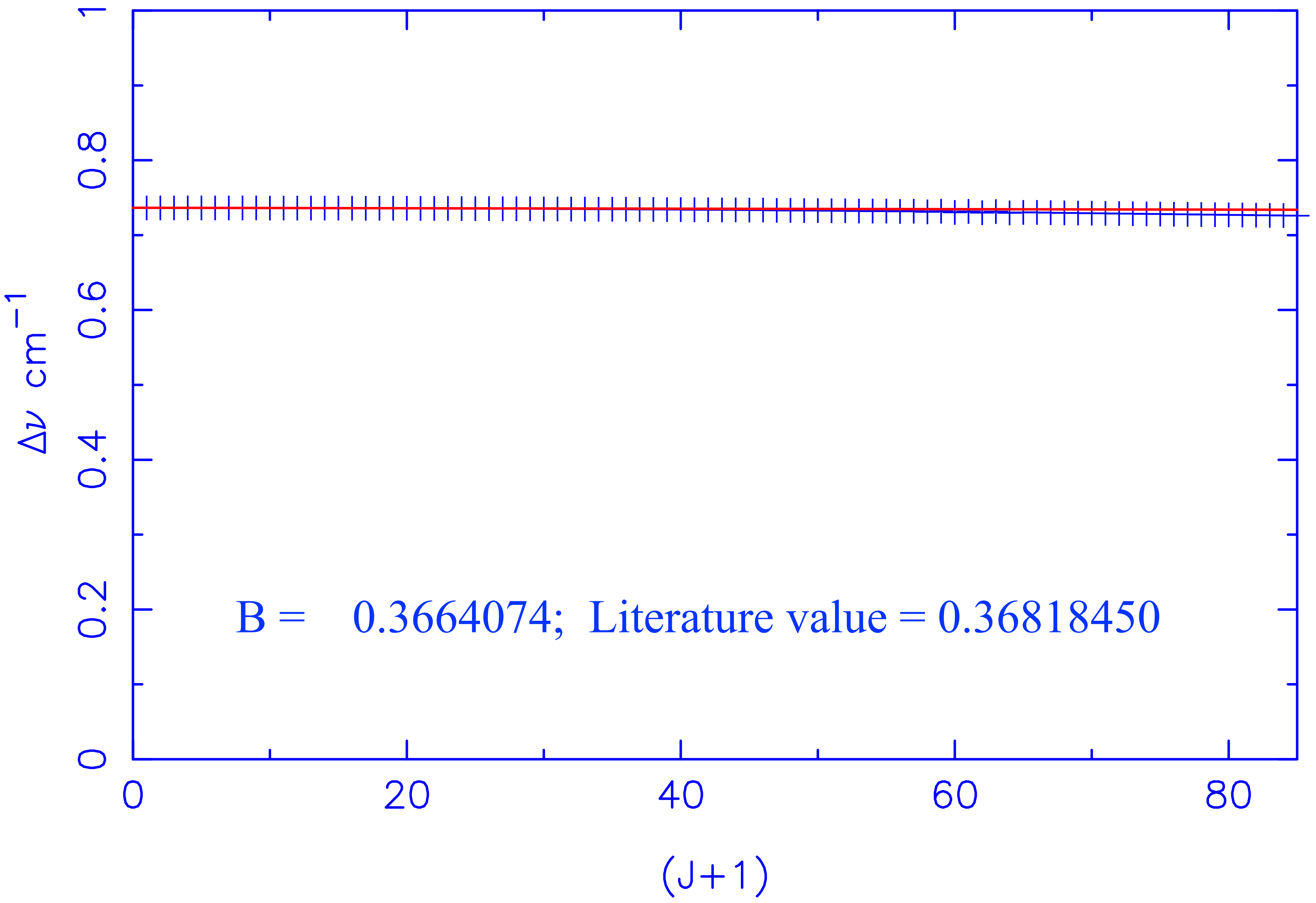


$^{16}O^{12}C^{18}O$ rotation band



B = 0.3680750; Literature value = 0.36818450

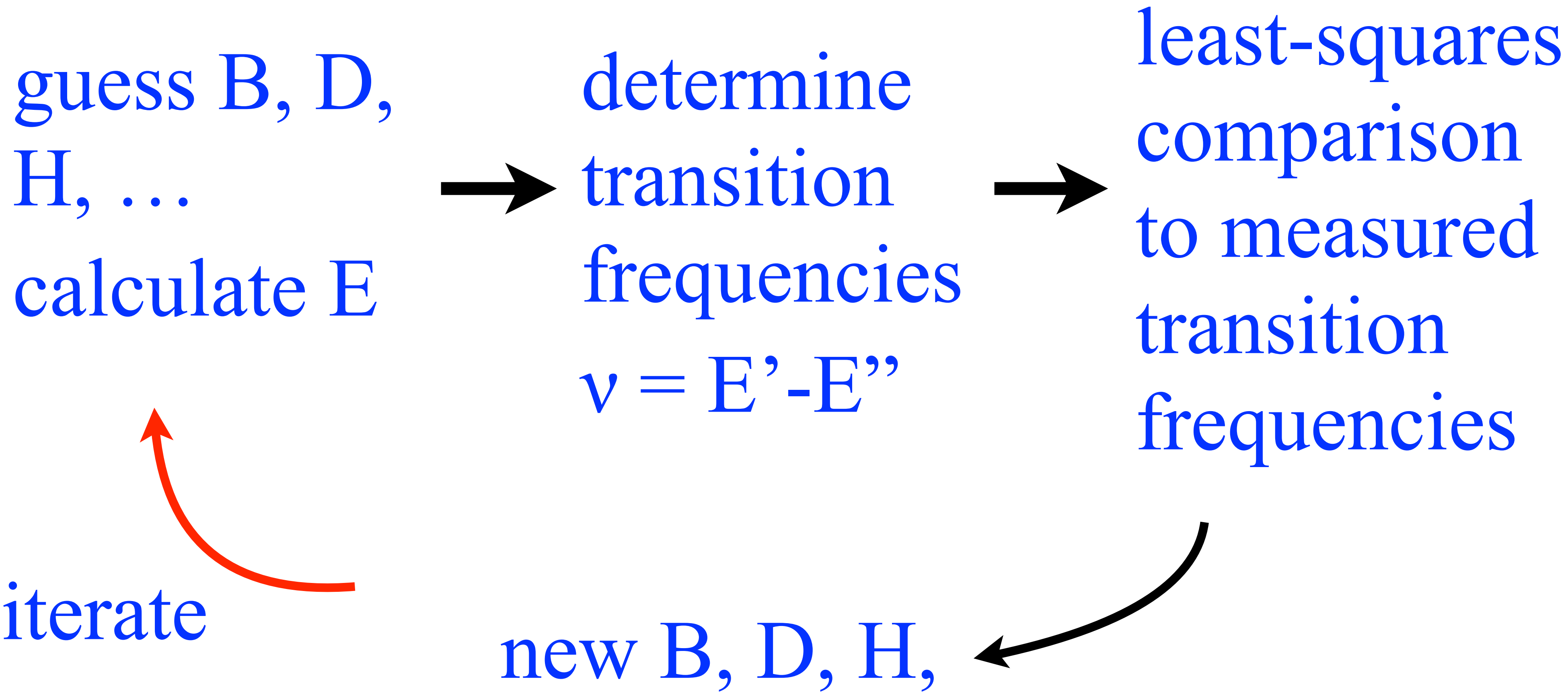
$^{16}O^{12}C^{18}O$ rotation band



B = 0.3664074; Literature value = 0.36818450

Rotational Energy of a Linear Molecule

$$E = BJ(J+1) - DJ^2(J+1)^2 + HJ^3(J+1)^3 + \cdots$$



guess B, D, H, …

calculate E

determine transition frequencies

$\nu = E' - E''$

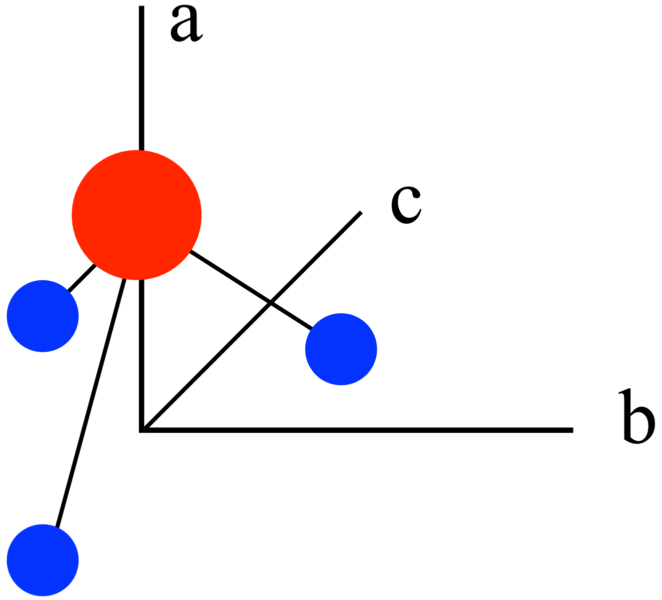
least-squares comparison to measured transition frequencies

new B, D, H,

iterate

Symmetric Top Molecules

Examples are NH_3, CH_3Cl, PH_3



$I_A \neq 0$

$I_B = I_C \neq 0$

Energy - Symmetric Top

$$A = \frac{h}{8\pi^2 c I_A} \qquad B = \frac{h}{8\pi^2 c I_B}$$

$$E(J,K) = BJ(J+1) + (A-B)K^2$$

J is the total angular momentum quantum number J = 0, 1, 2, …

K is the component of angular momentum about the figure axis:
K= J, J-1, J-2, … -J

