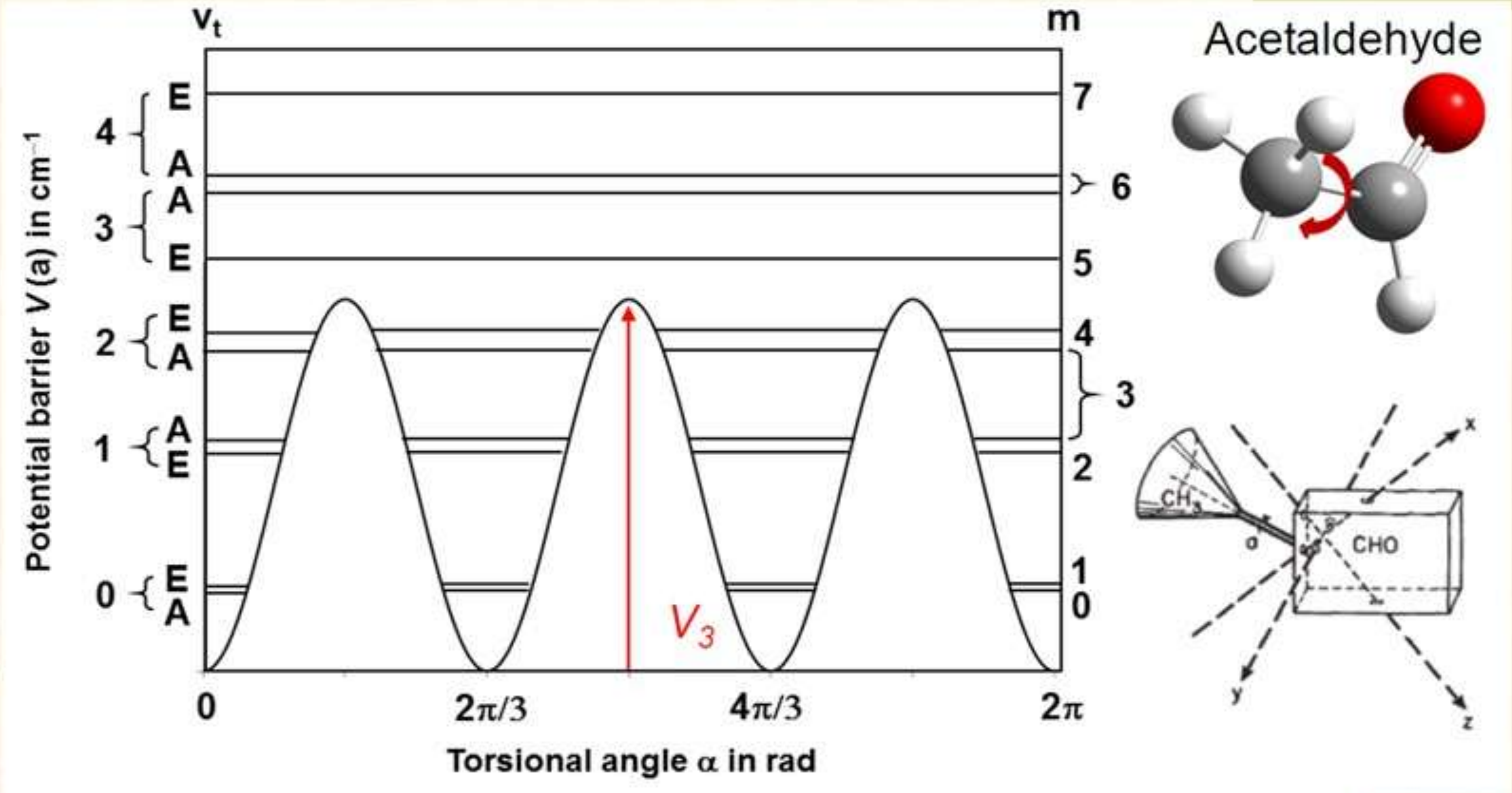
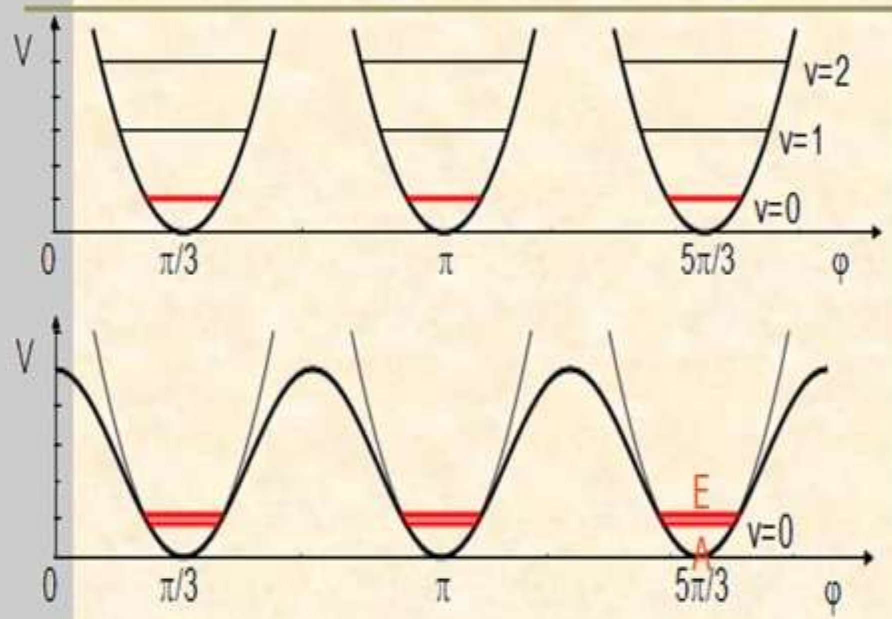
Internal rotation

