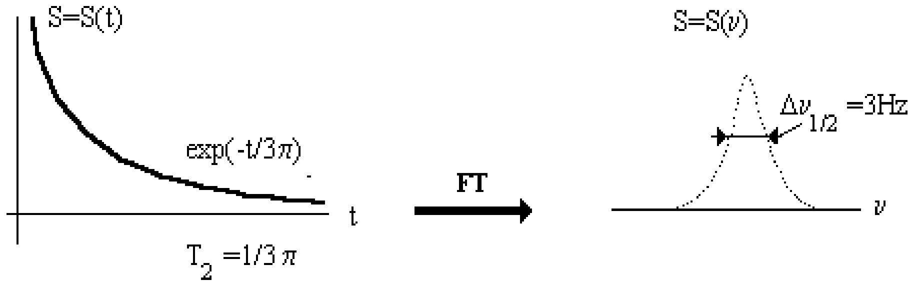
DATA PROCESSING

Let us start with a numerical example:

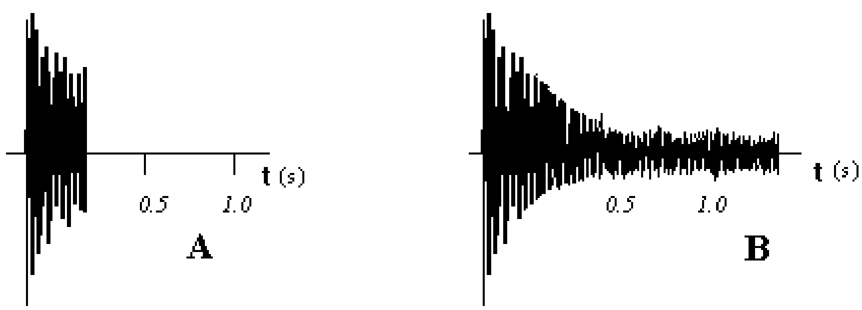


Typical line of $\Delta\upsilon_{1/2}$ =3Hz.= $(\pi T_2)^{-1}$ → $T_{2=}$ $(3\pi)^{-1} \approx 0{,}11$s

question #1: ideal acquisition time (t_a)?

memo: if t_a too short → A type FID is obtained (truncated)

if t_a too long → B type FID is obtained (too much noise)



answer #1: acquisition until the intensity of the FID is <1-2% of the initial value of S=S(t)

S(t) = exp(-t/T_2) and $T_2 \approx$ 0.11s → 0.01=exp(-t/0.11) → t=0,4-0,5s

memo: typical $t_{max} > 3T_2$ → in this case the suggested t_{max}>0,33s

question #2: size of the data vector **r**(t)?

memo $dw=Sw^{-1}$

e.g. Sw = 10 kHz → dw = 100 µs

Acquiring data for t=0,4-0,5s.

A new point at every 100 µs →≈ 5000 points to be stored

answer #2: **r**(t) should be 5k (5120 points)

conclusion: digital resolution 1.95Hz/point

question #3: what if t_{max} < 0,4-0,5s *consequence:* truncated data

question #4: what if t_{max} > 0,4-0,5s *consequence:* noise is collected

answer #4: to improve digital resolution < 1.95Hz/point zero fill

e.g. ≈1.00Hz/point zero fill up to 10 k

Typical processing steps (one-dimensional operations) along the recorded 1D-data

A time ($t_{acq.}$) domain complex vector **r**(t)

↓

suppression of solvent and remove DC offset

↓

apodize

↓

zero-fill

↓

scale first point

↓

discrete Fourier transform

↓

phase correction

↓

baseline correction

↓

A frequency domain function **f**(ν)

Typical processing steps along a 2D-data set

A time ($t_{acq.}$) domain complex vector **r**(t_1,t_2)

processing along t_2 (M complex vectors)

suppression of solvent and remove DC offset
apodize
zero-fill
scale first point
discrete Fourier transform
phase correction
baseline correction

r(t_1,ν_2)

processing along t_1 (N complex vectors)

apodize
zero-fill
scale first point
discrete Fourier transform
phase correction

f(ν_1,ν_2)

time domain signal $S = S(t)$

memo 1 : $FT\{S(t)\}$ ---> $S(\upsilon) = \int S(t) \exp(-i2\pi\upsilon t)\, dt$ $\quad 2\pi\upsilon = \omega$
memo 2 : $IFT\{S(\upsilon)\}$ ---> $S(t) = \int S(\upsilon) \exp(+i2\pi\upsilon t)\, d\upsilon$
memo 3 : $S(\upsilon)$ and $S(t)$ are Fourier pairs
memo 4 : FT and IFT are linear operations, therefore:
$FT\{cS(t)\} = c\, FT\{S(t)\}$ and $FT\{S(t)+Q(t)\} = FT\{S(t)\} + FT\{Q(t)\}$

theorems of FT relevant for NMR data processing:

A. similarity theorem:

$FT\{S(ct)\} = |c|^{-1} S(\omega/c) = |c|^{-1} S(2\pi\upsilon/c)$

Broadening the function in the time domain is narrowing it in the frequency domain

B time shifting theorem:

$FT\{S(t-\tau)\} = \exp(-i2\pi\upsilon\tau)\, S(\upsilon)$
Delaying in the time domain will induce a frequency-dependent phase shift

C frequency shifting theorem:

$FT\{S(t) \exp(-i2\pi\upsilon_o\tau)\} = S(\upsilon-\upsilon_o)$
frequencies can be shifted after acquisition

D convolution theorem:

$Q(t)*S(t) = \int Q(\tau)S(t-\tau)d\tau$ it's FT $FT\{Q(t)*S(t)\} = Q(2\pi\upsilon)*S(2\pi\upsilon)$
convolution of two functions (e.g. removal of residual solvent frequencies)

E Parseval's theorem:

$\int |S(t)|^2\, dt = \int |S(2\pi\upsilon)|^2\, d\upsilon$
The information content of the signal is identical both in the time and frequency domain. (no magic)

Apodization

description : apodizing the time domain signal
goal: to have a signal in the frequ domain with preferable line shape properties
comment: no magic (c.f. **E**)

1. Zero-filling

1.1.minimal zero-filling

fact: fast Fourier transformation (FFT) is faster than discrete Fourier transformation (DFT)

memo: DFT requires N*N steps
FFT requires $N*\log_2 N$ steps

problem: N must be equal to 2^m (m = 1,2,3,..,m)
solution: zero-filling up to the next 2^m
e.g. acquire k data point
attach to the end (2^m-k) zero

1.2.ideal zero-filling

add a 2^m zero at the end after minimal zero-filling
result: data size of $2^{(m+1)}$ points

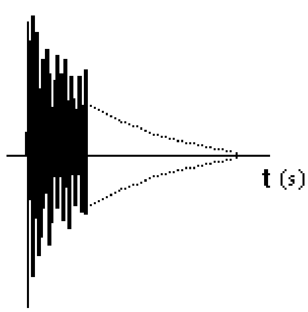
1.3.extra zero-filling

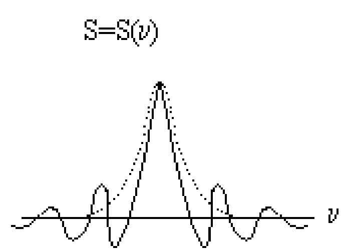
zero-filing more then $2^{(m+1)}$ points is just "cosmetic"

2. Apodization

source of problems invoking for apodization*:*

- -truncation artifacts (typical for non-acquisition dimension)
- -low signal-to-noise ratio (common for nD-experiments)
- -low resolution (often observed for nD-experiments)
- -not-ideal lineshape





answer in theory: **convolution in the frequency domain** with the most appropriate lineshape function { H(υ)}: S'(υ)=H(υ)*S'(υ).

answer in practice: **multiplication of the FID** with one or more window function(s) in the time-domain.

A: Not-shifted H(t) functions

A/1 an exponential: $H(t)=\exp(-\pi Ct)$

Example #1: The original $S(t)=\exp(-t/T_2)\exp(i2\pi\upsilon_{\mathbf{a}}t)$
after FT has a Lorentzian line shape with $\Delta\upsilon_{1/2}=B$ where $B = (\pi T_2)^{-1}$.

