From Lines to States without a Model

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What is it all about?

Typical Model Based Data Evaluation

- Chose appropriate model = Hamiltonian with parameters
  typical parameters: rotational constant, centrifugal distortion constant
- calculate parameter dependent lines Hamiltonian
- fit the calculated lines to the measured lines to get the parameter values

What is it all about?

CH_5^+: Prototype of a Floppy Molecule

- 120 different, energetically equivalent arrangements of the nuclei, only small energy barriers[1]
- Vibration and rotation not separable as common[2]
- First model only available for a short time

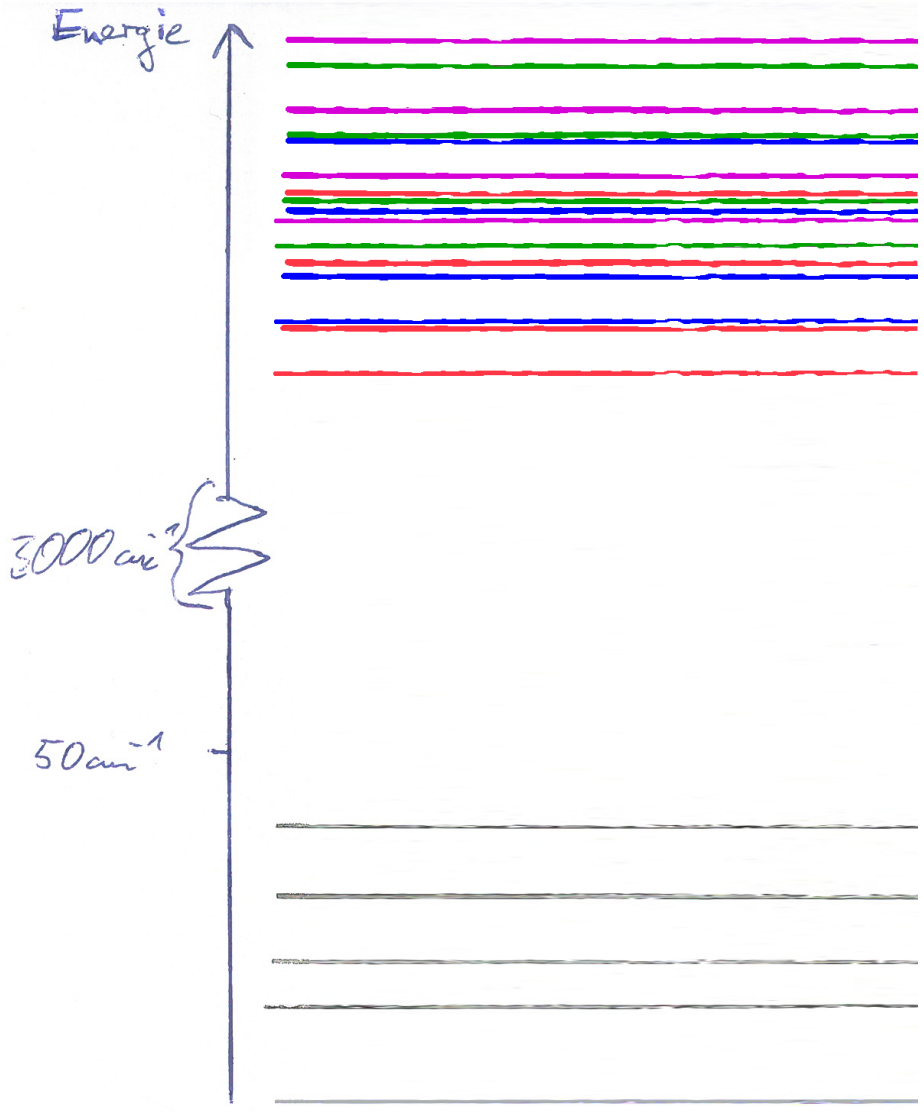
$\Longrightarrow$ Usual methods not usable

