NMR control overview

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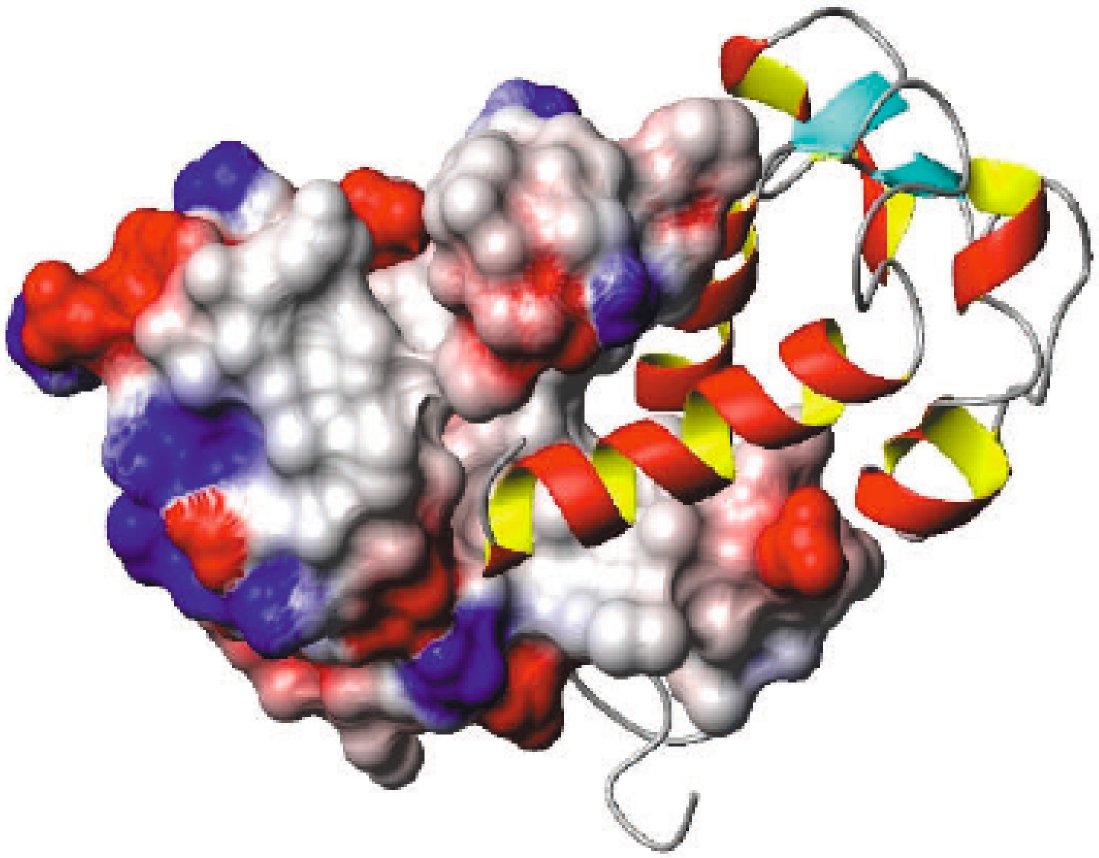
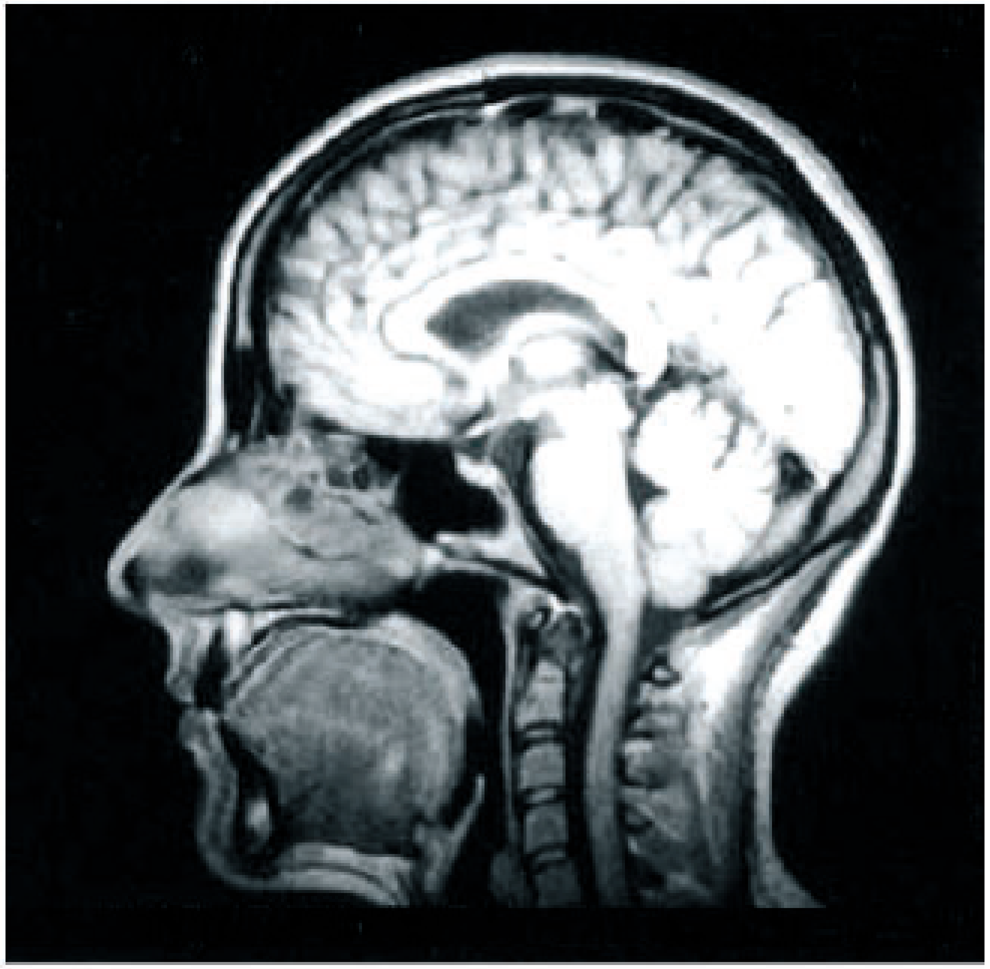
Topics

- magnetic moment of nuclear spins
- magn. vector/state function/density operator
- equations of motion
- NMR settings
- limitations of „standard“ liquid state NMR
- contributions to quantum computing
- control of spin and pseudo-spin systems

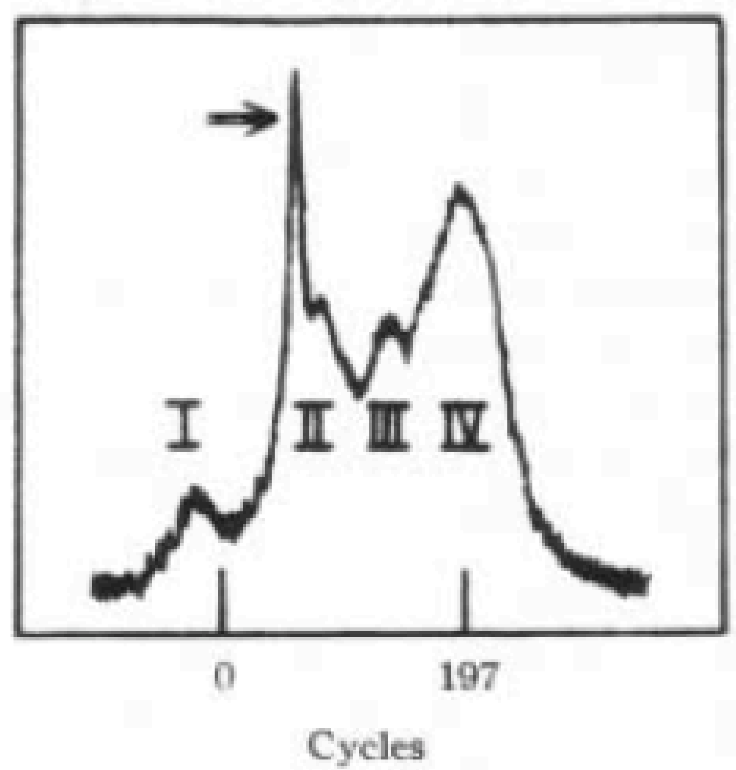




Nobel Prizes:

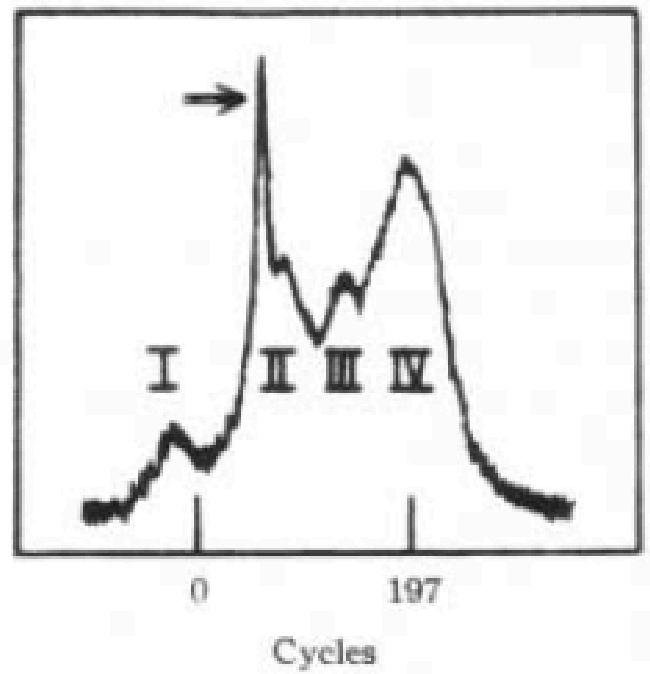
1952: Edward Purcell, Felix Bloch (Physics)
1991: Richard Ernst (Chemistry)
2002: Kurt Wüthrich (Chemistry)
2003: Paul Lauterbur, Peter Mansfield (Medicine)

First liquid state NMR spectrum of a protein



Ribonuclease
40 MHz

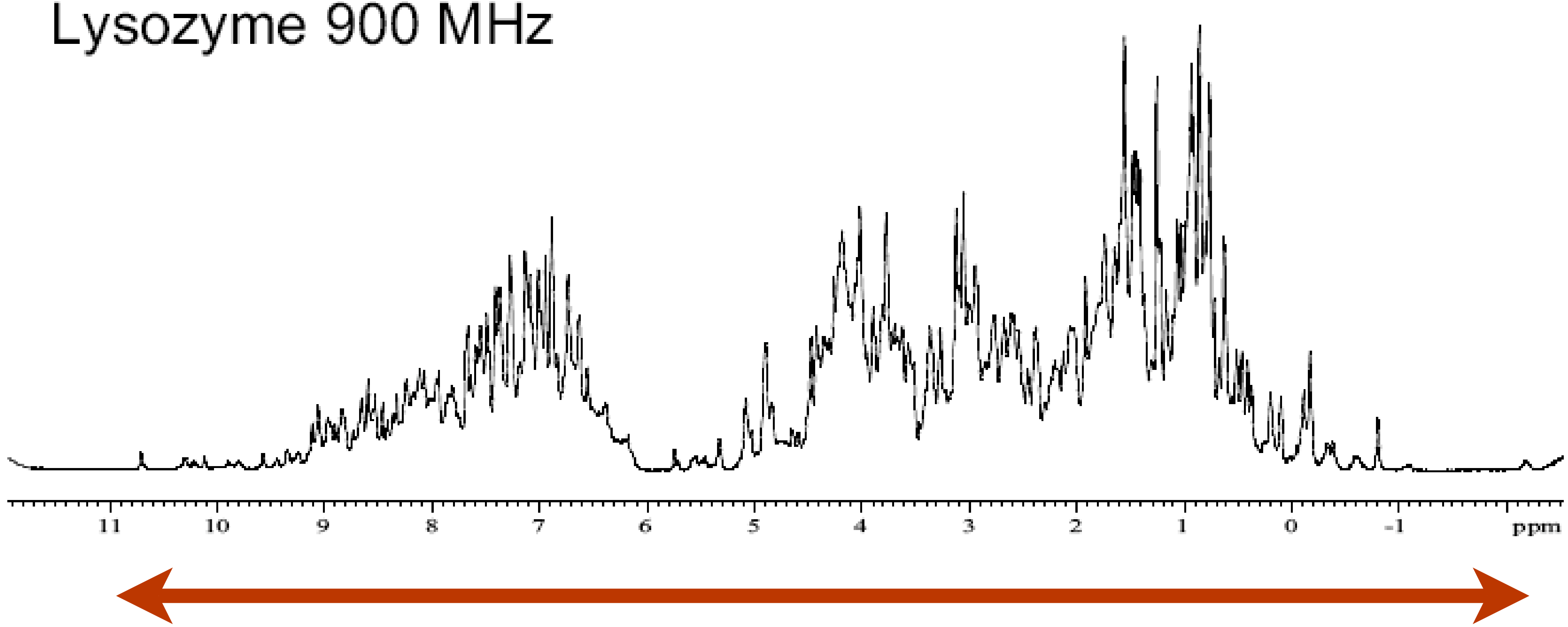
M. Saunders et al.
J.Amer.Chem.Soc. **1957**, *79*, 3289



Ribonuclease
40 MHz

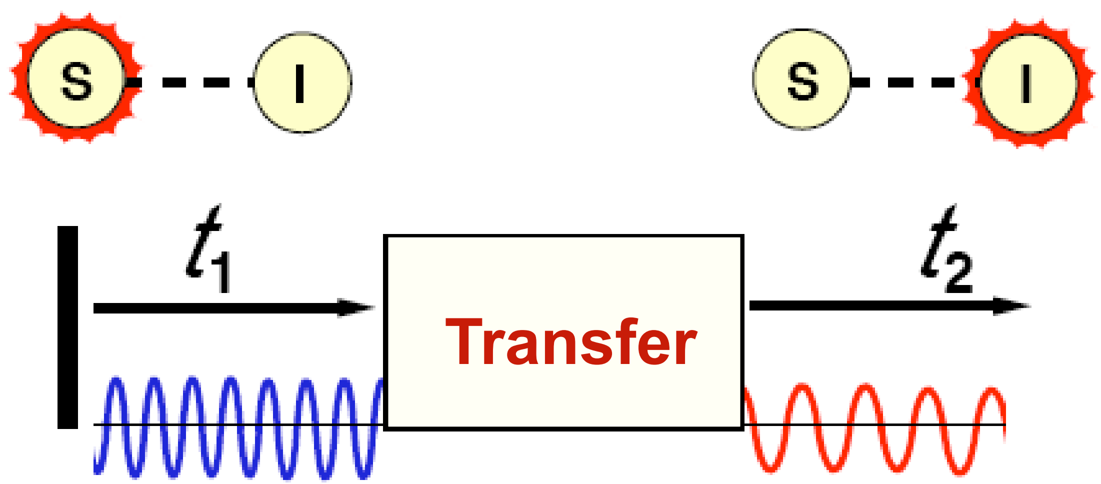
M. Saunders et al.
J.Amer.Chem.Soc. **1957**, *79*, 3289

