

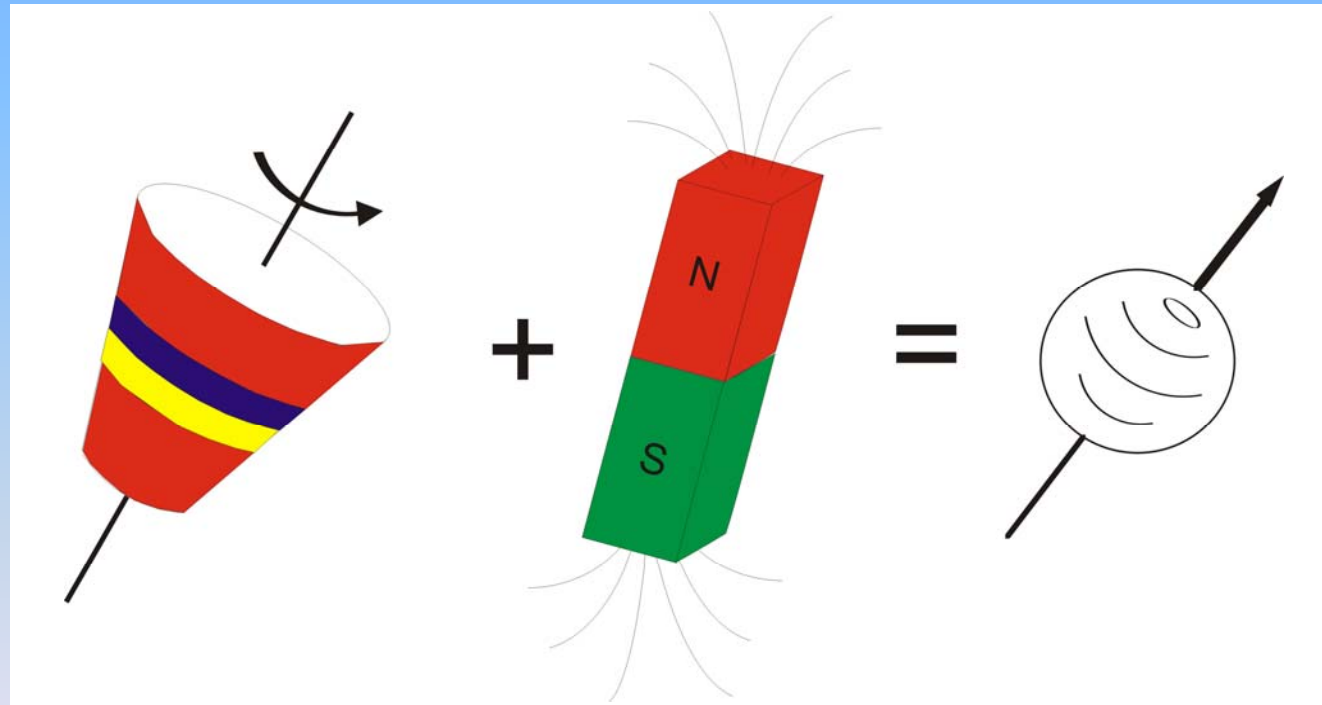
NUS: non-uniform sampling

Peter Schmieder

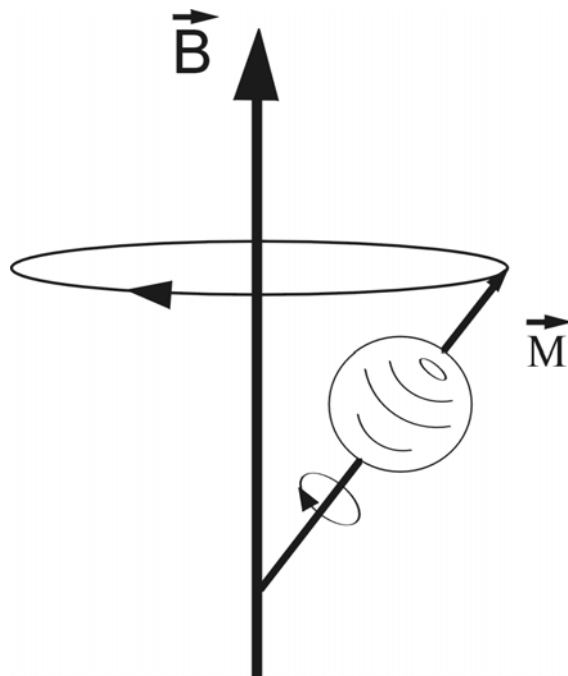
FMP, 10.10.2012



NMR-spectroscopy uses the nuclear spin that can be thought of as a mixture between gyroscope and magnet

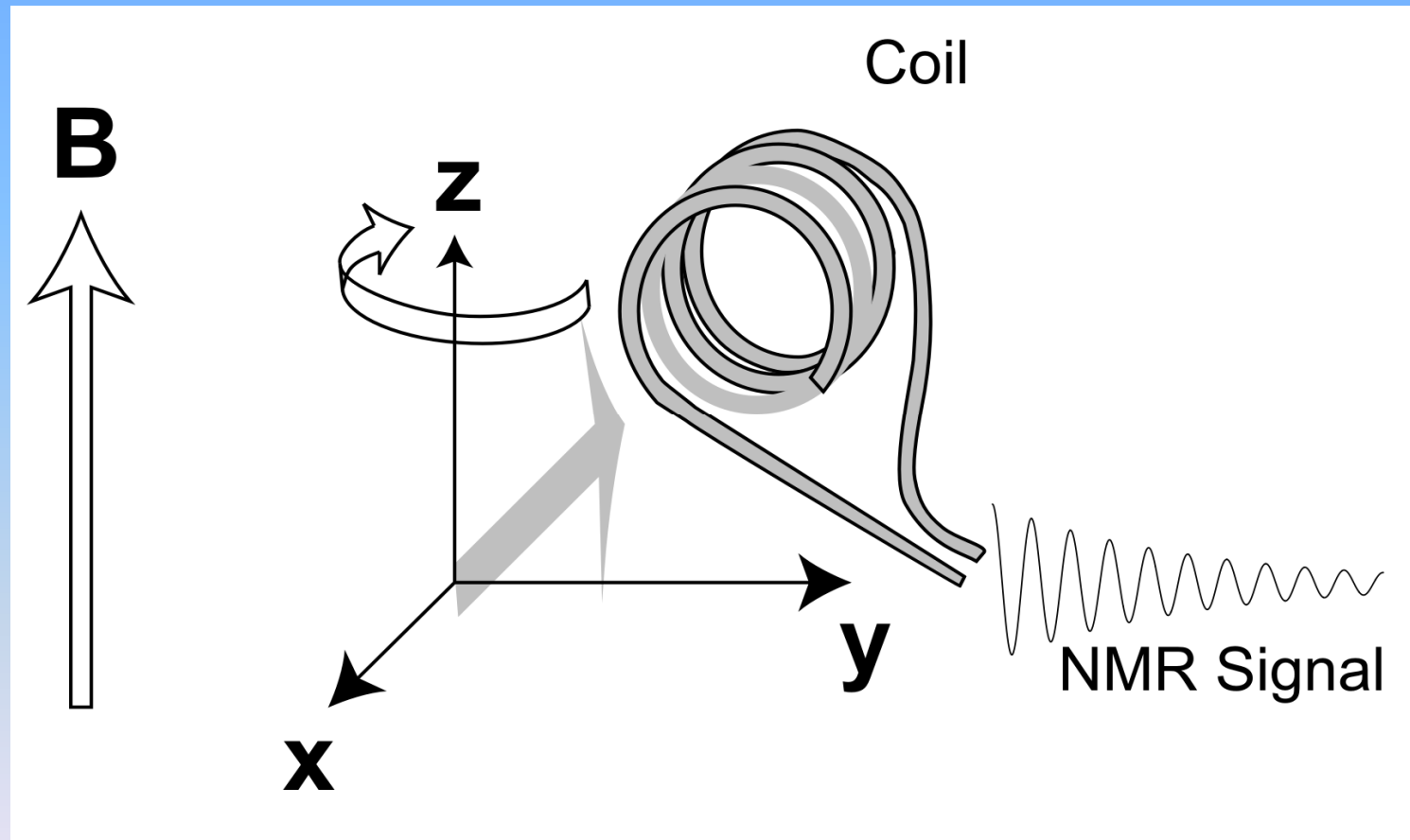


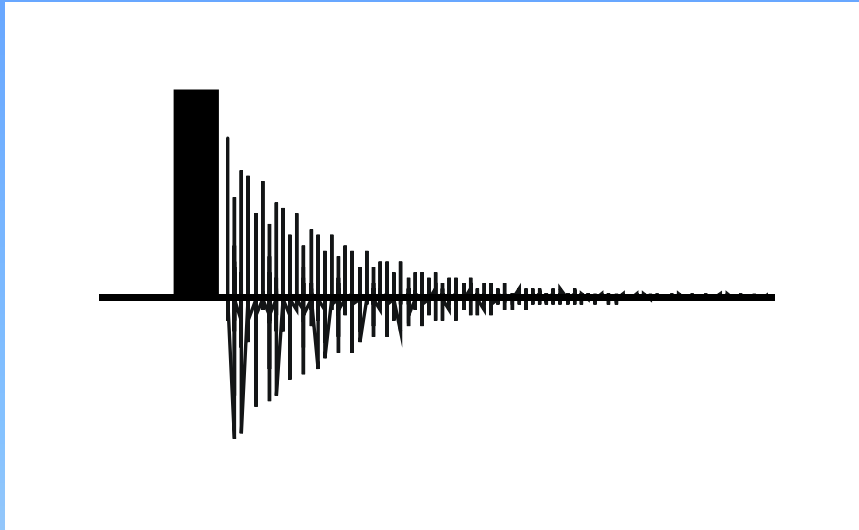
The frequency of the rotation of the spin in a magnetic field is what we are interested in



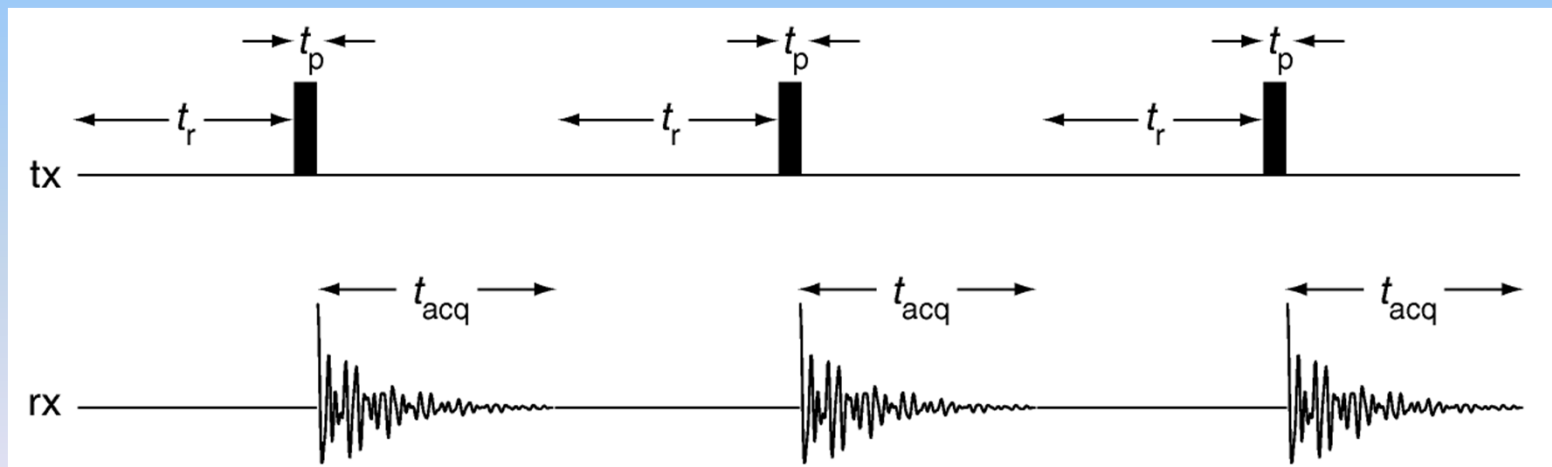
B_0 [Tesla]	ν_0 [MHz]
1.4	60
5.9	250
9.4	400
14.1	600
21.2	900

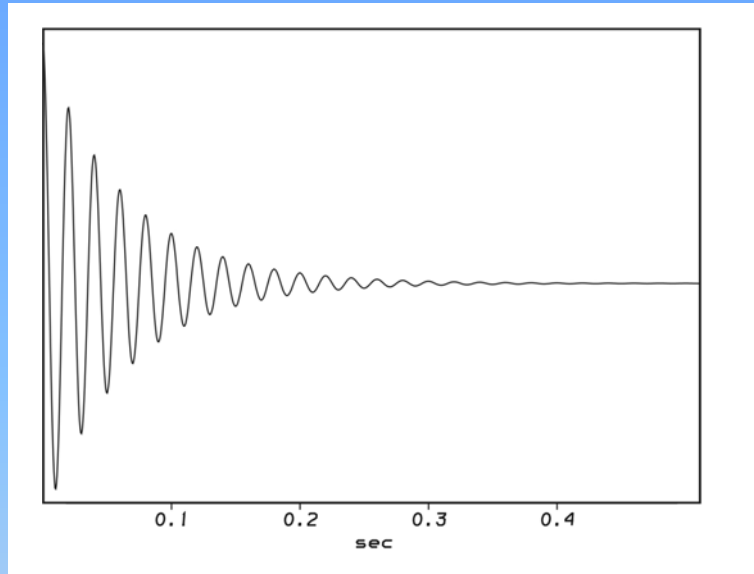
The frequency is measured by using the little magnet to induce a current in a coil





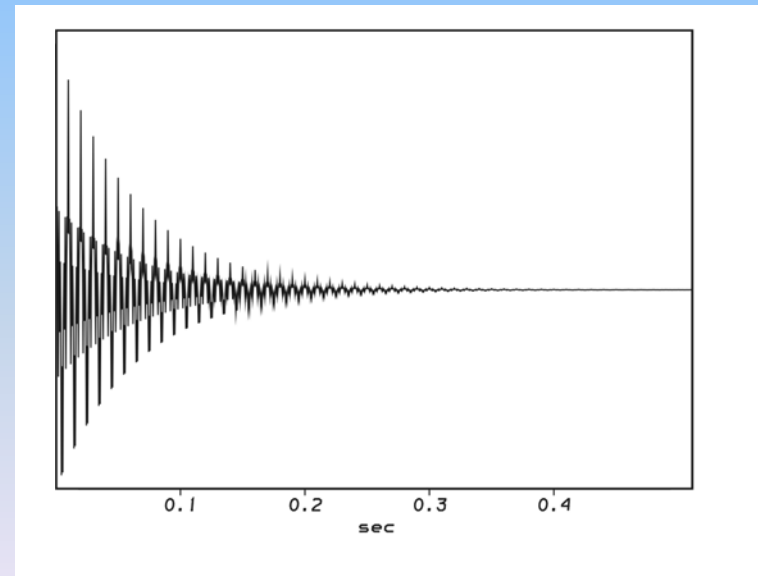
An RF-pulse is used to "start" the magnet. Because of signal-to-noise we repeat the excitation-detection



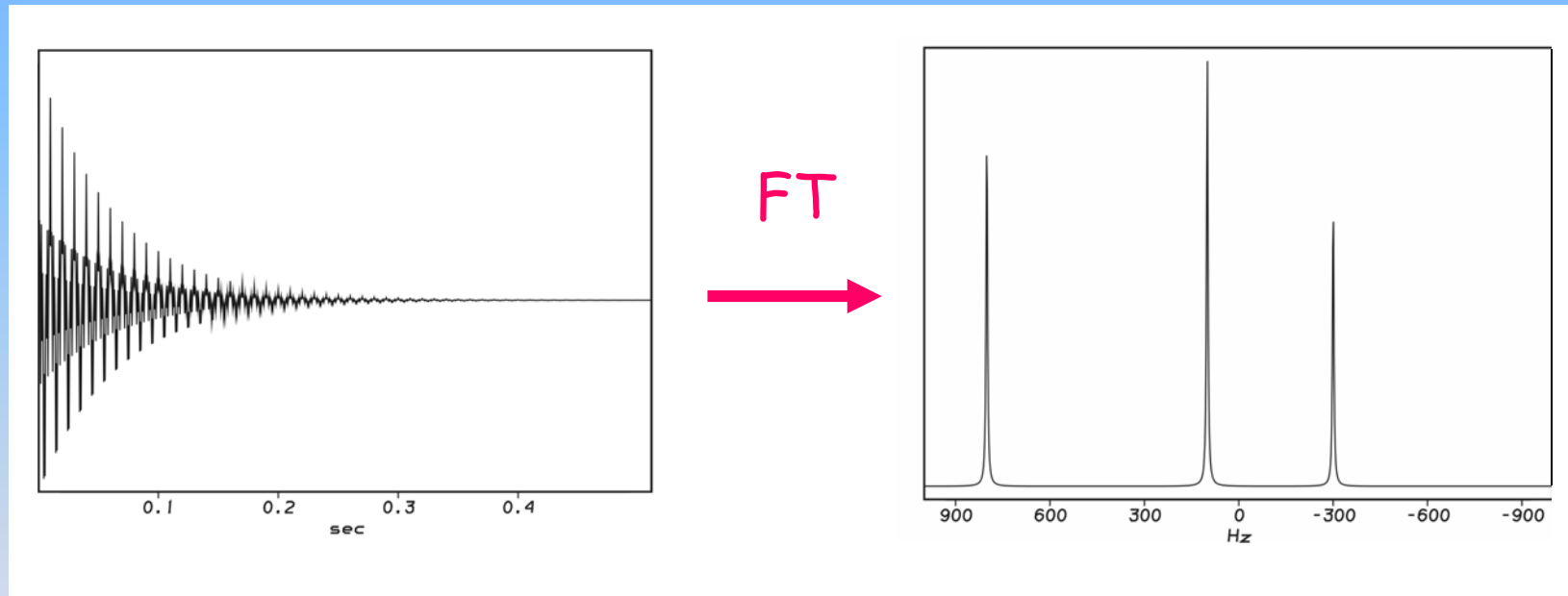


While the frequency of
one line is easy to
analyze from the time-
signal...