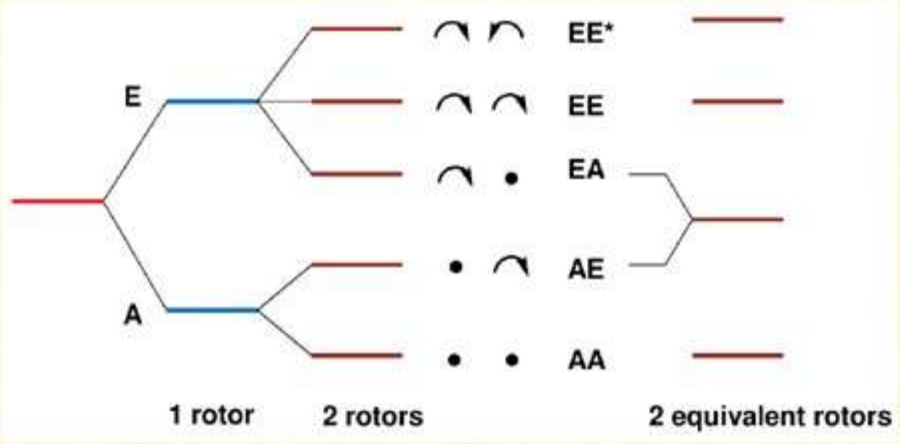


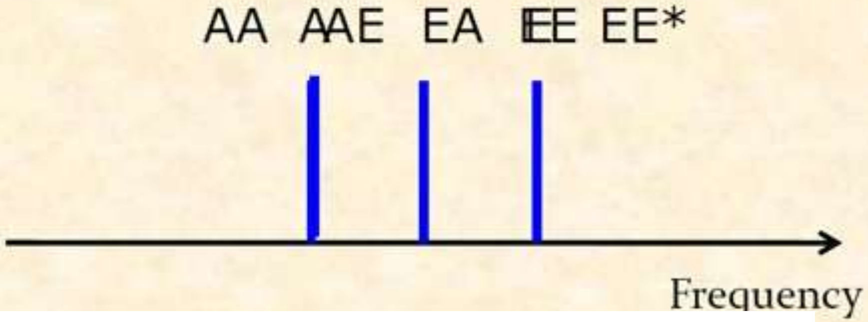
$$V(\alpha)=\frac{V_3}{2}(1-\cos 3\alpha)+\frac{V_6}{2}(1-\cos 6\alpha)+\cdots$$