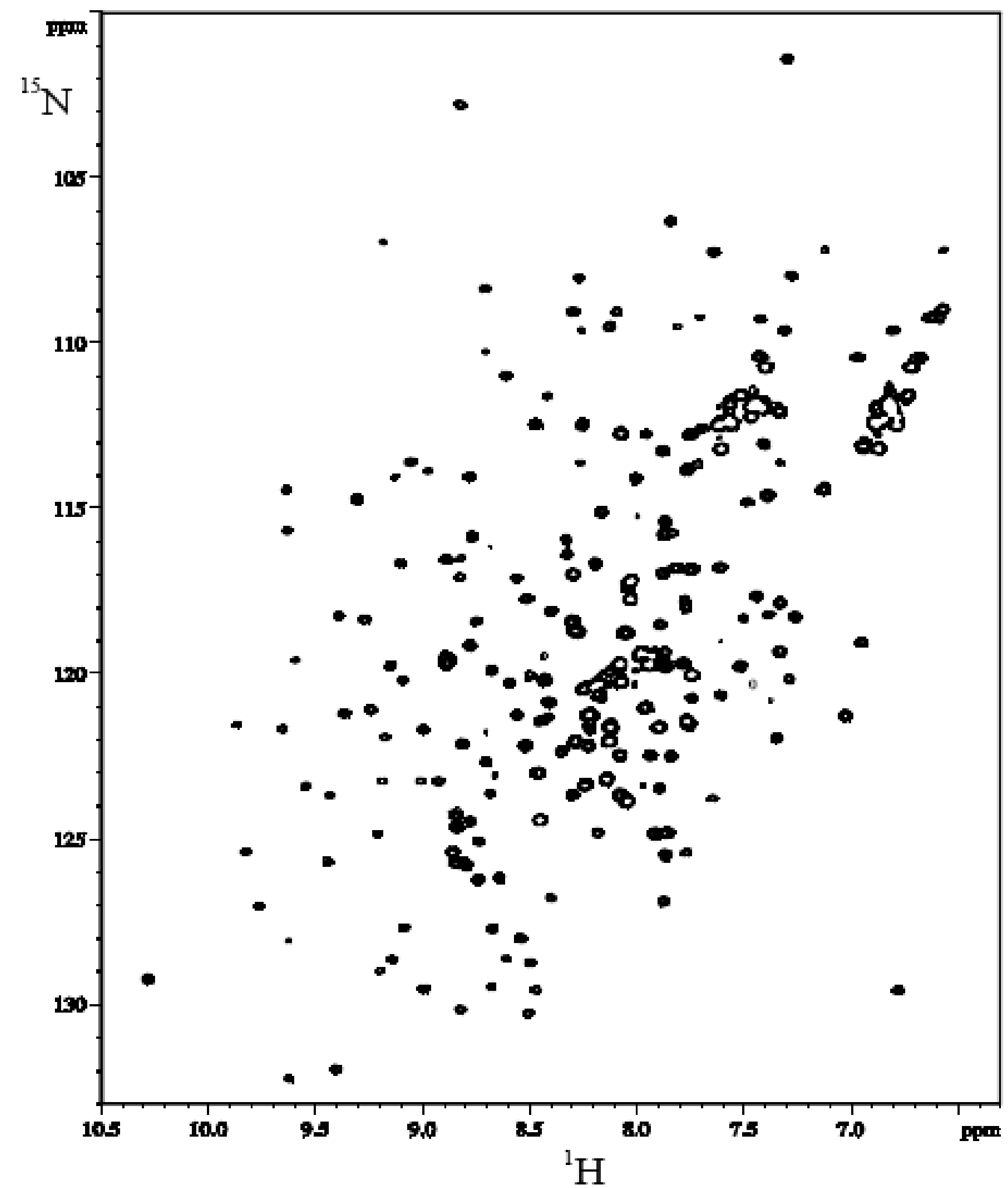
Lysozyme 900 MHz



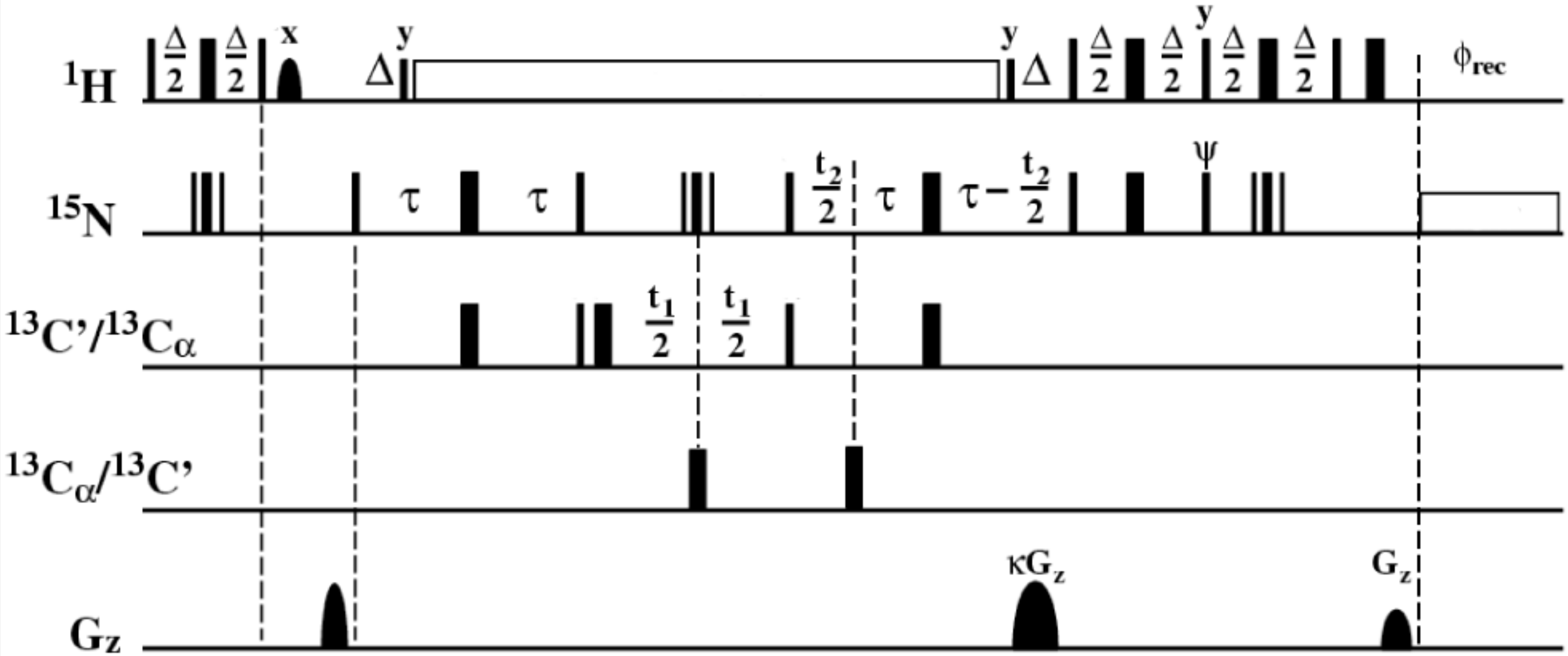
frequency dispersion: 10 kHz

Two-dimensional NMR

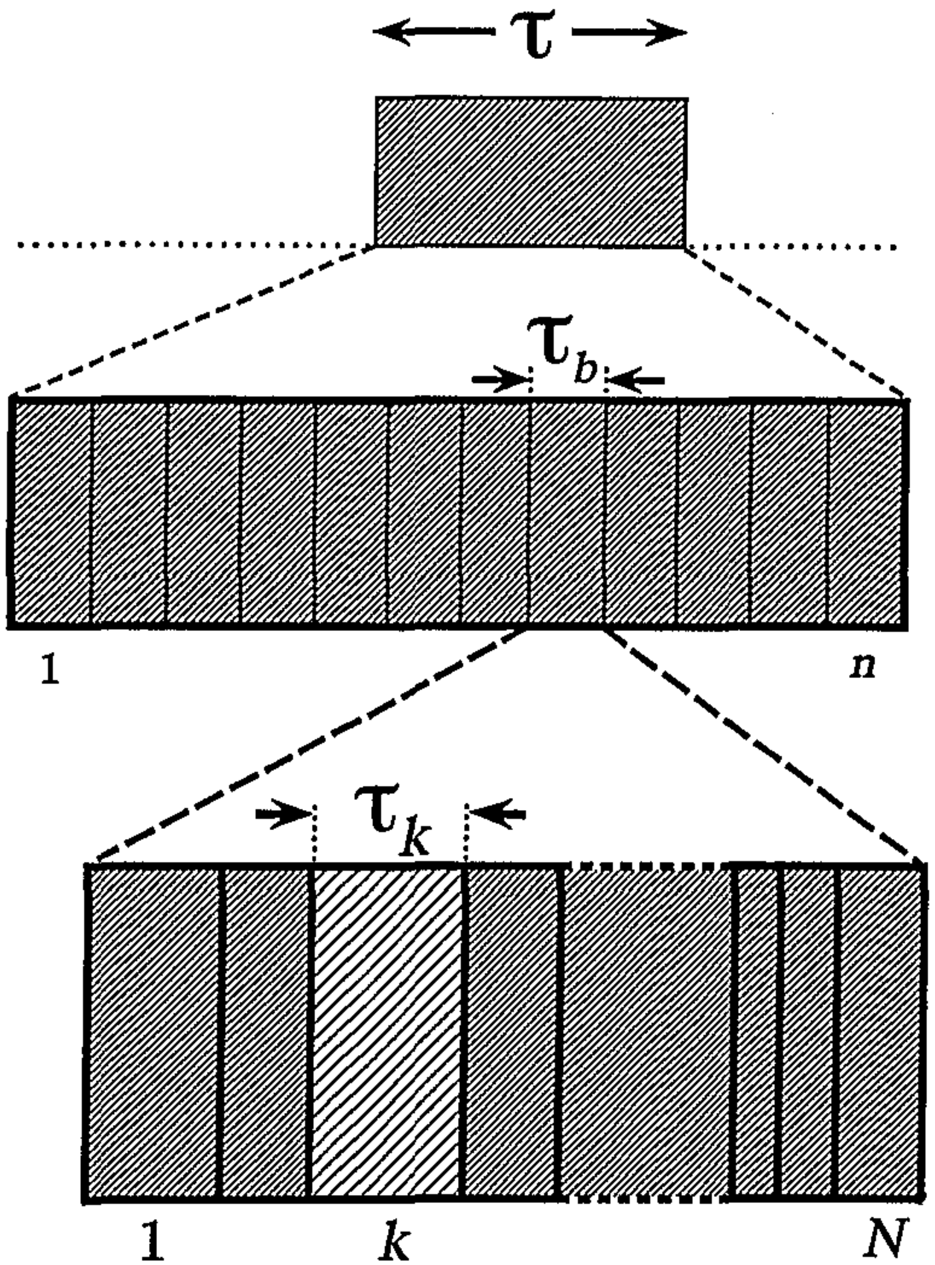




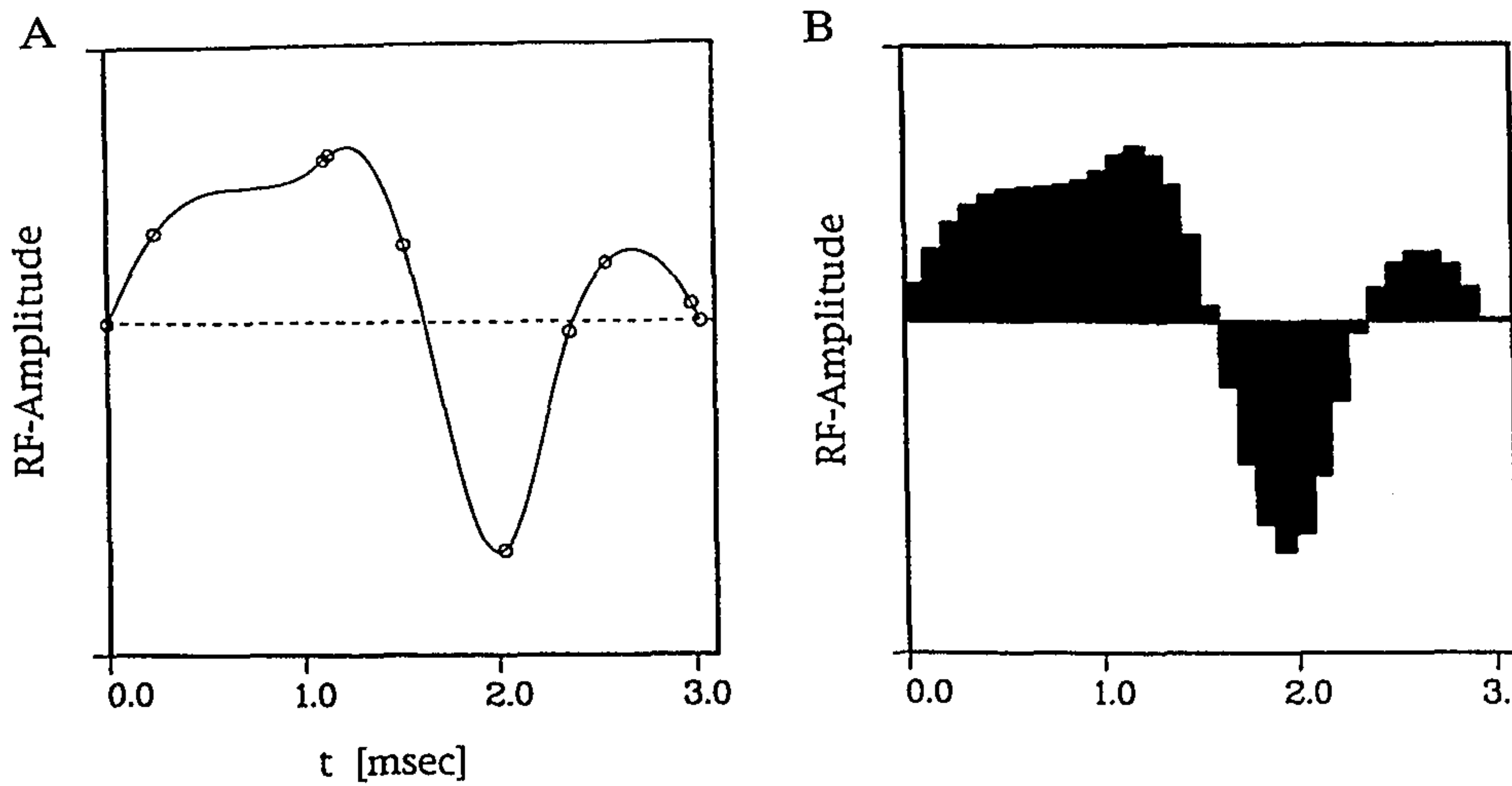
3D HNCO / HNCA

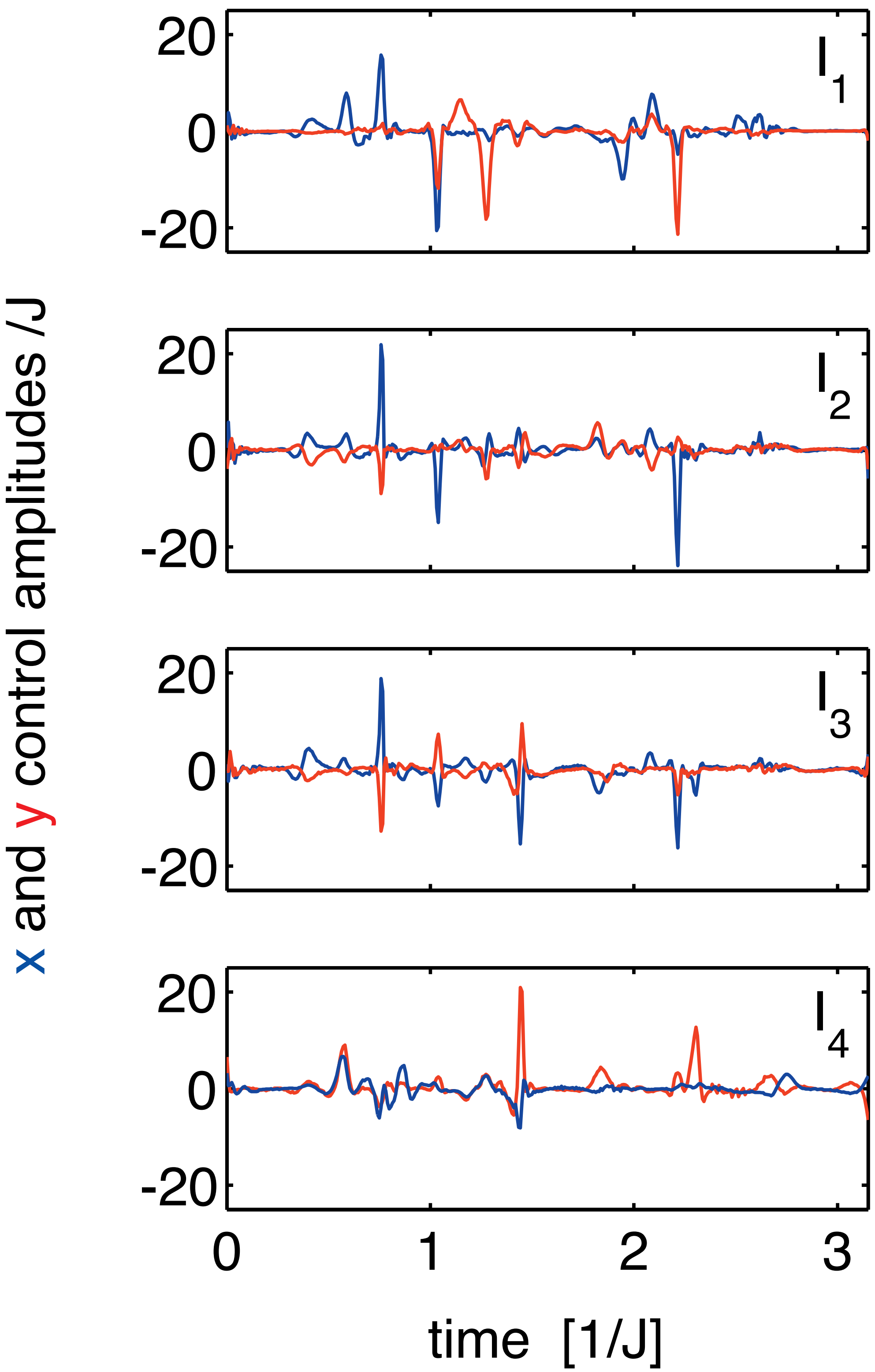


^1H
^{15}N
$^{13}C'/^{13}C_\alpha$
$^{13}C_\alpha/^{13}C'$
G_z
$\frac{\Delta}{2}$
x
y
Δ
τ
$\frac{t_2}{2}$
$\tau - \frac{t_2}{2}$
$\frac{t_1}{2}$
ψ
ϕ_{rec}
κG_z
G_z

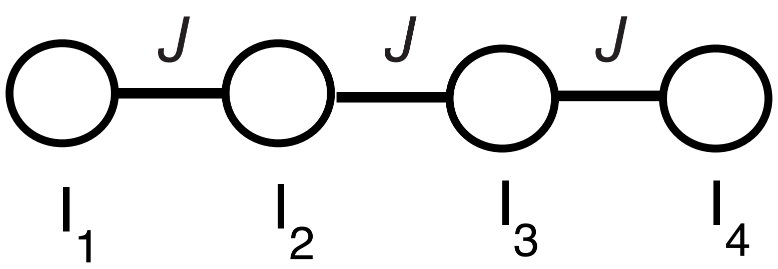


A square pulse may be completely characterized by the four parameters τ_k, ν_k^{rf}, B_k, and φ_k or, alternatively, by the four parameters α_k, ν_k^{rf}, ν_k^R, and φ_k. If the flip angles, frequencies, amplitudes, and phases of all N


A
B
RF-Amplitude
RF-Amplitude
0.0
1.0
2.0
3.0
0.0
1.0
2.0
3.0
t [msec]