Memo: Convolution in υ is multiplication in t

if $H(t)=\exp(-\pi Ct)$ is to be used (an exponential [Figure A/a]) then the new function is:

$$S'(t)=\exp(-t/T_2)\exp(i2\pi\upsilon_{\mathbf{a}}t)\ \exp(-\pi Ct)$$

After multiplication: $S'(t)=\exp-\{(\pi C+1/T_2)t\}\exp(i2\pi\upsilon_{\mathbf{a}}t)$.
After FT S'(t) has a Lorentzian lineshape with $\Delta\upsilon_{1/2}=B+C$ where $C+(\pi T_2)^{-1}$.
conclusion: the line has broadened by C, but S/N has improved (noise is broadened out)

Example #2:

if $H(t)=\exp(+\pi Ct)$ is to be used (an exponential for resolution enhancement) then the new function is:

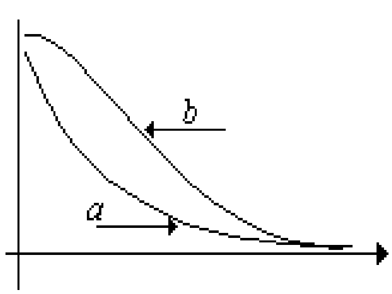
$$S'(t)=\exp(-t/T_2)\exp(i2\pi\upsilon_{\mathbf{a}}t)\ \exp(+\pi Ct)$$

After multiplication: $S'(t)=\exp-\{(-\pi C+1/T_2)t\}\exp(i2\pi\upsilon_{\mathbf{a}}t)$.
After FT the S'(t) has a Lorentzian lineshape with $\Delta\upsilon_{1/2}=B-C$ where $C-(\pi T_2)^{-1}$.
conclusion: The line is narrower to the expense of S/N.
In theory the line shape can be removed.

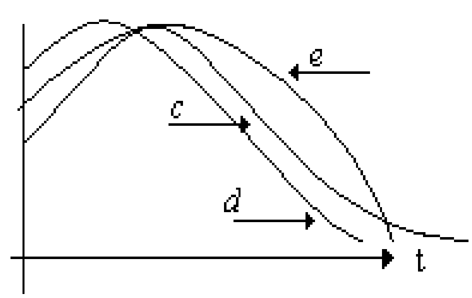
A/2 Gaussian : $H(t)=\exp\{-(kt)^2\}$

B: Shifted H(t) functions

B/1 Shifted Gaussian : **$H(t)=\exp\{-C(kt-k_1t)^2\}$**
B/2 Lorentzian to Gauss-transformation: **$H(t)=\exp\{\pi Ct\}\exp\{-(kt)^2\}$**
B/3 Sin bell: **$H(t)=\sin\{\pi([t+t_0]\backslash[t_{max}+t_0])\}$**



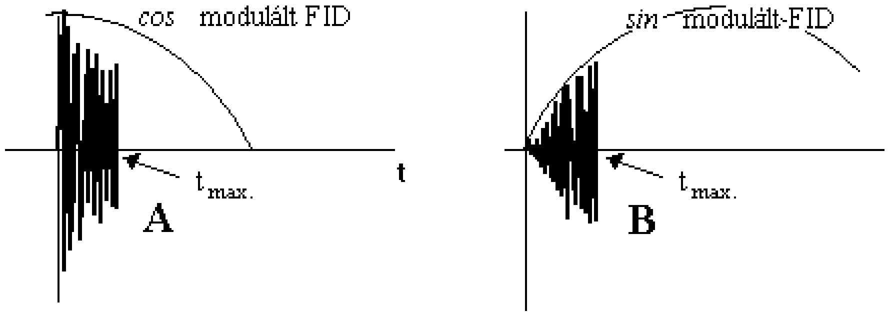
A



B

2.1. ideal apodization against truncation artifact

problem: data is often truncated:



consequence: the time domain signal is not reduced **smoothly** to zero -> the frequency domain signal contains truncation ripples.

answer: *use* apodization

the ideal filtering function: Dolph-Chebyshev function:

$IFT\ \{\cos[2(N-1)\cos^{-1}\{z_0\cos(\omega\Delta t/2)\}]/\cosh[2(N-1)\cos^{-1}\{z_0\}]\}$

where N:= sampled points

Δt:= sampling period

$z_0 := [\cos(\delta\Delta t/4)]^{-1}$

problem : too complex in its nature

application : use as benchmark for evaluating other filtering functions (e.g. Hamming funct., Kaiser Funct.)

2.2. maximize signal-to-noise

if $t_{max} > 3T_2$ then an exponential "line-broadening" function is used in the time-domain:

exp $(-\lambda t)$ where $\lambda \approx 1/T_2$, 2λ is the full-with at half-height of the Lorentzian

problems: exp $(-\lambda t)$ can optimise only the signal at λ frequ.

(For all other frequ. it is just an approach.)

makes the integration of the appodized function incorrect

often applied for acquisition dimension.

2.3. linear prediction