DOSY: Tips and Tricks

Detlef Moskau (2008)

DOSY: where is the challenge?

- Main problems with DOSY are:
  1. Compounds are not well resolved
  2. Signals are not well separated (‘wings’, ‘smilies’,…)
  3. Diffusion rates are wrong even when gradient calibration has been done
- Reasons:
  1. Compounds are not well resolved:
     - Differences in the diffusion rates are too small
     - Other transportation effect are overlaid with diffusion
     - Other transportation effects are larger that the diffusion
  2. Signals are not well separated:
     - Improper experiment conditions
     - DOSY processing parameters and preparation of data for DOSY calculation

DOSY: where is the challenge?

- Compounds are not well resolved:
  1. DOSY is a diffusion experiment
  2. All precautions for sample preparation etc. which are valid for diffusion experiments also apply for the DOSY experiment

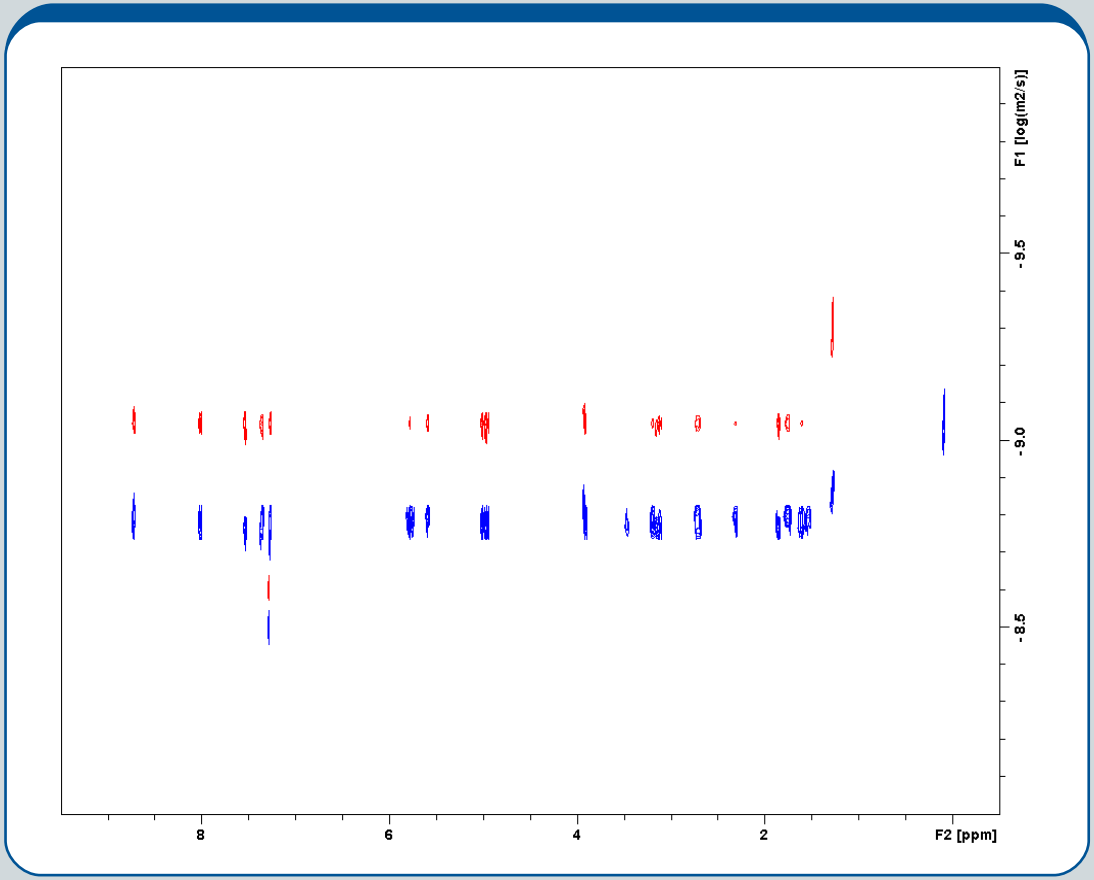
DOSY: understanding artifacts

- Quinine: DOSY and sample rotation:

  Non spinning

  Spinning

  J. Magn. Reson. **2001**, 48,153, Parella et. al.



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  Spinning

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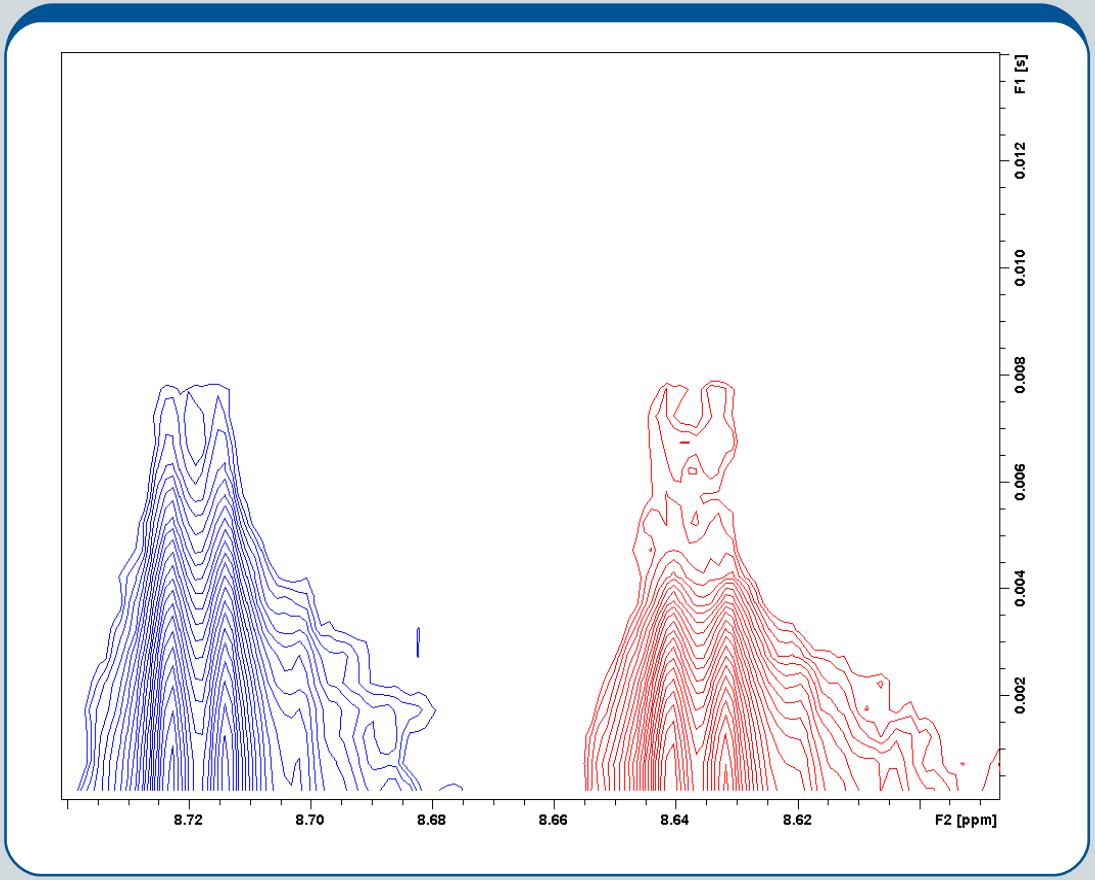
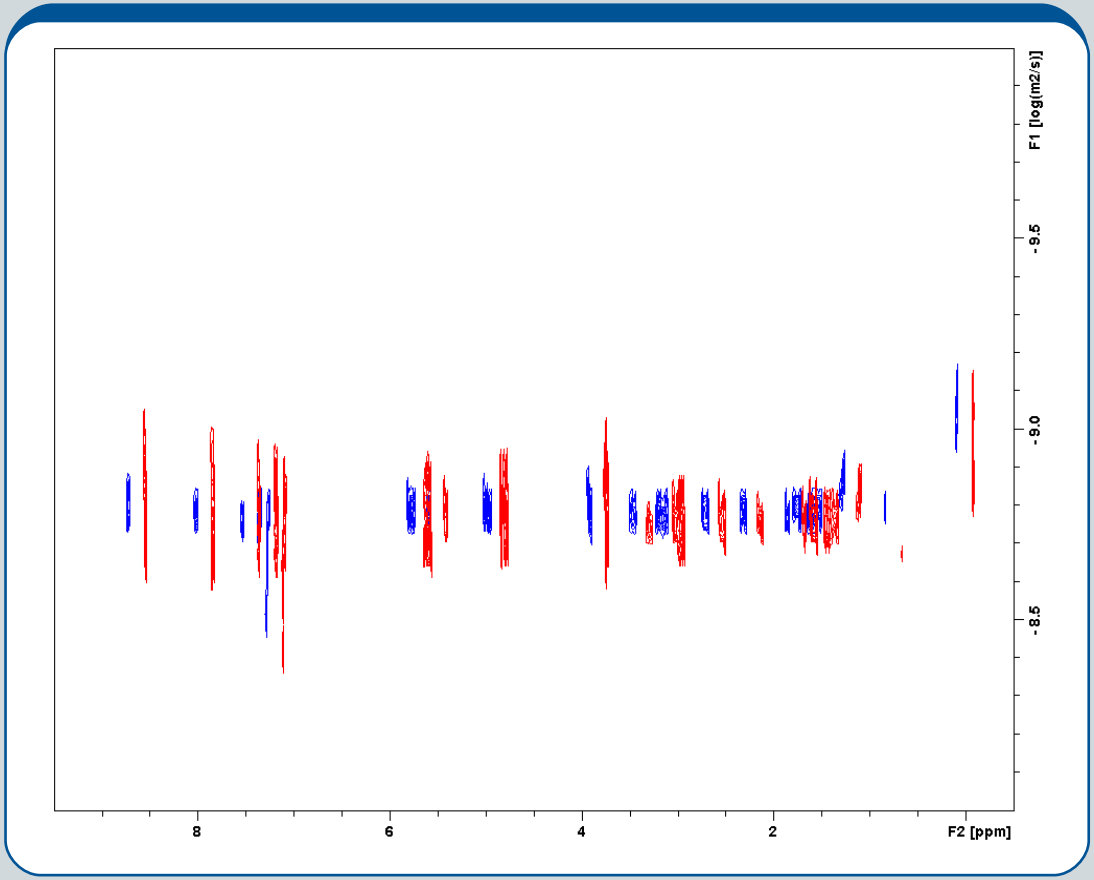