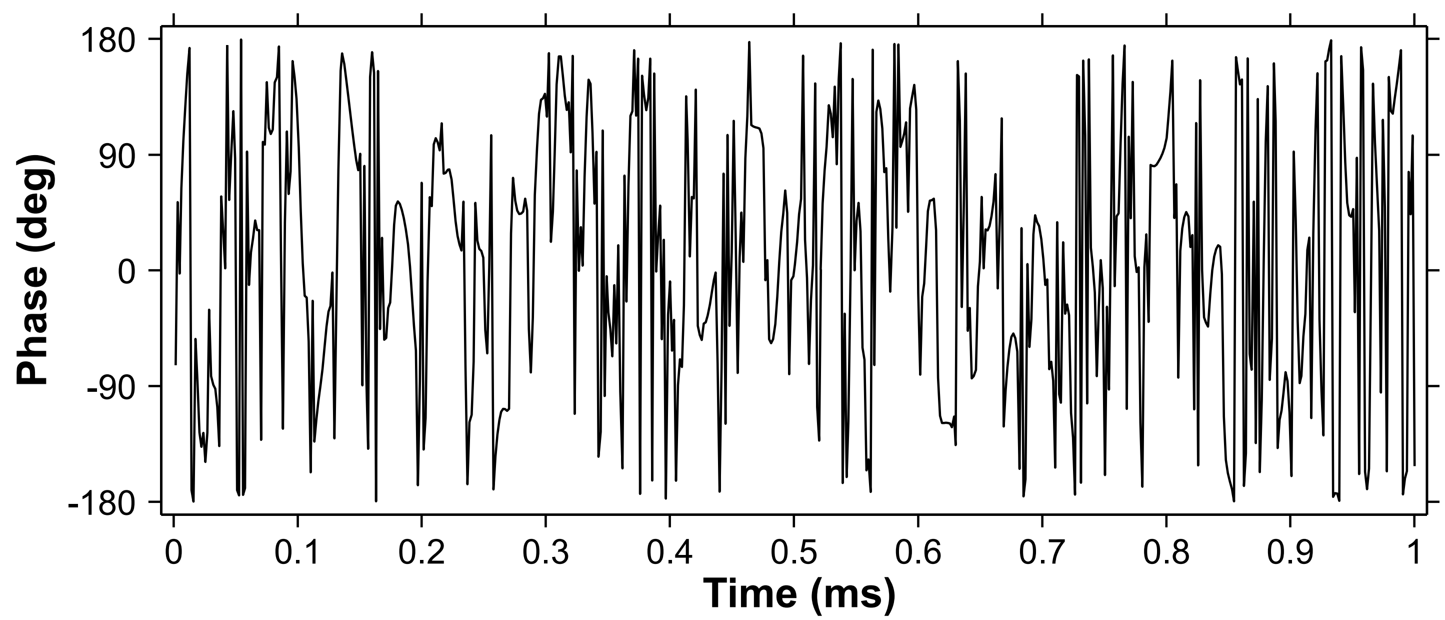
Pulse sequence for
time-optimal implementation
of the
quantum Fourier transform
for n=4 qubits



Schulte-Herbrüggen et al.
quant-ph/0502104

Robust broadband excitation pulse

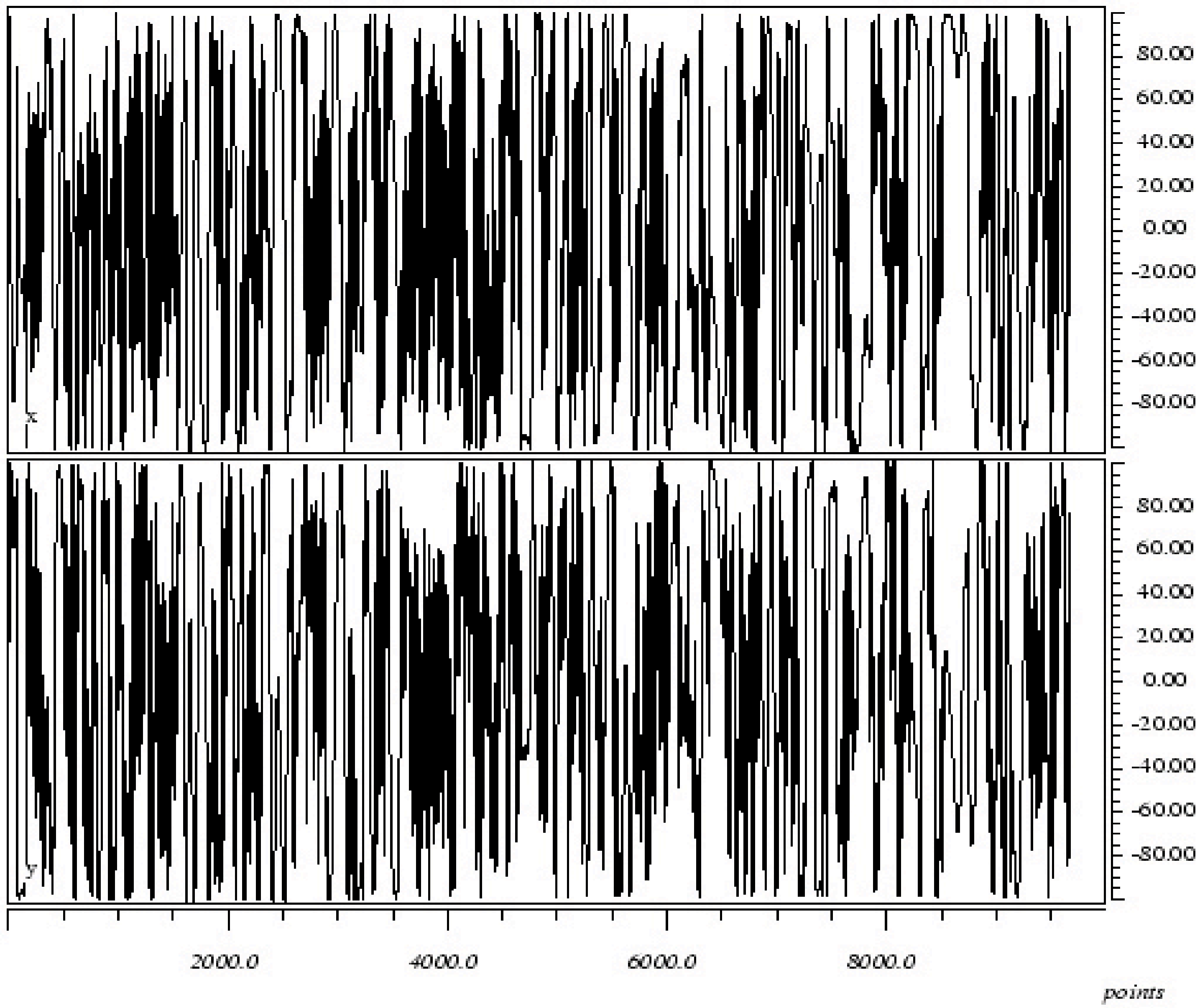
PM-BEBOP



bandwidth: 50 kHz

rf amplitude: 15 kHz

rf amplitude (x)



rf amplitude (y)

NMR comes in many different flavors ...

aggregation state:	liquid, liquid crystal, solid, ...
sample temperature:	high, ..., low
spin temperature:	high (mixed state), ..., low (pure state)
prepared initial state:	pseudo pure, 1 qubit model, ...
control:	rf, mw, laser, electrical, ...
molecule:	stable, chemical reaction
detection:	inductive, SQUID, electrical, optical ....

NMR (Nuclear Magnetic Resonance)

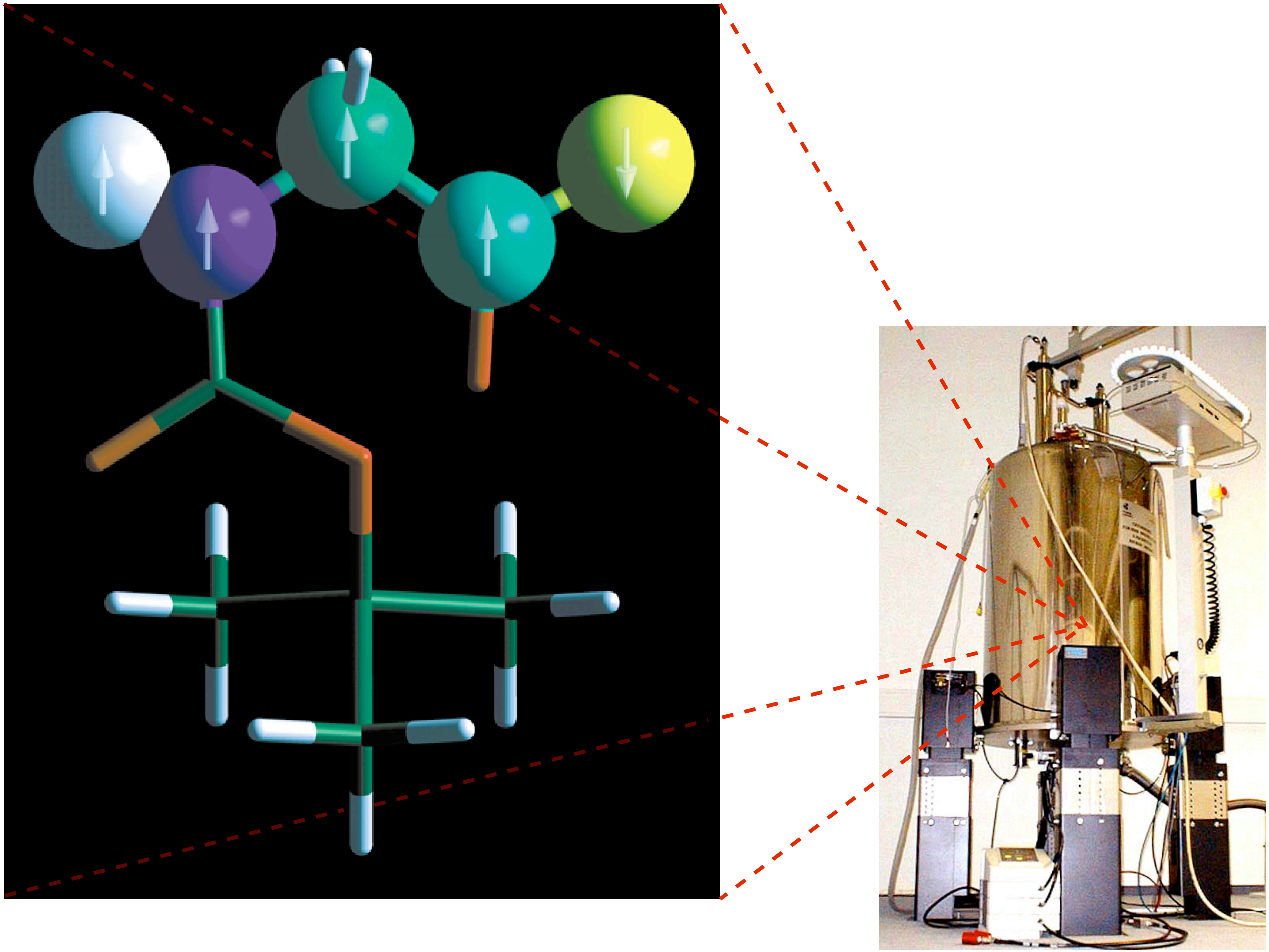
What is NMR?

How do you measure an NMR signal?

