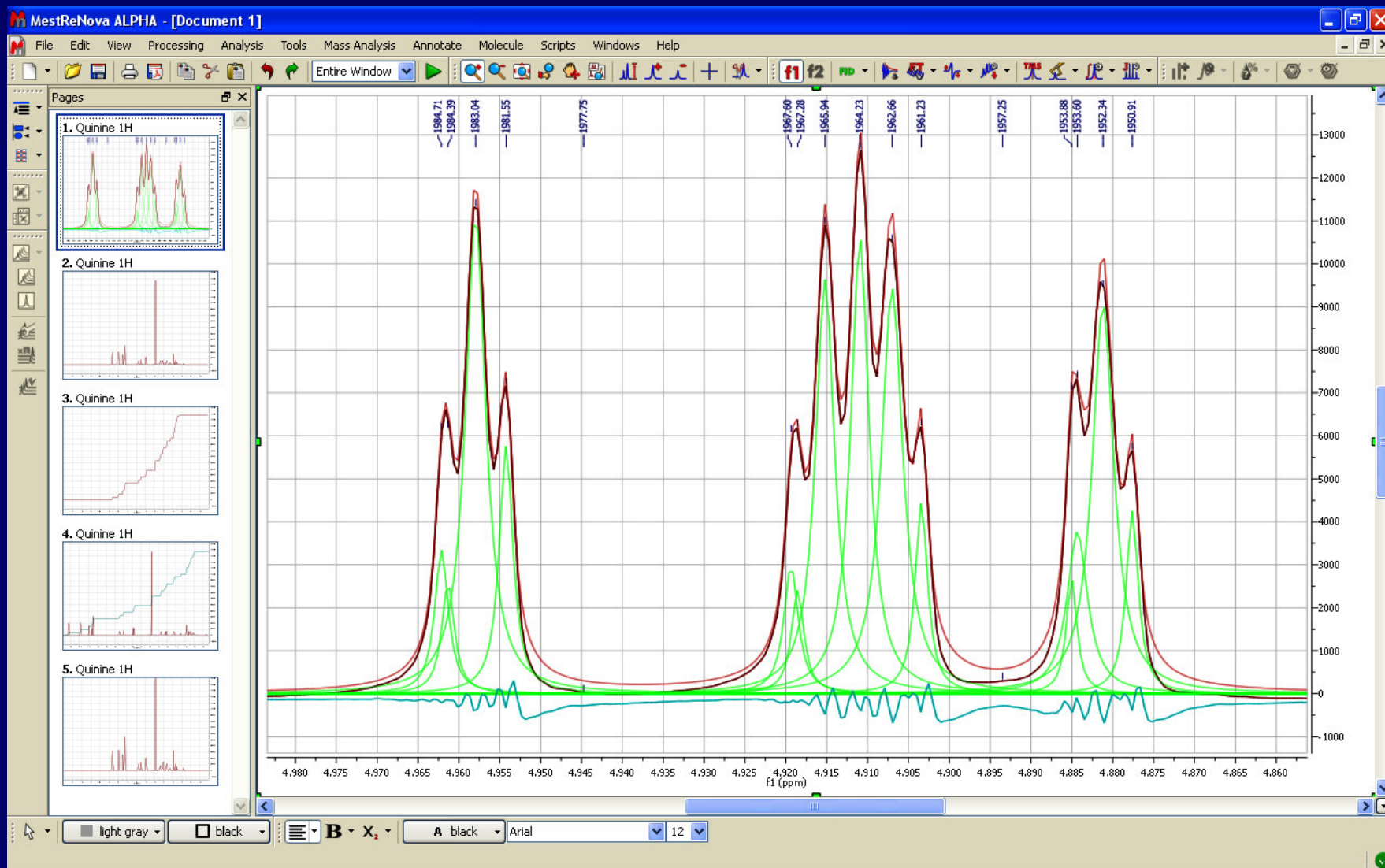


Peak shapes in NMR Spectroscopy

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I will touch upon these topics:

- Recent progress in automatic evaluation of NMR spectra: noise & linewidth estimate, Resolution Booster, J-Correlator, GSD
- **GSD** (Global Spectrum Deconvolution) is now **operative** !
- GSD residuals and the shapes of spectral peaks
- Classification of peak shape distortion sources
- Handling of peak shape distortions in GSD
- Perspectives of GSD

Fully automatic evaluation of NMR spectra: completed steps

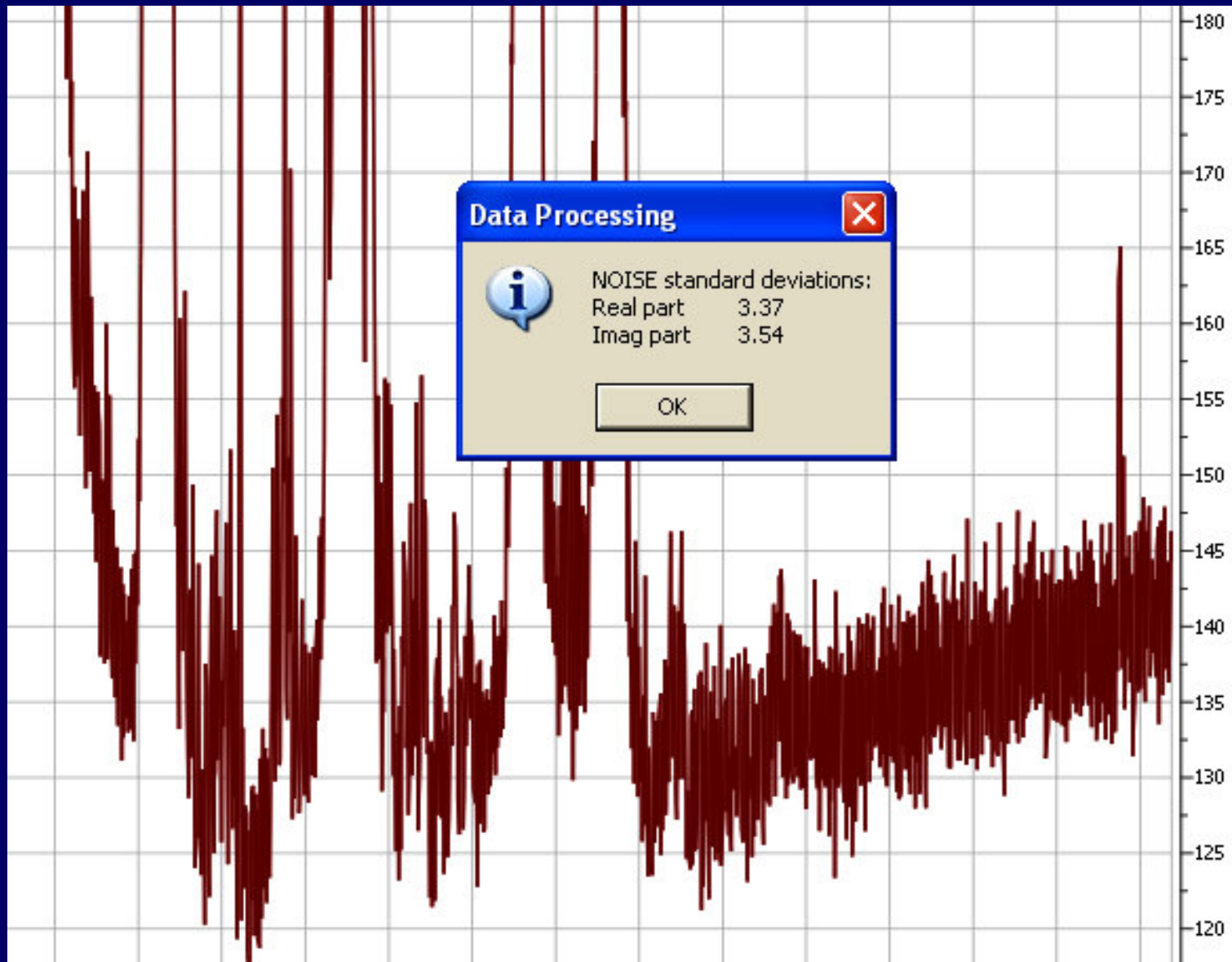
- ¹ **Robust Noise Estimator**
- ¹ **Robust Mean Linewidth Estimator**
- ² **RB: Resolution Booster**™
- ² **JC: J-Correlator**™
- ³ **GSD: Global Spectrum Deconvolution**