Lin and Swalen
Rev. Mod. Phys
1959

Internal rotation

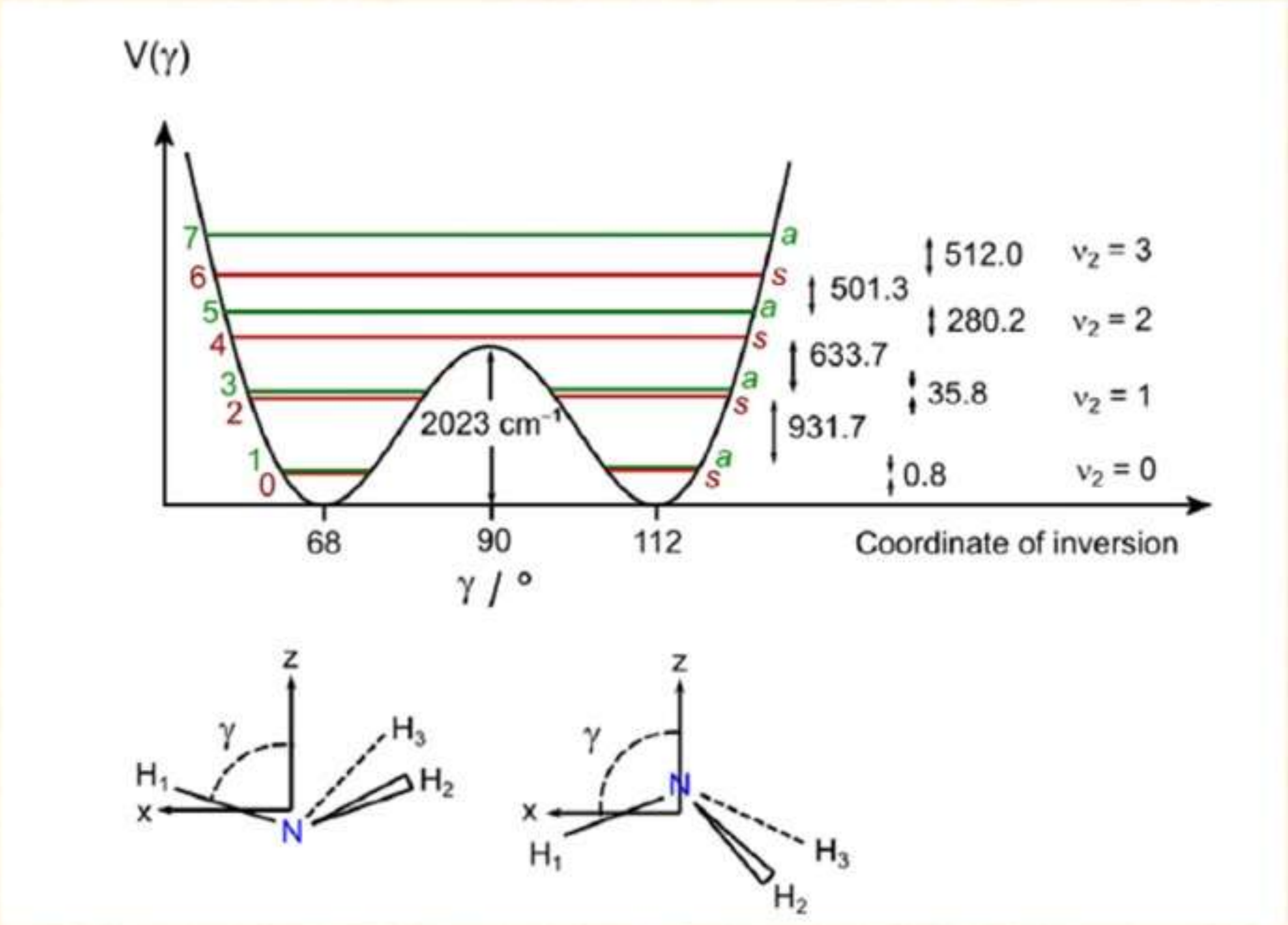






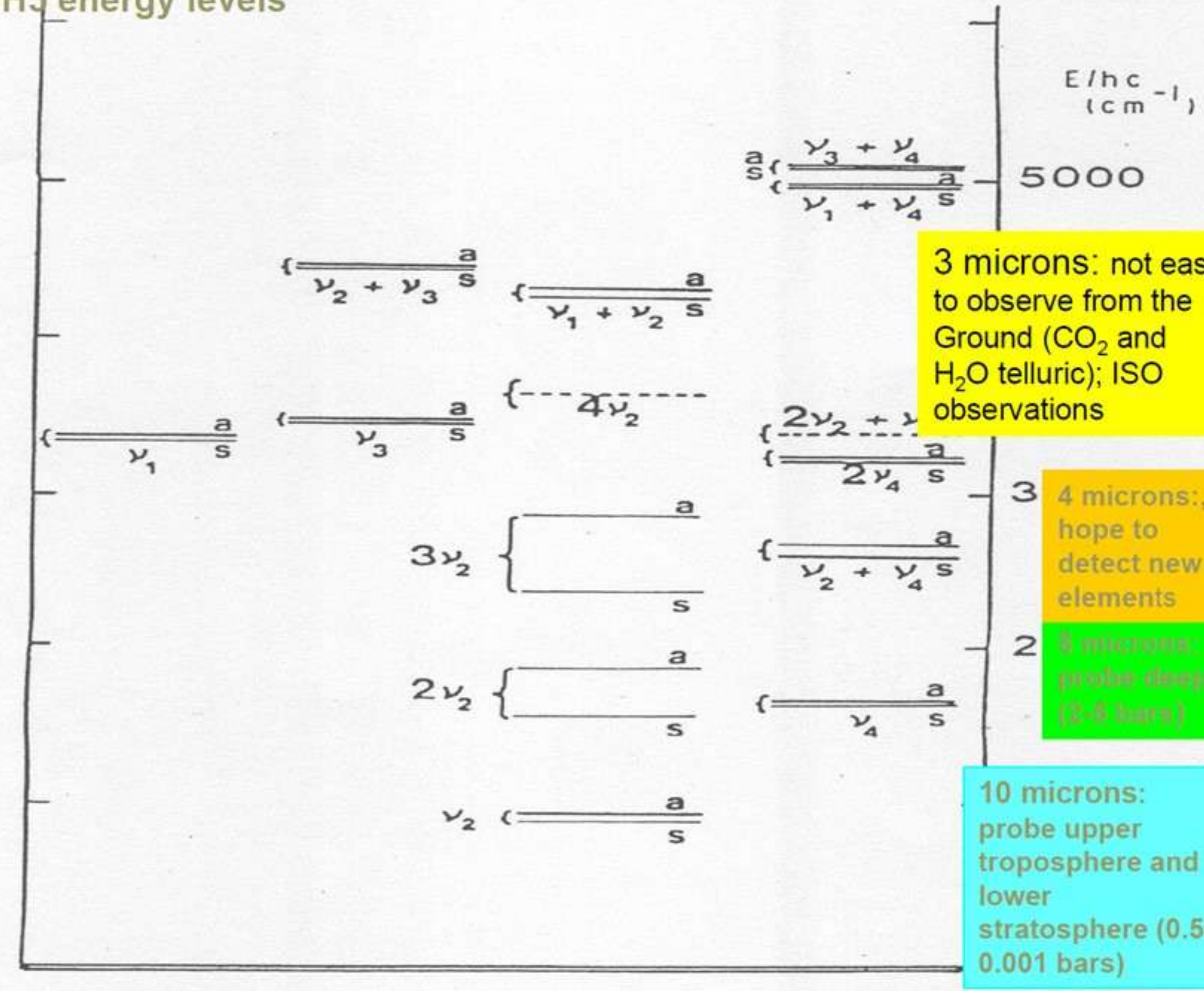
What makes NH_3 so hard???