Most simple case: a single spin

More interesting: coupled spins

Pulse sequences



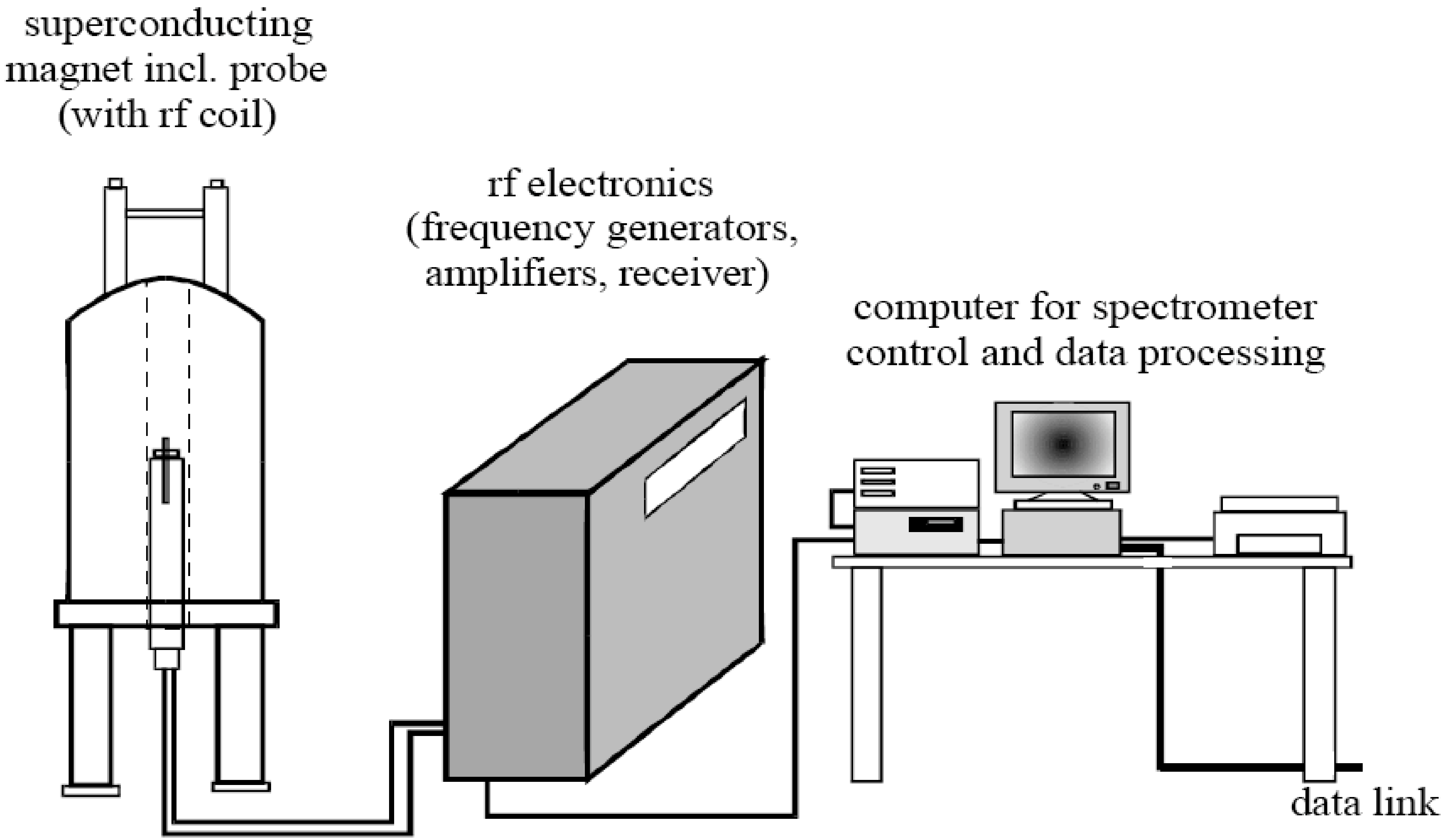
How do you measure an NMR signal?

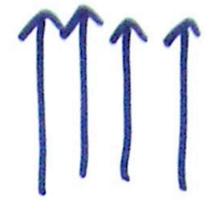
NMR Magnet

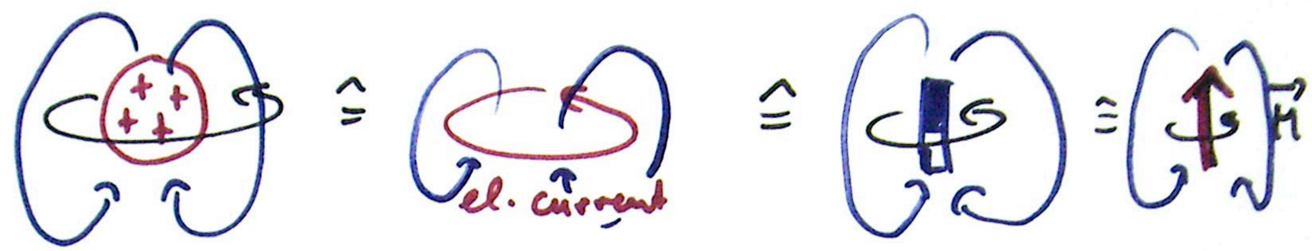
Magnetic field: 14 Tesla

^{1}H resonance frequency: 600 MHz

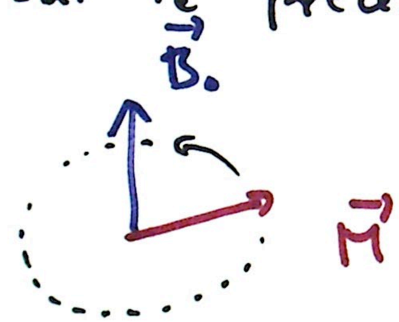
How do you measure an NMR signal?



Magnetic field $\vec{B}_0$  ↑ z axis

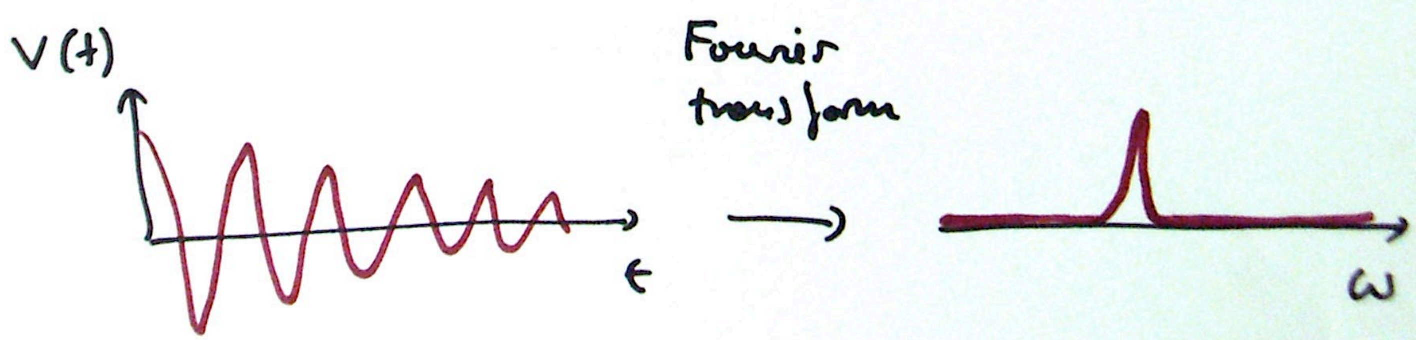


rotating magnet does not align with magn. field but it precesses (spinning top analogy)



Precession frequency $\omega = -\gamma B_0$

Precessing Magnetization induces Voltage V(t) in detection coil



Single Molecule with one spin 1/2

$$|\psi\rangle = \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = c_1 |\uparrow\rangle + c_2 |\downarrow\rangle$$

$$\frac{d}{dt}|\psi\rangle = -i\mathcal{H}|\psi\rangle \qquad \mathcal{H} = \omega I_z$$

$$|\psi(0)\rangle \longrightarrow |\psi(t)\rangle = \underbrace{e^{-i\mathcal{H}t}}_{U} |\psi(0)\rangle \quad \text{if } \mathcal{H} = \text{const.}$$

$$\langle A(t)\rangle = \langle \psi(t)|A|\psi(t)\rangle$$

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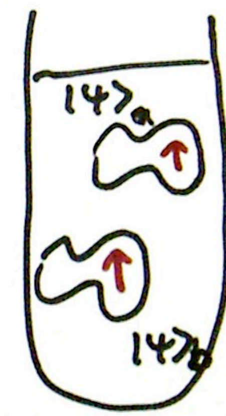
ensemble of e.g. two (or 10^{18}) molecules, each with one spin 1/2



$$\langle A\rangle_a \rightarrow \overline{\langle A\rangle} \leftarrow \langle A\rangle_b$$

$$\rho = \overline{|\psi\rangle\langle\psi|} = \begin{pmatrix} \overline{c_1 c_1^*} & \overline{c_1 c_2^*} \\ \overline{c_2 c_1^*} & \overline{c_2 c_2^*} \end{pmatrix}$$

$$\frac{d}{dt}\rho = -i[\mathcal{H}, \rho]$$

$$\rho(0) \longrightarrow \rho(t) = \underbrace{e^{-i\mathcal{H}t}}_{U} \rho(0) \underbrace{e^{i\mathcal{H}t}}_{U^+} \quad \text{if } \mathcal{H} = \text{const.}$$

$$\langle A(t)\rangle = \mathrm{tr}(A\rho(t))$$

"Spin operators" $I_x = \frac{1}{2}\sigma_x = \frac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$

$I_y = \frac{1}{2}\sigma_y = \frac{1}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$

$I_z = \frac{1}{2}\sigma_z = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$

$\uparrow$

Pauli Operators

magnetization vector

$$\vec{M} = \begin{pmatrix} M_x \\ M_y \\ M_z \end{pmatrix} \sim \begin{pmatrix} \langle I_x \rangle \\ \langle I_y \rangle \\ \langle I_z \rangle \end{pmatrix}$$

---

for example: $\rho(0) = \frac{1}{2}\begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}$

$$\boxed{\mathcal{H} = \omega I_z = \frac{\omega}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}}$$

$$U = e^{-i\mathcal{H}t} = \exp\begin{pmatrix} -i\omega t/2 & 0 \\ 0 & i\omega t/2 \end{pmatrix} = \begin{pmatrix} e^{-i\omega t/2} & 0 \\ 0 & e^{i\omega t/2} \end{pmatrix}$$

$$\rightsquigarrow \rho(t) = U\rho(0)U^+ = \frac{1}{2}\begin{pmatrix} e^{-i\omega t/2} & 0 \\ 0 & e^{+i\omega t/2} \end{pmatrix}\begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}\begin{pmatrix} e^{i\omega t/2} & 0 \\ 0 & e^{-i\omega t/2} \end{pmatrix}$$

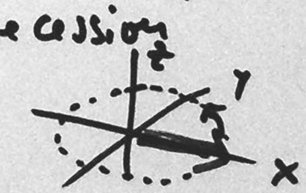
$$= \frac{1}{2}\begin{pmatrix} 1 & e^{-i\omega t} \\ e^{i\omega t} & 1 \end{pmatrix}$$

$$\langle I_x \rangle = \mathrm{tr}\left(I_x \rho(t)\right) = \frac{1}{4}\mathrm{tr}\left\{\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 1 & e^{-i\omega t} \\ e^{i\omega t} & 1 \end{pmatrix}\right\} = \frac{1}{2}\cos(\omega t)$$

$$\langle I_y \rangle = \frac{1}{2}\sin(\omega t)$$

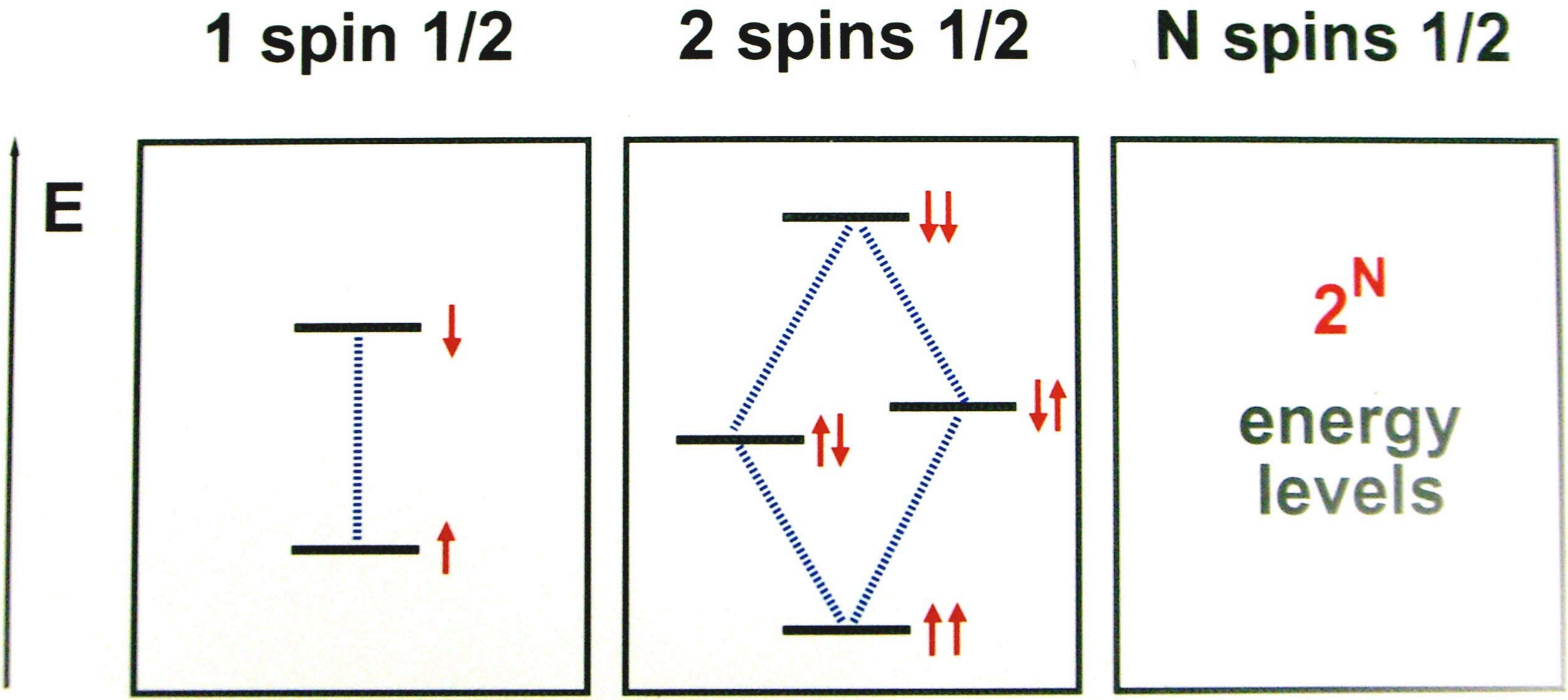
$$\langle I_z \rangle = 0$$

"precession"



$$\rightsquigarrow \vec{M}(t) \sim \frac{1}{2}\begin{pmatrix} \cos(\omega t) \\ \sin(\omega t) \\ 0 \end{pmatrix}$$

Energy levels



Isolated Spin Systems

1 Spin 1/2

2 Spins 1/2

State function:

$$|\Psi_I\rangle = c_1|\uparrow\rangle + c_2|\downarrow\rangle$$

0 1

$$|\Psi_{IS}\rangle = c_1|\uparrow\uparrow\rangle + c_2|\uparrow\downarrow\rangle + c_3|\downarrow\uparrow\rangle + c_4|\downarrow\downarrow\rangle$$

00 01 10 11

Magnetization vectors: *(Bloch, 1946; Feynman et al., 1957)*

$$\vec{M}_I$$

$$(\vec{M}_I + \vec{M}_S + \ldots)$$

Equation of Motion

$$|\dot{\Psi}\rangle = -\,i\,\mathbf{H}\,|\Psi\rangle$$

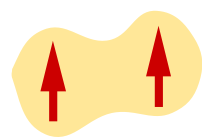
(time-dependent Schrödinger equation)