DOSY: understanding artifacts

- Quinine: DOSY at two different gas flows:

  525 l/h

  670 l/h



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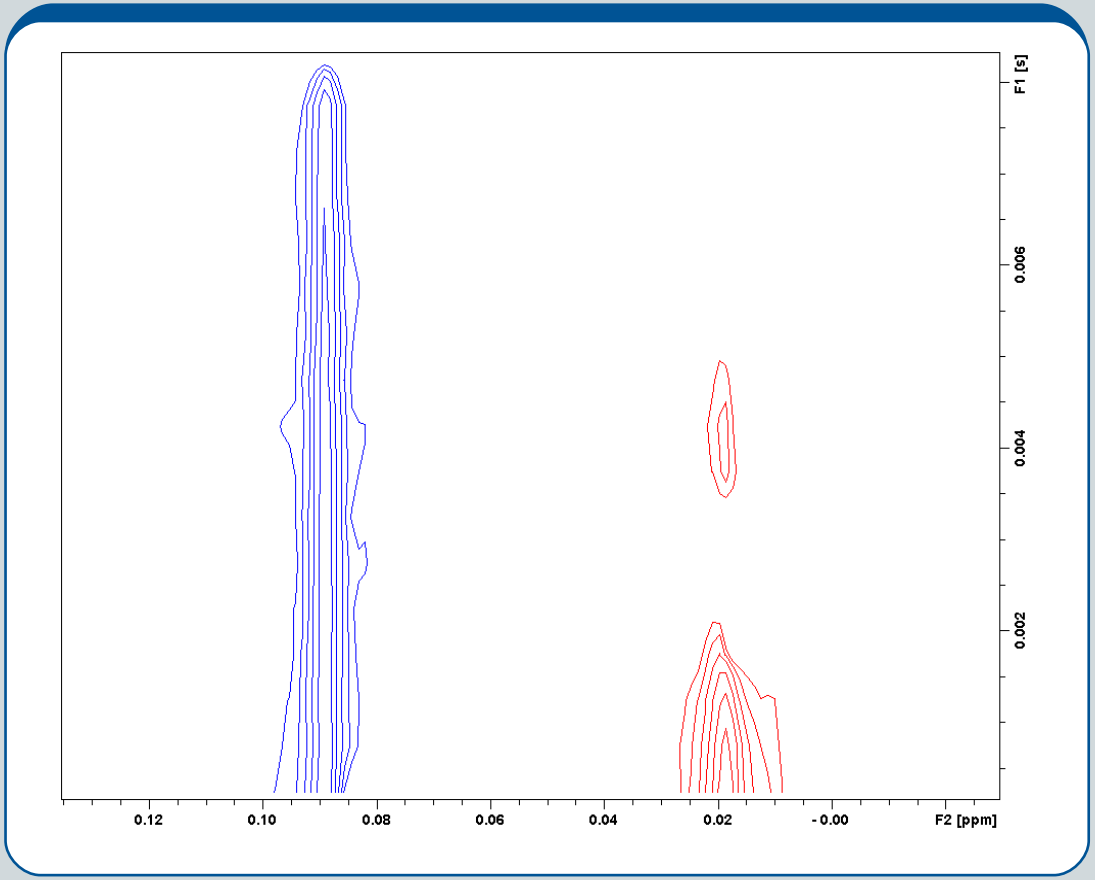
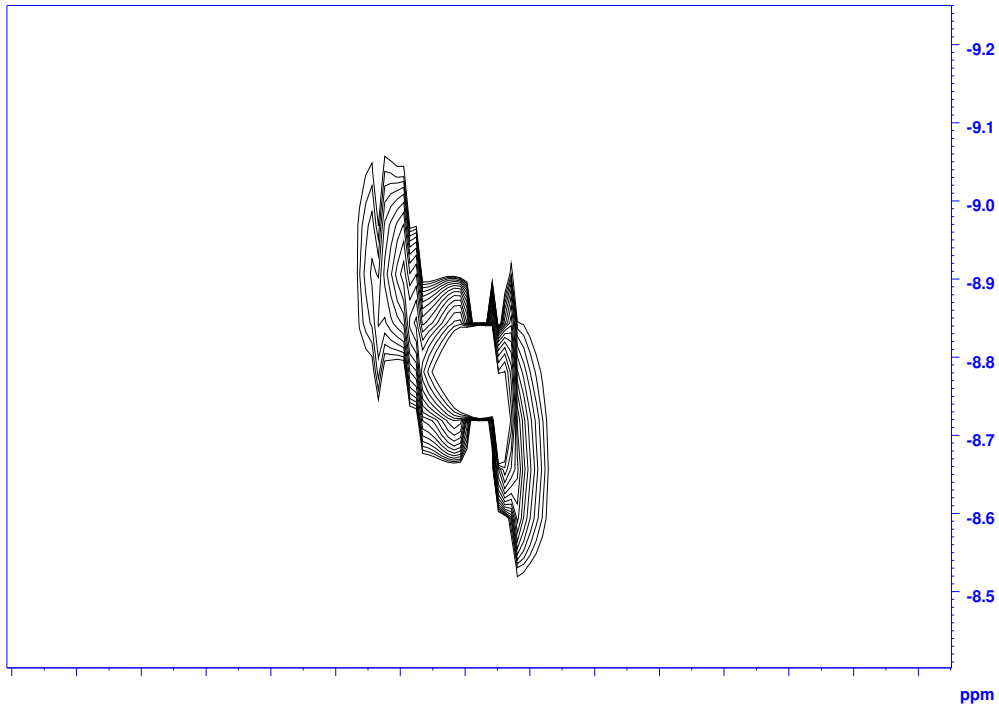