Large amplitude motion : inversion



NH$_3$ ENERGY LEVELS

NH3 energy levels



3 microns: not easy to observe from the Ground (CO$_2$ and H$_2$O telluric); ISO observations

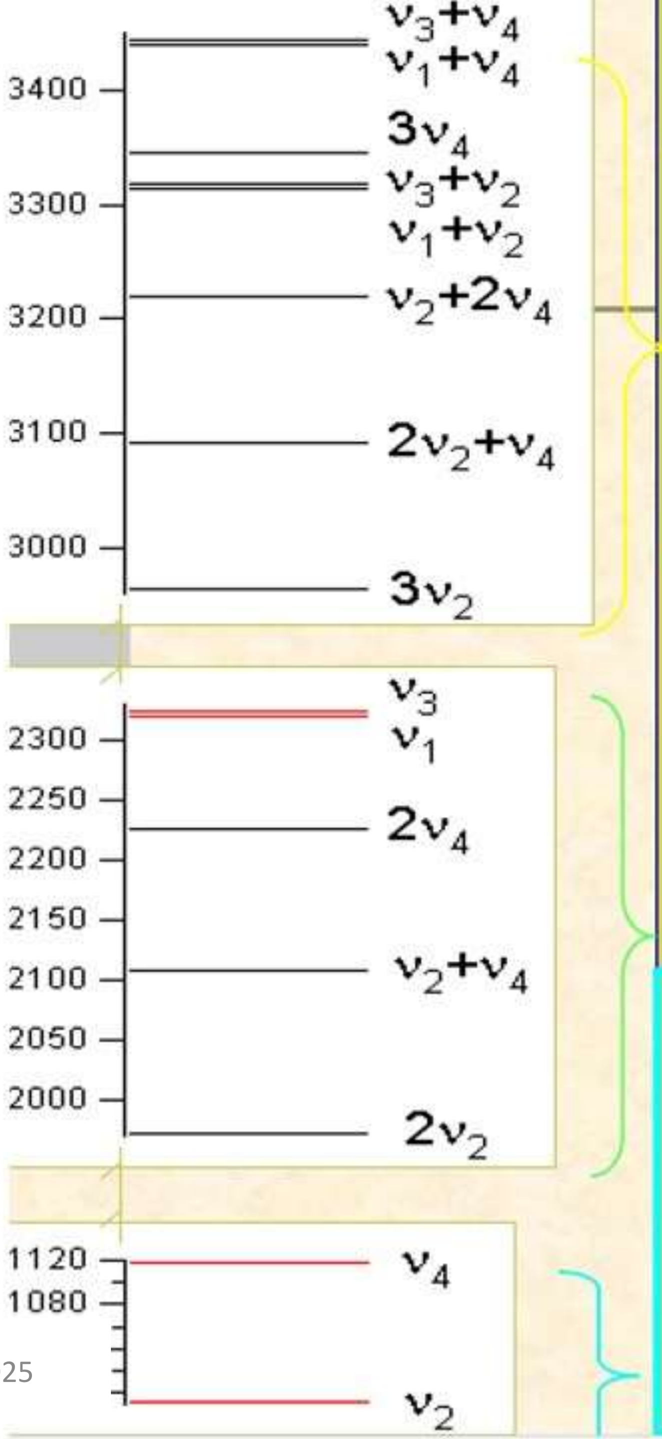
4 microns:, hope to detect new elements

5 microns: probe deep (2-6 bars)