Unitary Transformation

$$|\Psi\rangle(0) \xrightarrow{U} |\Psi\rangle(t)$$

with $|\Psi\rangle(t) = U\,|\Psi\rangle(0)$ **and** $U\,U^{\dagger} = 1$

Isolated quantum system



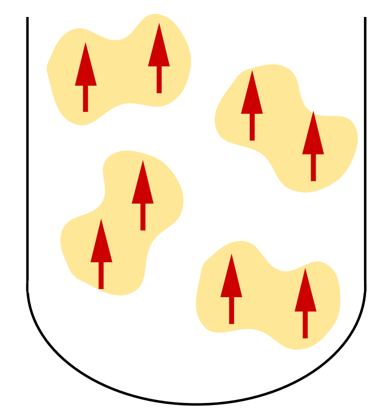
Pure state $|\Psi\rangle$

Measurement:

random *eigenvalue* of observable

(collapse of state function)

Ensemble of quantum systems



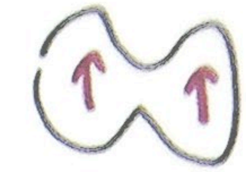
Density operator $\rho = \overline{|\Psi\rangle\langle\Psi|}$

Measurement:

expectation value of observable

(no collapse of state functions)

single molecule with two spins 1/2



$$|\psi\rangle = \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = c_1 |\uparrow\uparrow\rangle + c_2 |\uparrow\downarrow\rangle + c_3 |\downarrow\uparrow\rangle + c_4 |\downarrow\downarrow\rangle$$

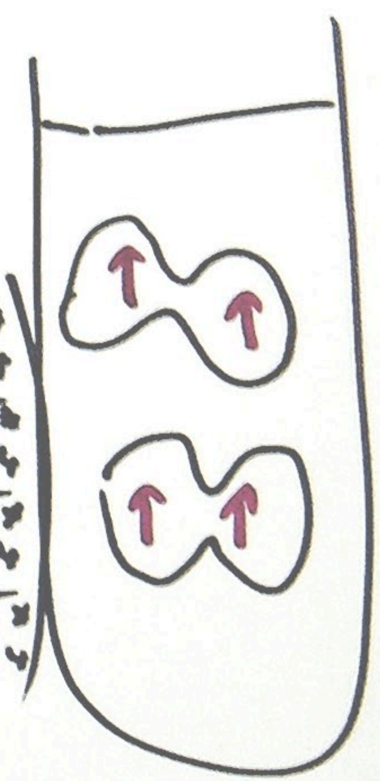
"weak J coupling"

$$\mathcal{H} = \omega_I \underbrace{I_z}_{\frac{1}{2}\sigma_z \otimes \mathbb{1}} + \omega_S \underbrace{S_z}_{\frac{1}{2}\mathbb{1} \otimes \sigma_z} + 2\pi J \underbrace{I_z S_z}_{\frac{1}{4}\sigma_z \otimes \sigma_z}$$

---

ensemble of molecules with two spins 1/2

$$\rho = \overline{|\psi\rangle\langle\psi|} = \overline{\begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} (c_1^* \; c_2^* \; c_3^* \; c_4^*)} = \begin{pmatrix} \overline{c_1 c_1^*} & \overline{c_1 c_2^*} & \overline{c_1 c_3^*} & \overline{c_1 c_4^*} \\ \overline{c_2 c_1^*} & \overline{c_2 c_2^*} & \overline{c_2 c_3^*} & \overline{c_2 c_4^*} \\ \overline{c_3 c_1^*} & \overline{c_3 c_2^*} & \overline{c_3 c_3^*} & \overline{c_3 c_4^*} \\ \overline{c_4 c_1^*} & \overline{c_4 c_2^*} & \overline{c_4 c_3^*} & \overline{c_4 c_4^*} \end{pmatrix}$$

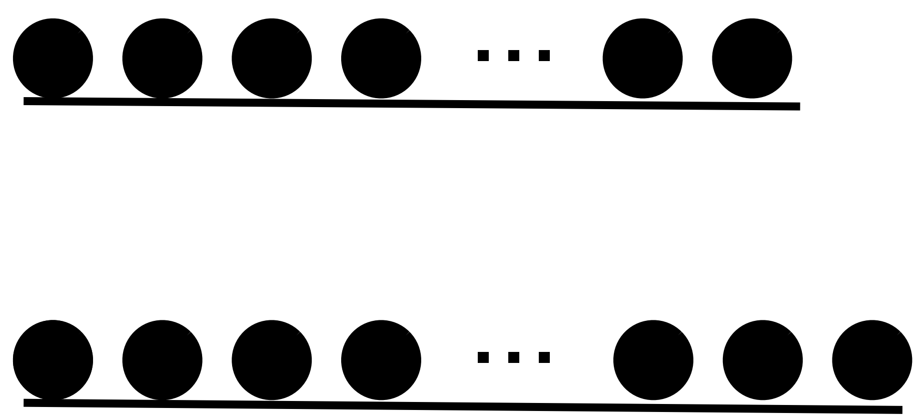


Thermal equilibrium density operator

for one spin 1/2:

$$\rho \approx \frac{1}{2}\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} + \frac{1}{2}\begin{bmatrix} \alpha_i & 0 \\ 0 & -\alpha_i \end{bmatrix}$$

with $\alpha_i = \hbar\omega_i/2kT \approx 10^{-5} \ll 1$



Thermal equilibrium density operator

for one spin 1/2:

$$\rho \approx \frac{1}{2}\begin{bmatrix}1 & 0\\ 0 & 1\end{bmatrix} + \frac{1}{2}\begin{bmatrix}\alpha_i & 0\\ 0 & -\alpha_i\end{bmatrix}$$

for two spins 1/2:

$$\rho \approx \frac{1}{4}\begin{bmatrix}1 & 0 & 0 & 0\\ 0 & 1 & 0 & 0\\ 0 & 0 & 1 & 0\\ 0 & 0 & 0 & 1\end{bmatrix} + \frac{1}{4}\begin{bmatrix}\alpha_1+\alpha_2 & 0 & 0 & 0\\ 0 & \alpha_1-\alpha_2 & 0 & 0\\ 0 & 0 & -\alpha_1+\alpha_2 & 0\\ 0 & 0 & 0 & -\alpha_1-\alpha_2\end{bmatrix}$$

with $\alpha_i = \hbar\omega_i/2kT \approx 10^{-5} \ll 1$

Thermal equilibrium density operator for n spins 1/2

$$\rho_{th} \approx \frac{\exp(-H/\mathrm{k}T)}{Tr(\exp(-H/\mathrm{k}T))} \approx \frac{1}{N}(\mathbf{1} - \frac{H}{\mathrm{k}T}) \qquad \text{for } \|H\| \ll \mathrm{k}T.$$

$$\approx \frac{1}{N}(\mathbf{1} - \sum_{l=1}^{n} \alpha_l I_{lz})$$

with $\alpha_l = \frac{\hbar\omega_l}{\mathrm{k}T}$ $\qquad N = 2^n$

Boltzmann's constant k

$$I_{lz} = \frac{1}{2}\mathbf{1} \otimes \ldots \otimes \mathbf{1} \otimes \sigma_z \otimes \mathbf{1} \otimes \ldots \otimes \mathbf{1}$$

where the Pauli matrix σ_z appears as the l^{th} term in the product.

Equation of Motion

$$\dot{\rho} = -i\,[\mathbf{H},\rho] \quad \left(+ \;\hat{\hat{\Gamma}}\,\rho \right)$$

(Liouville-von Neuman Equation)

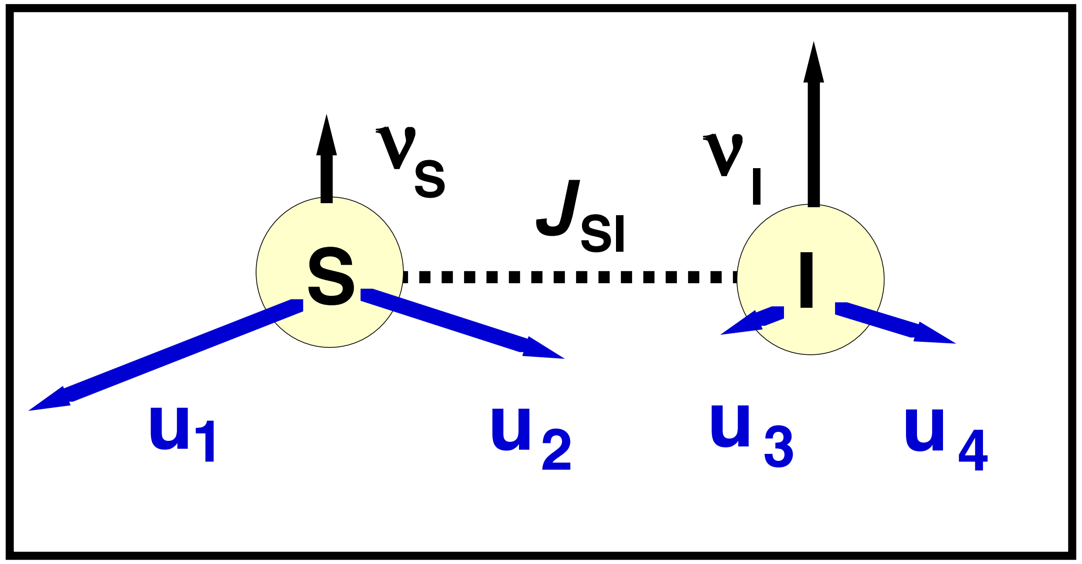
Unitary Transformation

$$\rho(0) \xrightarrow{\boldsymbol{U}} \rho(t)$$

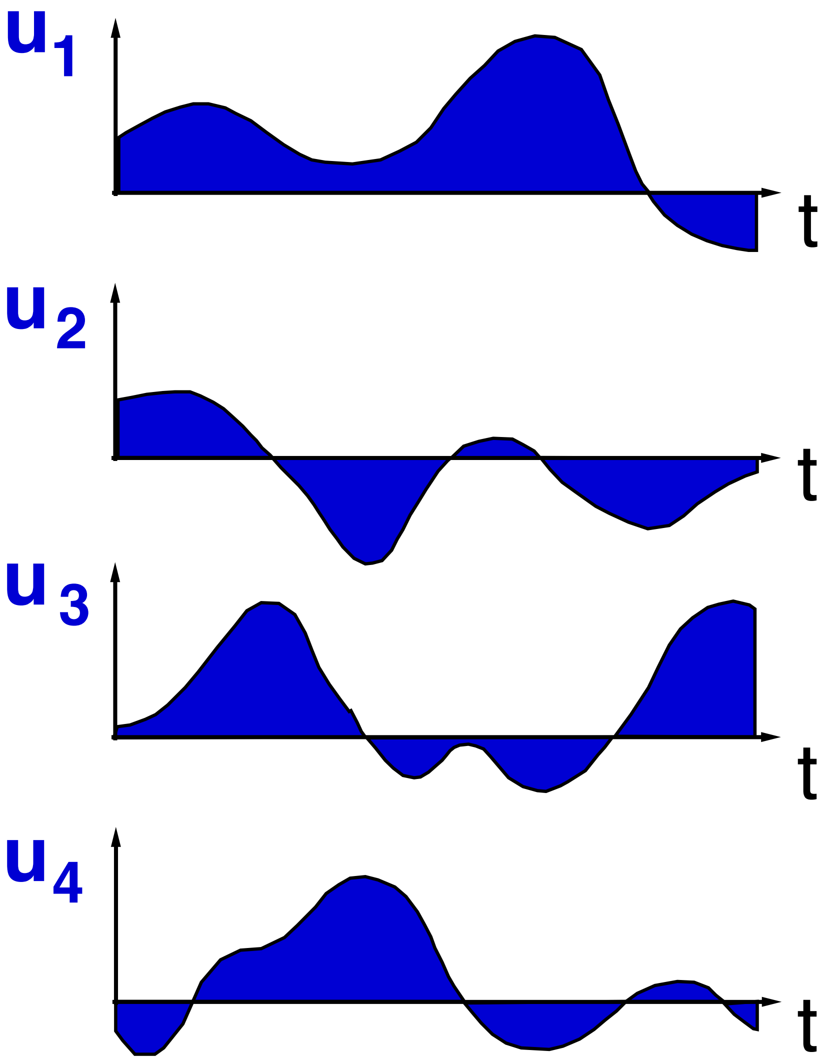
with $\rho(t) = \boldsymbol{U}\,\rho(0)\,\boldsymbol{U}^{\dagger}$ **and** $\boldsymbol{U}\,\boldsymbol{U}^{\dagger} = 1$


BRUKER
900
BRUKER

Control Parameters $u_k(t)$



$$H_0 + \sum_k u_k(t)\, H_k$$



Design of NMR Pulse Sequences

Theoretical Tools:
- Average Hamiltonian Theory
- Effective Hamiltonian
- Toggling Frame
- Multiple Rotating Frame
- Density Operator Formalism
- Product Operator Formalism

Building Blocks:
- Square Pulses
- Shaped Pulses (Gaussian, e-SNOB)
- Heteronuclear Decoupling Sequences (WALTZ-16)

Consider:
- RF Inhomogeneity
- Miscalibration of Pulses
- Relaxation
- Non-Resonant Effect of RF Pulses (Bloch-Siegert-Shift)

Goal: **Short, Robust Pulse Sequences with a Minimum of Pulses**

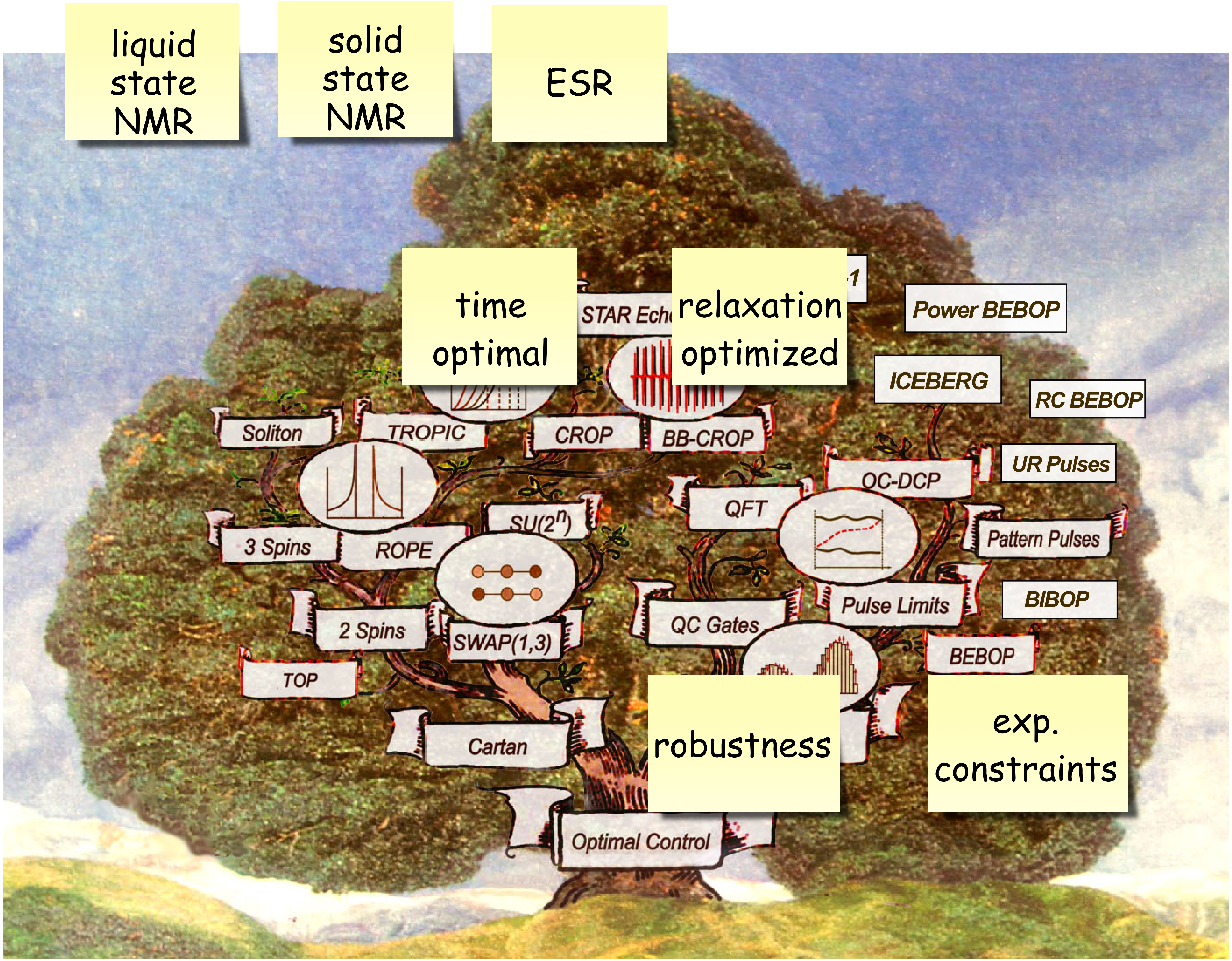
→ Optimal Control Meth.