DOSY: understanding artifacts

- Doped water with ^{13}C-MeOH: DOSY

Typical ‘smilies’ are visible



DOSY: optimizing results

- Doped water with ^{13}C-MeOH:

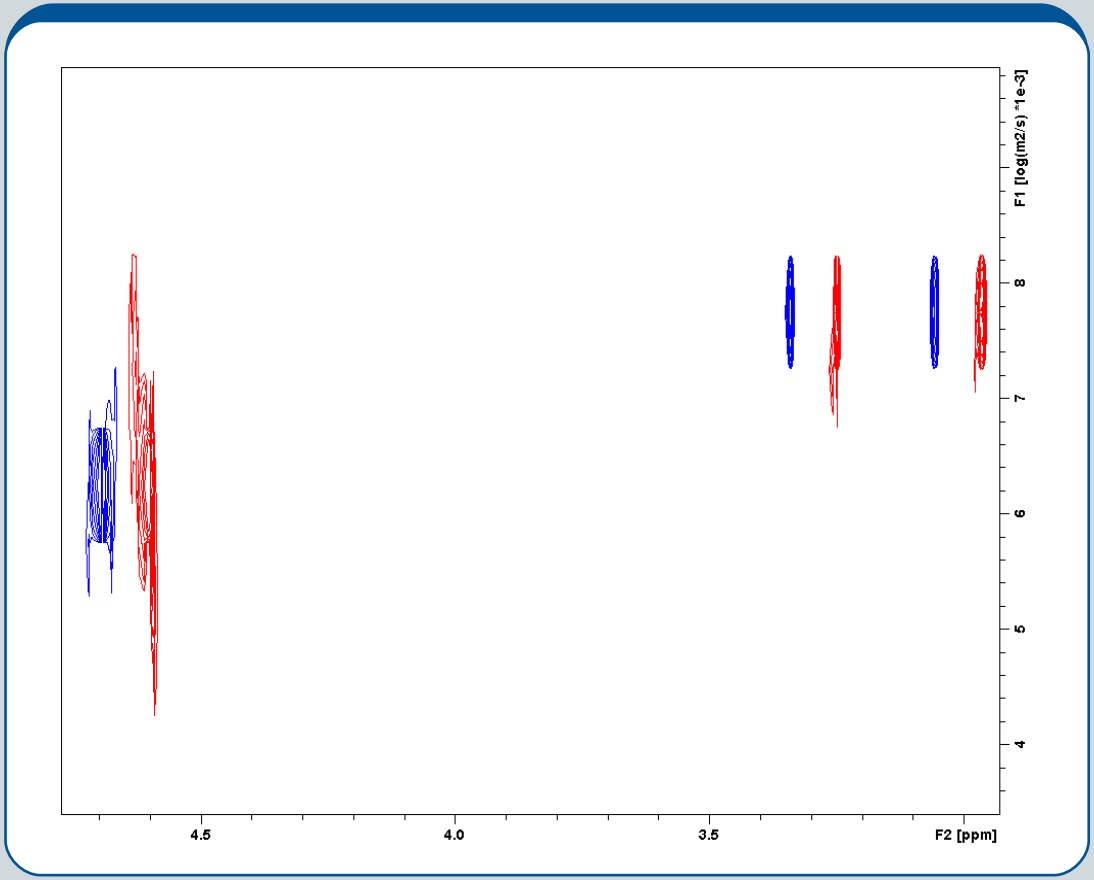
  DOSY 90° composite pulses

  Spatial selective excitation in B_1-homogeneous region

  Allows reduction of smilies

  red: standard LEDBPGP2S

  blue: CP- LEDBPGP2S



DOSY: optimizing results

- Doped water with ^{13}C-MeOH:

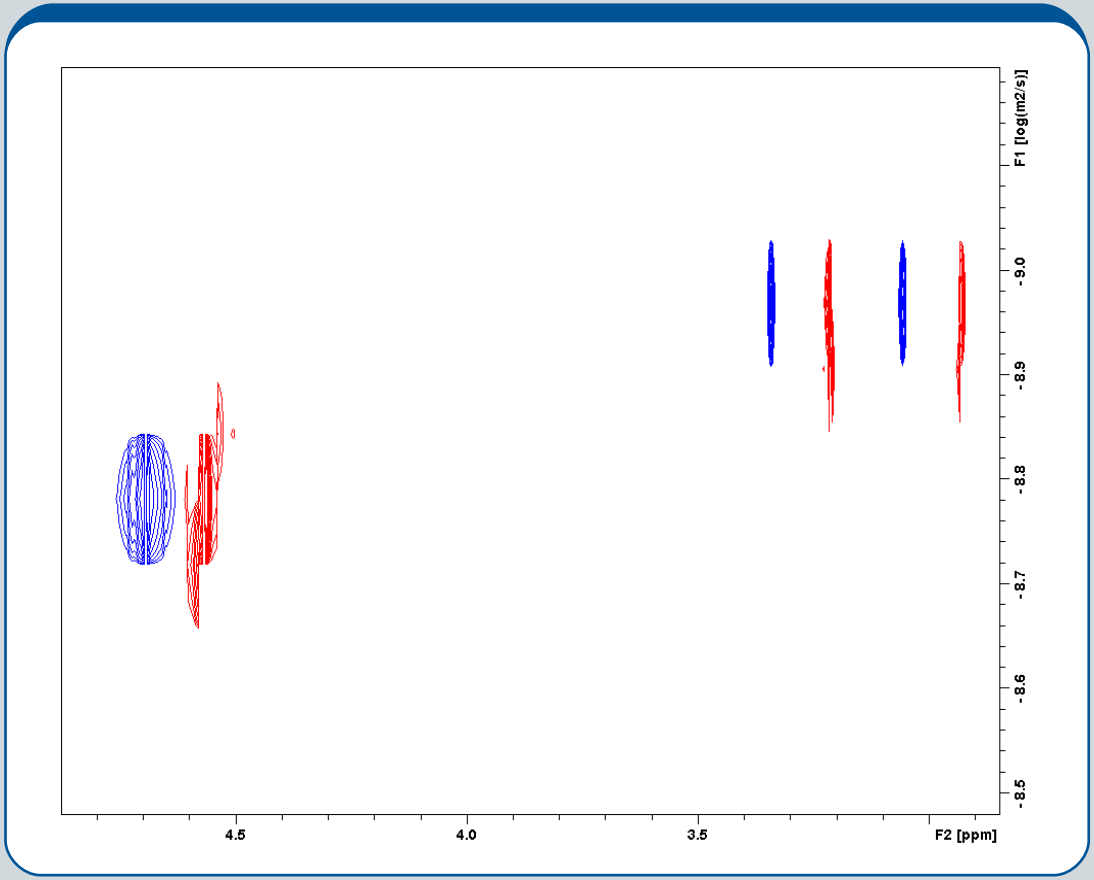
  DOSY 90° composite pulses

  Spatial selective excitation in B_1-homogeneous region

  Allows reduction of smilies

  red: xf2, abs2 and dosy2d

  blue: xf2, abs2, deconvolution and dosy2d



DOSY: optimizing results

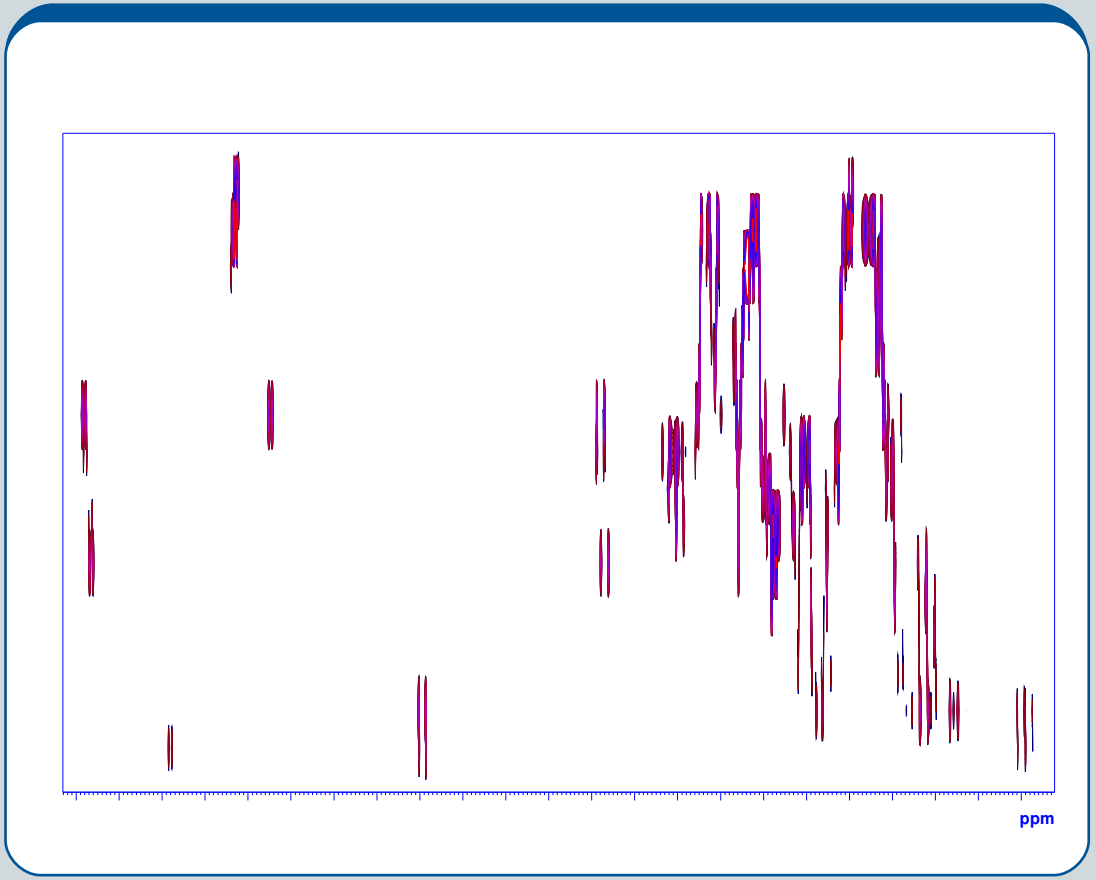
The AU program deconxf2.dmo

```
....
TIMES(td1)
      i=i+1;
      DATASET(name, expno_save, procno_save, disk, user);
      RSR(i, 1000);
      DATASET(name, expno, 1000, disk, user);
      DATASET2(name, expno, 999, disk, user);
      GDCON;
      DATASET(name, expno, 999, disk, user);
      HT;
      WSR(i,procno_save,expno,name,user,disk);
END;
......
```