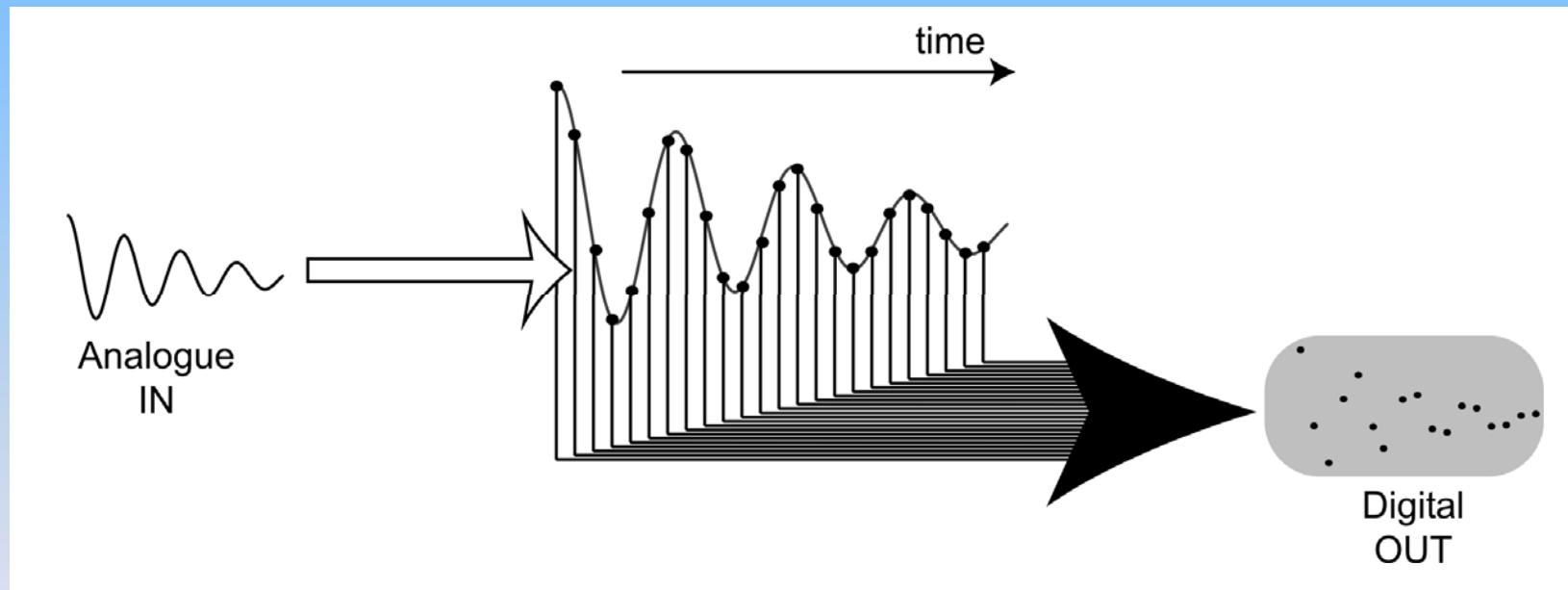
...it is difficult from
more than one

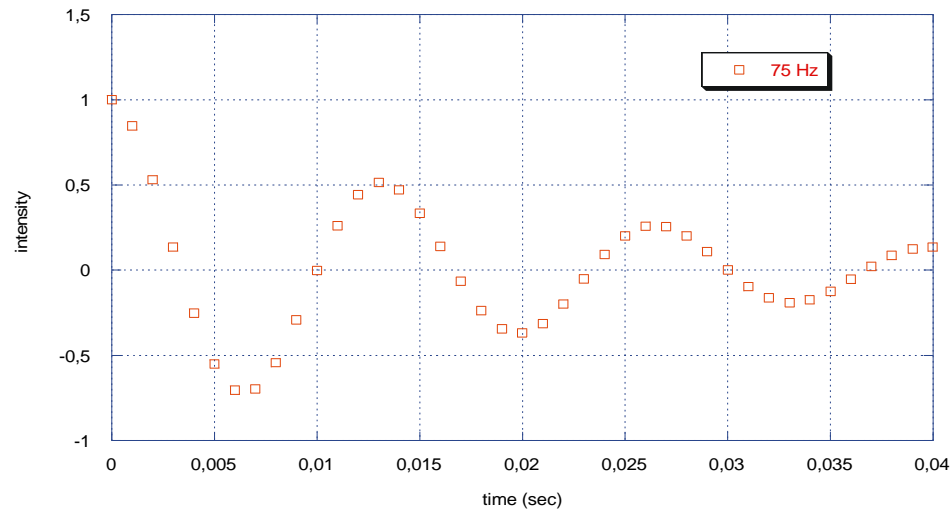


That's why we do a Fourier-Transformation !



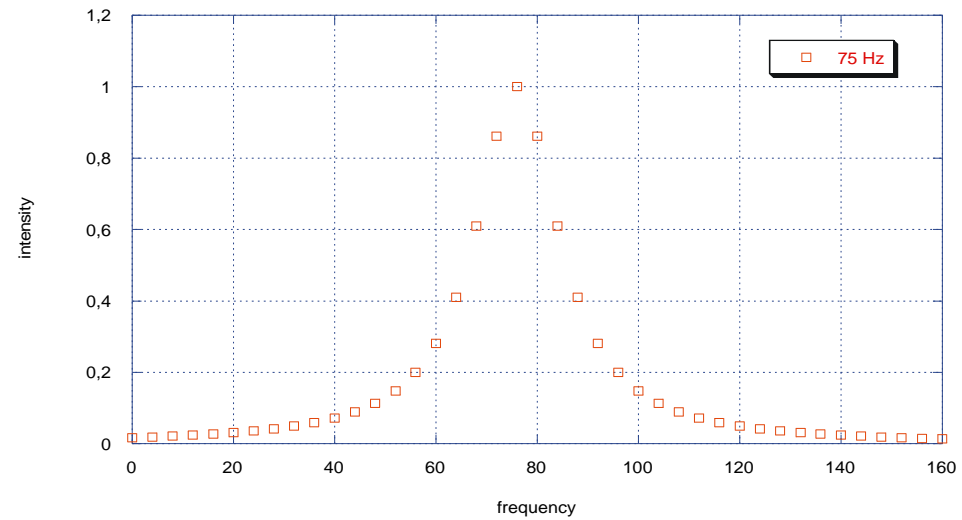
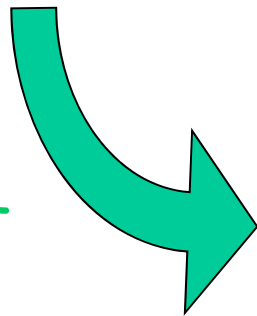
For which we have to digitize the signal.
Then we can use the DFT or FFT to process
data fast.



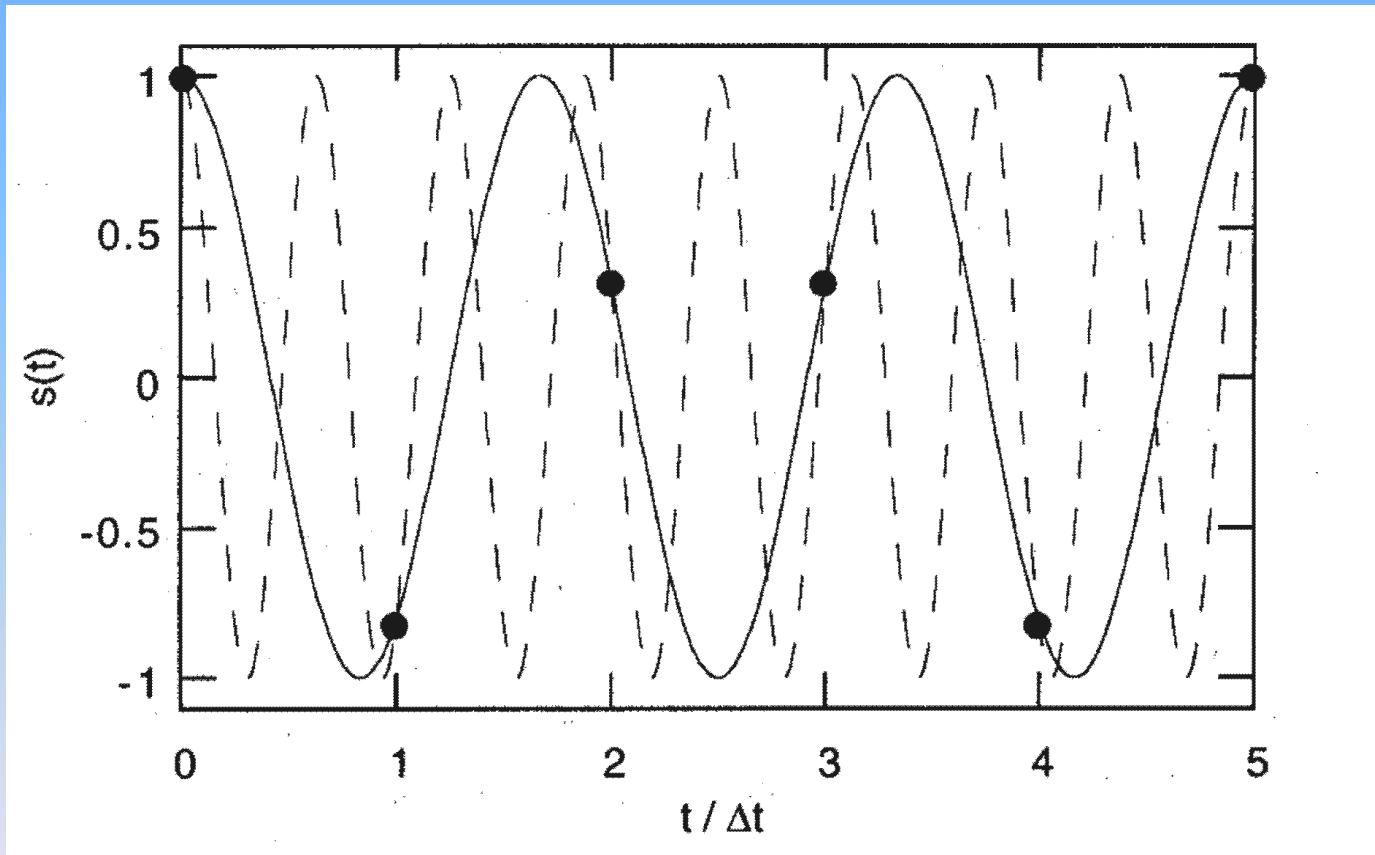


The DFT only
sorts points

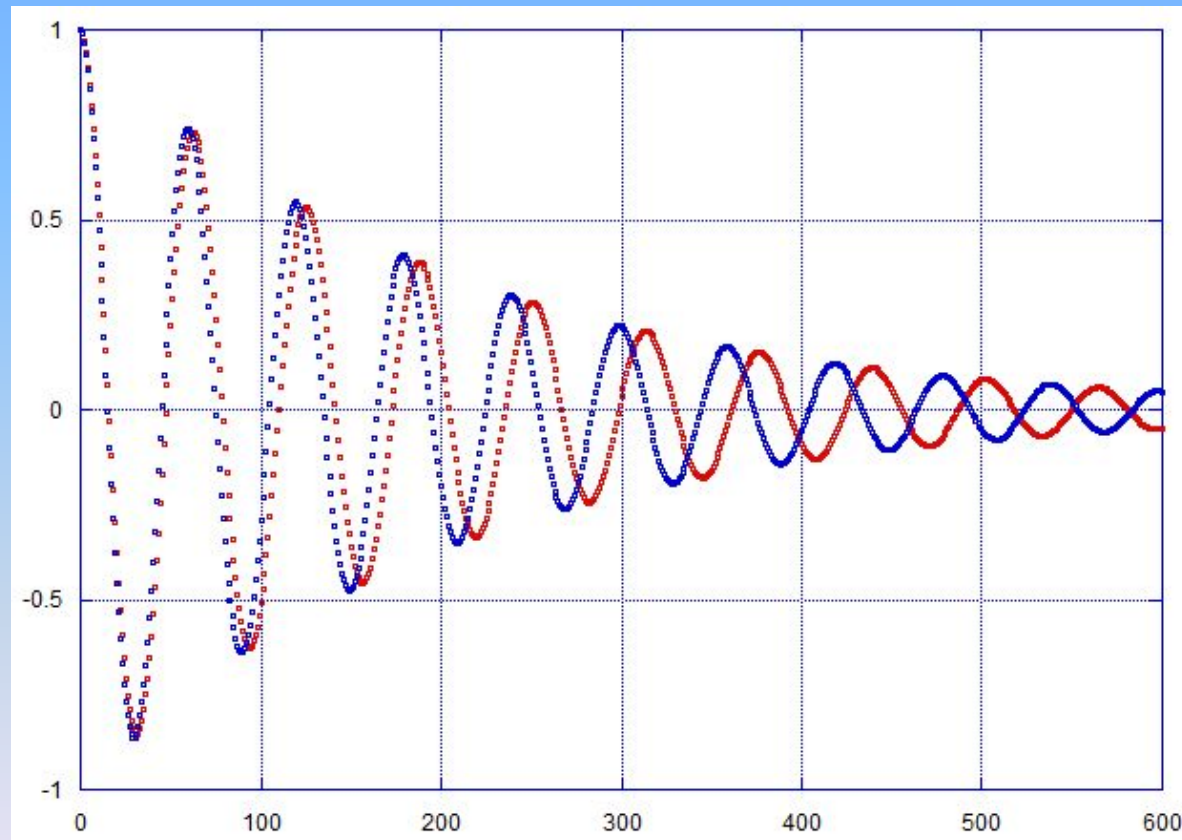
FT



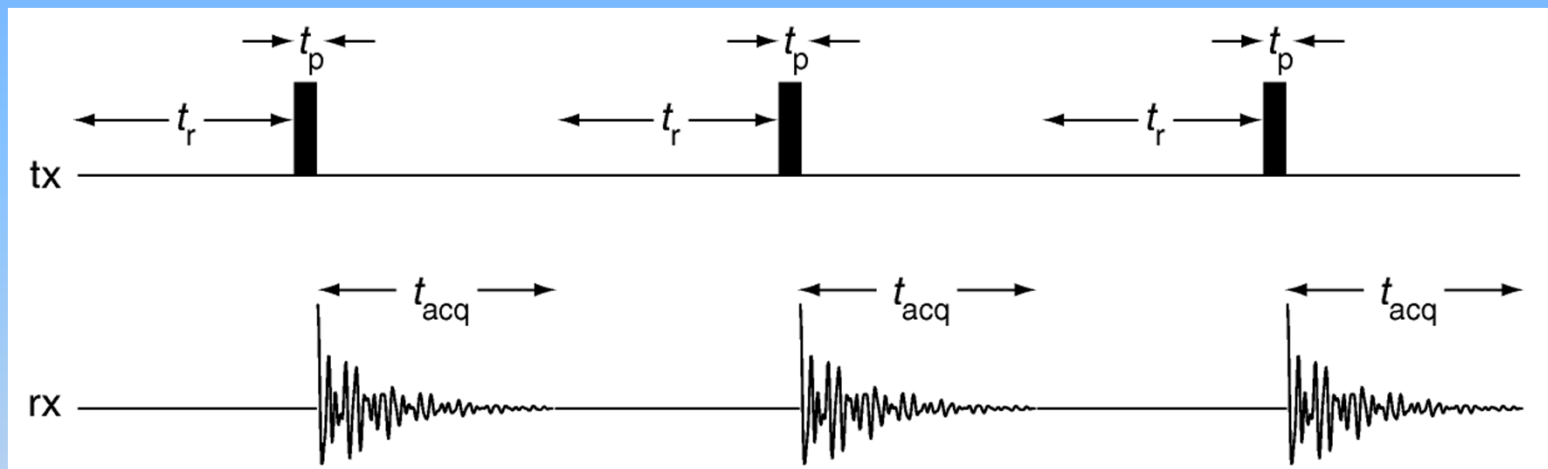
The maximum frequency that we want to detect determines the sampling rate: Nyquist condition



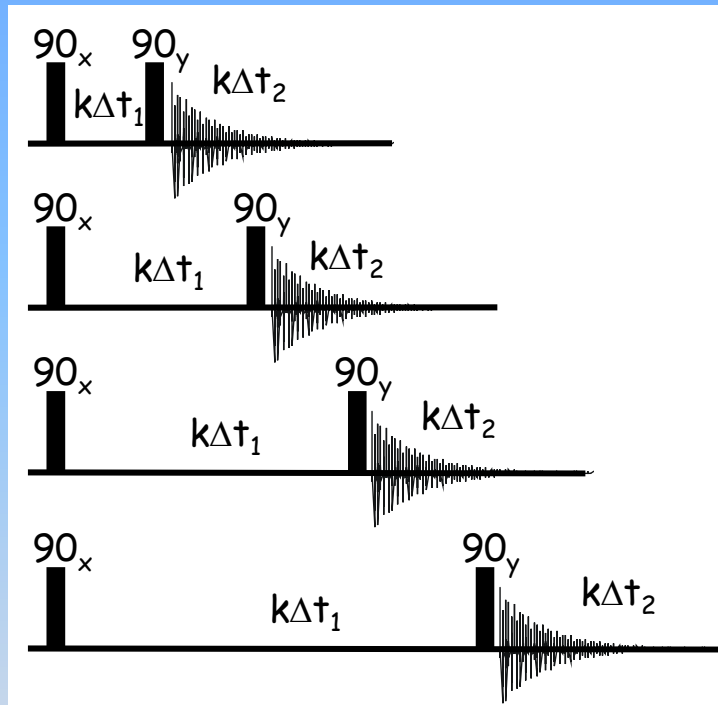
What about resolution, i.e. separating two lines ?
To do that we have to sample many points !