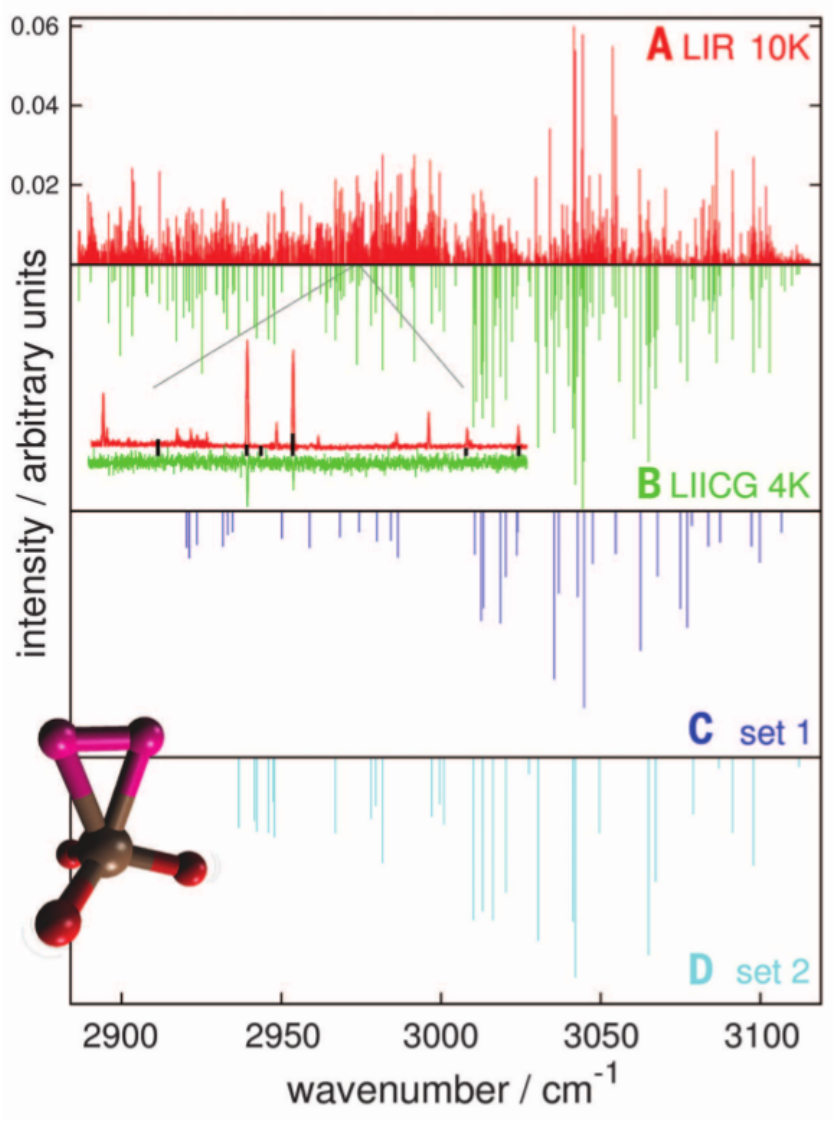
[1] Huang et al. 2006, Kumar et al. 2006, Jin et al. 2006

[2] Schmiedt et al. 2015

What happened so far?

Measurements

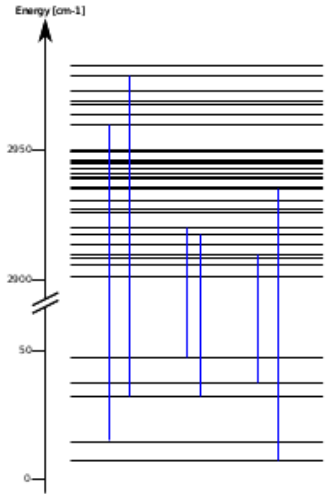
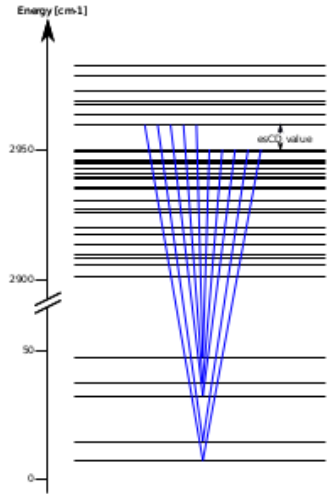
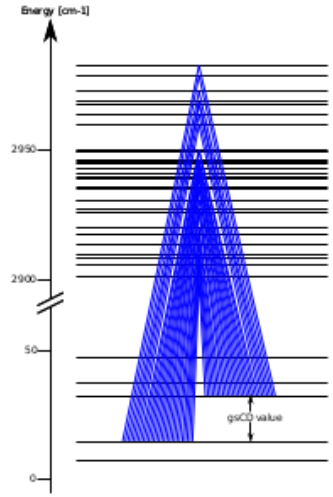