¹ to be published

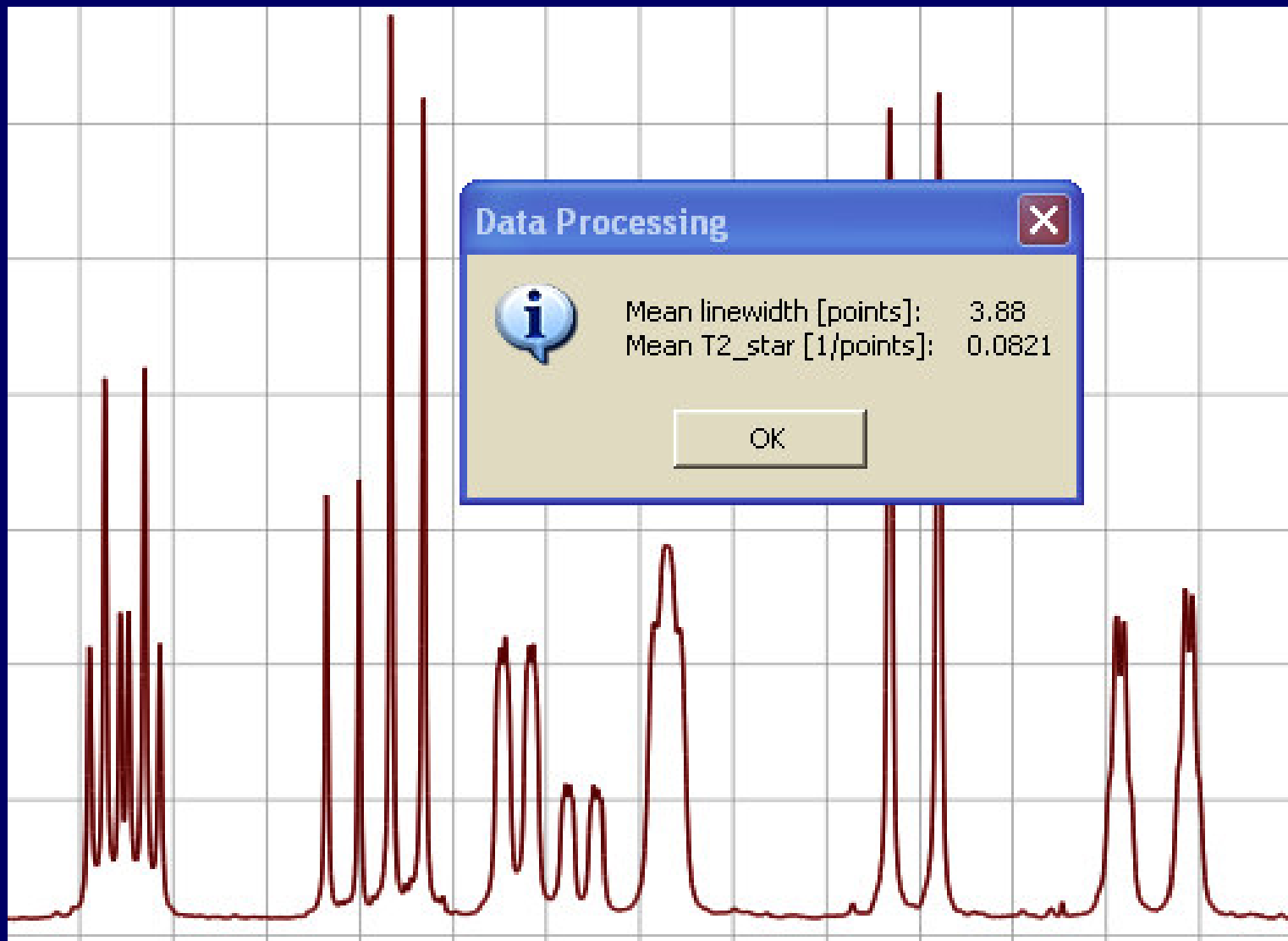
² ENC 2008 posters: see www.ebyte.it/stan/SS_Posters.html