10 microns: probe upper troposphere and lower stratosphere (0.5-0.001 bars)

PH_3 energy levels

As NH_3, PH_3 presents an inversion energy level



-The band $3\nu_2$:

-Low resolution of line positions (Maki et al. JCP 1973)

- The octad bands:

New line positions and intensities measurements (Butler et al., JMS 2006)

The Global analysis of the Dyad, pentad and octad bands: (Nikitin et al., JMS 2009)

• The $2\nu_2/\nu_2+\nu_4/2\nu_4/\nu_1/\nu_3$ pentad:

-Frequencies: rms=**0.009 cm^{-1}** up to J=16

(Tarrago et al. **JMS**, 1992, Ulenikov and al. **JMS**, 2002)

-Intensities: rms= **13%** (Tarrago et al. **JMS**, 1992

•The ν_2/ν_4 dyad:

-Frequencies: rms=**0.0004cm^{-1}** up to J=22

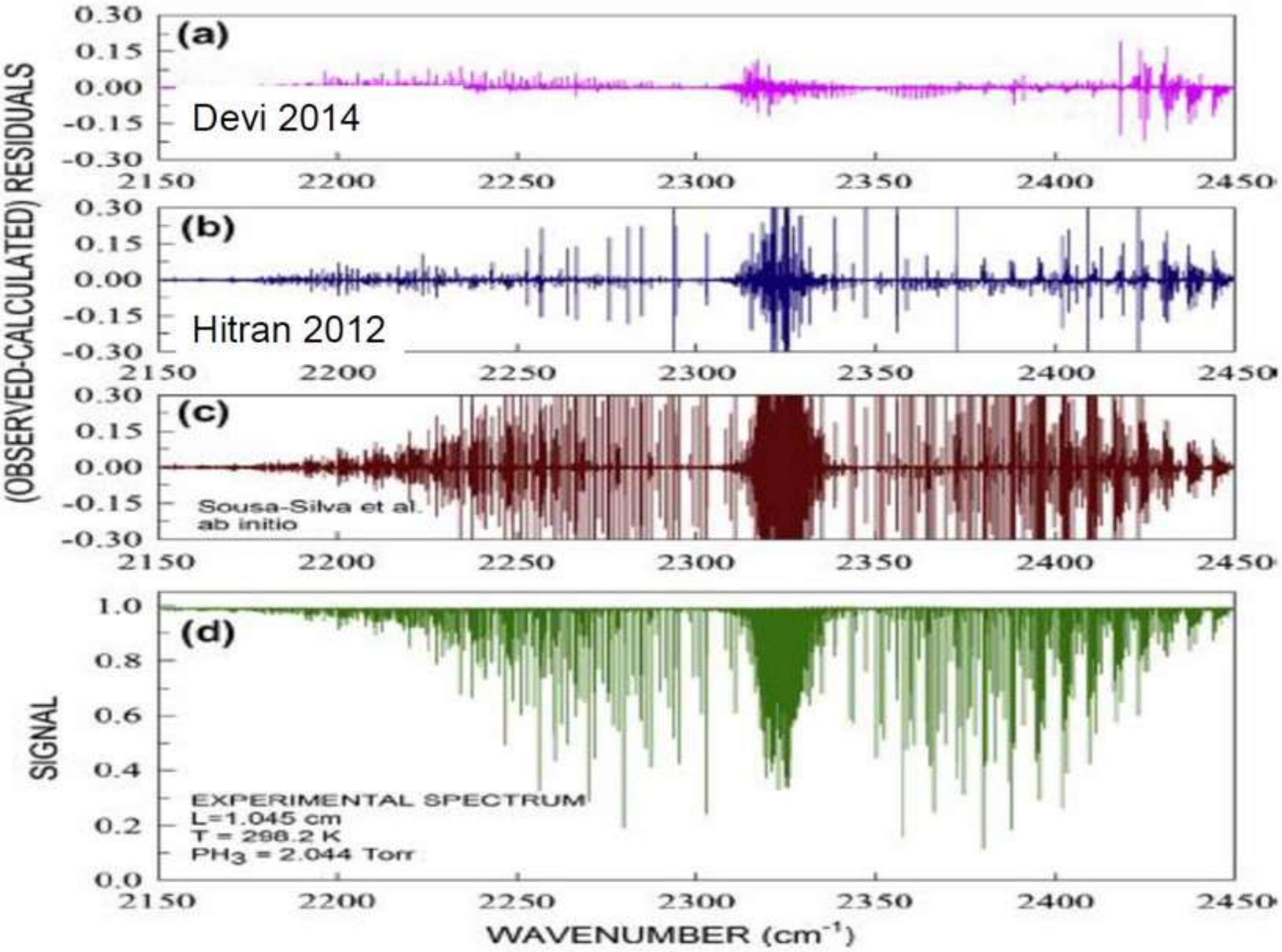
(Fusina and al, **J.Mol.Struc.**,2000)