Asvany et al. 2005

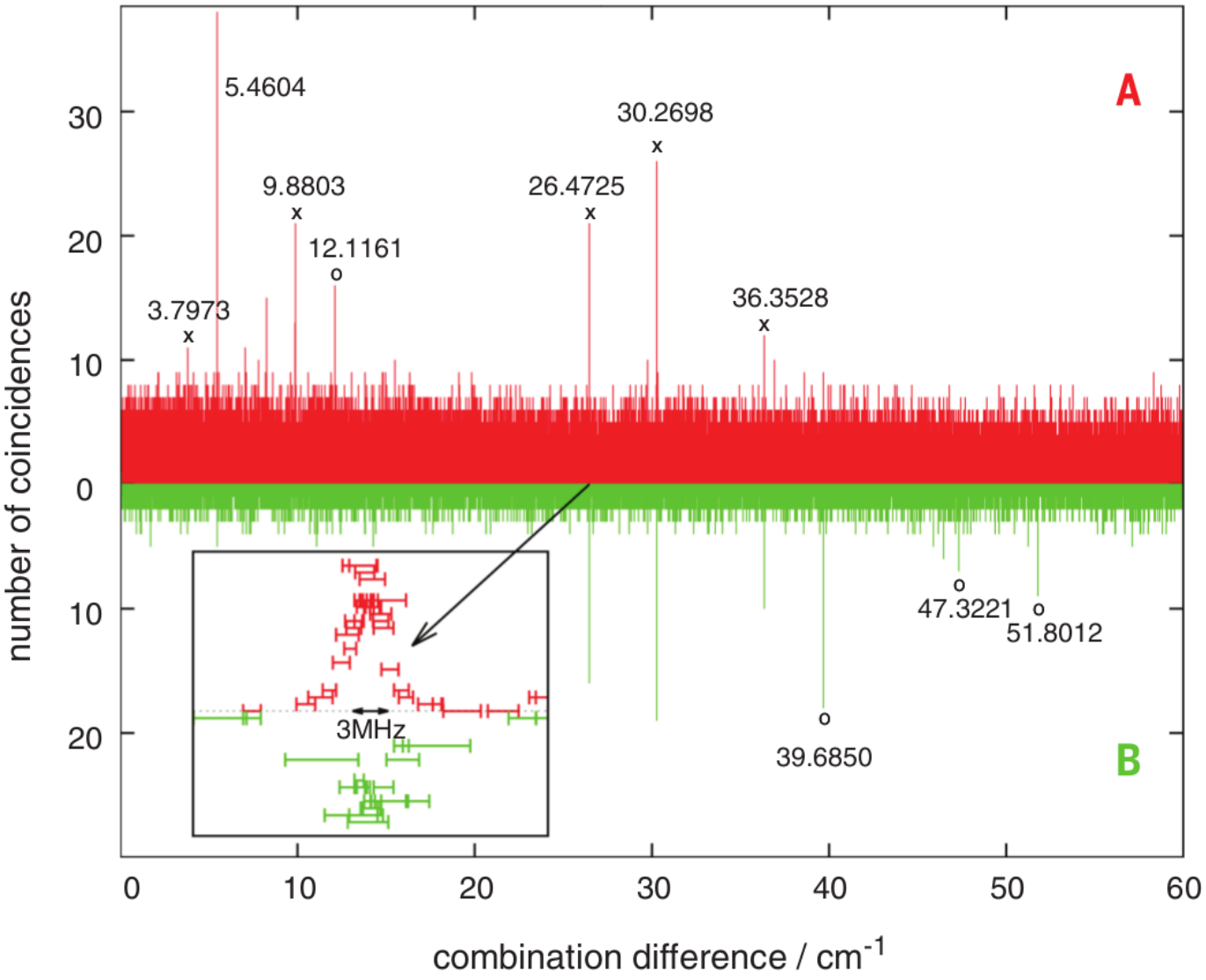
What happened so far?

Data Evaluation using Combination Differences (CDs)

	accidental CD (aCD)	**excited state CD (esCD)**	**ground state CD (gsCD)**
			
Meaning	no	energy difference between two vibrationally excited states	energy difference between two vibrational ground states
Typical number of occurrence	~ 1	$\lesssim$ #vibrational ground states	$\lesssim$ #vibrationally excited states

What happened so far?