DOSY: optimizing results

- DOSY spectrum, mixture of four sugars
- Experiment conditions:
  - 40 mm filling height
  - LED sequence with composite pulses
  - Processing: xf2, abs2 dosy2d

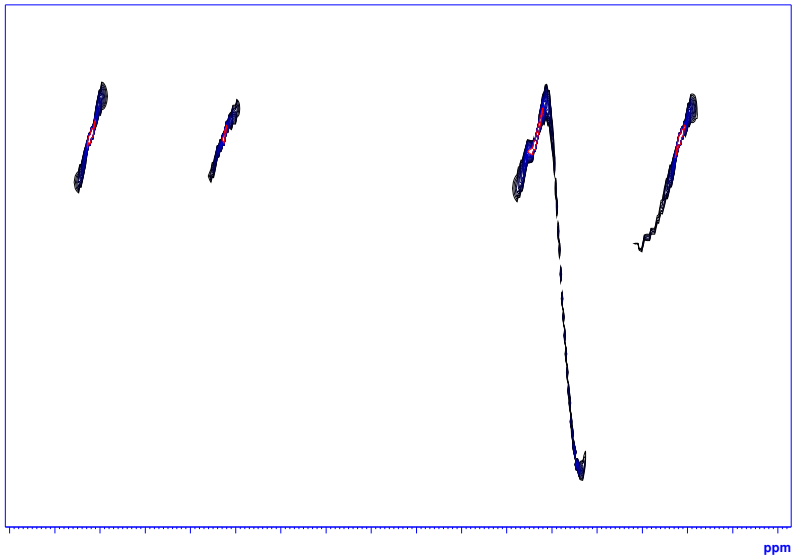
Can‘t we do a better job???