-Intensities: rms=**2%** (Brown and al., **JMS**, 2001)

-Linewidth: self Broadening coefficients

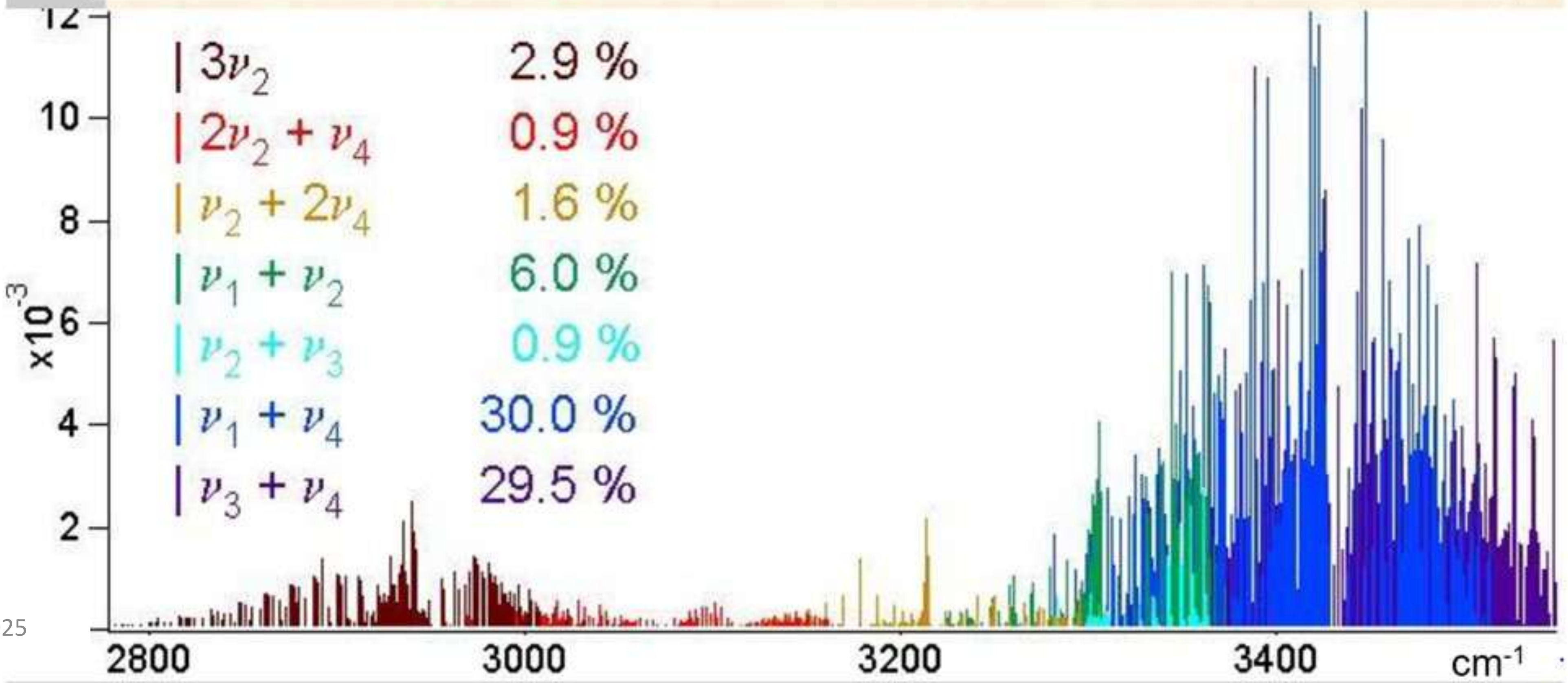
(J. Salem and al, JMS, 2004)

Observed-calculated in the pentad region



ANALYSIS OF THE 3 MICRON REGION :

- Data 2750 - 3600 cm^{-1} : 8075 line positions and intensities obtained by L. R. Brown and R. Butler (Kitt Peak FTS, spectral resolution of 0.0115 cm^{-1}).
- Analysis of spectra: 4095 lines identified.
- 7 vibrational states simultaneously analysed
- 79% of intensity of region accounted for, - Unassigned state is $3\nu_4$



Isotopes

Isotopes can be treated as regular molecular structures : isotopic ratio have no reason to be similar to Solar System values (Warning : terrestrial databases include the « standard » terrestrial ratio)