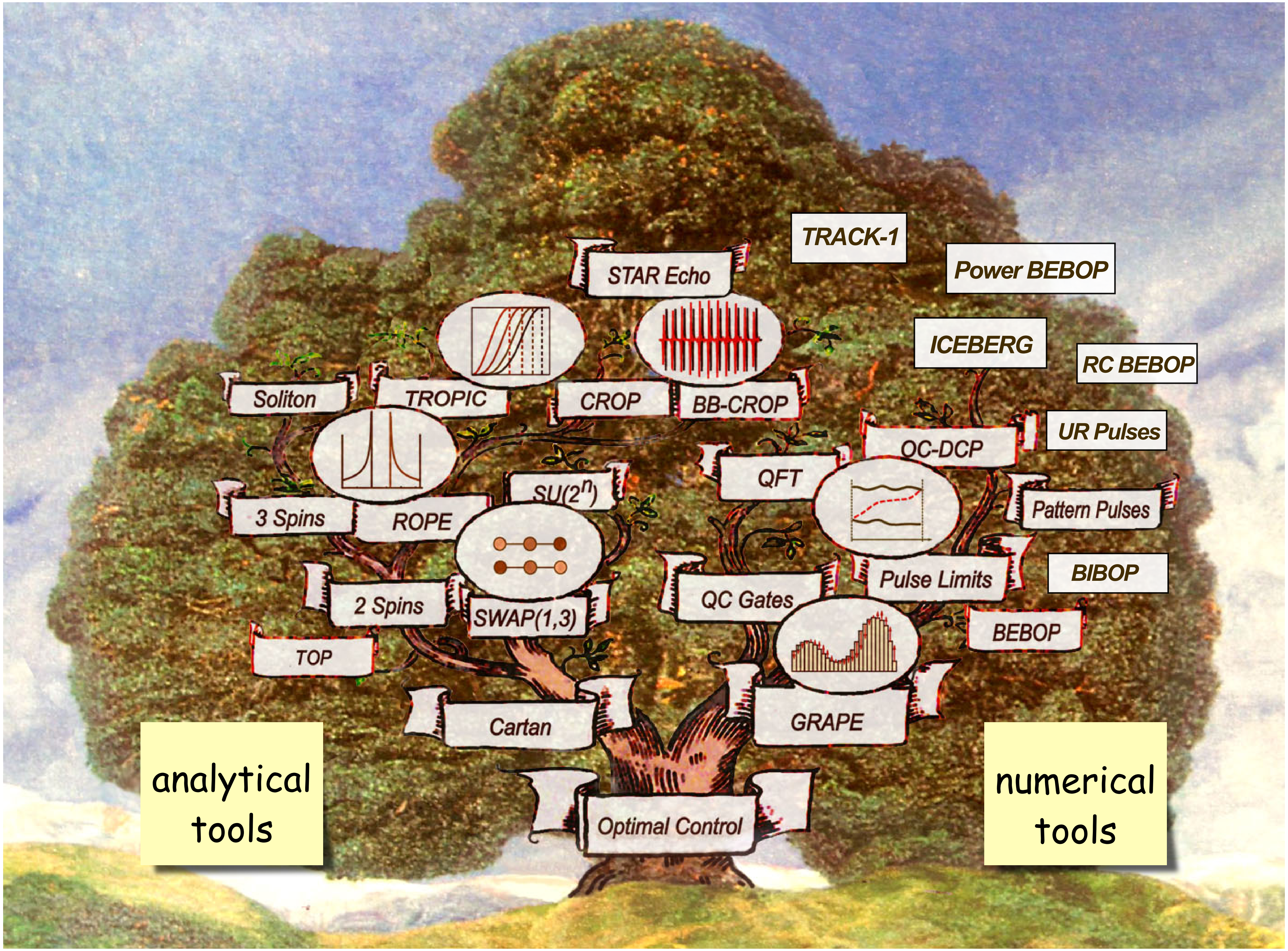
Optimal control in NMR: band-selective excitation and inversion

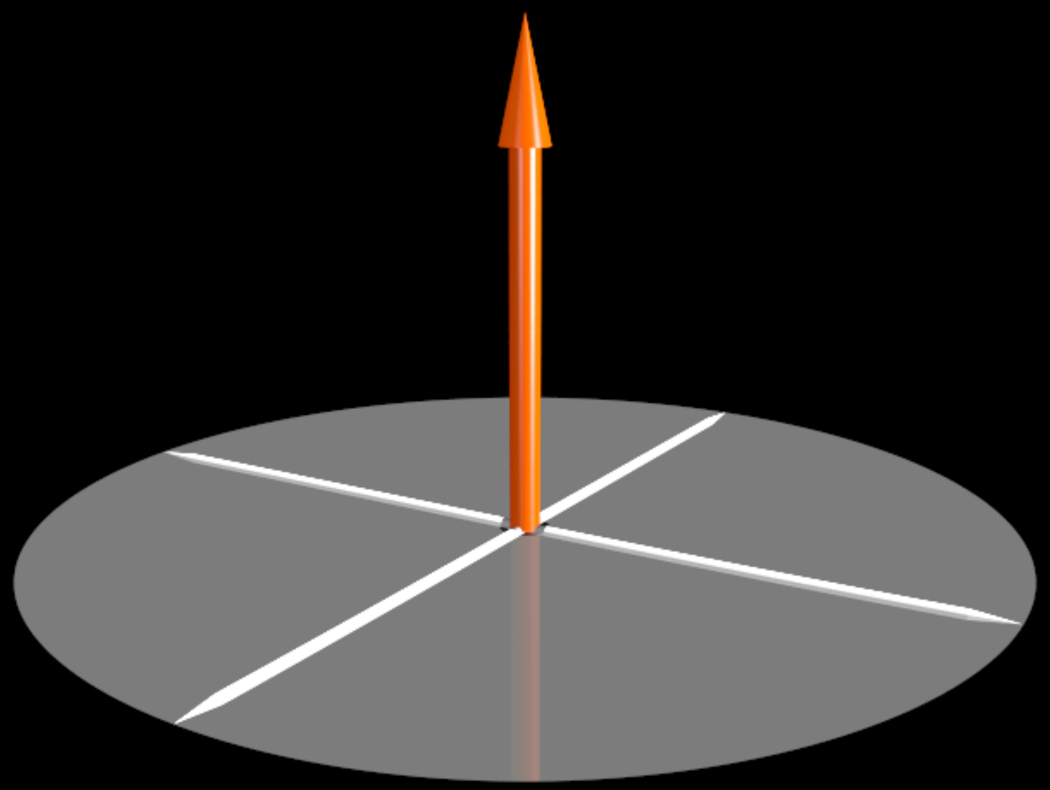
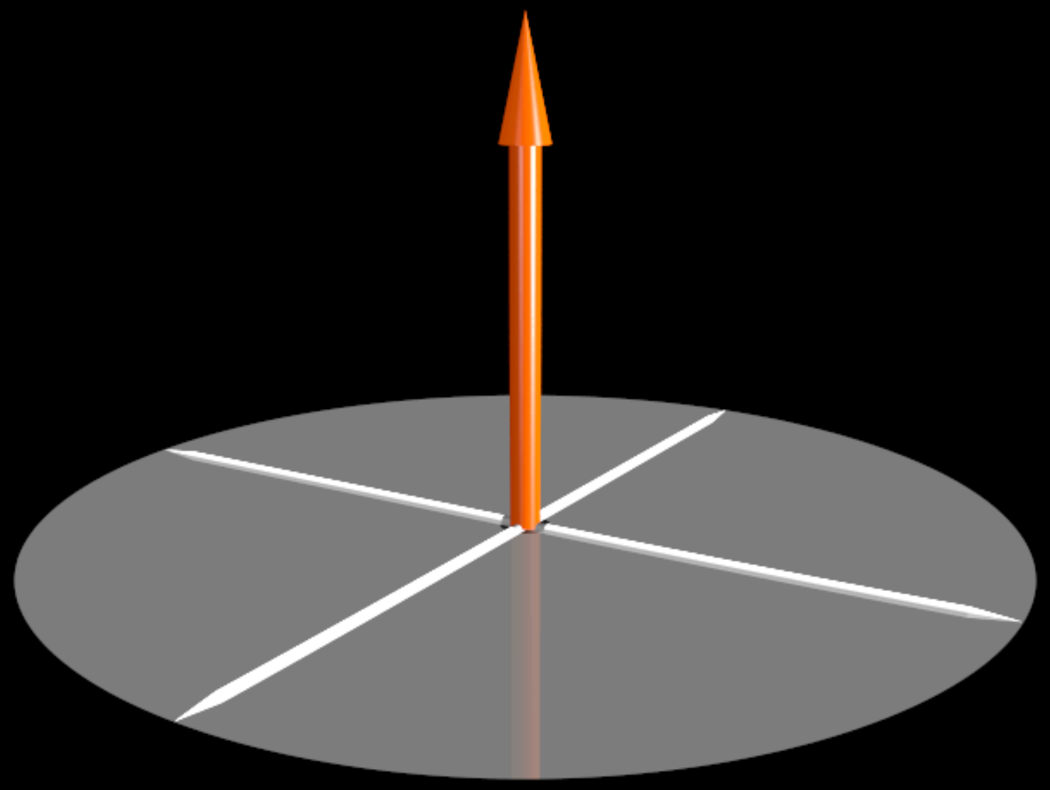
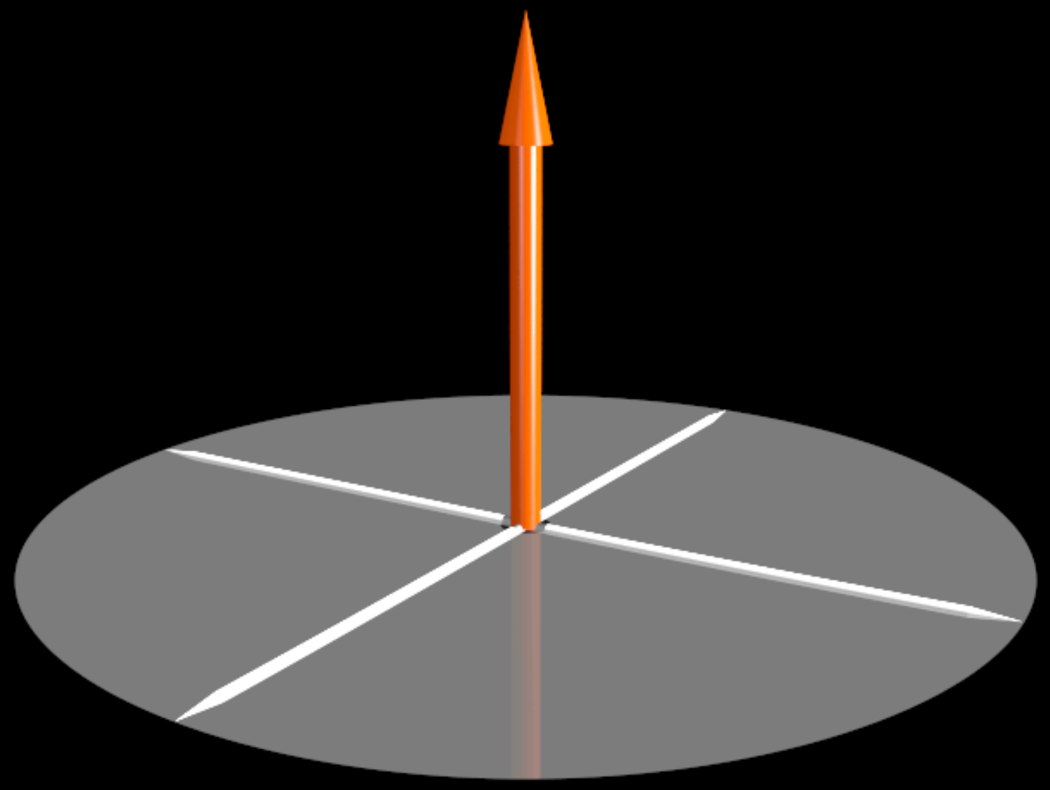
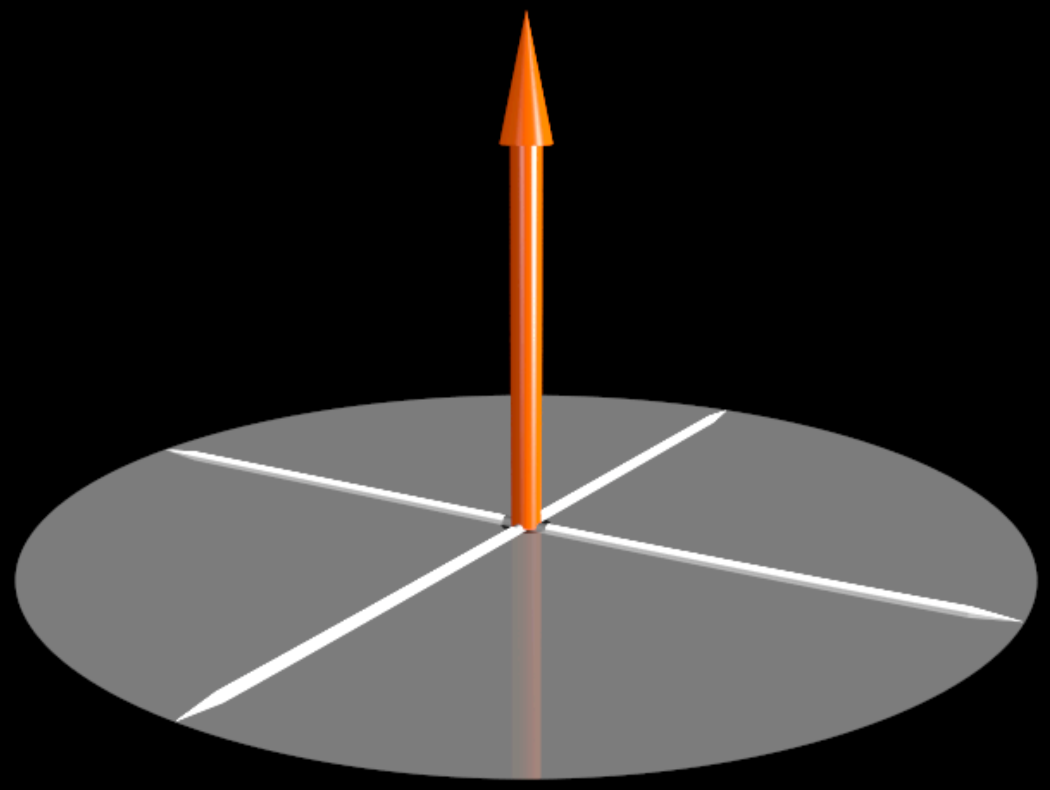
S. Conolly, D. Nishimura, A. Macovski, Optimal control solutions to the magnetic resonance selective excitation problem, IEEE Trans. Med. Imaging MI-5 (1986) 106–115.