This comes for free in a 1D !

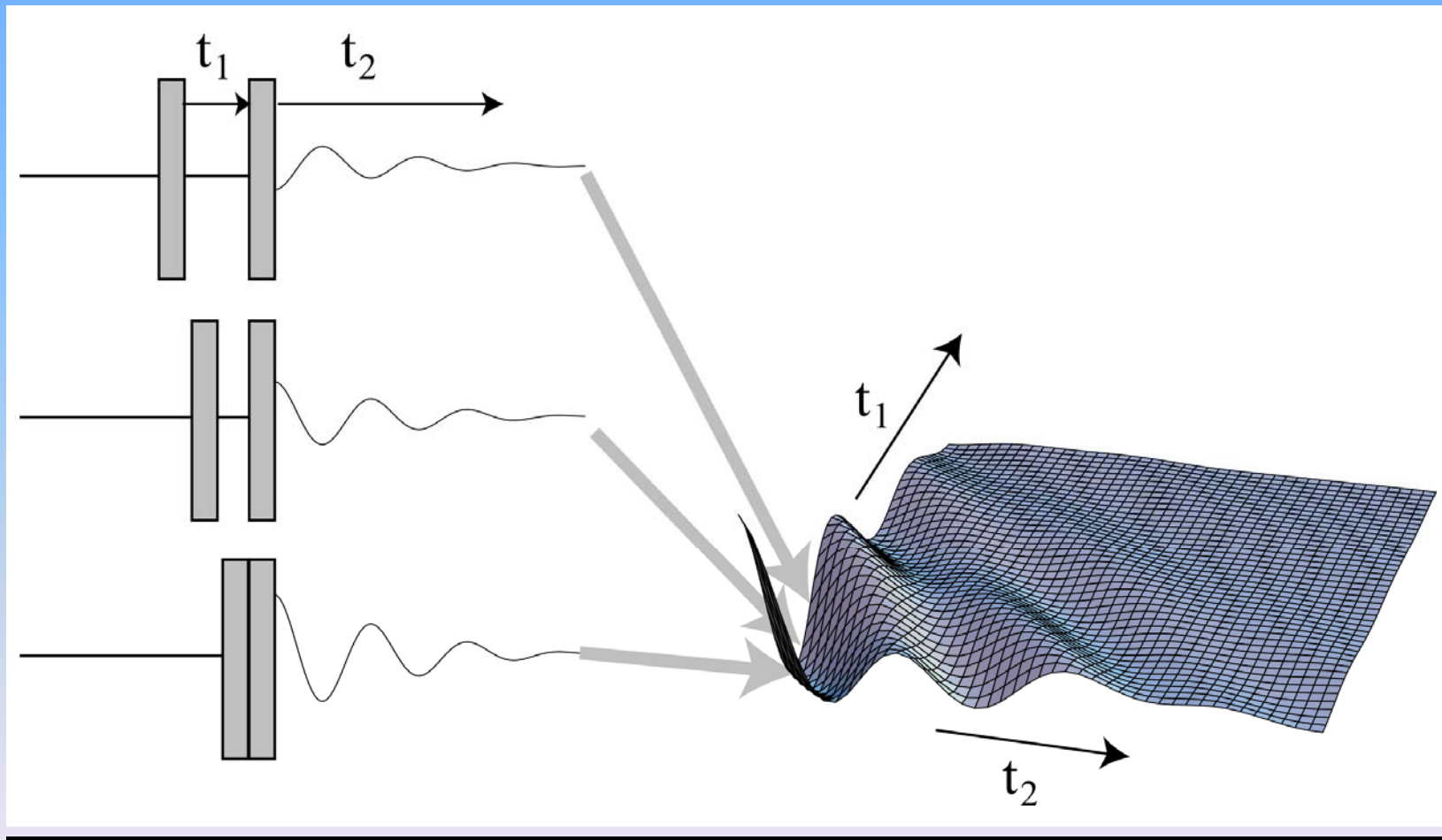


If t_{acq} gets longer one can shorten t_r

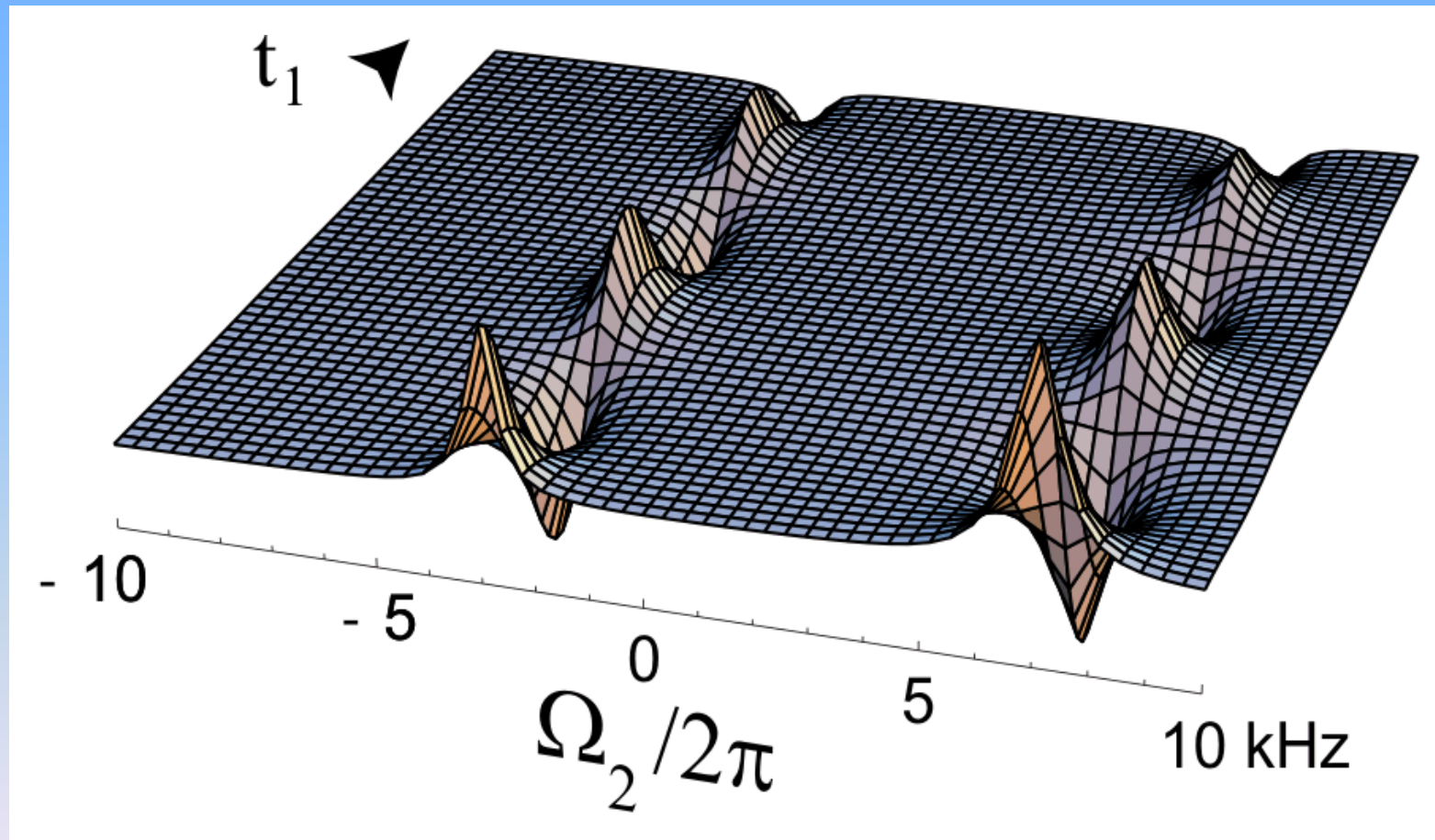


A multidimensional spectrum is created by repetitive recording of a one-dimensional spectrum with systematic changes in the pulse-sequence....