Data Evaluation using CDs at two Temperatures: CD spectra



Asvany et al. 2015

Model-less Data Evaluation

Common Approaches and Plausible Reasoning Made Systematic

- Simplification based (Moruzzi)
- Temperature based
- Mixed: Temperature, combinatorics and plausible reasoning

New: Data evaluation completely based on combinatorics

Comparison: $\rightarrow$ Bonus track

What is New?

Results from my Diploma Thesis

- Further development of the CD spectra
  - CD spectra as kernel density estimators
    - ★ Problem and idea
    - ★ Choice of the kernel
    - ★ Choice of the bandwidth
  - Using scaling behavior for noise cancellation $\rightarrow$ Bonus track
- From CD peaks to states — a new method
  - Reconstruction of the vibrational ground states
  - Rekonstruction of the vibrationally excited states

Further Development of the CD Spectra

CD as kernel density estimators: Problem and Idea

Problem: CD values have measurement errors
$\Longrightarrow$ How to count?

Answer of Asvany et al.: #neighboring CDs within the error
$\Longrightarrow$ New Problem$\rightarrow$ Bonus track

Finding: CD spectra are kernel density estimators (KDEs)
$\Longrightarrow$ Application of common knowledge about kernel density estimators
(see for instance: M. P. Wand and M. C. Jones. Kernel Smoothing. Chapman & Hall/CRC, 1995)

Further Development of the CD Spectra

What is a KDE?