³ First version became operative **last week**

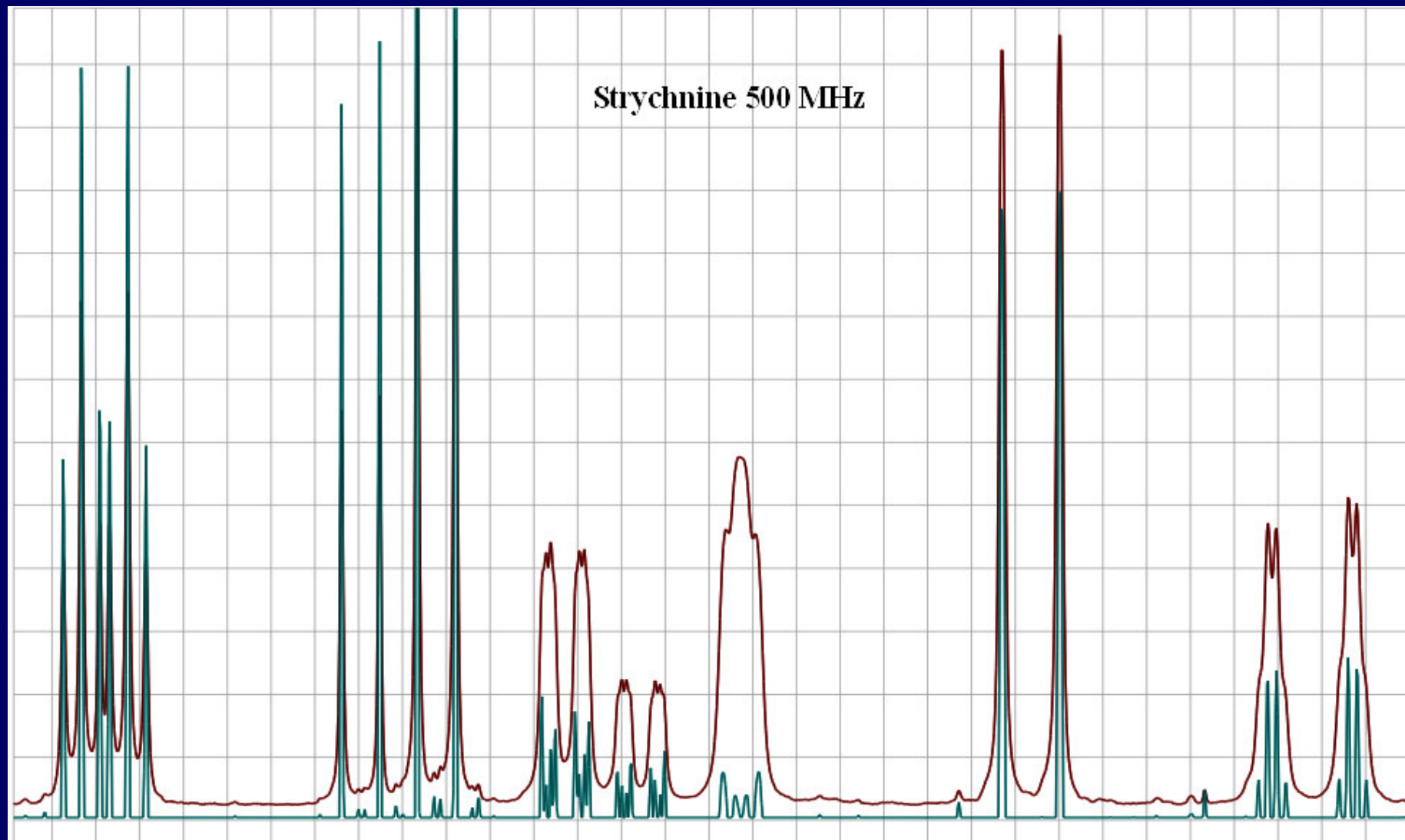
Noise Estimator



Harmonic-mean Linewidth Estimator

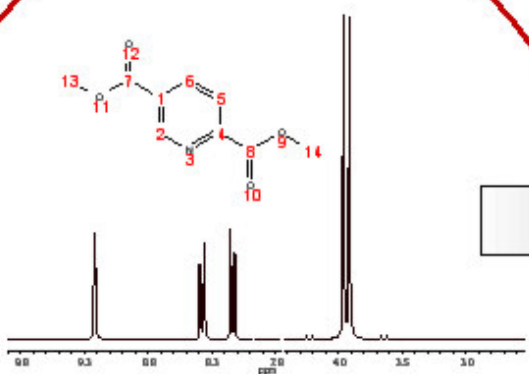


Example of Resolution Booster

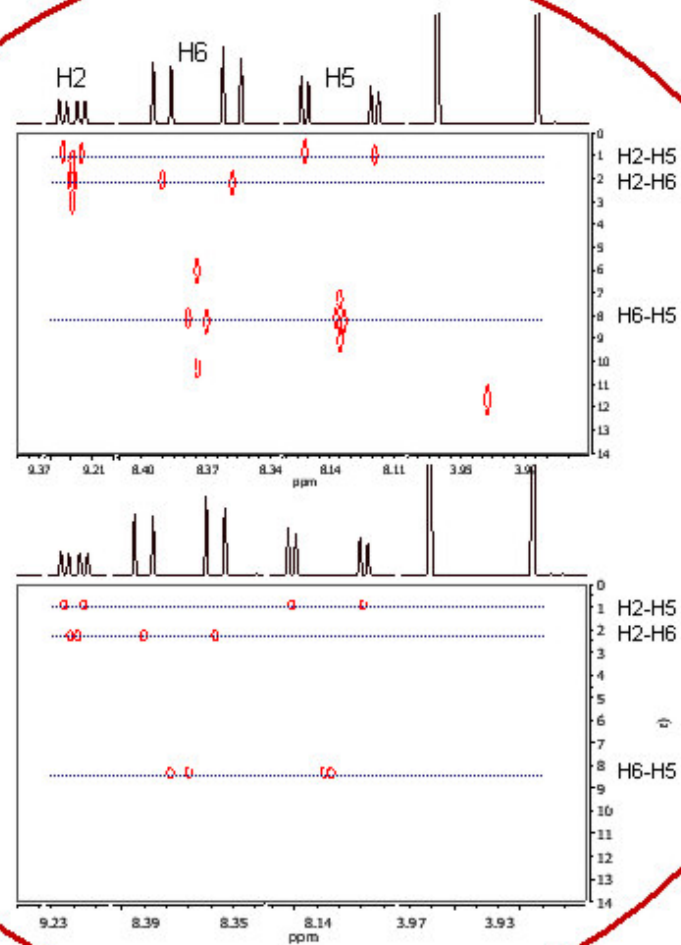


Example of J-Correlator

From 1D NMR to 2D NMR



JC



What is GSD ?

The idea is very simple:

Spectra contain peaks and artifacts => Let us carry out automatic multiplet deconvolution of the whole spectrum to recognize and extract all peaks and discard artifacts

Problems which need to be solved:

- Recognition of all significant peaks before fitting
- Assignment of realistic *a-priori* bounds to peak parameters
- Fitting of hundreds of parameters in a reasonable time

Resulting objects:

- * List of peaks (center, height, width, phase, shape)
- * Synthetic spectrum
- * Array of residues

Why must peaks be recognized and boxed-in prior to any fitting ?

Spectral peaks have *approximately* Lorentzian shapes:

$$P(h, \Omega, \Delta; \nu) = h L((\nu - \Omega) / (\Delta / 2))$$

$$L(x) = 1 / (1 - ix)$$

All nearly complete sets of Lorentzian-shaped functions are approximately linearly dependent