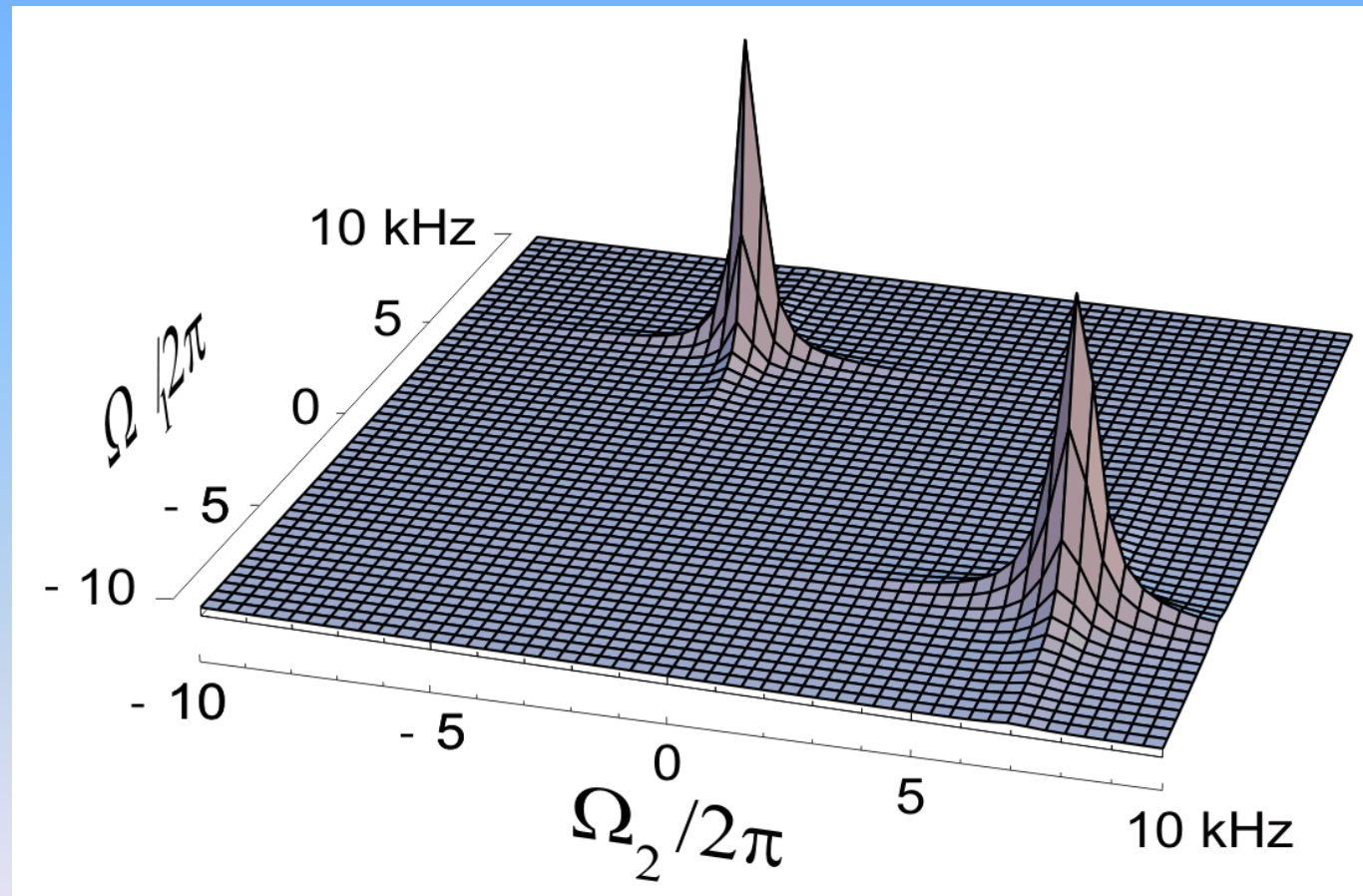
....resulting in a two-dimensional FID

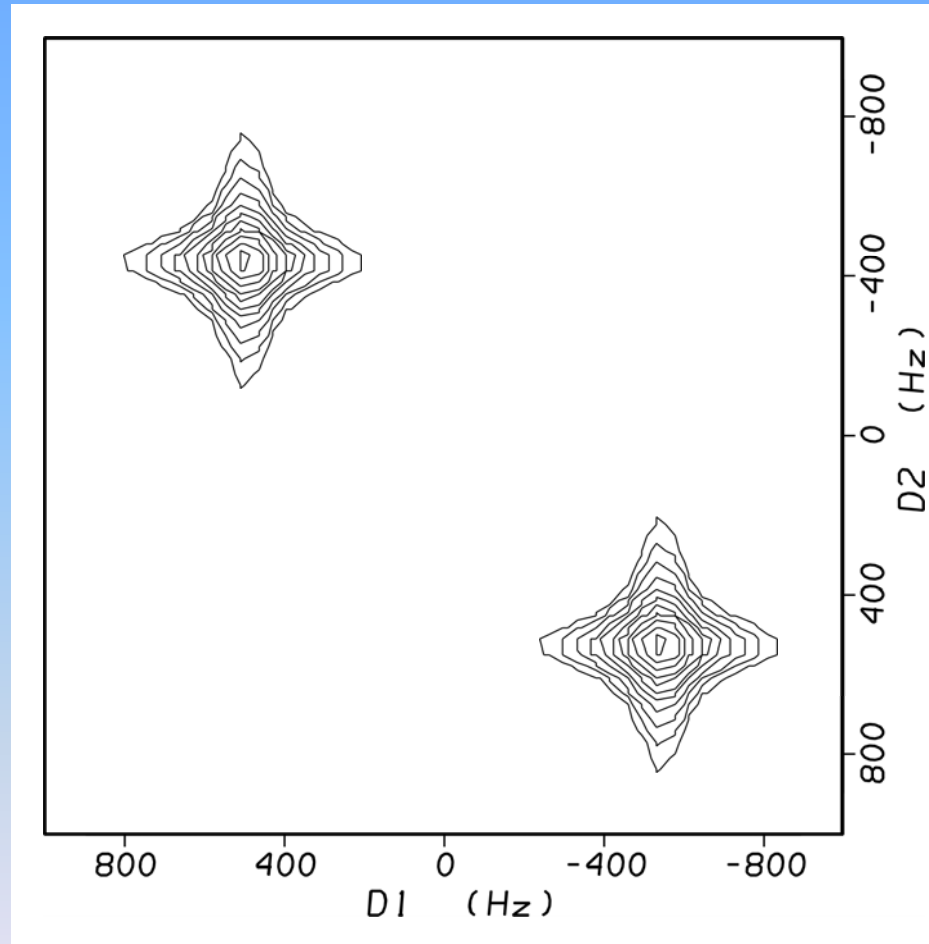


The first FT yields the „interferogram“

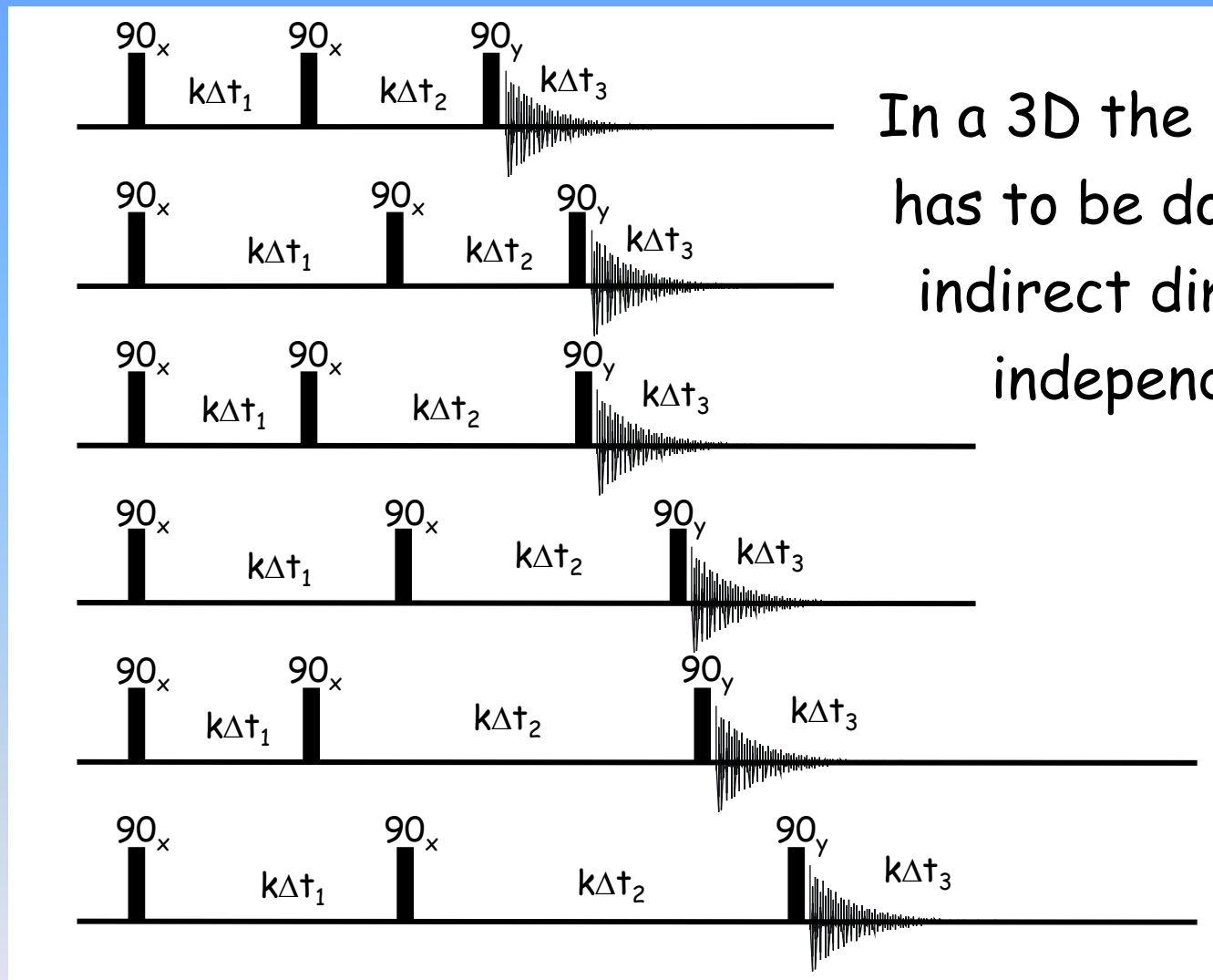


The second FT yields the two-dimensional spectrum





Spectra are usually viewed as contour plots



In a 3D the repetition
has to be done in two
indirect dimensions
independently

That is why multidimensional spectra take so much longer

1D, 1024 points, 8 scans

12 sec

2048 points do **not** (!!) take longer

2D, 1024 x 1024, 8 scans

4,3 hours

1024 x 2048 points take 8,6 hours

3D, 1024 x 128 x 128, 8 scans

54,6 hours

4D, 1024 x 32 x 32 x 32, 8 scans

109,2 hours

4D, 1024 x 128 x 128 x 128, 8 scans

291 days

The reason is the DFT !

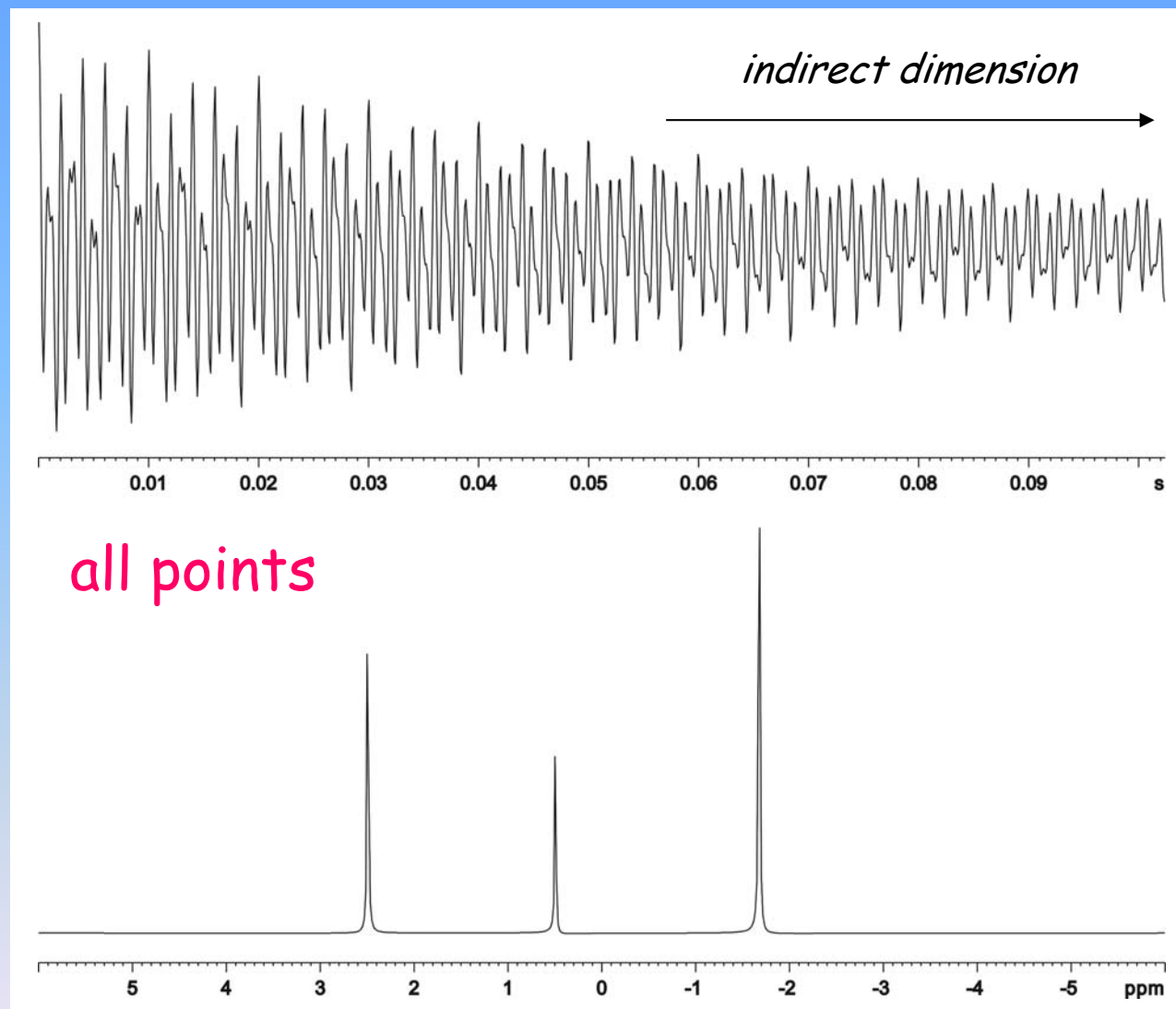
The DFT is fast but also has some limitations:

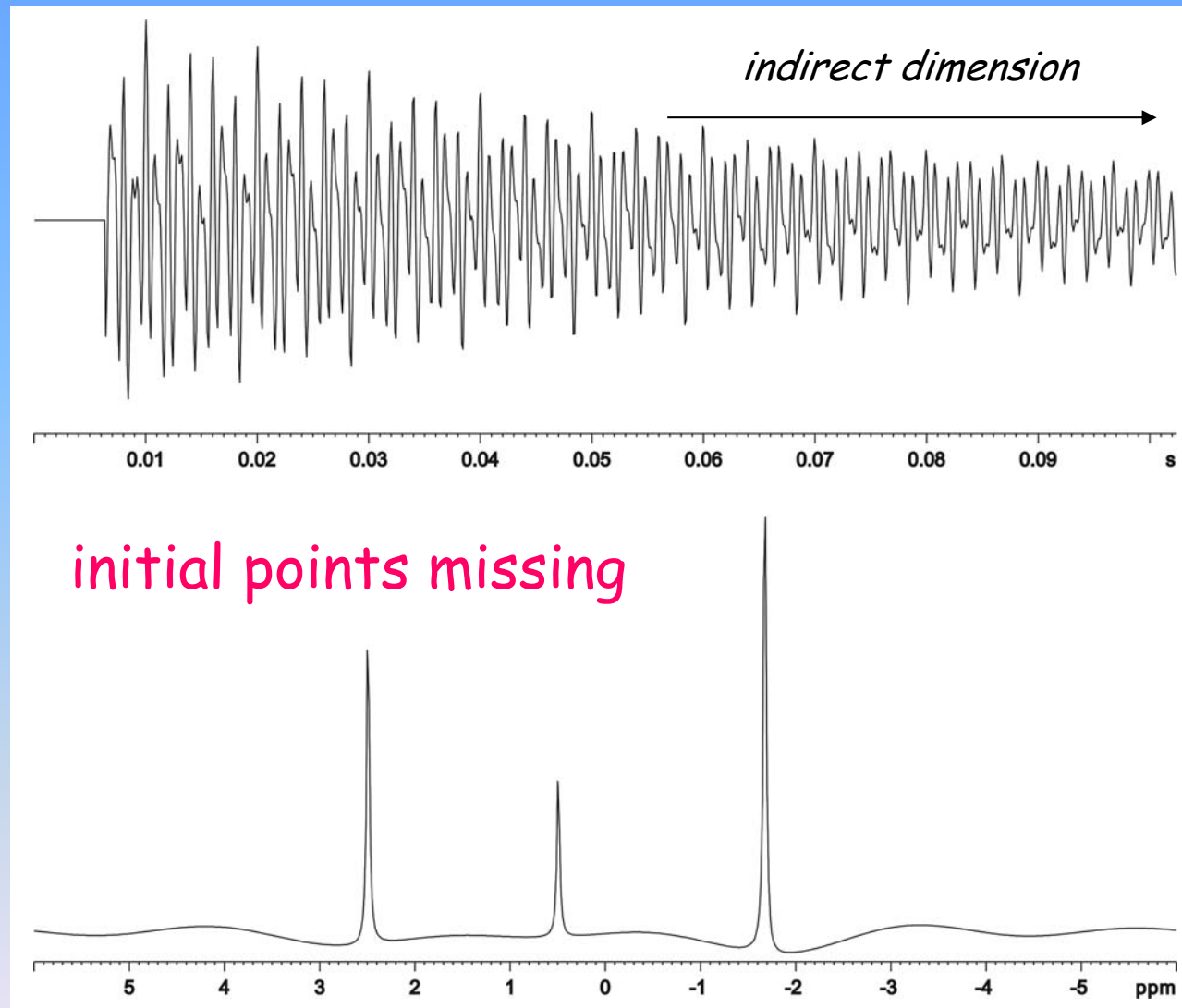
Points have to be sampled in equidistant intervals

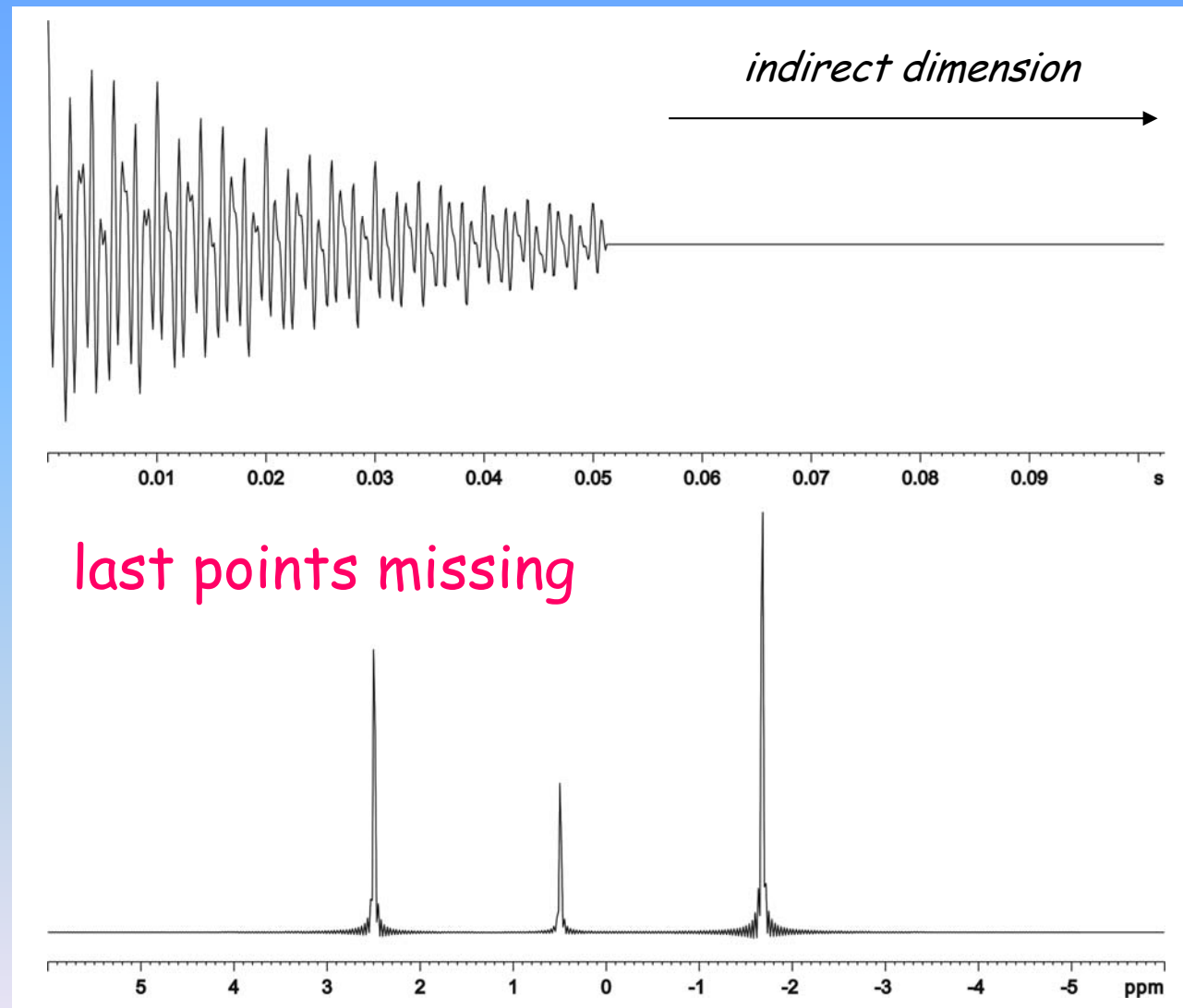
The distance between points determines the maximum frequency that can be sampled