$$\varrho(E) = \frac{1}{n}\sum_i K_b(E - CD_i)$$

n: #CDs

K_b: kernel function of bandwidth b

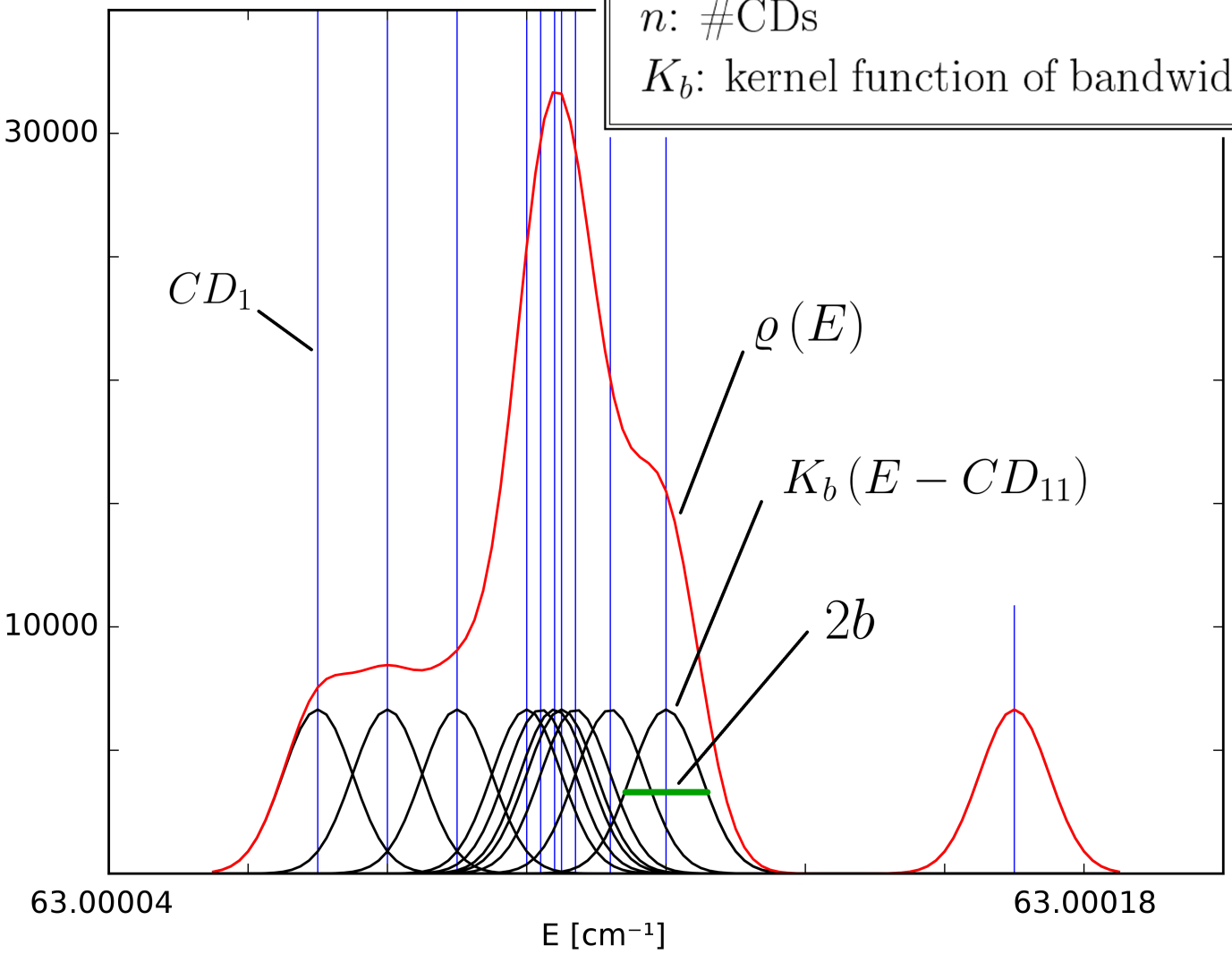