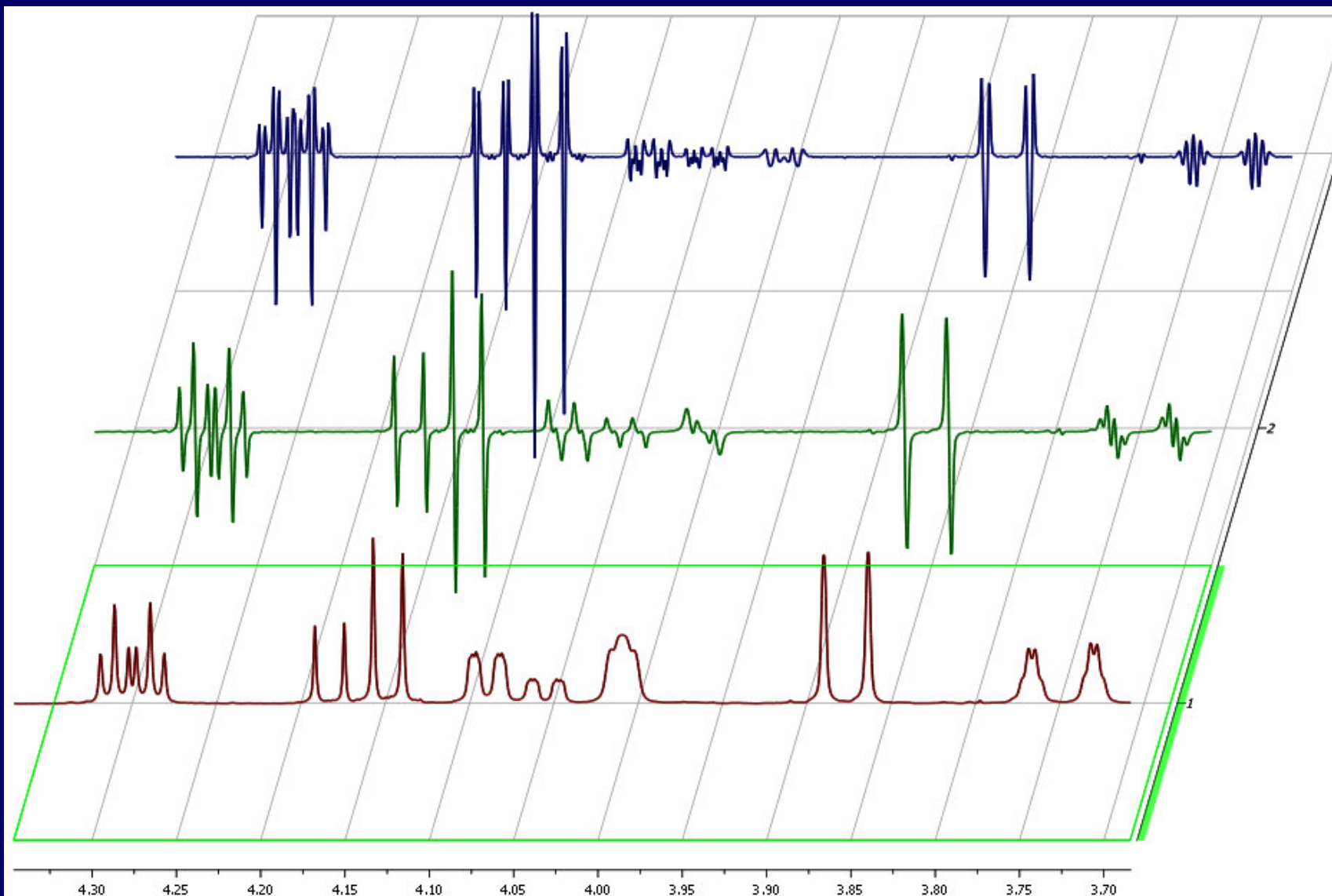
A consequence:

Lorentzian deconvolutions are numerically ill defined

A Lorentzian peak can be approximated very well by three or five different Lorentzian peaks (=> acute danger of **peak spawning**).

Recognition of significant peaks

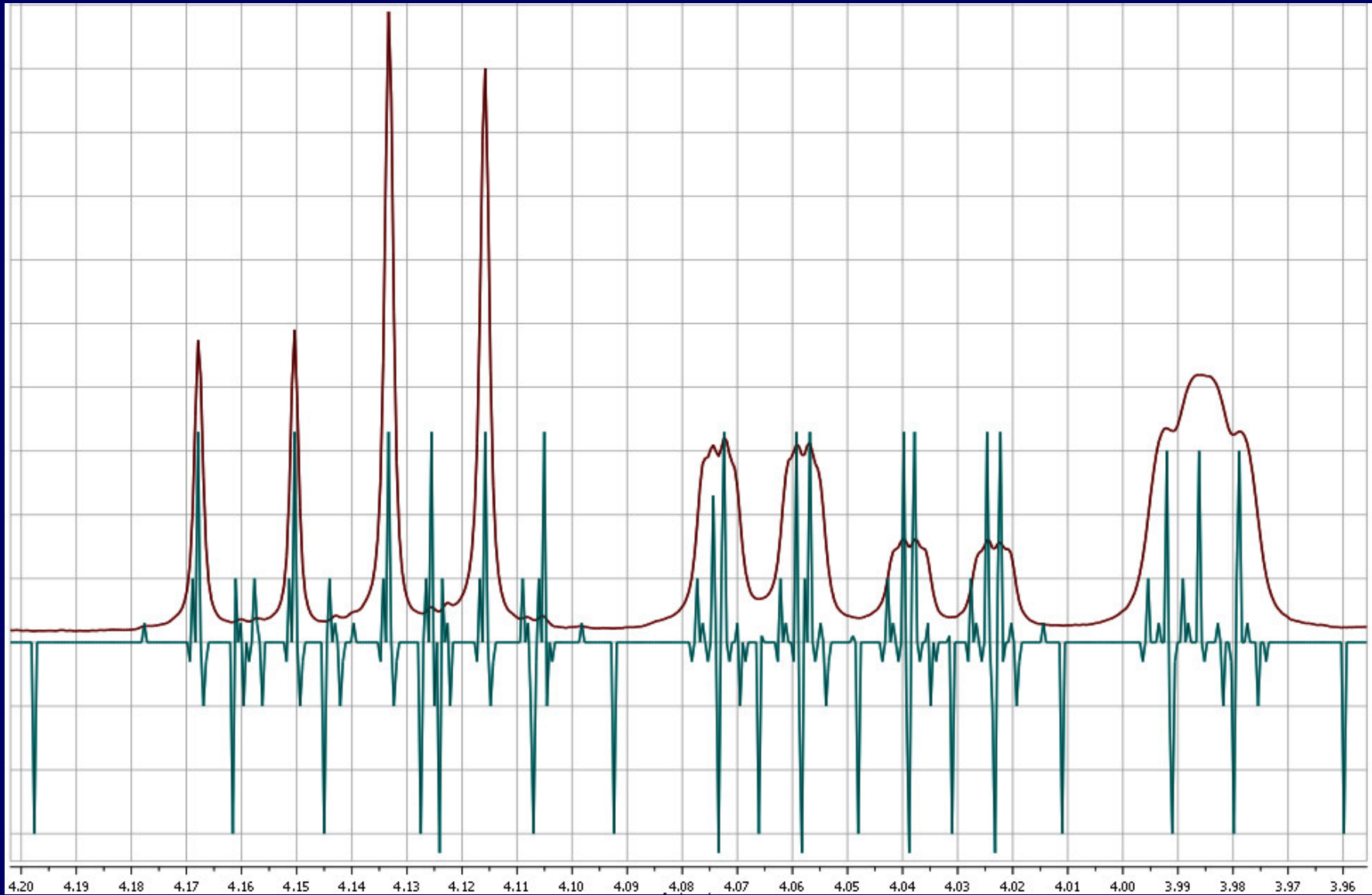
(1) Calculation of derivatives



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Recognition of significant peaks