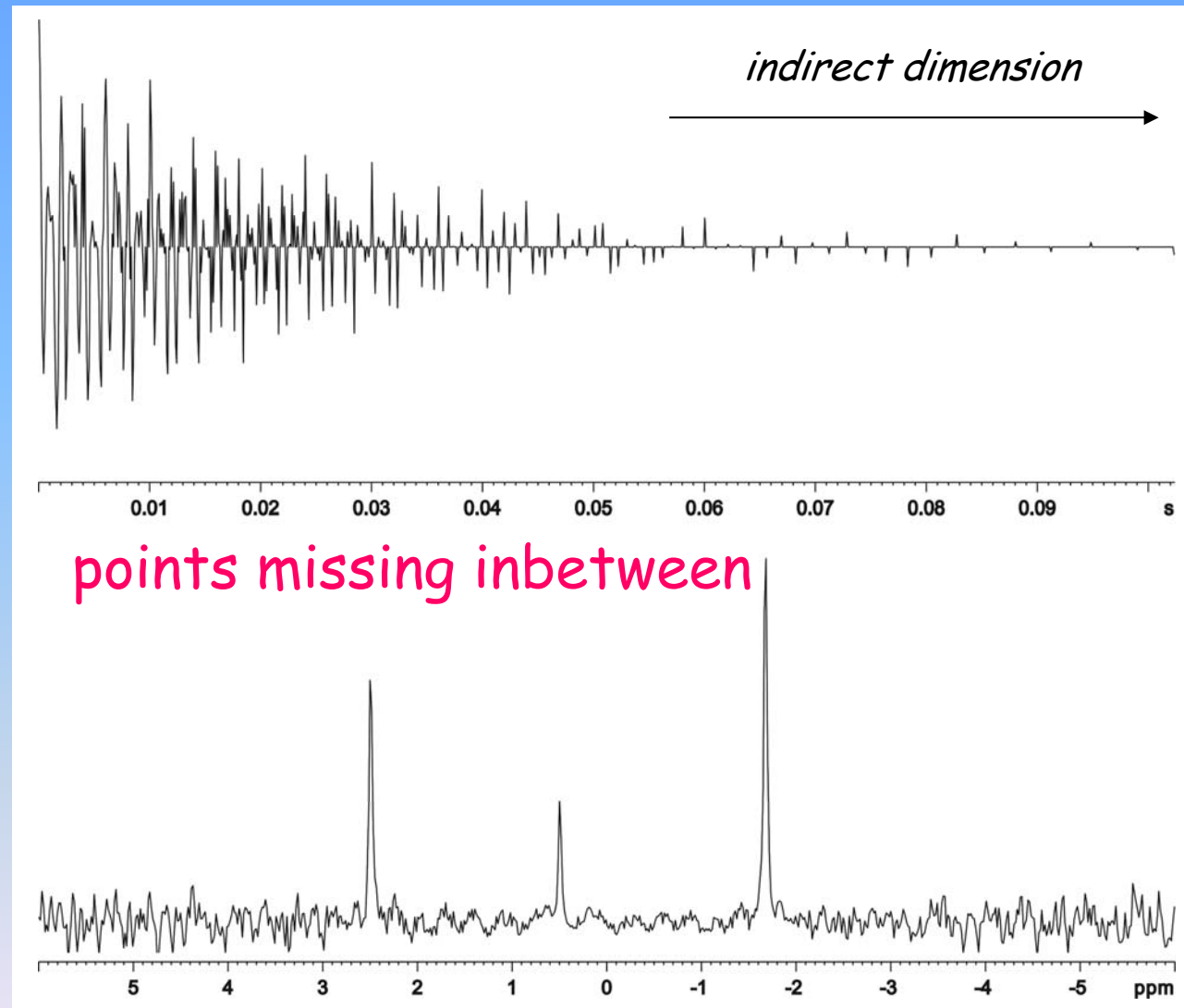
Missing points at the beginning, in the end or in the center cause distortions

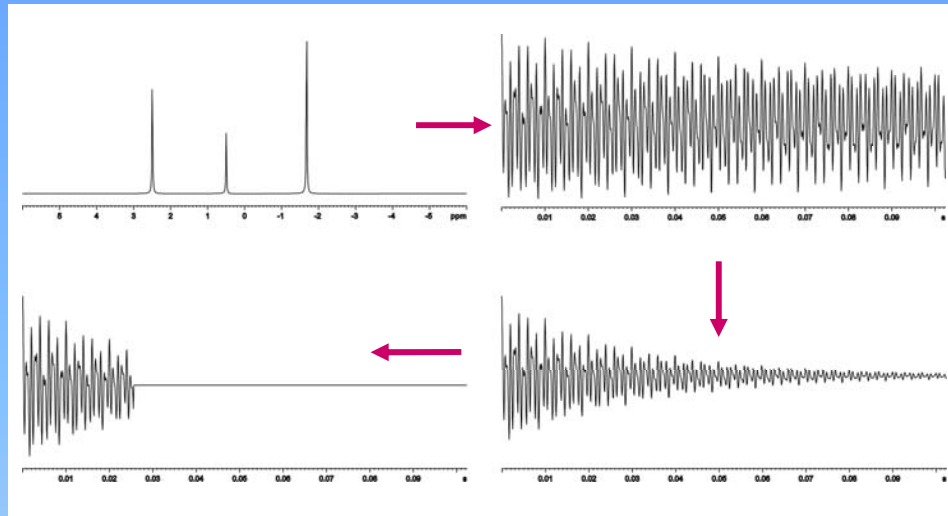
Good resolution in nDs requires long experiment time !!



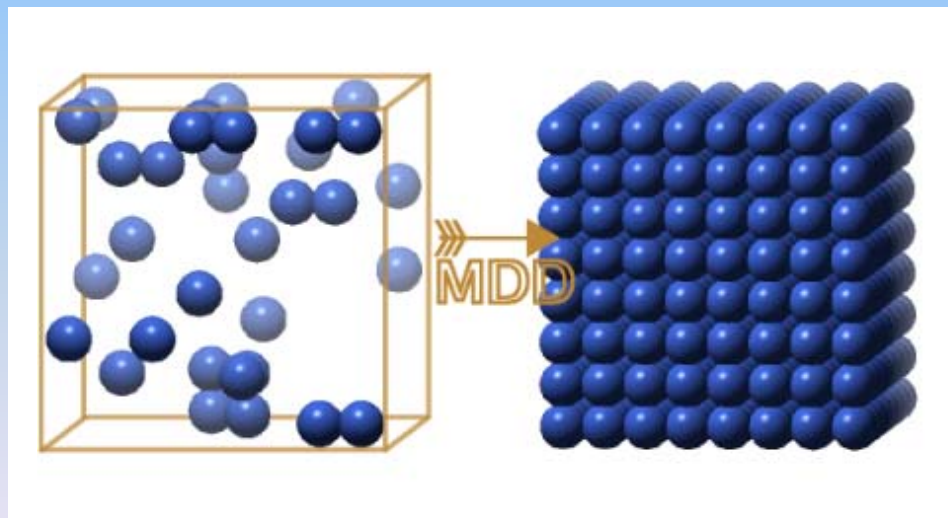






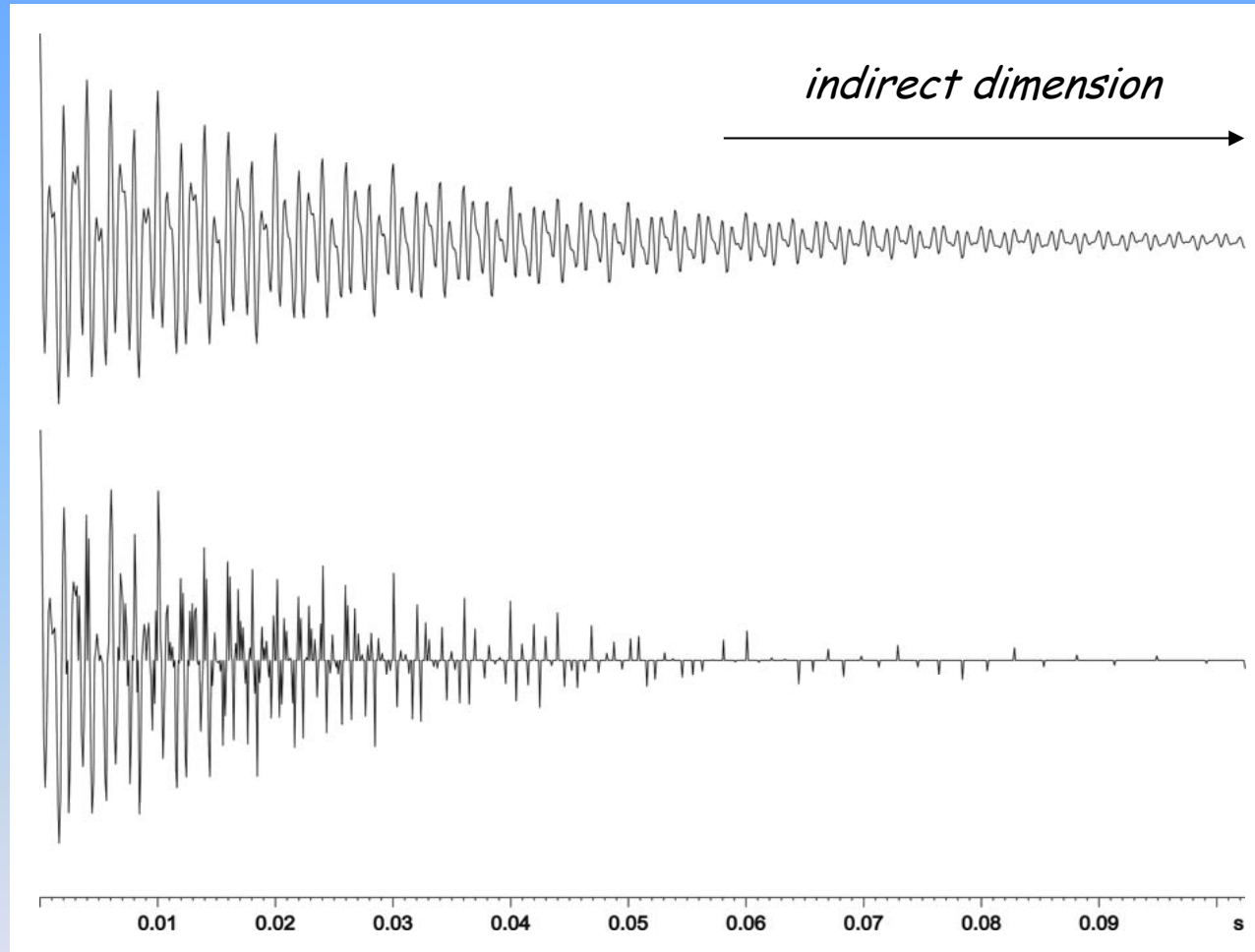


Maximum-Entropy
Reconstruction



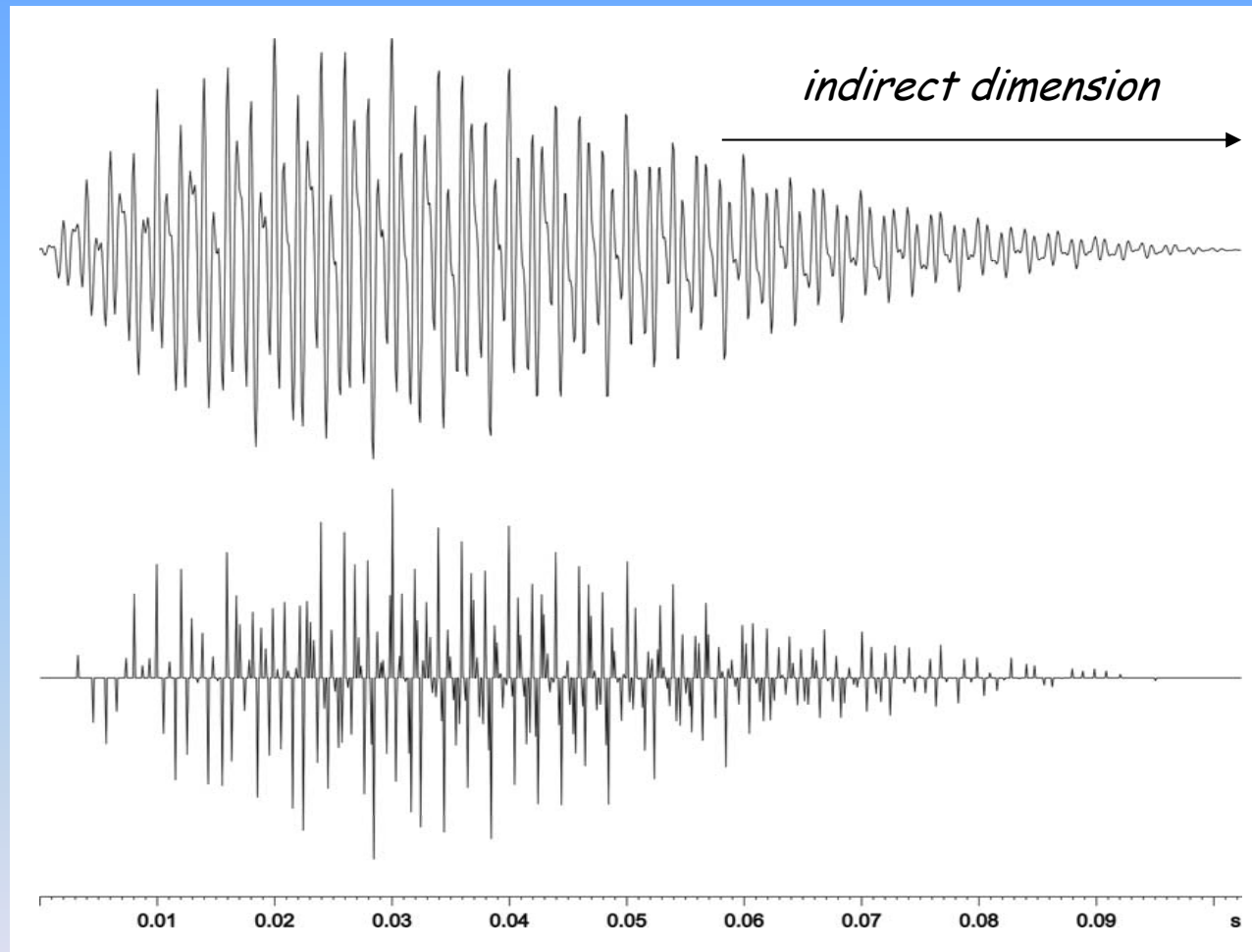
Multi-Dimensional
Decomposition

exponentially-decaying signal



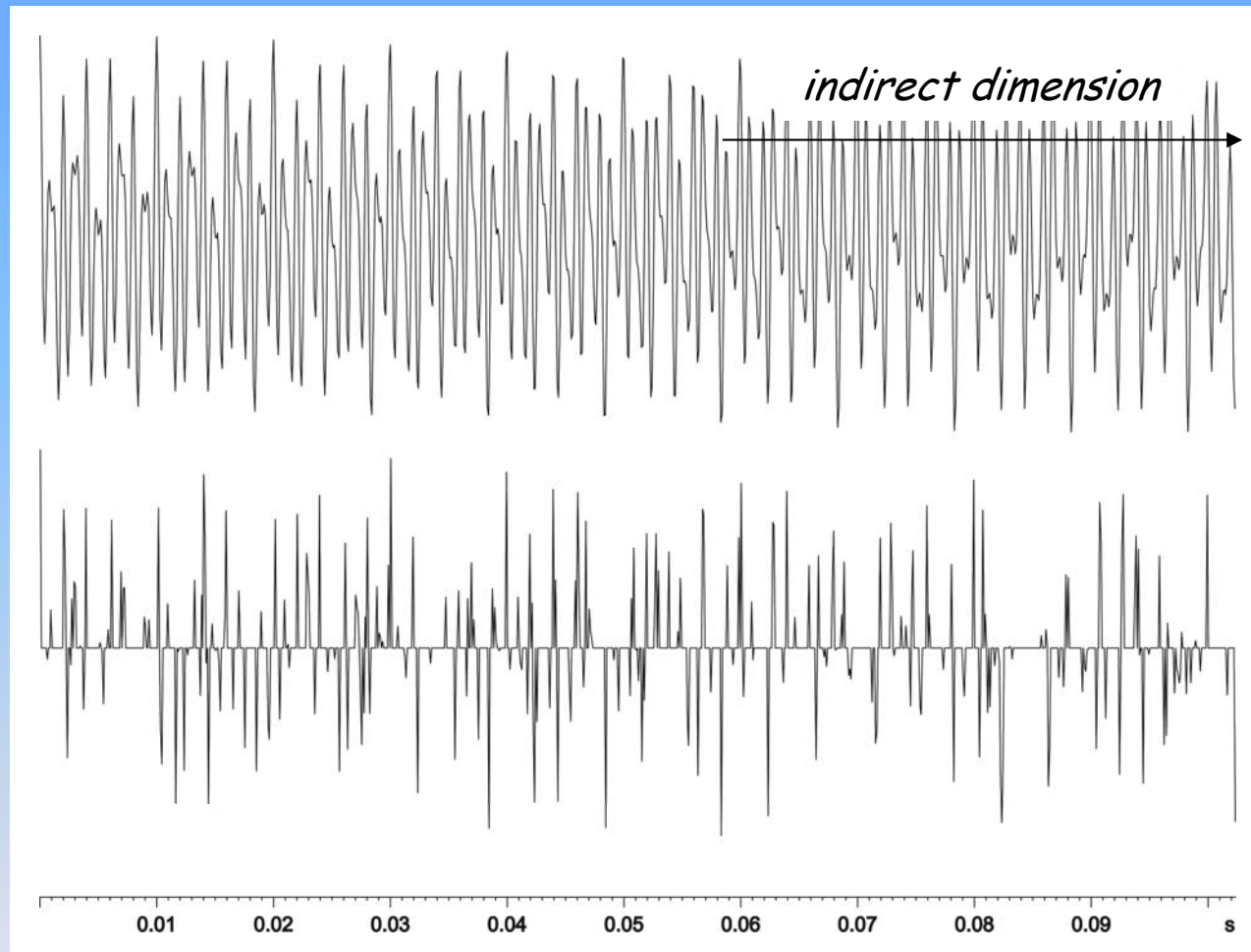
J.C.J. Barna et al. *J. Magn. Reson.* **73**, 69-77 (1987)

sine-modulated signal (e.g. cosy-experiment)