Figure based on Wand et al., 1995, Fig.~2.2

Further Development of the CD Spectra

Choice of the Kernel

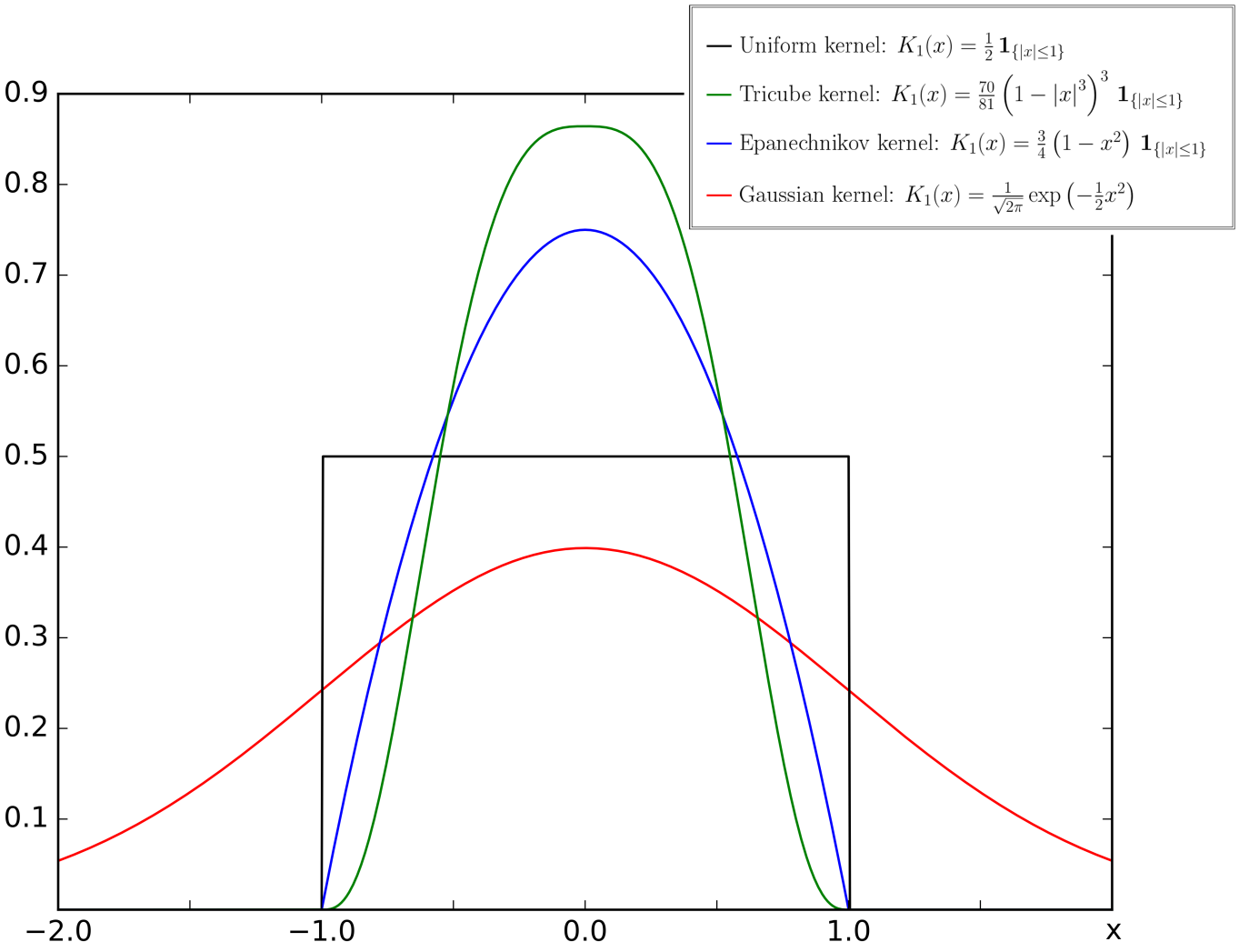


Figure inspired by Wand et al. 1995, Fig.~2.7