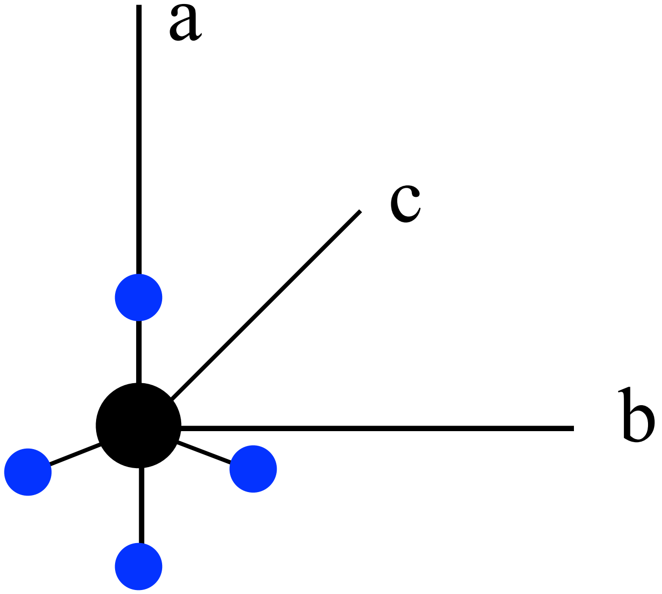
Energy - Symmetric Top

$$E(J,K) = BJ(J+1) + (A-B)K^2$$

when Coriolis and other resonances are accounted for the energy expression is much more complicated. See Poynter RL, Margolis JS. The ground state far infrared spectrum of NH_3 . Mol Phys 1983;48:401-18.

Spherical Top Molecules

Examples are CH_4, CCl_4, SF_6



$$I_A = I_B = I_C$$

Energy - Symmetric Top

$$B = \frac{h}{8\pi^2 c I_B}$$

$$E(J) = BJ(J+1)$$

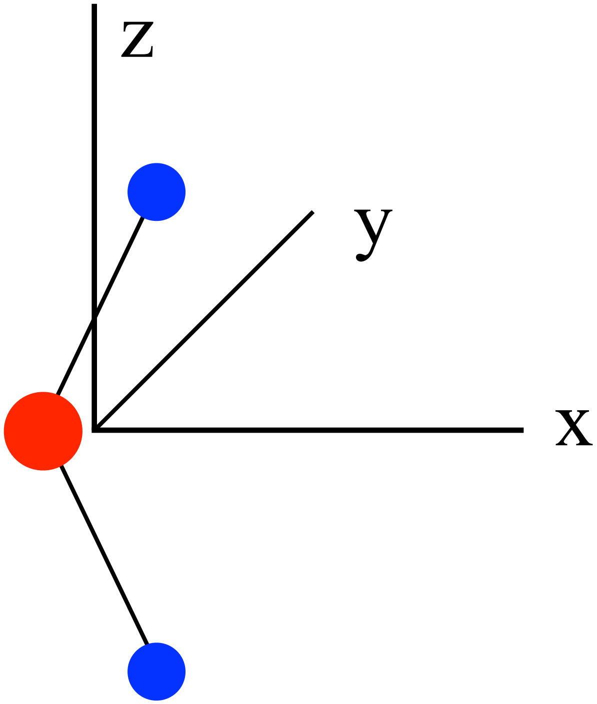
J is the total angular momentum quantum number J = 0, 1, 2, …

Note inclusion of resonances gives a much more complicated Hamiltonian.

see
Jean-Paul Champion, Gérard Pierre, Hubert Berger, Jean Cadot, Vibration-rotation energies of harmonic and combination levels in tetrahedral XY_4 molecules: Analysis of the $2\nu_2$ and $\nu_2 + \nu_4$ bands of $^{12}CH_4$,Journal of Molecular Spectroscopy 79, 281–294 (1980).

Asymmetric top molecules

Examples are H_2O, HNO_3, H_2CO, O_3, …



$$I_A \neq I_B \neq I_C \neq 0$$

Energy - Asymmetric Top

$$A = \frac{h}{8\pi^2 c I_A} \qquad B = \frac{h}{8\pi^2 c I_B} \qquad C = \frac{h}{8\pi^2 c I_C}$$

$$E(J, K_a, K_c) = complicated$$

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