P. Schmierer et al. *J. Biomolec. NMR* 3, 569-576 (1993)

non-decaying signal (e.g. ct-experiment)



P. Schmierer et al. *J. Biomolec. NMR* 4, 483-490 (1994)

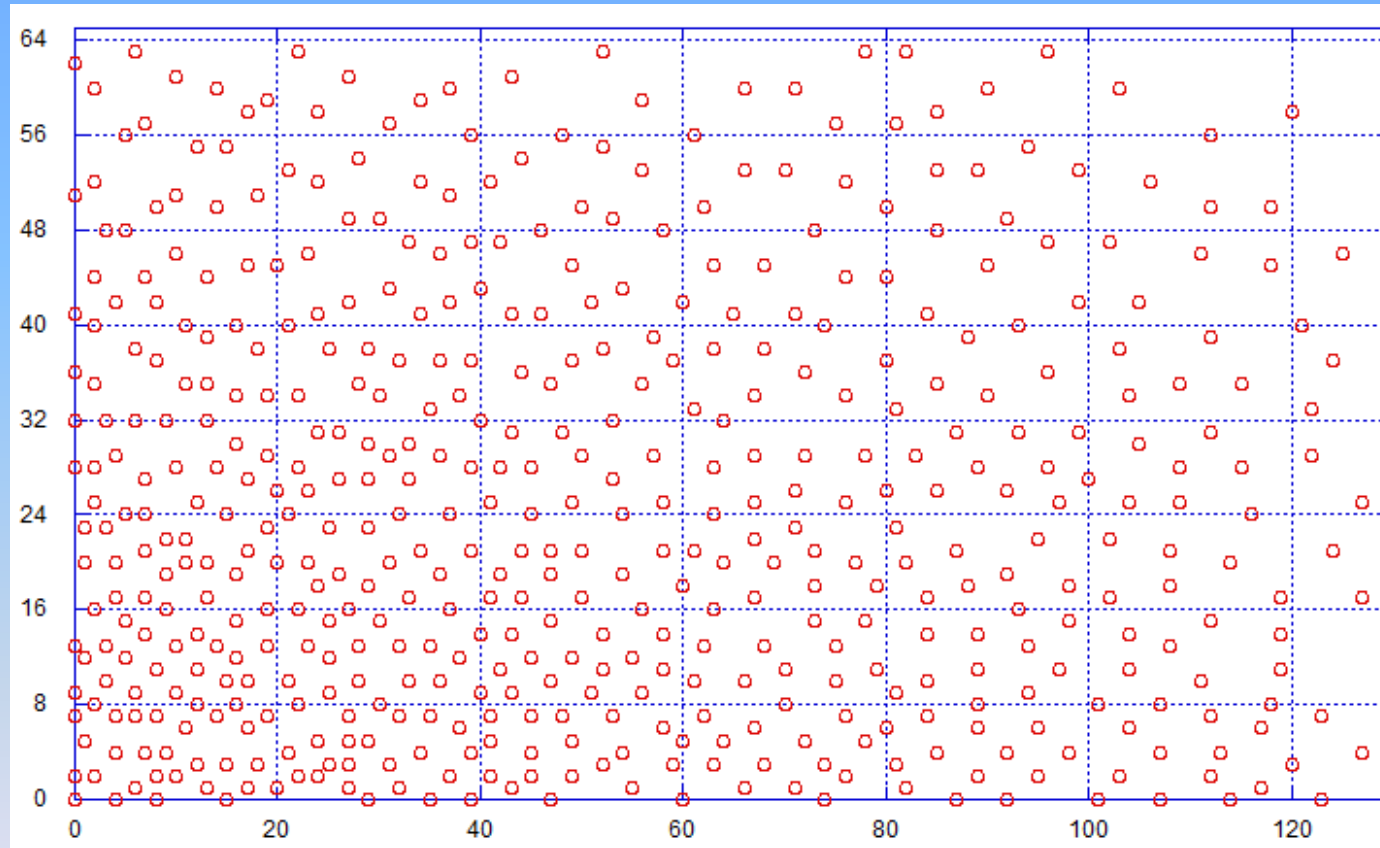
In 3D there are two indirect dimensions

64 x 128 complex points



exponentially-decaying signals in 3D

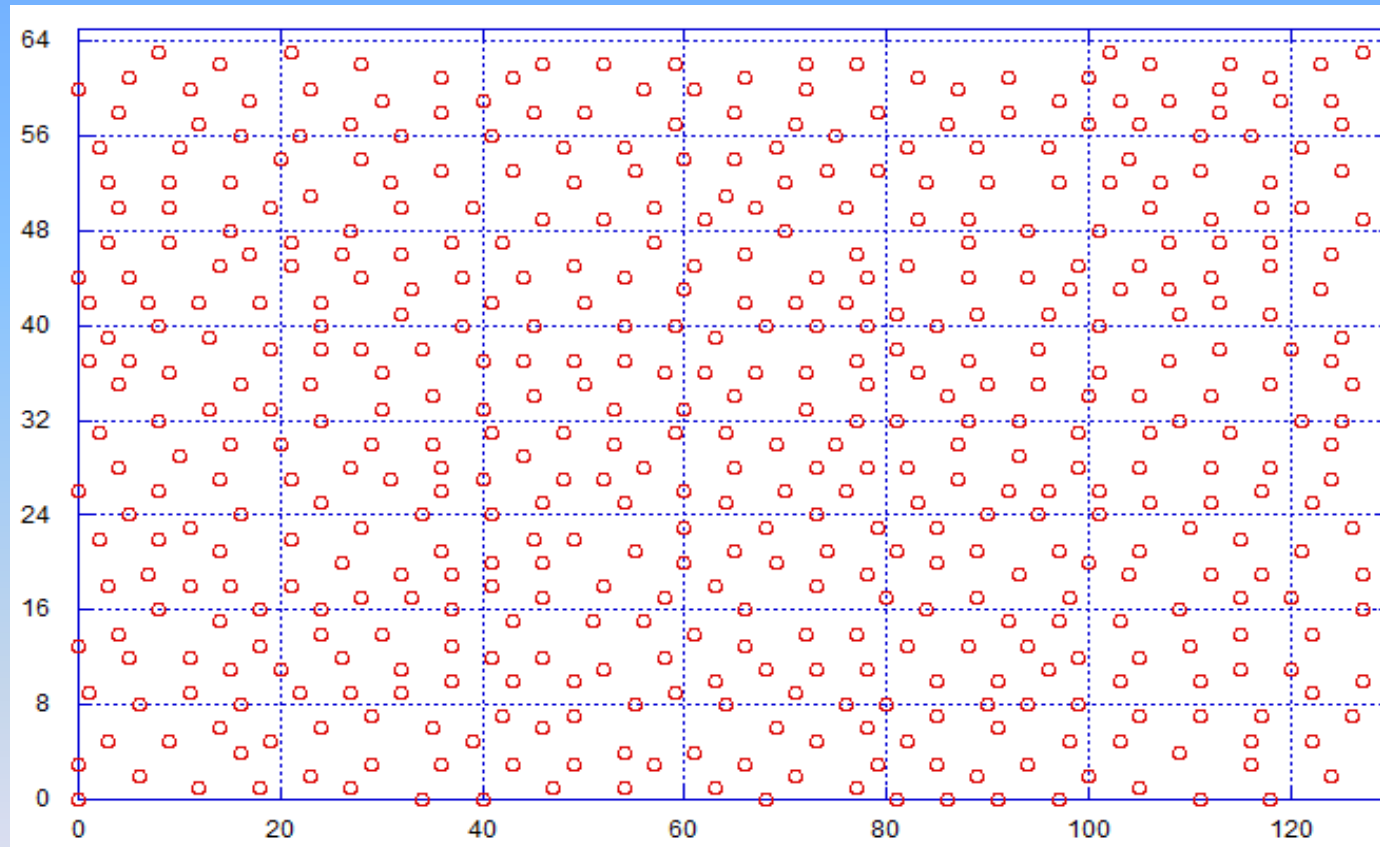
512 out of 8192 (64 × 128) complex points



A.S. Stern et al. *J. Am. Chem. Soc.* **124**, 1982-1993 (2002)

non-decaying signal in 3D

512 out of 8192 (64 × 128) complex points



A.S. Stern et al. *J. Am. Chem. Soc.* **124**, 1982-1993 (2002)

sampling limit

the sample provides sufficient S/N and the data have to be recorded far too long to achieve enough resolution

NUS can drastically shorten the experiment time

sensitivity limit

the sample requires an extended experiment time to achieve a sufficient S/N anyway and the required resolution can easily be obtained

NUS can provide more flexibility

ct-HNCA of SH3 @900 MHz

We are clearly in the sampling limit !

^{13}C : the ct-delay is 27 msec, the increment is 132 μsec

we can collect 200 complex points (400 FIDs)

^{15}N : the ct-delay is 22 msec, the increment is 220 μsec

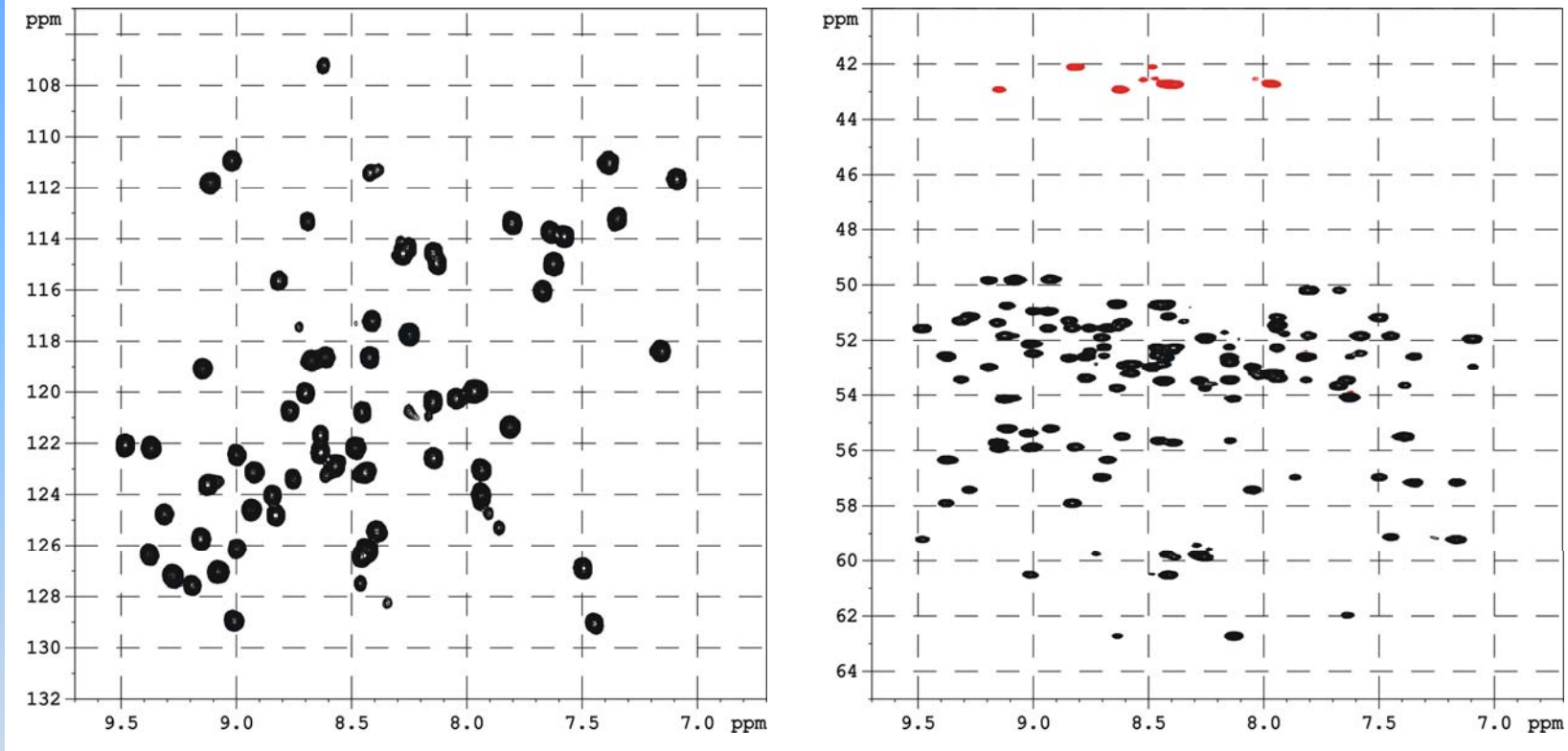
we can collect 100 complex points (200 FIDs)

The full 3D would therefore consist of 80 000 FIDs

Assuming 4 scans and 0.8 sec relaxation delay this amounts to 80

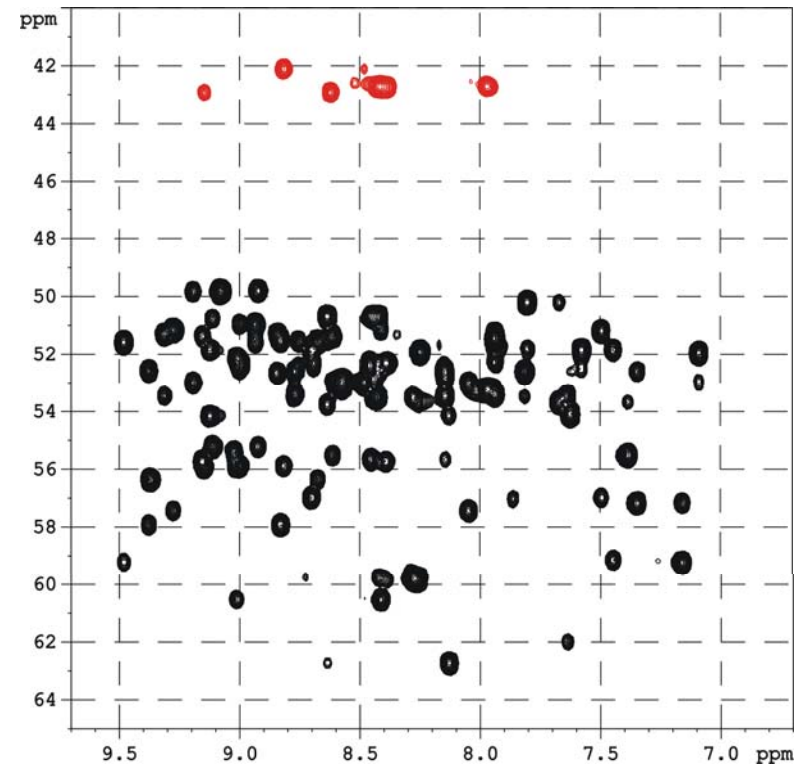
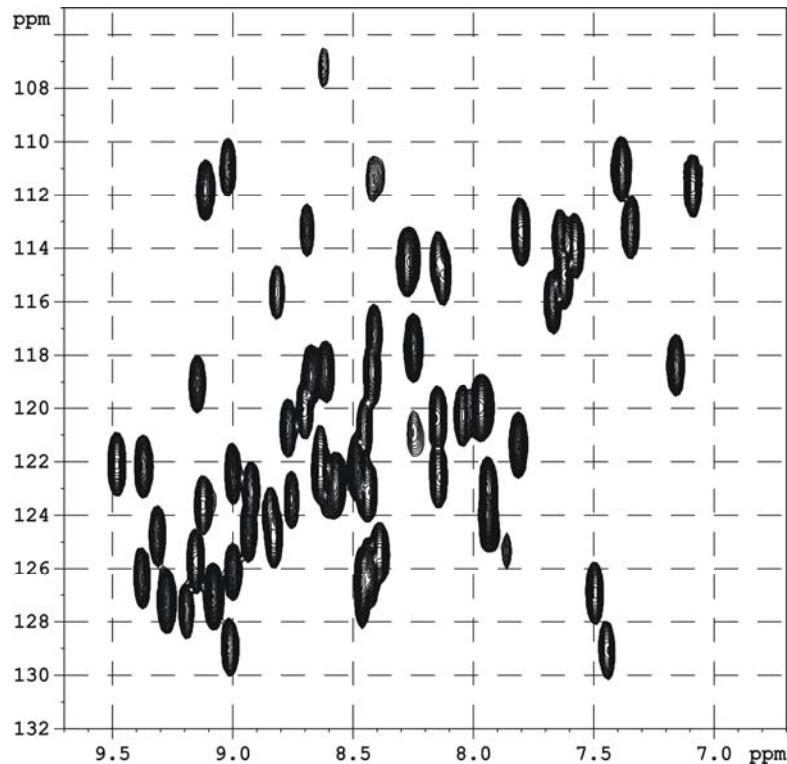
hours, while 1 hour is enough for S/N !