Further Development of the CD Spectra

Choice of the Bandwidth

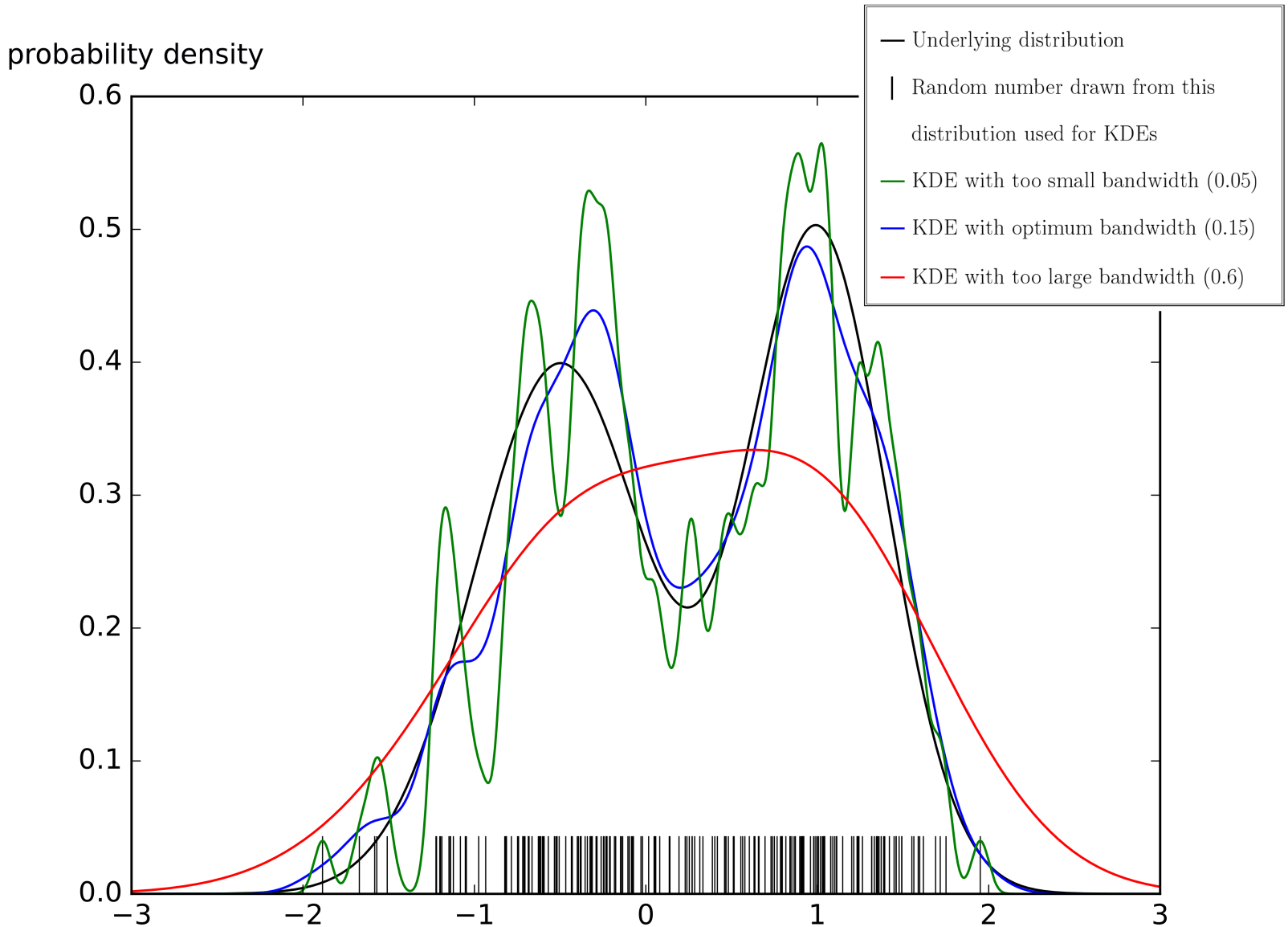
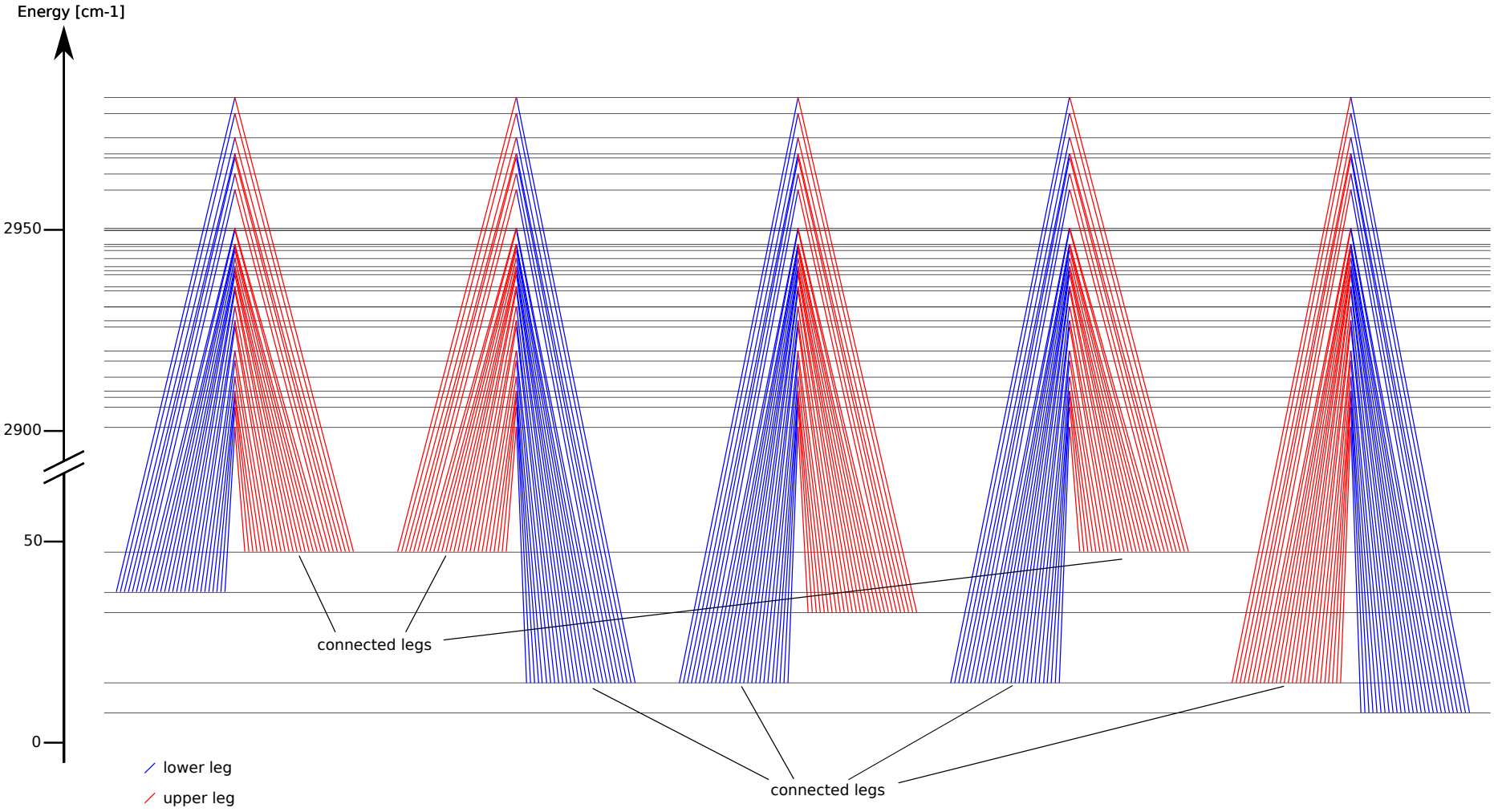