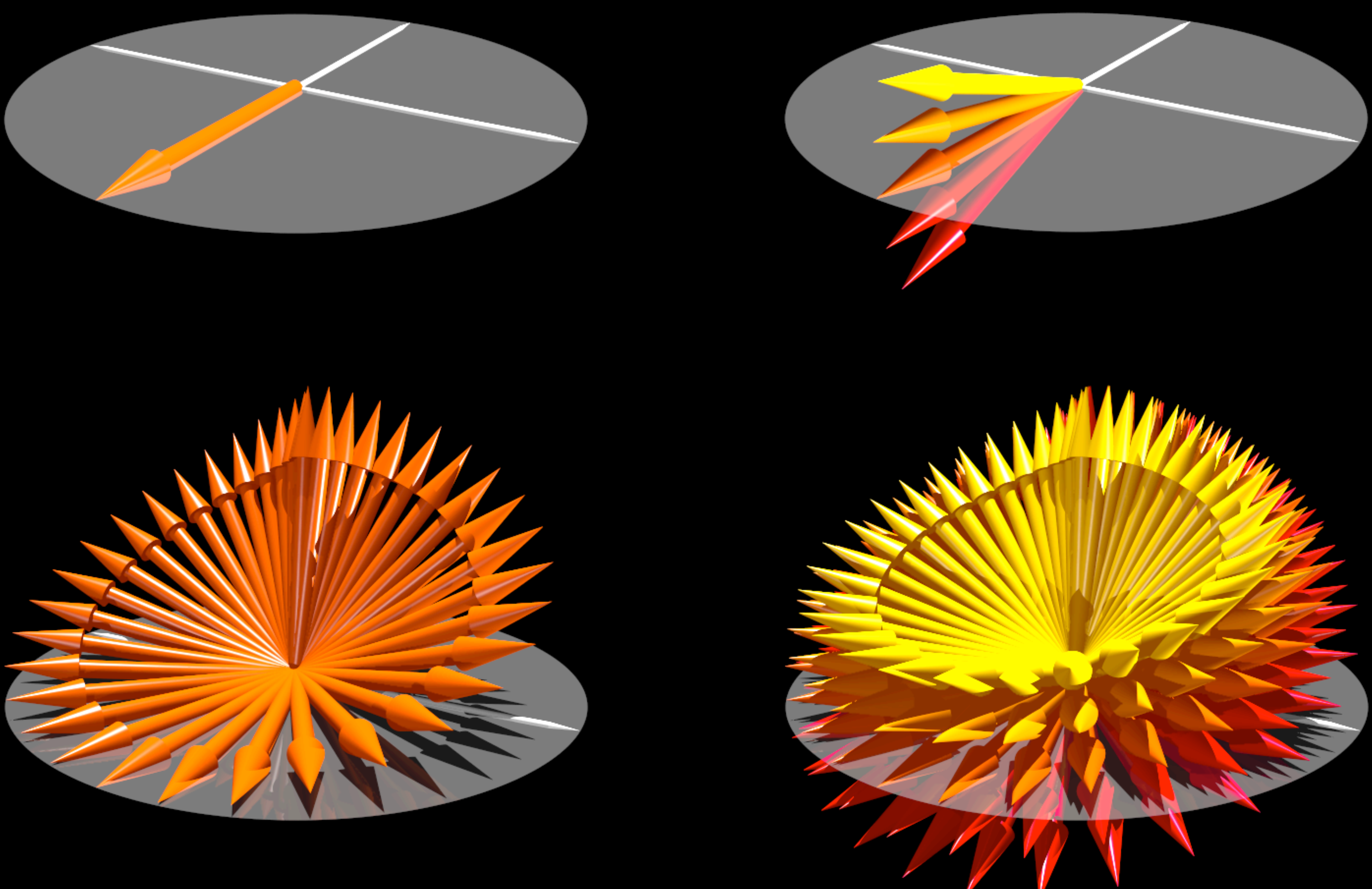
J. Mao, T.H. Mareci, K.N. Scott, E.R. Andrew, Selective inversion radiofrequency pulses by optimal control, J. Magn. Reson. 70 (1986) 310–318.

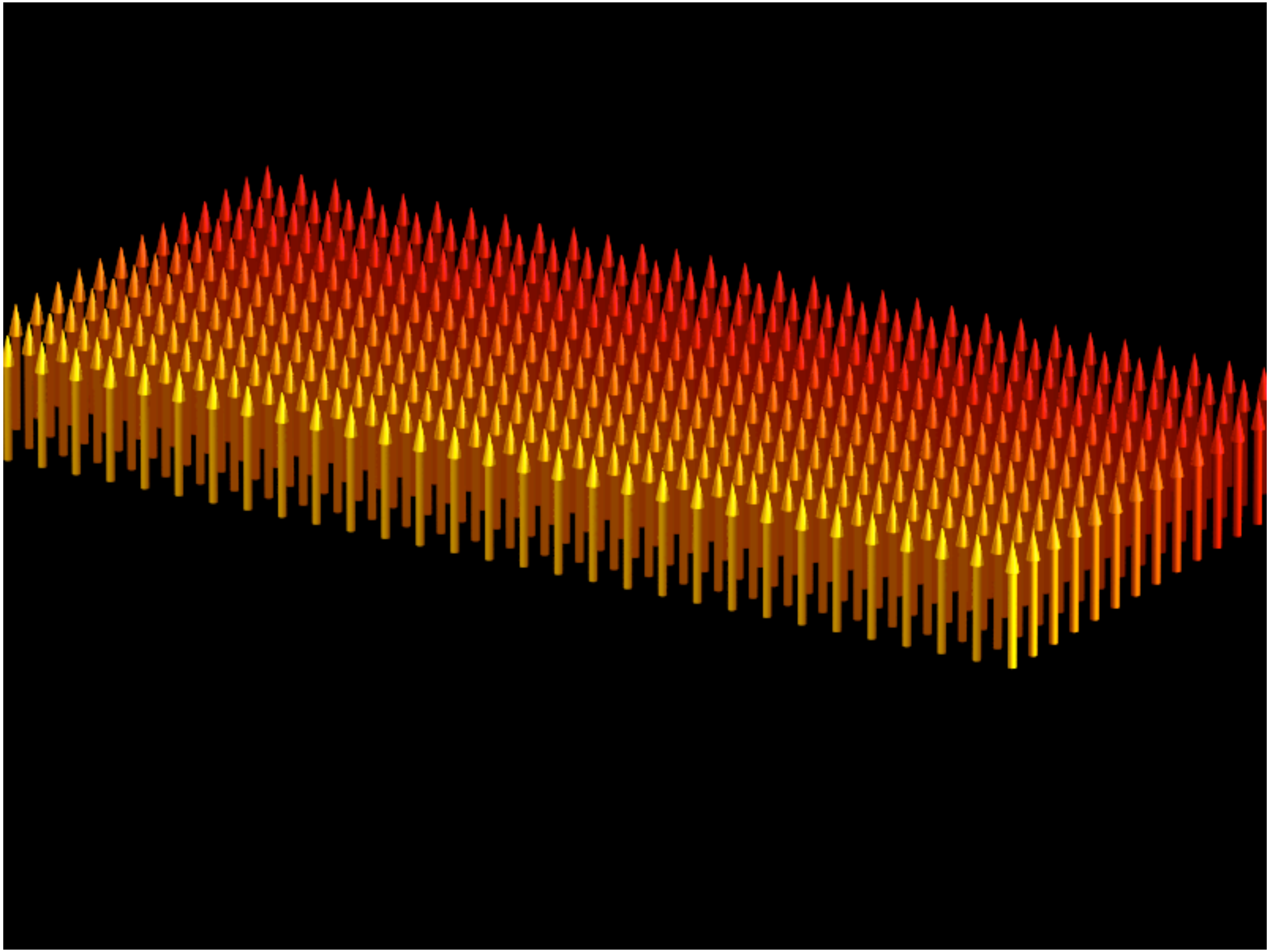
D. Rosenfeld, Y. Zur, Design of adiabatic selective pulses using optimal control theory, Magn. Reson. Med. 36 (1996) 401–409.

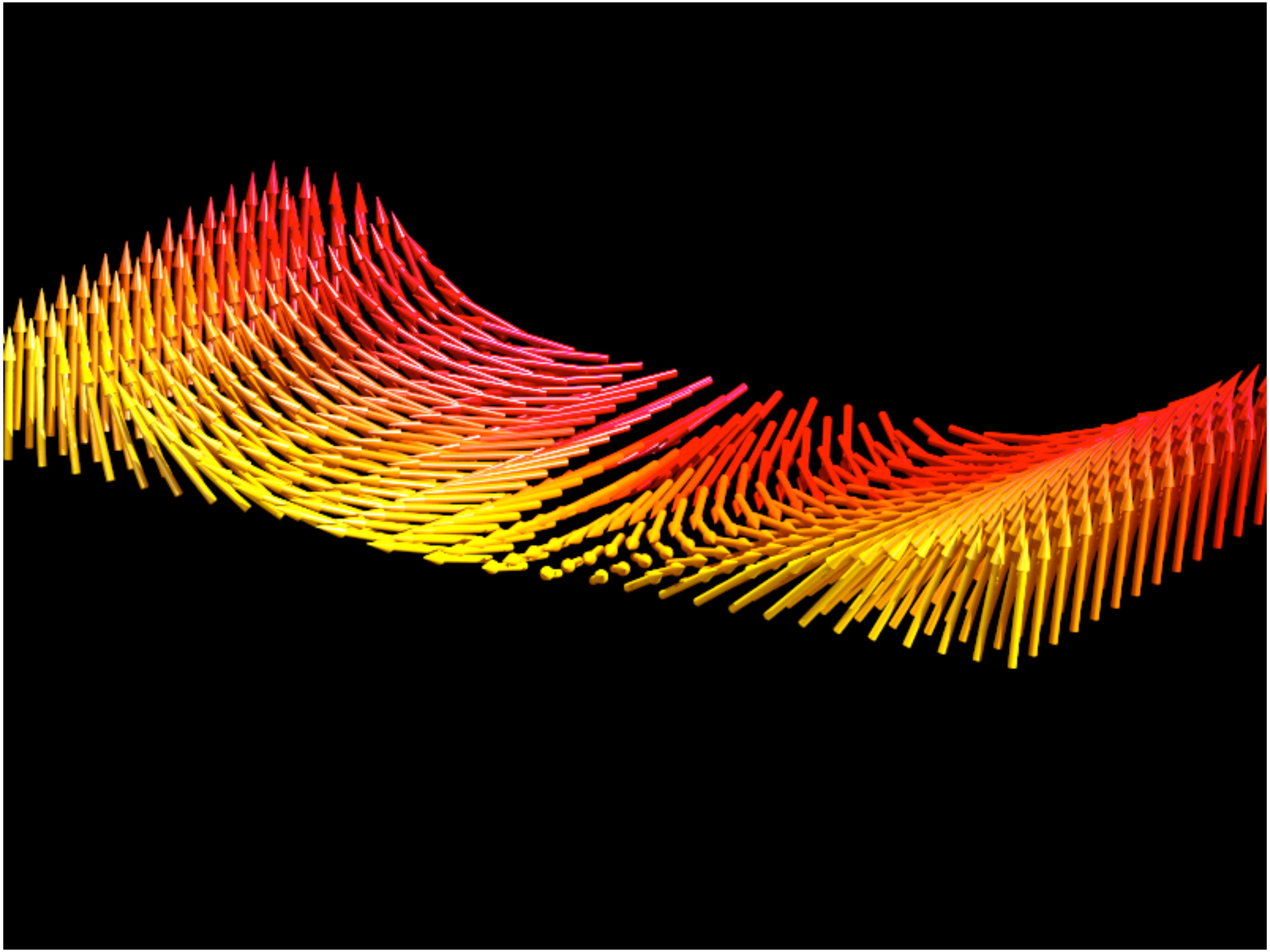

liquid state NMR
solid state NMR
ESR
time optimal
relaxation optimized
robustness
exp. constraints
STAR Ech
Power BEBOP
ICEBERG
RC BEBOP
UR Pulses
Soliton
TROPIC
CROP
BB-CROP
OC-DCP
QFT
Pattern Pulses
3 Spins
ROPE
$SU(2^n)$
2 Spins
SWAP(1,3)
QC Gates
Pulse Limits
BIBOP
BEBOP
TOP
Cartan
Optimal Control


TRACK-1
Power BEBOP
STAR Echo
ICEBERG
RC BEBOP
Soliton
TROPIC
CROP
BB-CROP
UR Pulses
OC-DCP
SU(2^n)
QFT
3 Spins
ROPE
Pattern Pulses
Pulse Limits
BIBOP
2 Spins
SWAP(1,3)
QC Gates
BEBOP
TOP
Cartan
GRAPE
analytical tools
numerical tools
Optimal Control