ct-HNCA of SH3 @900 MHz



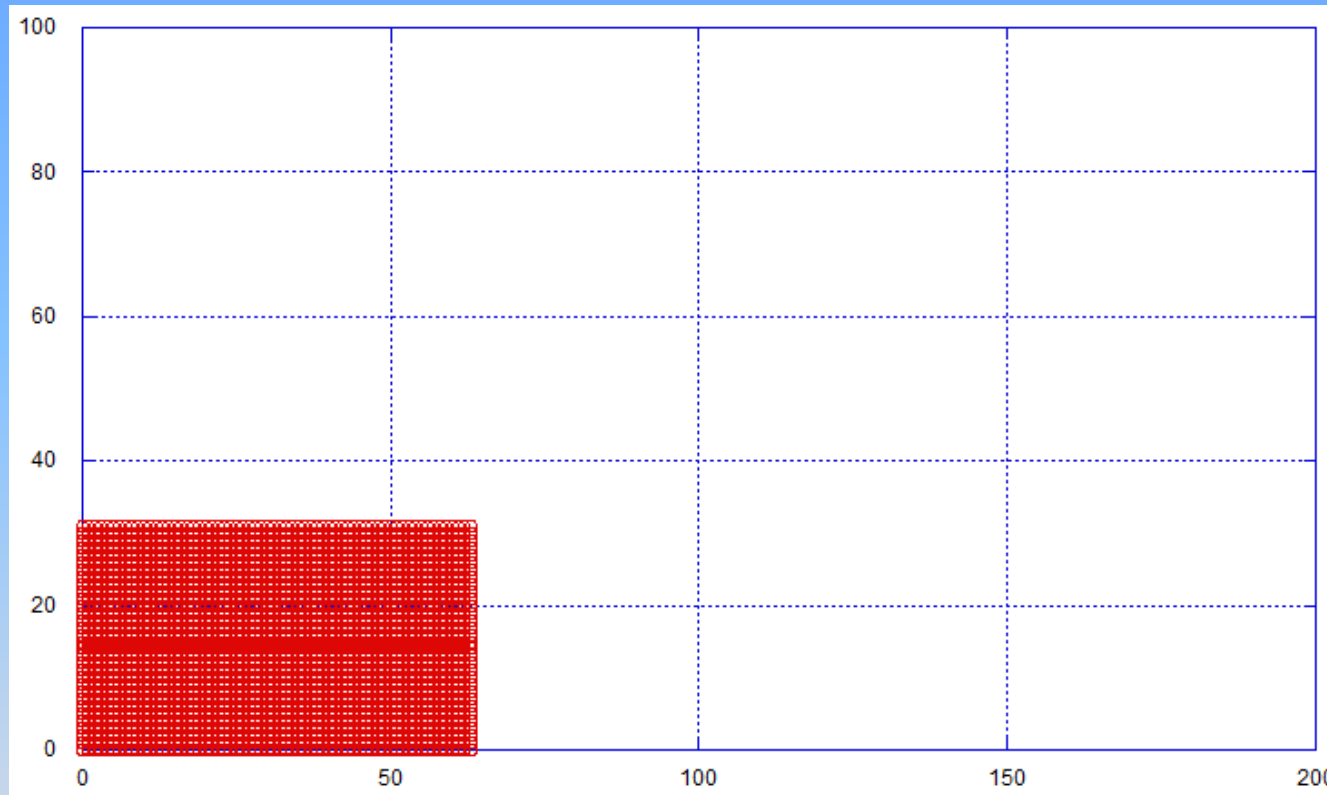
Projections of a dataset with $100^* \times 200^* = 20\,000$ full points, i.e. 80 hours spectrometer time

ct-HNCA of SH3 @900 MHz



if we cut this to 8 hours "classically" ($32^* \times 64^* = 2048$ full points) we
have less resolution

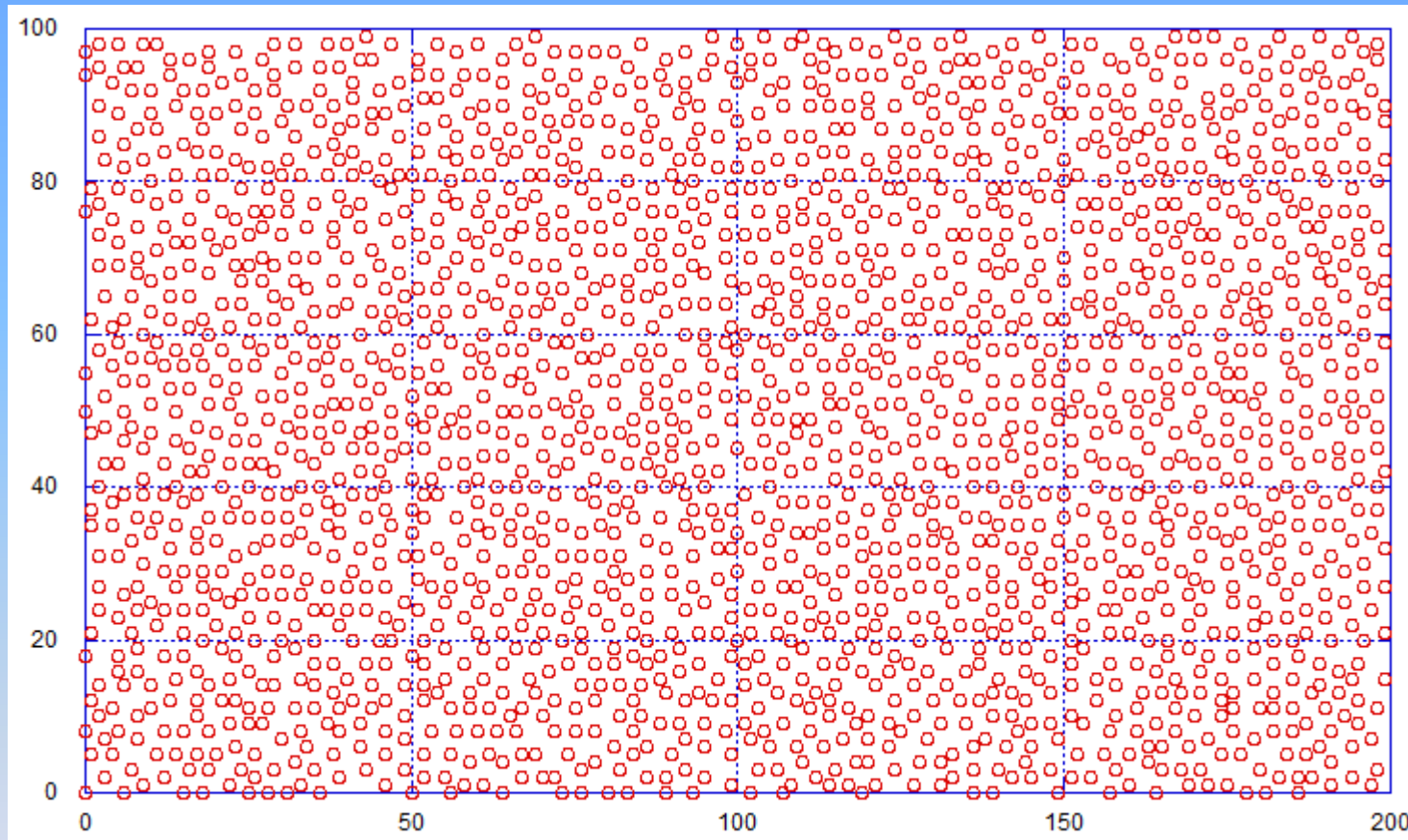
ct-HNCA of SH3 @900 MHz



by cutting to 8 hours the sampling is drastically reduced:

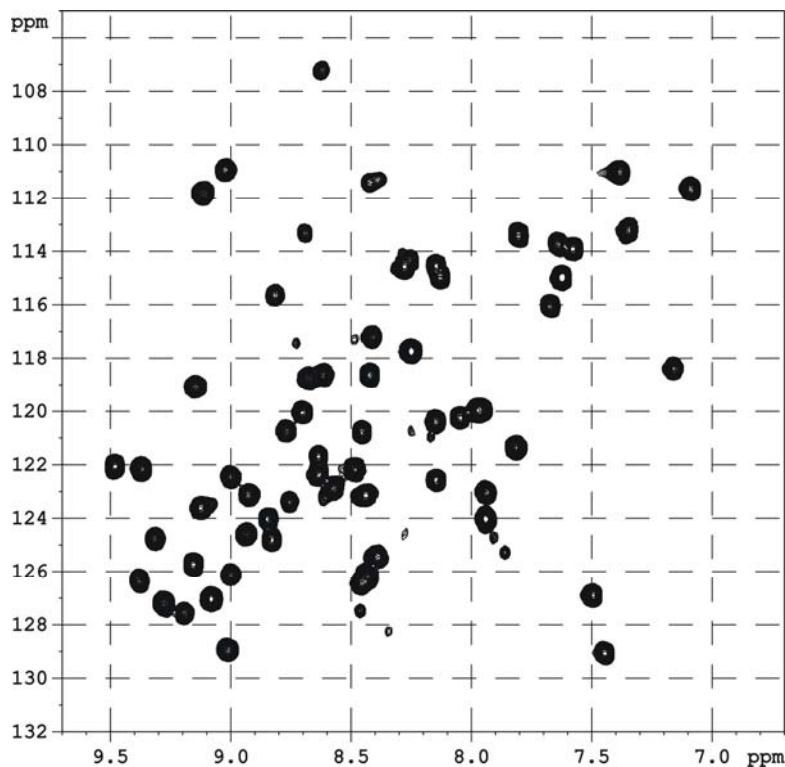
$$32^* \times 64^* = 2048 \text{ full points}$$

ct-HNCA of SH3 @900 MHz

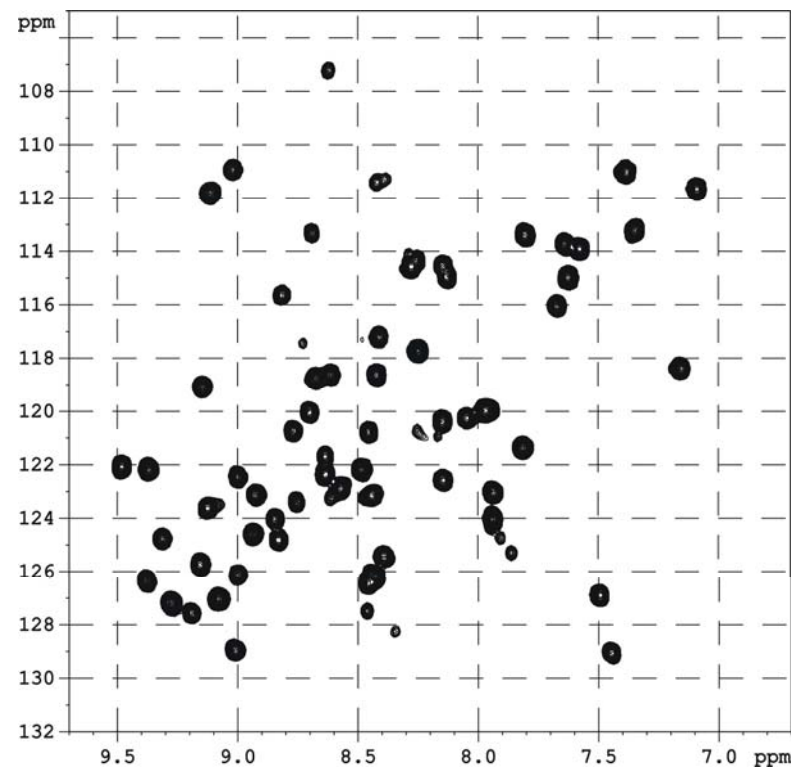


2048 out of 20000 (10.2%)