Figure based on Wand et al. 1995, Fig.~2.3

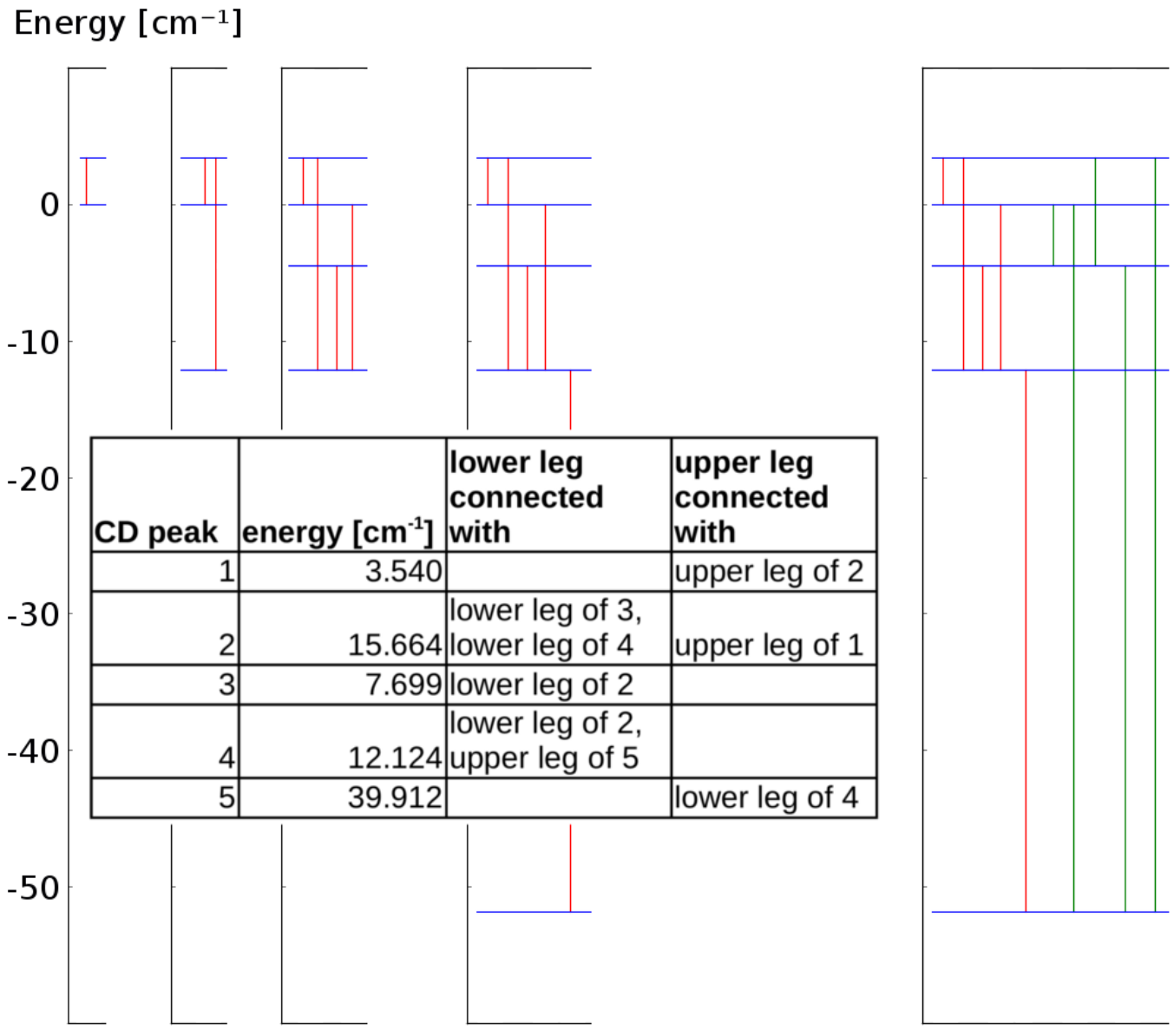
From CD Peaks to States



Selection rules and by mistake assigned aCDs are neglected in this sketch.

From CD Peaks to States

Reconstruction of the Vibrational Ground States



CD peak	energy [cm^{-1}]	lower leg connected with	upper leg connected with
1	3.540		upper leg of 2
2	15.664	lower leg of 3, lower leg of 4	upper leg of 1
3	7.699	lower leg of 2	
4	12.124	lower leg of 2, upper leg of 5	
5	39.912		lower leg of 4

From CD Peaks to States

Reconstruction of the Vibrationally Excited States