Special case : some isotopes change the symmetry of the molecule and can therefore have a very different spectroscopy – ex. CH_3D

Emission and absorption coefficients

Calculation of transition probabilities =>

* related to the molecular dipole momentum of the molecule

- Depends on the population of the emitting/absorbing level
- Basis : spontaneous, stimulated and absorption coefficients (Einstein coefficients)
- Emission and radiation : Enstein relations A_{ij}, B_{ij}, B_{ji}

Boltzmann distribution

Spectral absorption coefficient

Types of line broadening

See

- Hanson, Summer School on Combustion and the Environment, June 19-24, 2022, Princeton, NJ, USA

https://cefrc.princeton.edu/sites/g/files/toruqf1071/files/documents/Lecture%20Notes%20-%20Hanson.pdf

Additional complexities in radiative transfer

1. Far wings effects

2. Collision Induced absorptions

Far wings effects

Very strong lines can dominate the opacity very far from line center: the Lorentz line shape reaches the limit of validity when applied too far from line center

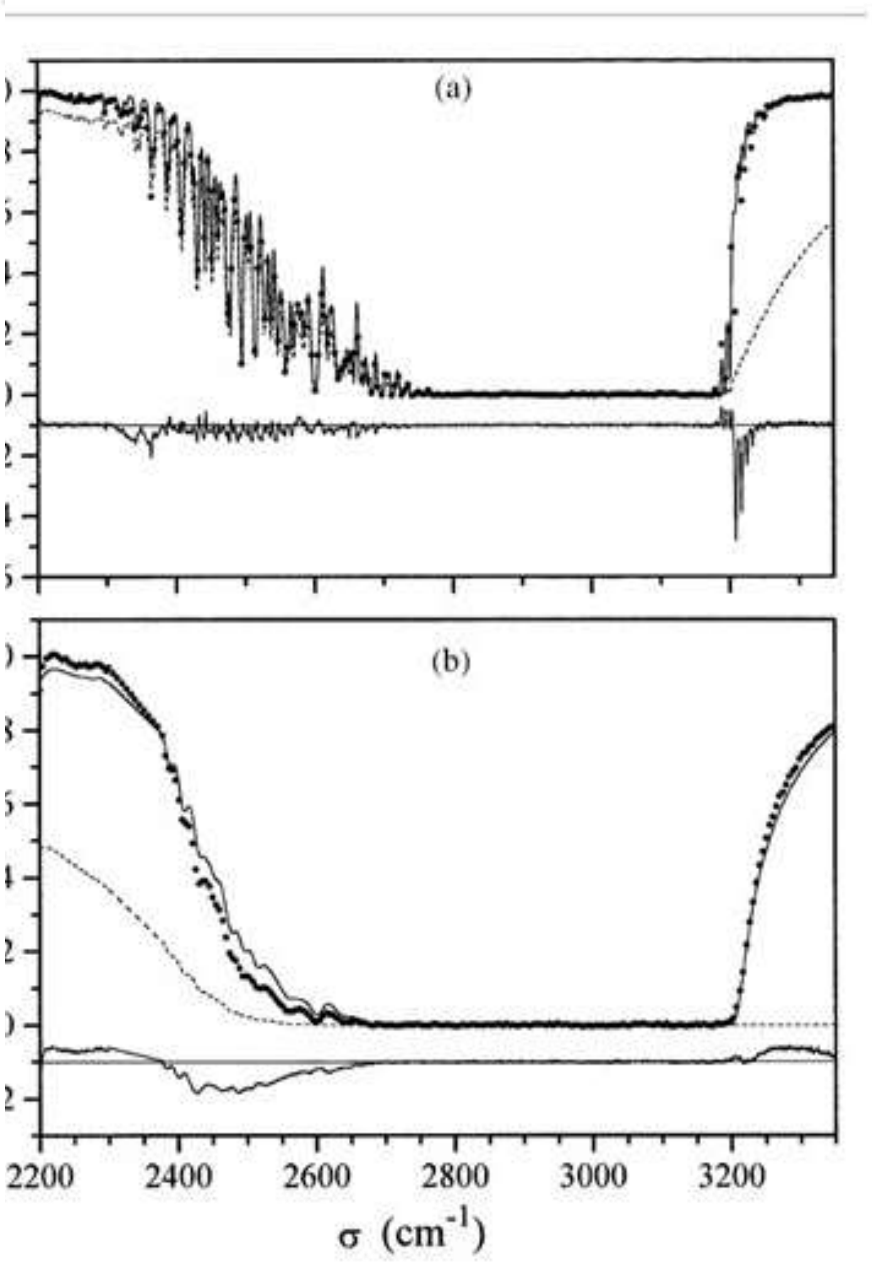


Fig. 1. Transmissions of CH_4–H_2 mixtures at room temperature (297 K) for a 3 m long path. ● are measured values. —— and - - - - have been calculated with the χ factor of Eq. (2) and purely lorentzian line shapes ($\chi=1$), respectively. (a) $d_{CH_4}=0.919$ Am, $d_{H_2}=25.0$ Am. (b) $d_{CH_4}=1.84$ Am, $d_{H_2}=163$ Am. Measured-calculated residuals are given below the spectra.