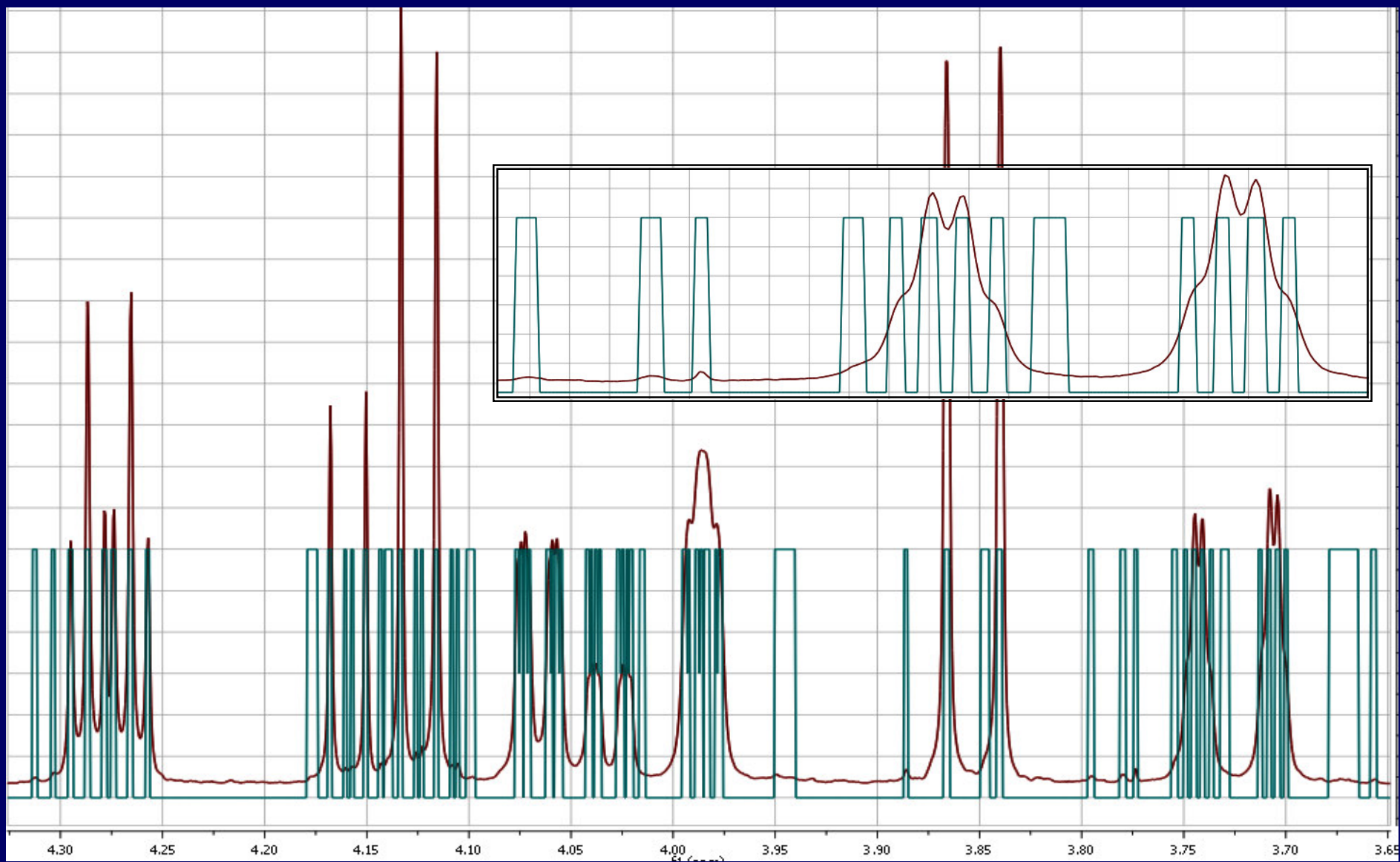
(2) Marking special points [local extremes of derivatives 0,1,2]



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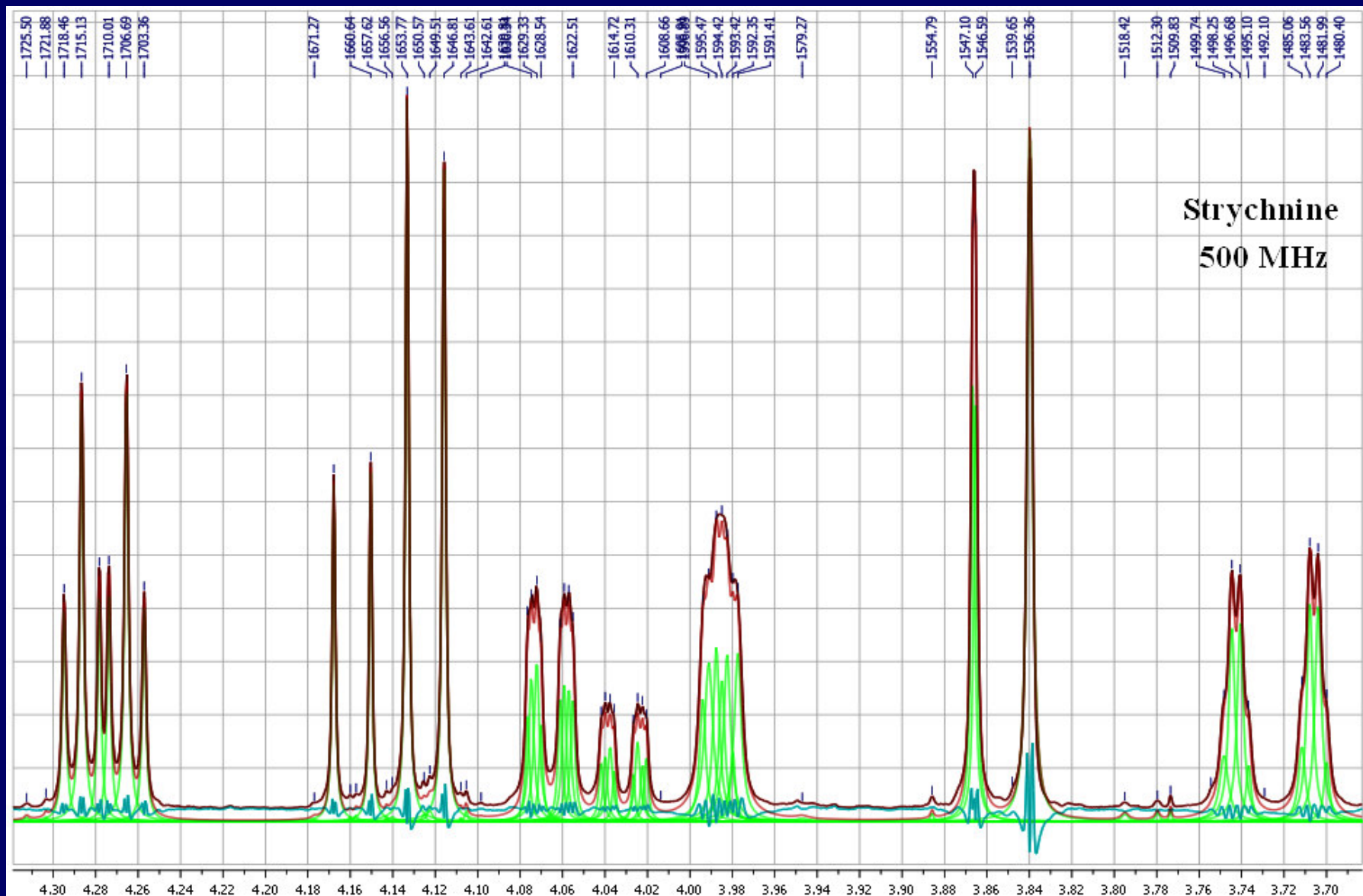
Recognition of significant peaks:

(3) Boxing-in of recognizable peaks (251 in this case)



Fitting of *all* parameters of *all* the peaks

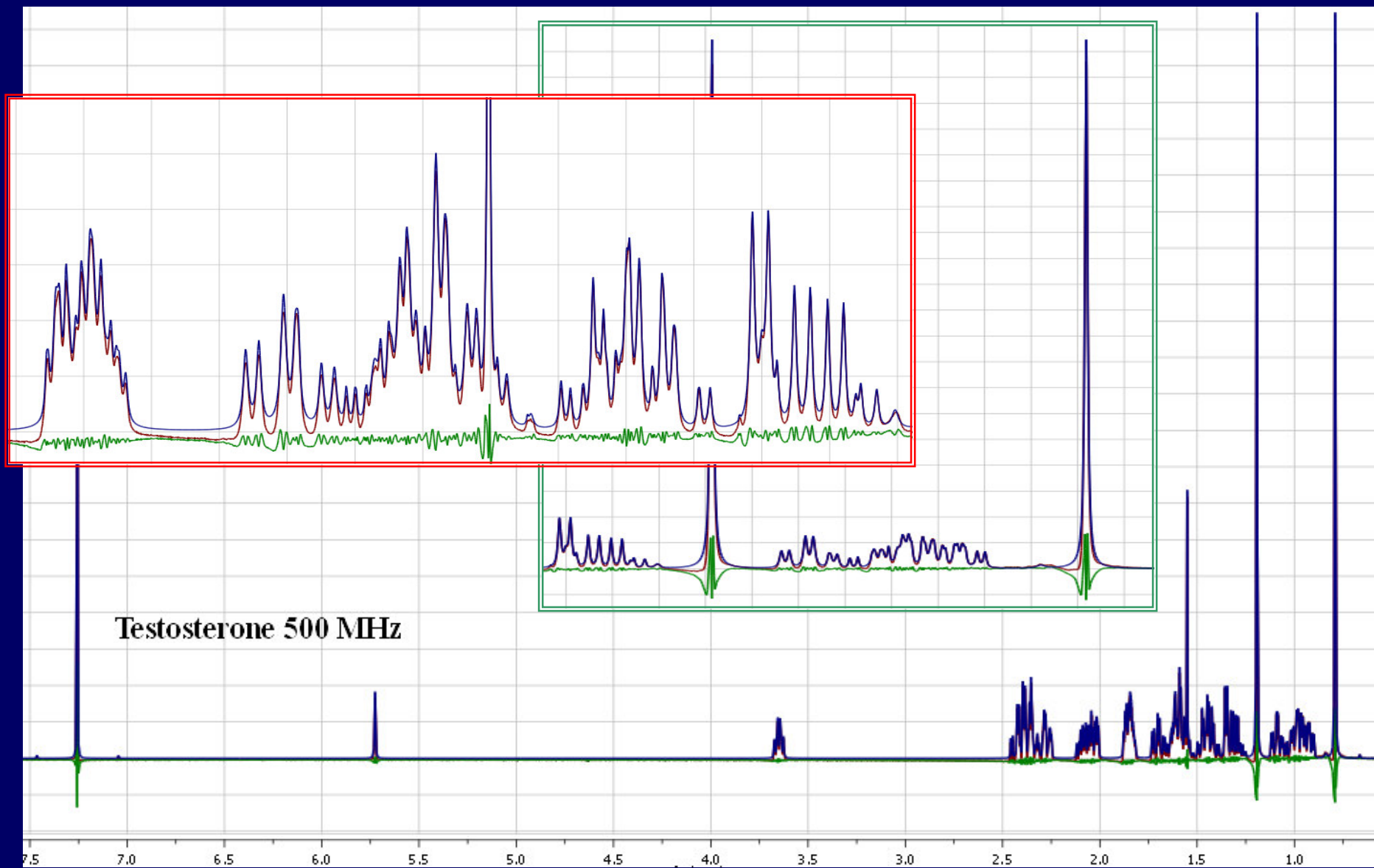
Peak-by-peak passages => linear dependence on number of peaks



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Simple GSD without splitting

200 peaks, 5 passages, about 5 seconds



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Sources of peak-shape deviations from Lorentzian

1. Magnetic field inhomogeneity (shimming)
2. Magnetic field noise (ebyte.it/library/docs/nmr06a/NMR_FieldNoise_Fid.html)
3. Sample spinning (dtt0)
4. Sample temperature gradients (up to 0.01 ppm/deg)
5. FID weighting before FT (Voight and other profiles)
6. Distorsions due to Discrete Fourier Transform (cyclic condition)
7. Overlap of miriads of transitions in coupled spin systems
8. Relaxation effects (e.g., methyl lines contain 3 transitions of different widths)
9. Molecular dynamics effects (chemical exchange, limited mobility)
10. etc ...