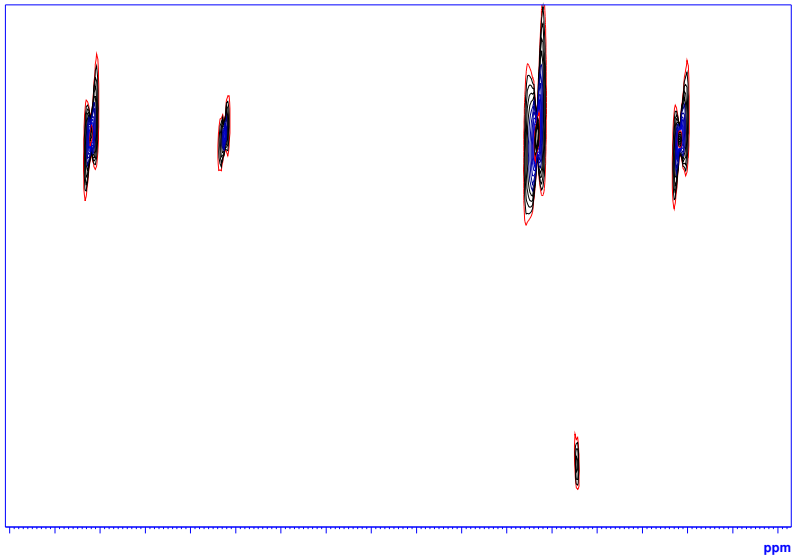
DOSY: optimizing results

LWF: broadening in diffusion dimension, reduces truncation artifacts

LWF 0.3, SpiSup 1



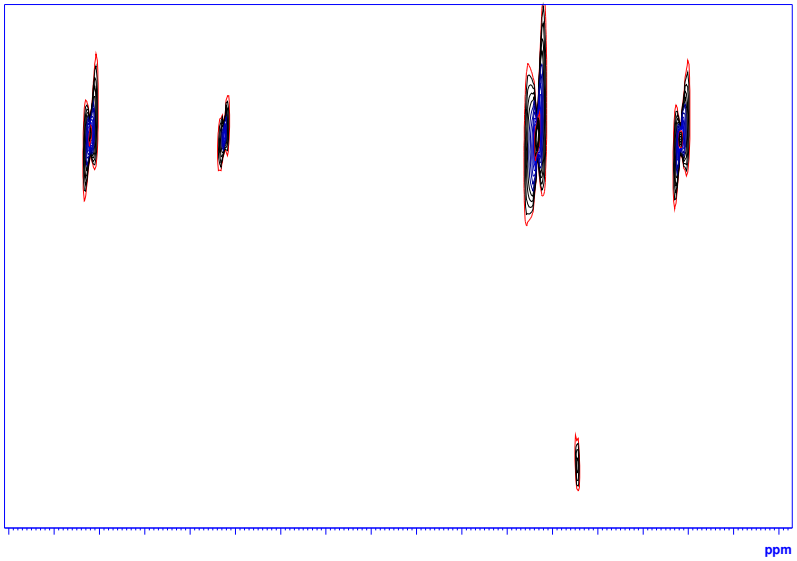
LWF 4, SpiSup 1



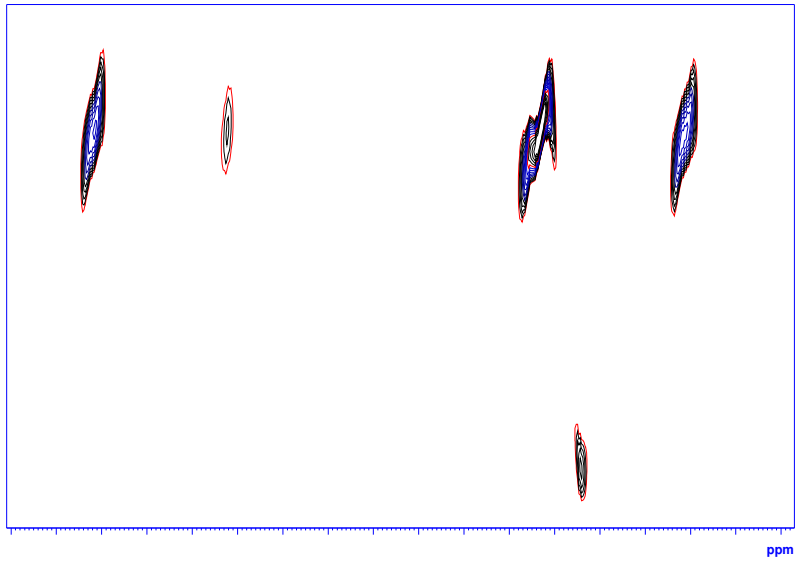
DOSY: optimizing results

SpiSup: broadening in chemical shift dimension, reduces tails

LWF 4, SpiSup 1



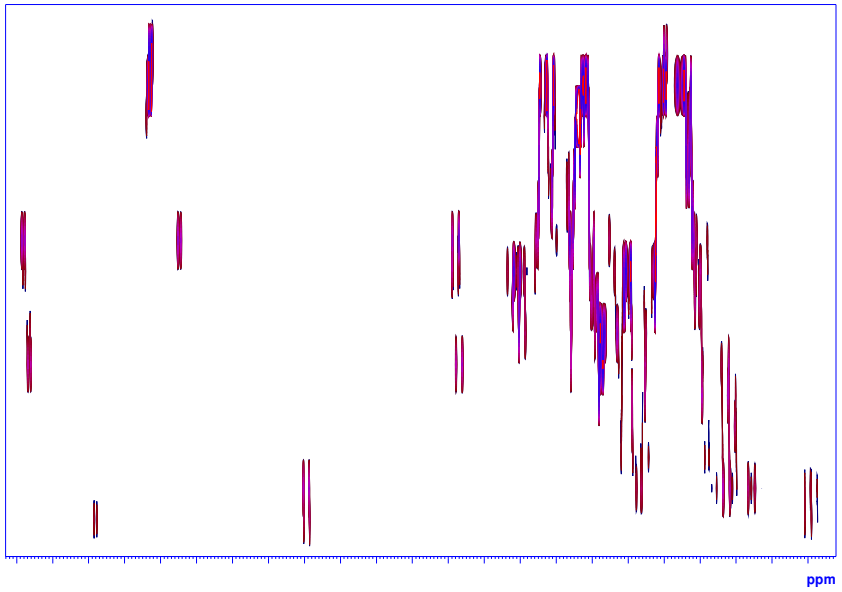
LWF 4, SpiSup 100



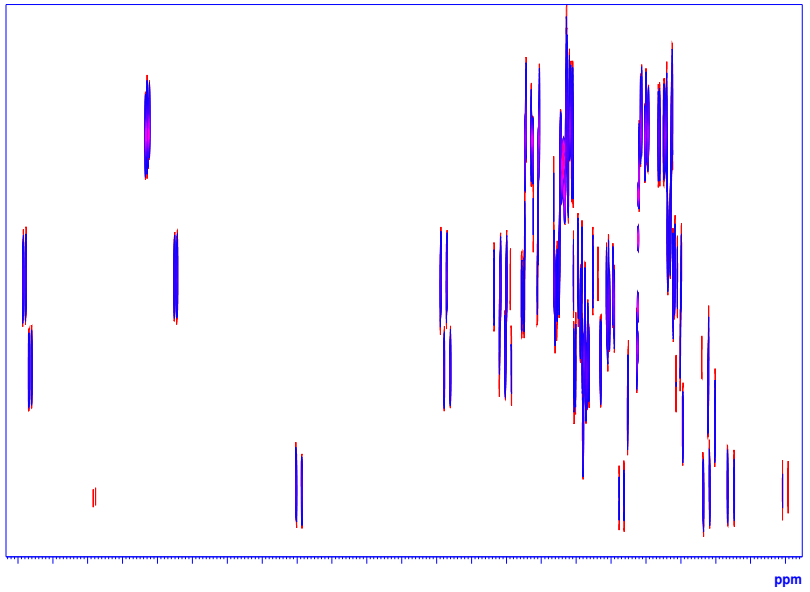
DOSY: optimizing results

SpiSup and LWF: optimized for sample

LWF 1, SpiSup 1



LWF 4, SpiSup 100

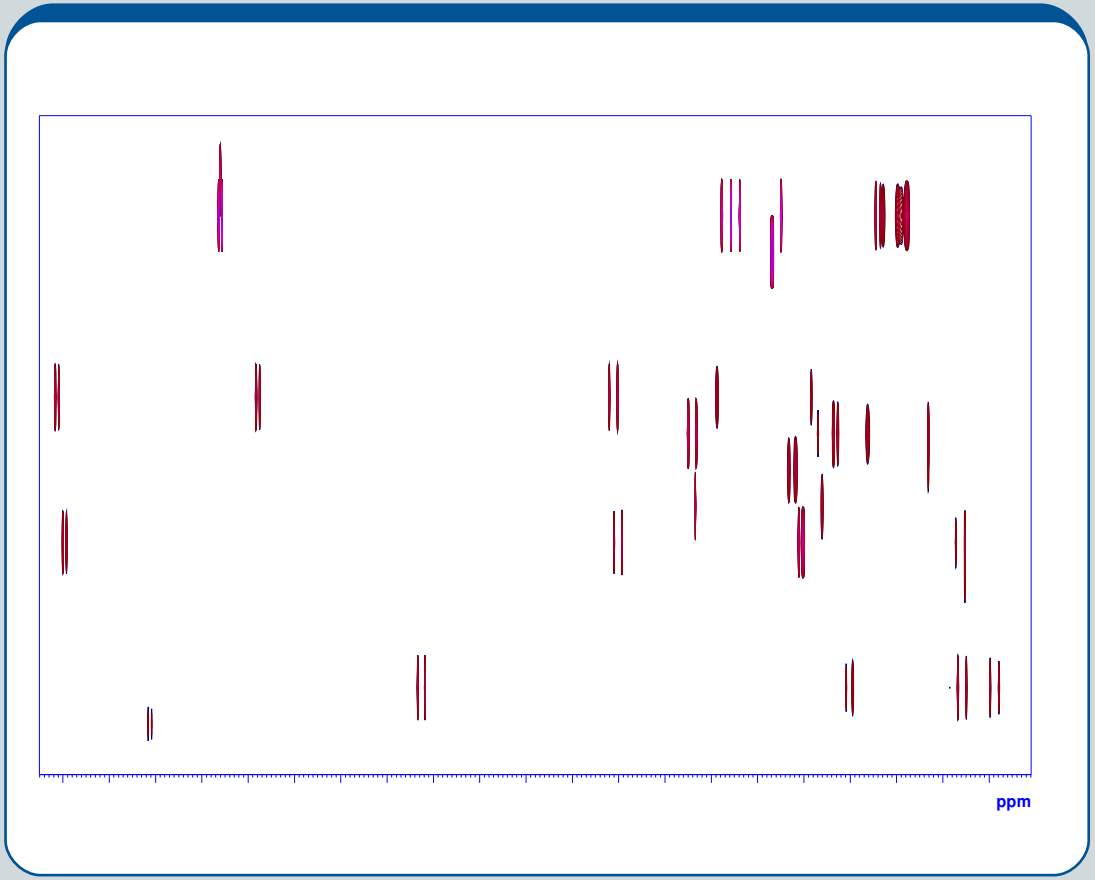


DOSY: optimizing results

- DOSY spectrum, mixture of four sugars
- Experiment conditions:
  - 40 mm filling height
  - LED sequence with composite pulses
  - Processing: xf2, abs2 dosy2d
  - And:

2D-deconvolution!

Peak list might be cleaned up first.....



Summary Tips and Tricks: Sample and VT

- Run the DOSY experiment under conditions which exclude or at least minimize any additional transport effect beside diffusion.
- Transport effect could be:
  - Convection:
    - Use sample filling height 40 mm
    - Reduce temperature for low-viscosity solvents
    - Reduce temperature gradient (higher VT gasflow)
    - Use small diameter tubes.
    - Try with sample rotation
  - Sample vibrations:
    - Reduce gasflow
    - Do not use the blue spinner

Summary Tips and Tricks: Pulse Sequence

- The DOSY ‘wings’ seems to be generated at the inhomogeneous region of the sample:
  - Do not record / excite inhomogeneous region:
    - Use composite 90° pulses

Summary Tips and Tricks: Processing

- The DOSY ‘wings’ can be reduced by deconvolution:
  - Optimized LWF and SPISUP together with using different window functions
  - 1D deconvolution of rows prior DOSY calculation:
    - Fast for simple spectra
    - Time consuming for complex spectra
    - Quality of the DOSY is given by the quality of the deconvolution
  - 2D deconvolution of the DOSY spectrum:
    - Nice spectra, but:
    - Relies on quality of peak list