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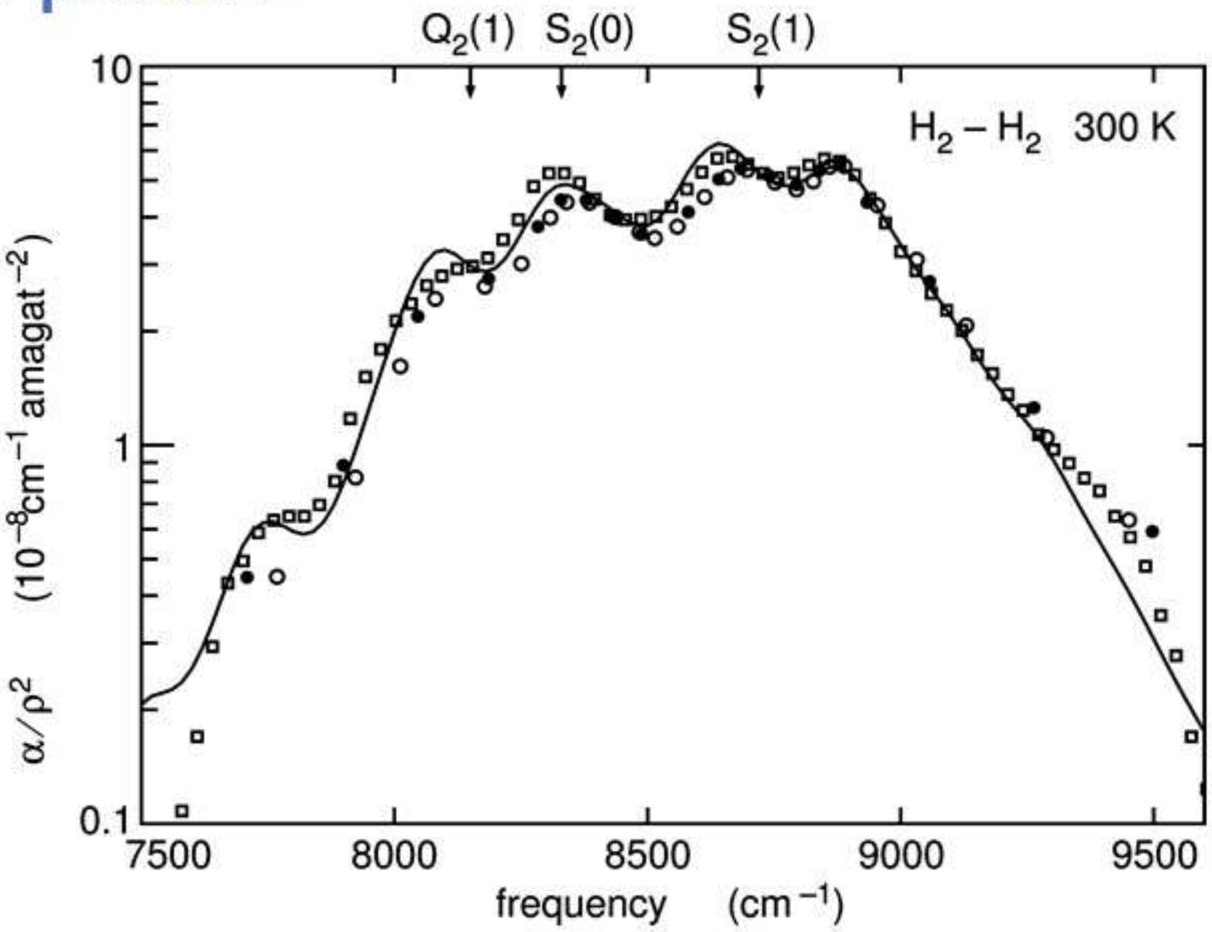
Hartmann et al, 2002

Collision induced absorption

The continuum of atmospheric spectra, outside strong molecular bands, is dominated by quadrupolar effects from homopolar diatomic molecules like N_2 or H_2



Abel et al., J. Phys. Chem. A 2011, 115, 25, 6805–6812

Databases: how to compute a spectroscopic database ?

- Example = Hitran extraction
- How to retrieve the database ?
  - Schrödinger equation in Born-Oppenheimer approximation
  - Calculation of a database ⇔ calculation of the hamiltonian of the molecule
- Practical approaches :
  - combination of prediction/experiments => parametrized hamiltonian
  - Ab initio calculations
  - What is the necessary accuracy for practical use ?