ct-HNCA of SH3 @900 MHz

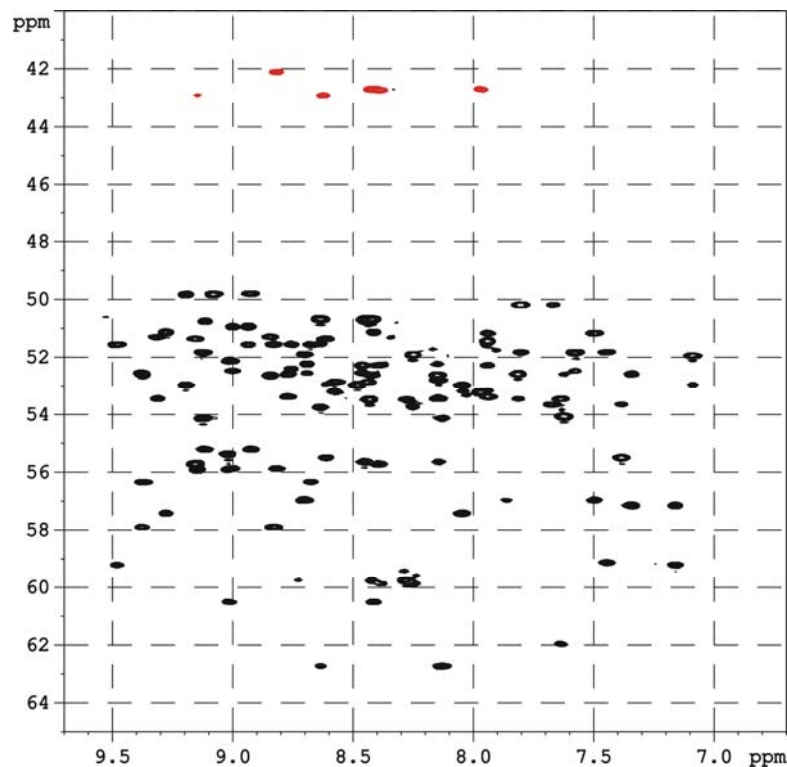


8 hours instead of 80

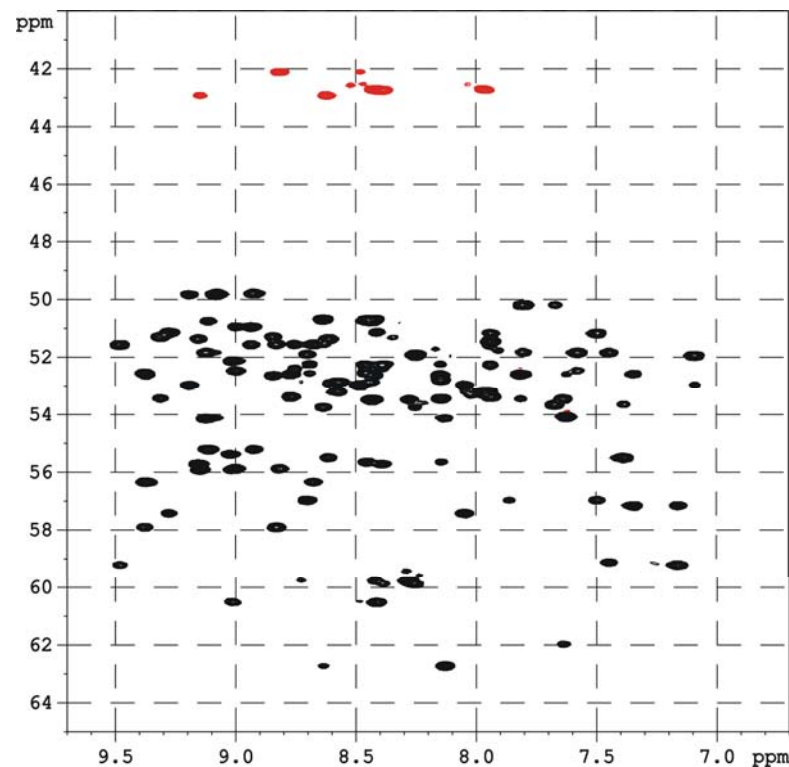


traditional

ct-HNCA of SH3 @900 MHz

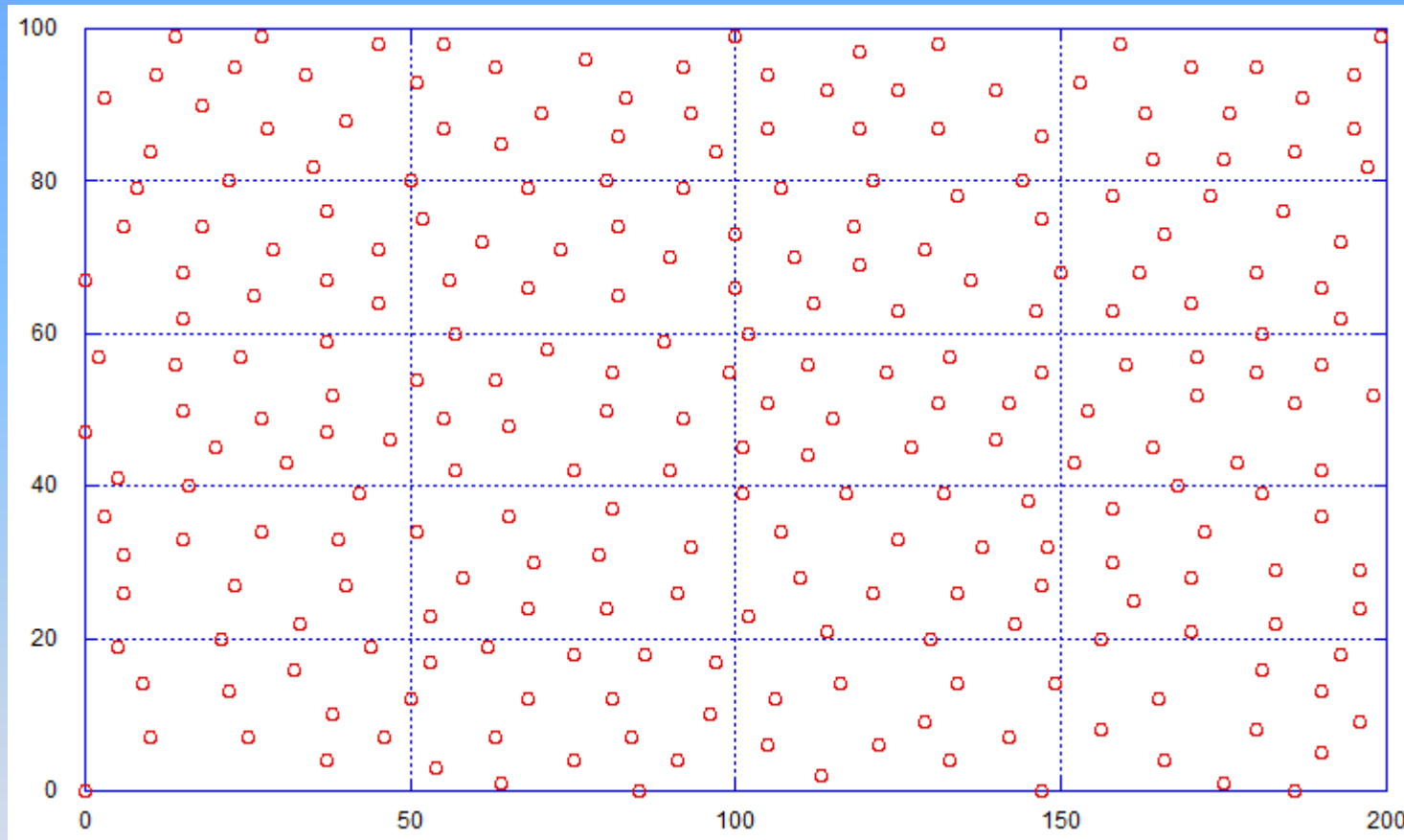


8 hours instead of 80



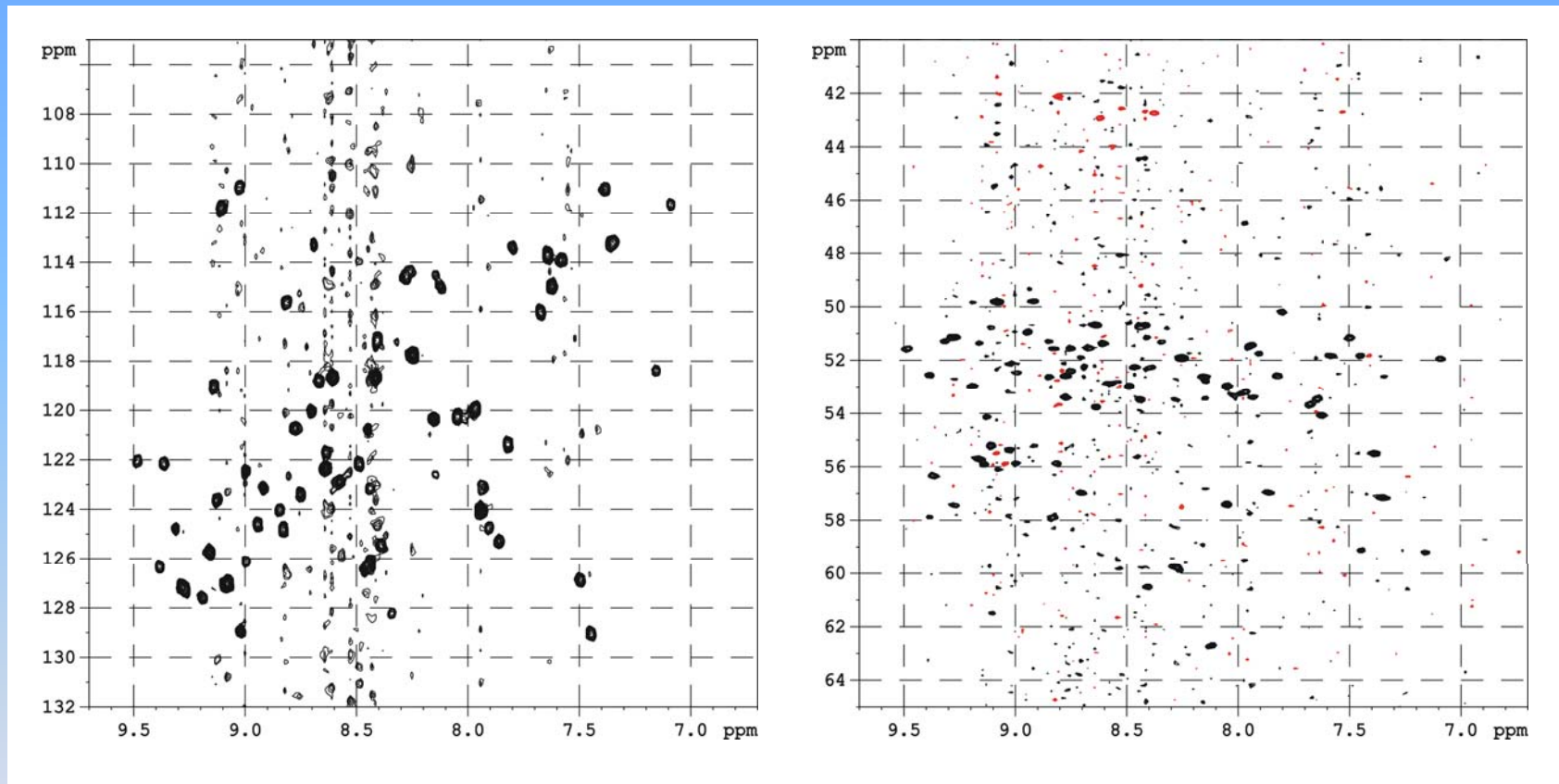
traditional

ct-HNCA of SH3 @900 MHz



256 out of 20000 (1.3%)

ct-HNCA of SH3 @900 MHz



256 out of 20 000: 1 hour instead of 80

Acquisition of NUS data in topspin 3.1

Experiment

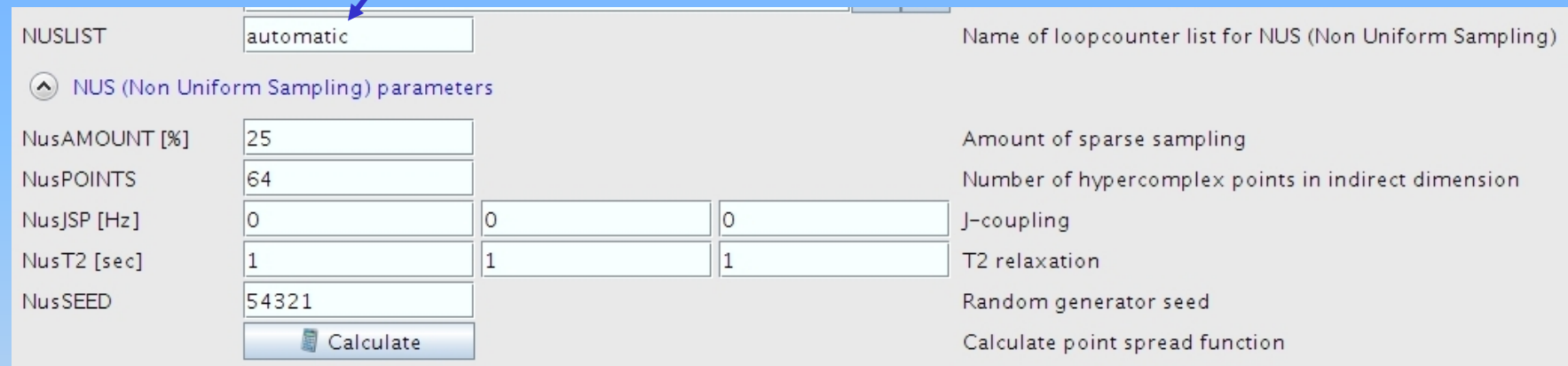
PULPROG	MFhncowg_nus_psf	...	E	Current pulse program
AQ_mod	DQD			Acquisition mode
FnMODE	States	States		Acquisition mode for 2D, 3D etc.
FnTYPE	traditional(planes)			nD acquisition mode for 3D etc.
TD	1024	32	32	Size of fid
DS	4			Number of dummy scans
NS	16			Number of scans
TD0	1			Loop count for 'td0'

Experiment

PULPROG	MFhncowg_nus_psf	...	E	Current pulse program
AQ_mod	DQD			Acquisition mode
FnMODE	States	States		Acquisition mode for 2D, 3D etc.
FnTYPE	non-uniform_sampling			nD acquisition mode for 3D etc.
TD	1024	32	32	Size of fid
DS	4			Number of dummy scans
NS	16			Number of scans
TD0	1			Loop count for 'td0'

Acquisition of NUS data in topspin 3.1

NUSLIST is the sampling schedule, which can also be created independently (it is a vc-list)



NUSLIST	automatic	Name of loopcounter list for NUS (Non Uniform Sampling)		
NUS (Non Uniform Sampling) parameters				
NusAMOUNT [%]	25	Amount of sparse sampling		
NusPOINTS	64	Number of hypercomplex points in indirect dimension		
NusJSP [Hz]	0	0	0	J-coupling
NusT2 [sec]	1	1	1	T2 relaxation
NusSEED	54321	Random generator seed		
<input type="button" value="Calculate"/>				Calculate point spread function

Parameter to create the sampling schedule:
NusAMOUNT gives the percentage of points
(NusPOINTS) selected

Acquisition of NUS data in topspin 3.1

0 0
56 5
43 92
22 8
41 8
58 30
59 3
5 31
12 19
4 43
39 4
2 8
11 26
8 46
11 21
50 41
8 63
9 27
50 8
17 43
51 86
24 31
6 67
11 93
4 4
9 5
10 39
40 75
52 54
61 34
54 10
10 37
...

The points in the NUSLIST are also ordered randomly so that reasonable processing is possible without waiting for the experiment to finish.

The list is stored in the dataset under the name "nuslist"

How many points have been recorded is stored in the parameter NusTD for each dimension while the TD only gives the maximum number of points

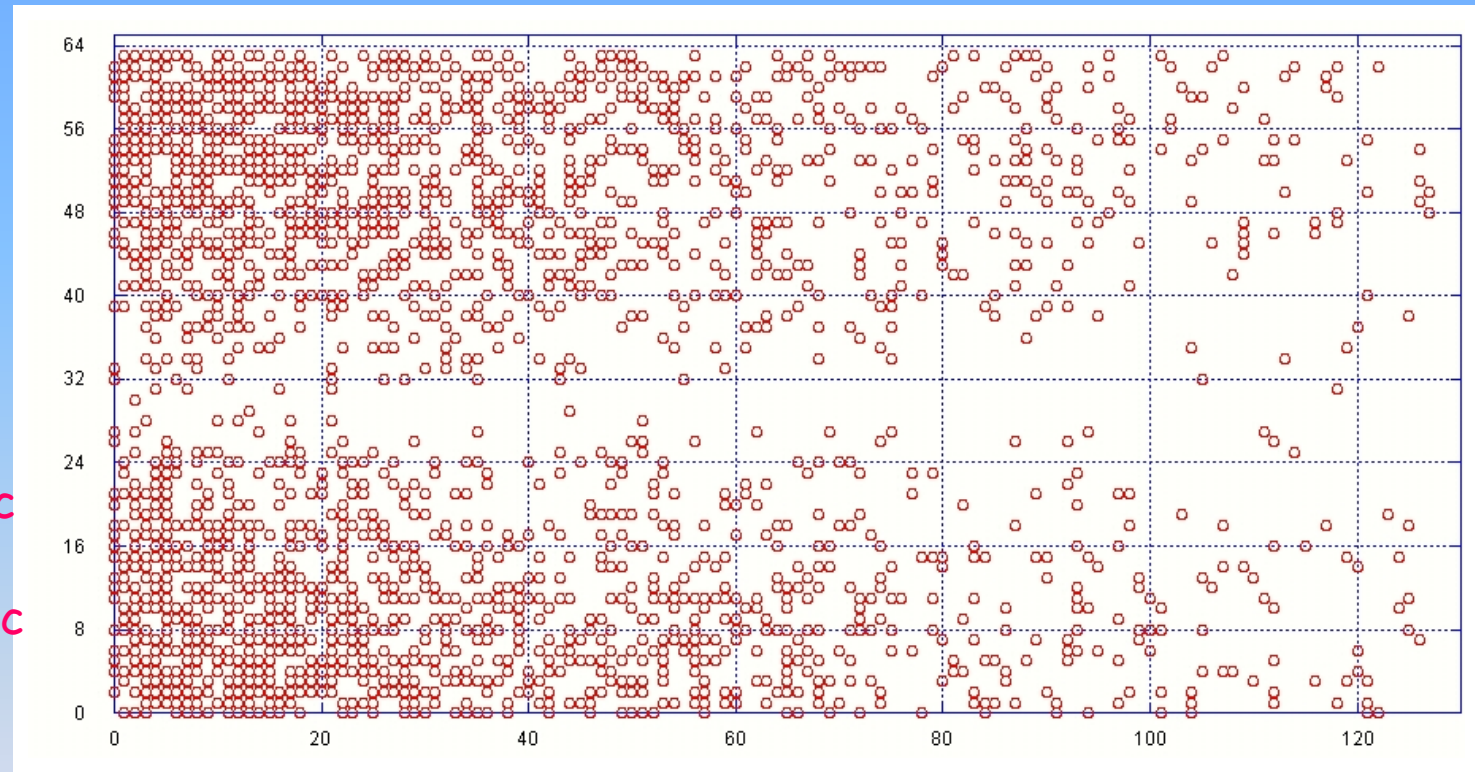
Acquisition of NUS data in topspin 3.1

NUSLIST	automatic	Name of loopcounter list for NUS (Non Uniform Sampling)		
NUS (Non Uniform Sampling) parameters				
NusAMOUNT [%]	25	Amount of sparse sampling		
NusPOINTS	64	Number of hypercomplex points in indirect dimension		
NusJSP [Hz]	0	0	0	J-coupling
NusT2 [sec]	1	1	1	T2 relaxation
NusSEED	54321	Random generator seed		
	<input type="button" value="Calculate"/>	Calculate point spread function		

Parameter to adjust the sampling schedule:
NusJSP if a cosine-modulation due to coupling is present
NusT2 if there is a decay due to relaxation

Acquisition of NUS data in topspin 3.1

using NusJSP and NusT2



$t_{\max} = 20 \text{ msec}$
 $J = 50 \text{ Hz}$
 $1/2J = 10 \text{ msec}$

$t_{\max} = 15 \text{ msec}$
 $T_2 = 5 \text{ msec}$

Processing of NUS data in topspin 3.1

NUS is recognized by the command **ftnd** and **mdd** is started automatically

ftnd

NAME

ftnd - nD processing including Fourier transform ($\geq 3D$)

DESCRIPTION

The command *ftnd* processes nD data performing fid baseline correction, linear prediction, window multiplication, Fourier transform and phase correction. The command automatically recognizes the data dimensionality and handles data of dimension $\geq 3D$. In TOPSPIN 2.1, *ftnd* has been tested by Bruker on 3D, 4D, 5D and 6D data. Note that 3D data can also be processed with the conventional commands *tf3*, *tf2*, *tf1* and *ft3d*.

As an example, *ftnd* is described here for a 4D dataset. It takes the following three arguments:

- *<direction>*
the direction(s) to be processed. Allowed values are:
 - 0 : all directions, in the order defined by AQSEQ
 - 4321, 4312, 4231, 4213, 4132, 4123 : all directions in specified order
 - 4, 3, 2, or 1 : F4, F3, F2 or F1, respectively.

„ftnd 0“

Thank you