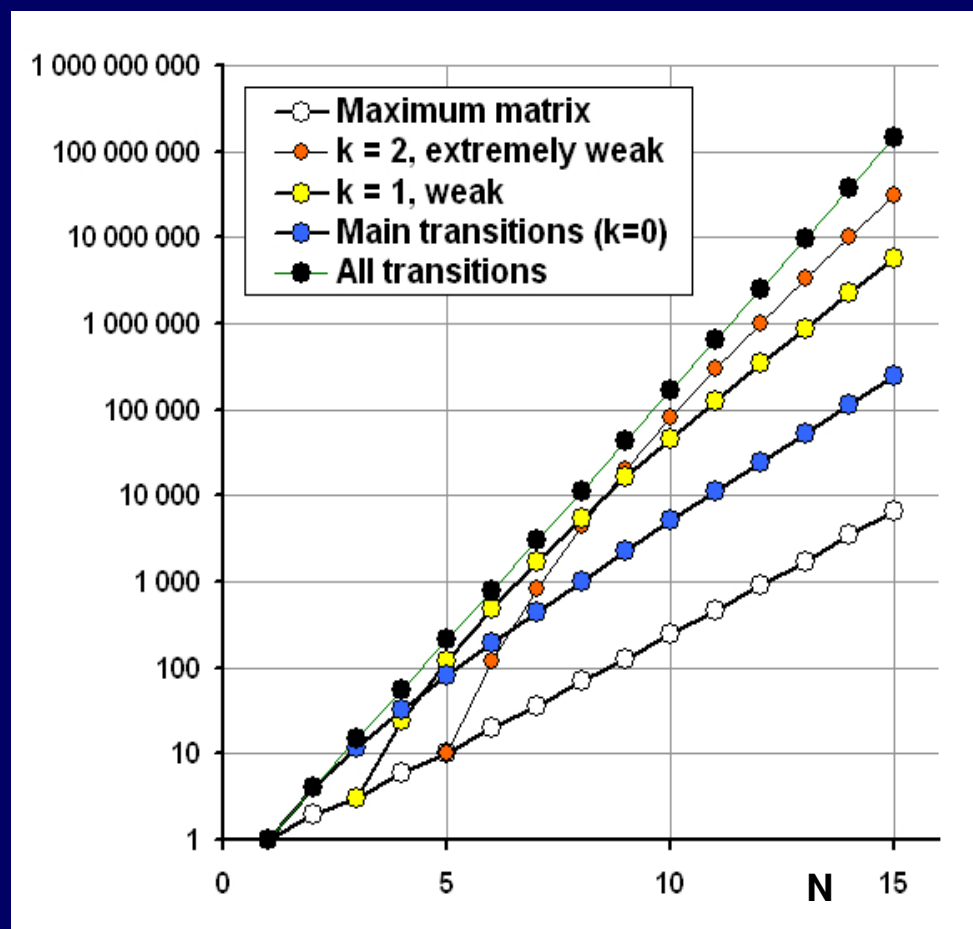
Overlap of transitions

Spectral peaks are really envelopes of transitions:

Even in molecules of modest size the number of distinct peaks is tens to thousands times smaller than that of quantum transitions.

⇒

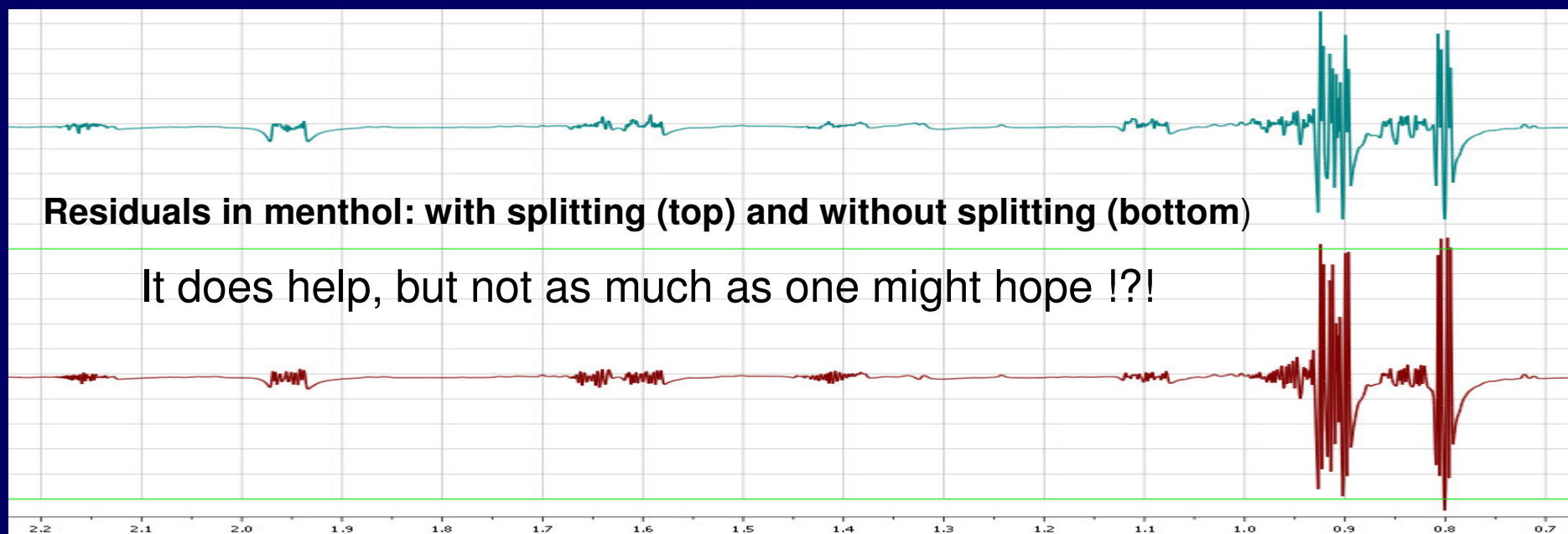
Every peak is an envelope of a large number of transitions and its shape is dominated by the coupling pattern of the spin system.



An unresolved Lorentzian doublet: a crude but versatile peak-shape model

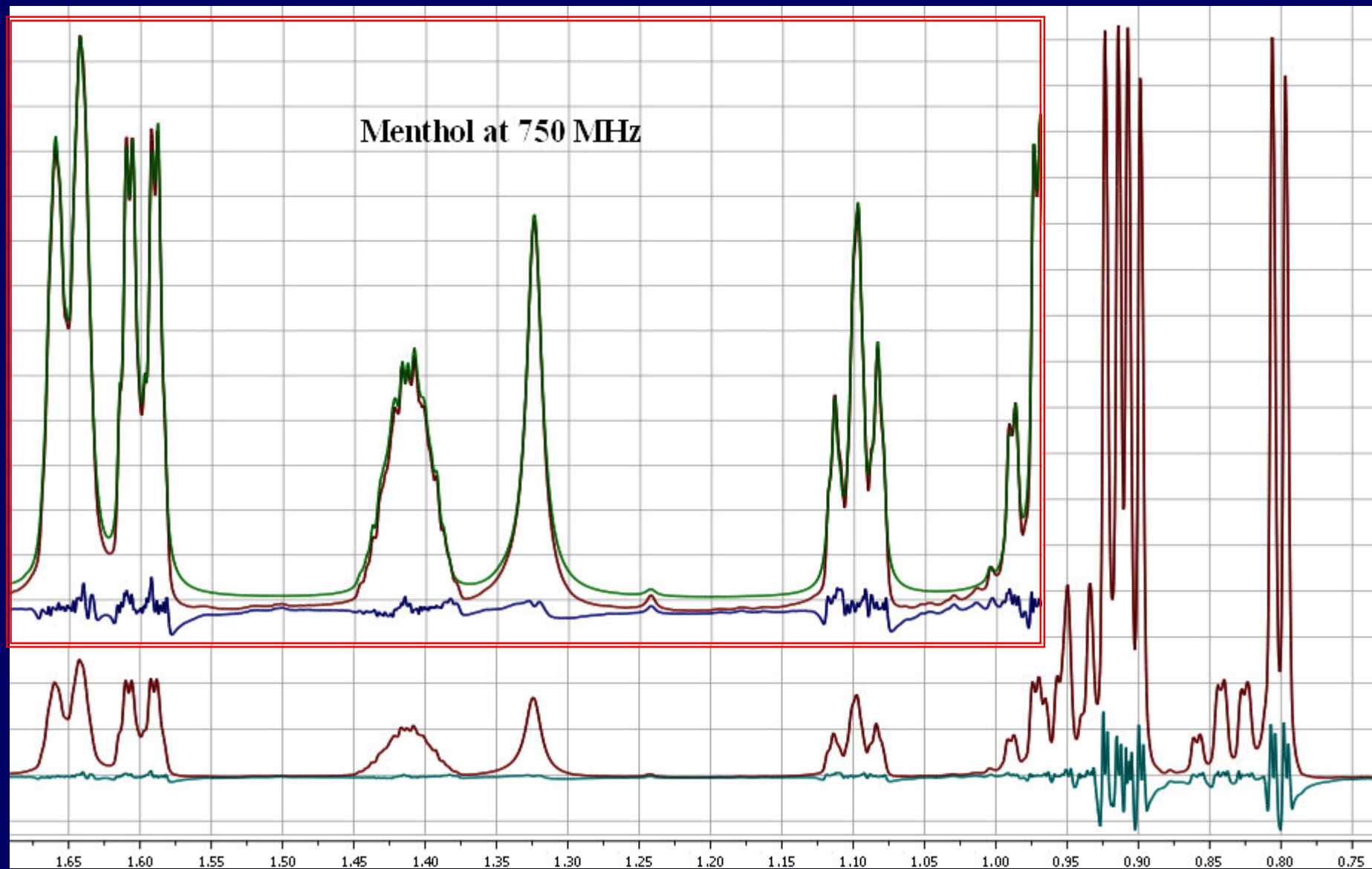
It can be shown that a finely split (unresolved) Lorentzian doublet can closely approximate peak shape distortions due to most weighting functions (Voight profiles), many shimming and relaxation effects (T_2^* dispersion), and at least some of the transition overlap effects.

Hence the most obvious approach to improving GSD quality is
peak splitting



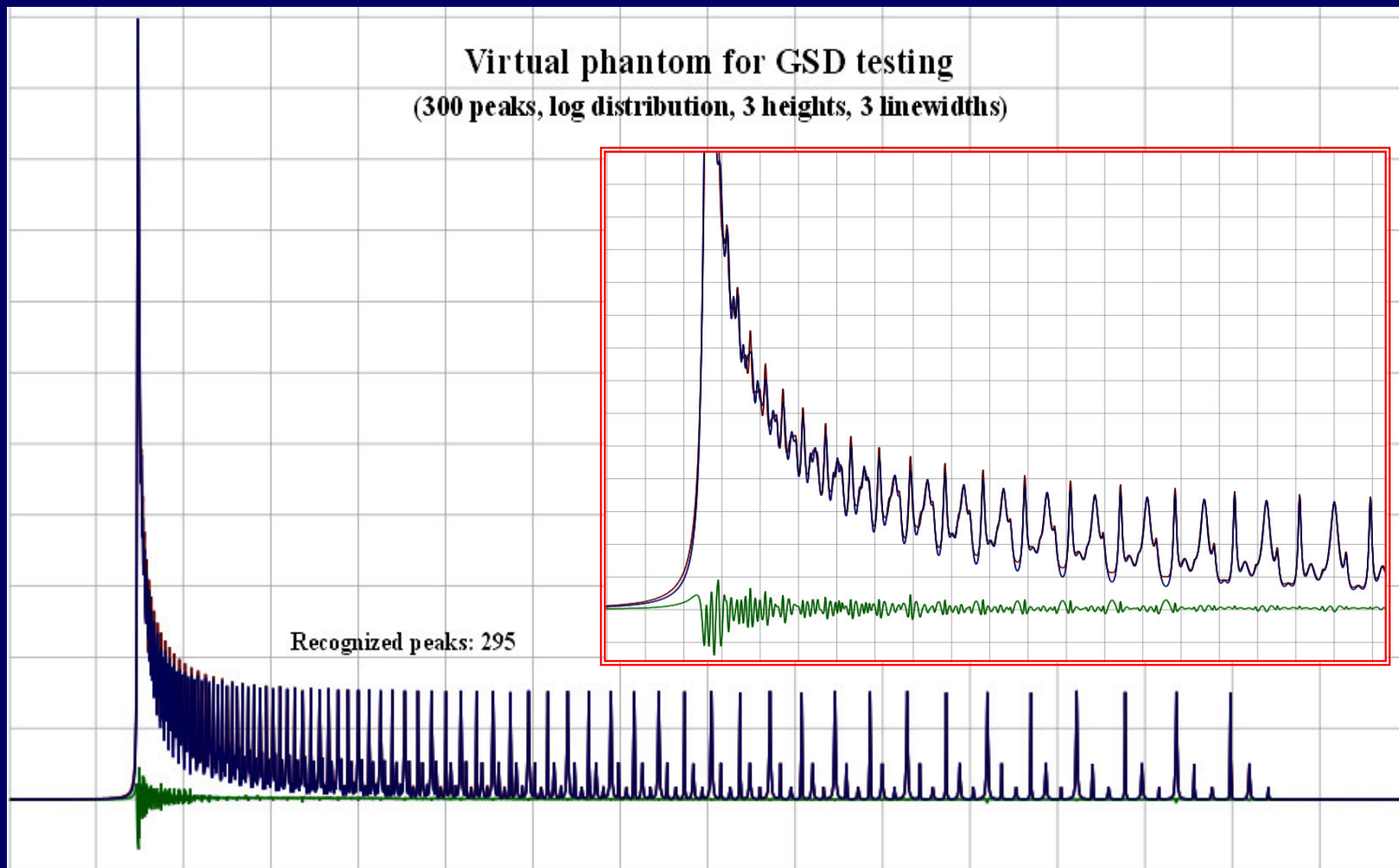
Example of a full GSD with splitting

Without splitting 181 peaks, with splitting 286



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GSD development tools



Conclusions and perspectives

Global Spectrum Deconvolution is now running and usable,
even though some more work on reducing the residuals is needed

The residuals are generally peak- or multiplet-specific and therefore reflect real lineshape deviations from the ideal, not limitations of the GSD algorithm itself.

GSD will become the most important tool for:

- * Quantitative analysis with automatic/manual peak editing
- * Molecular structure verification and/or elucidation

The abstract and slides of this talk are available at
[www.ebyte.it/stan/Talk MMCE 2009.html](http://www.ebyte.it/stan/Talk_MMCE_2009.html)

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