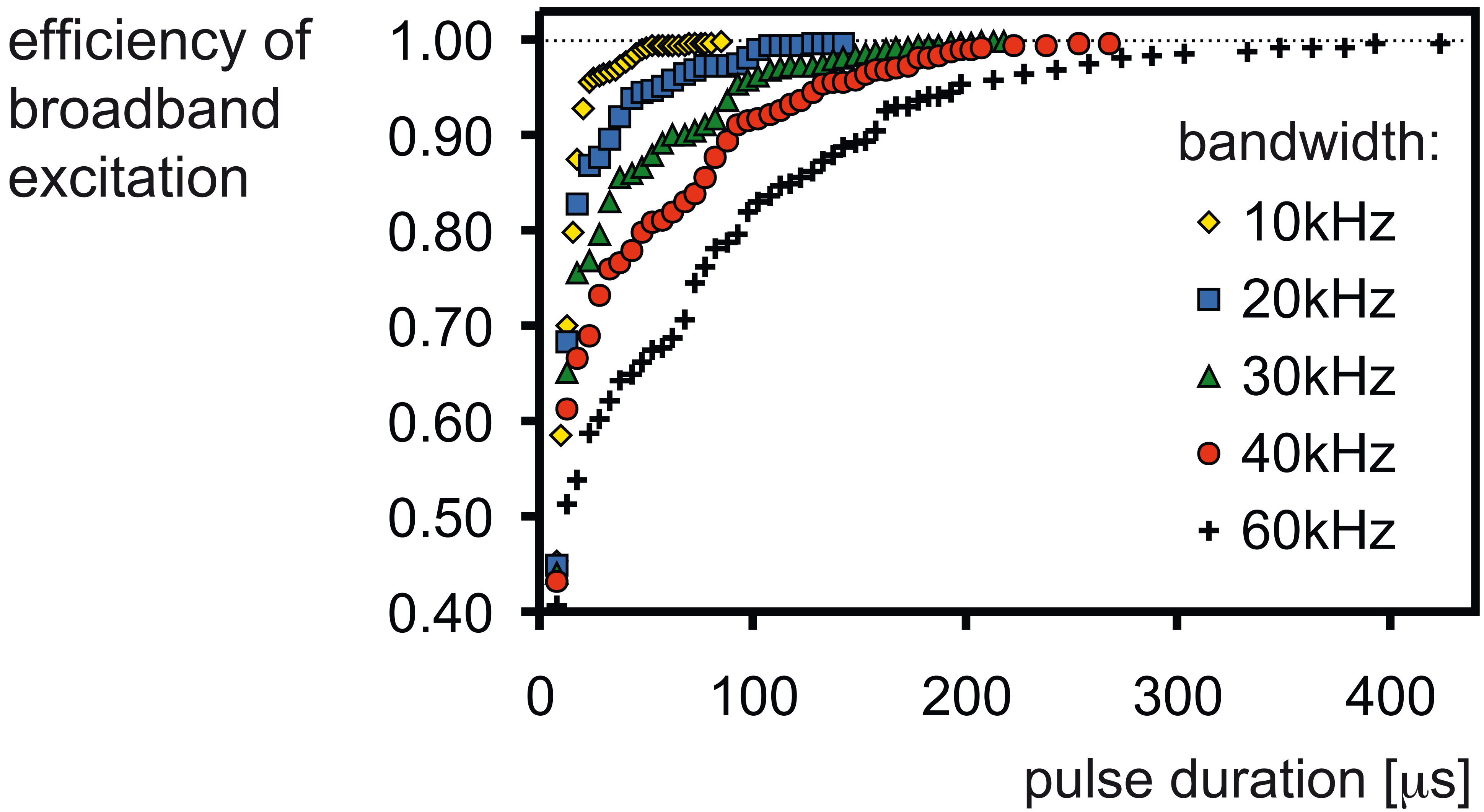











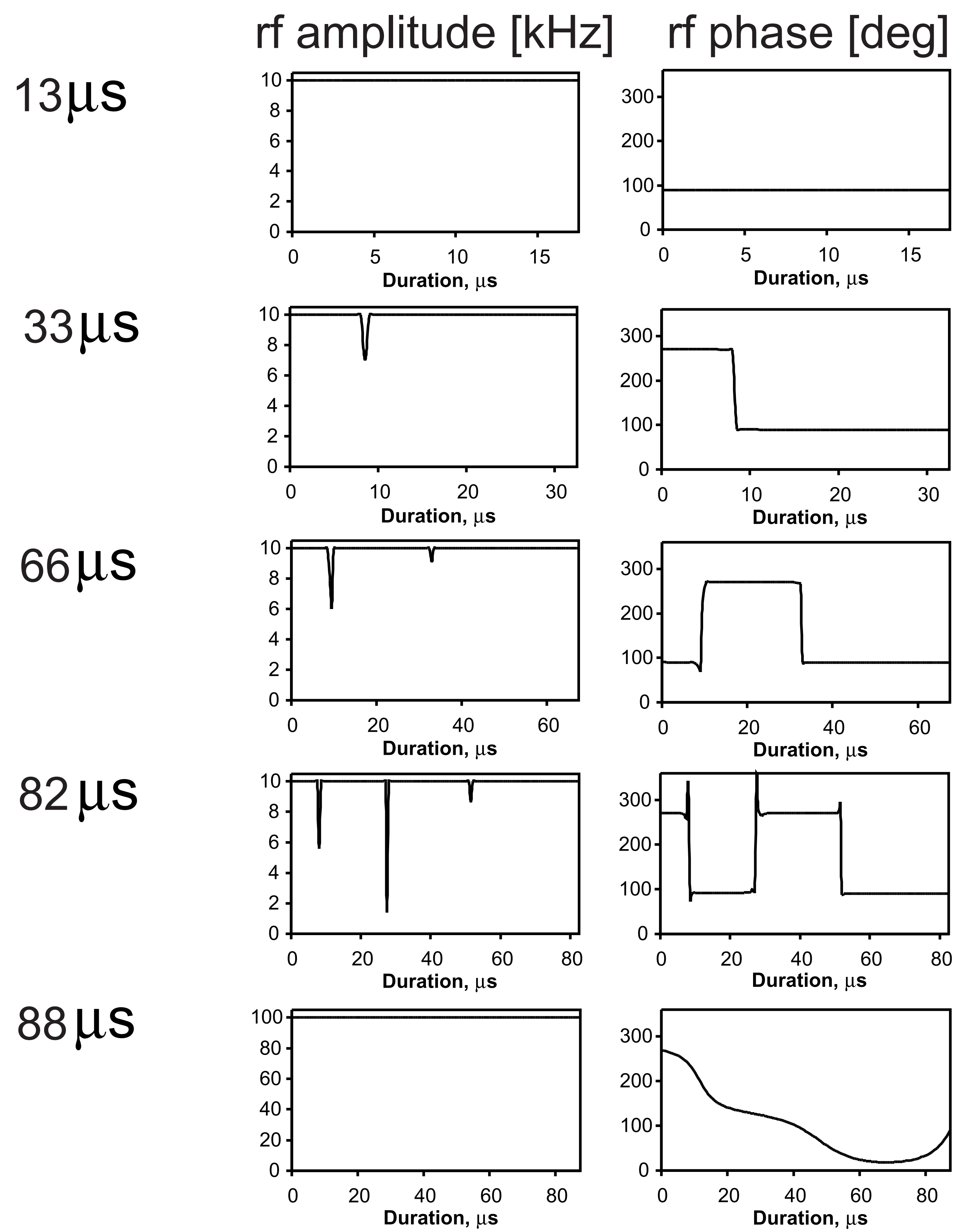
Larger excitation bandwidths require longer pulses for same performance



max. rf amplitude: 10 kHz

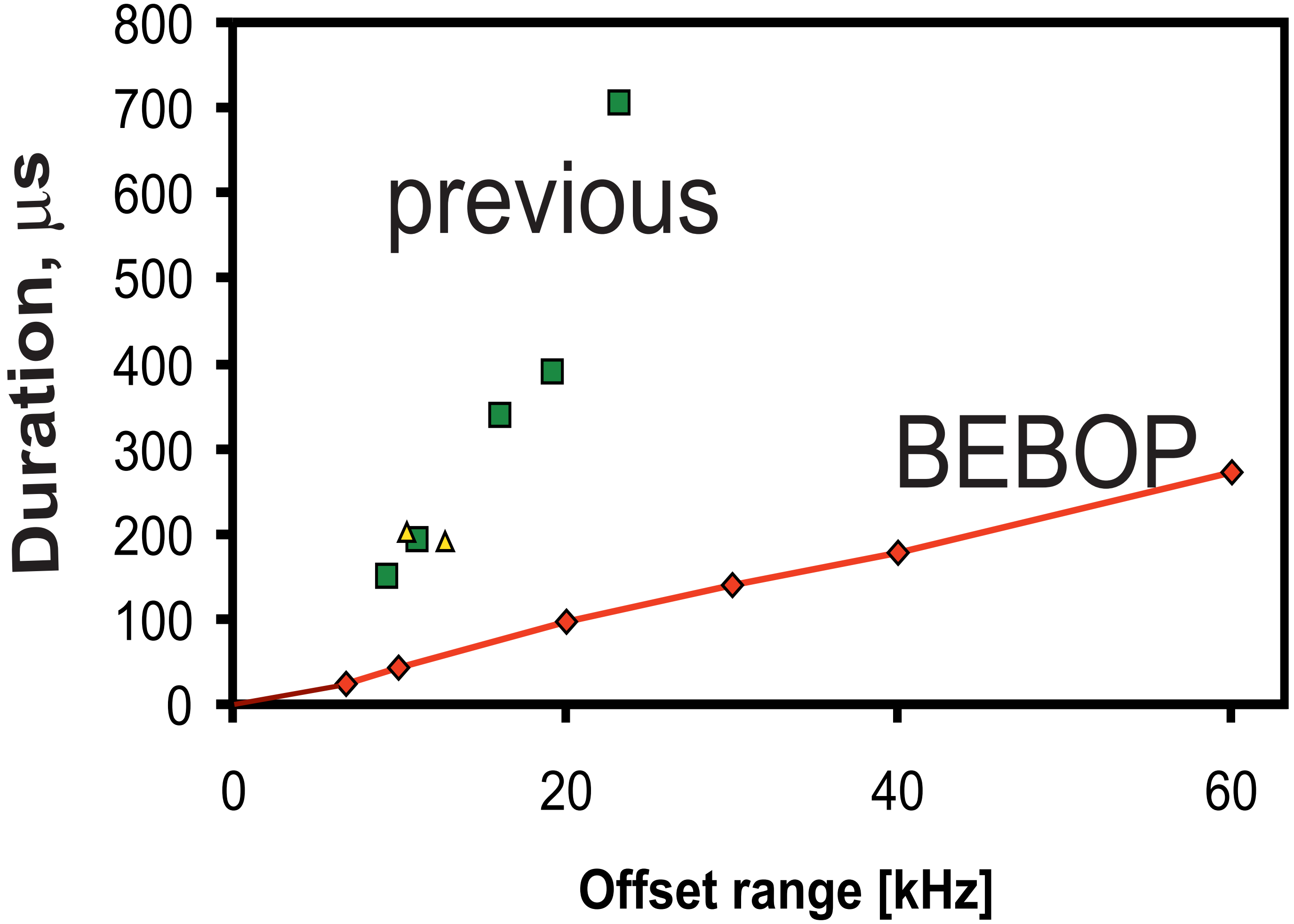
Kobzar, Skinner, Khaneja, Glaser, Luy (2004)

Longer pulse durations allow for more complex phase variations



excitation bandwidth: 20 kHz
no rf inhomogeneity

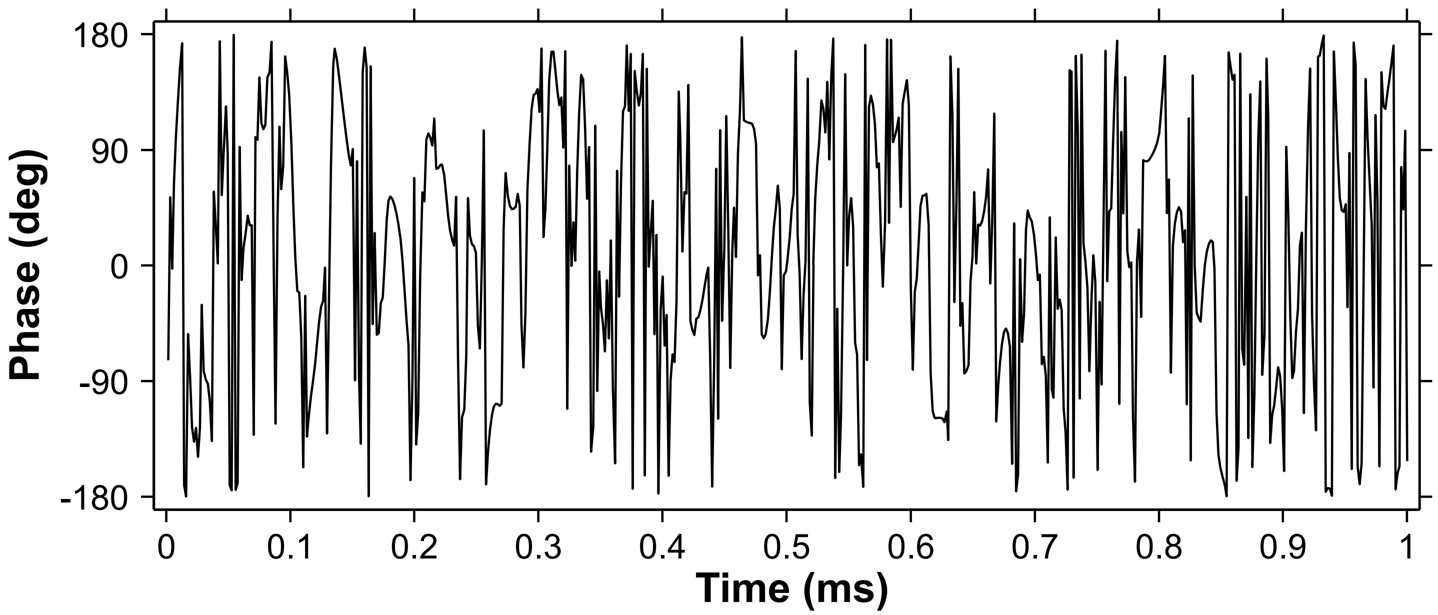
Pulse duration as a function of offset range

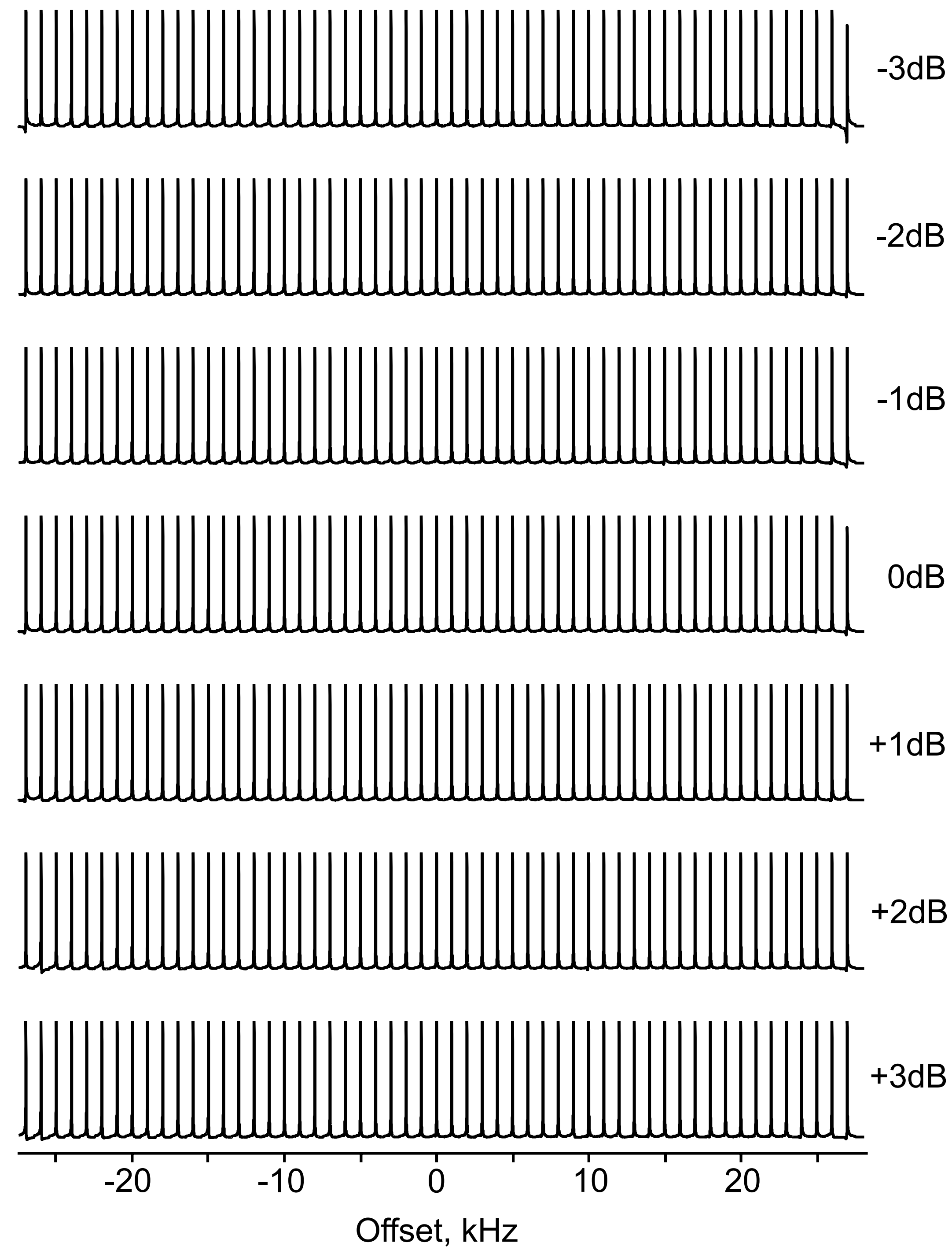


(excitation efficiency: 98%, max. rf amplitude: 10 kHz, no rf inhomogeneity)

Robust broadband excitation pulse

PM-BEBOP

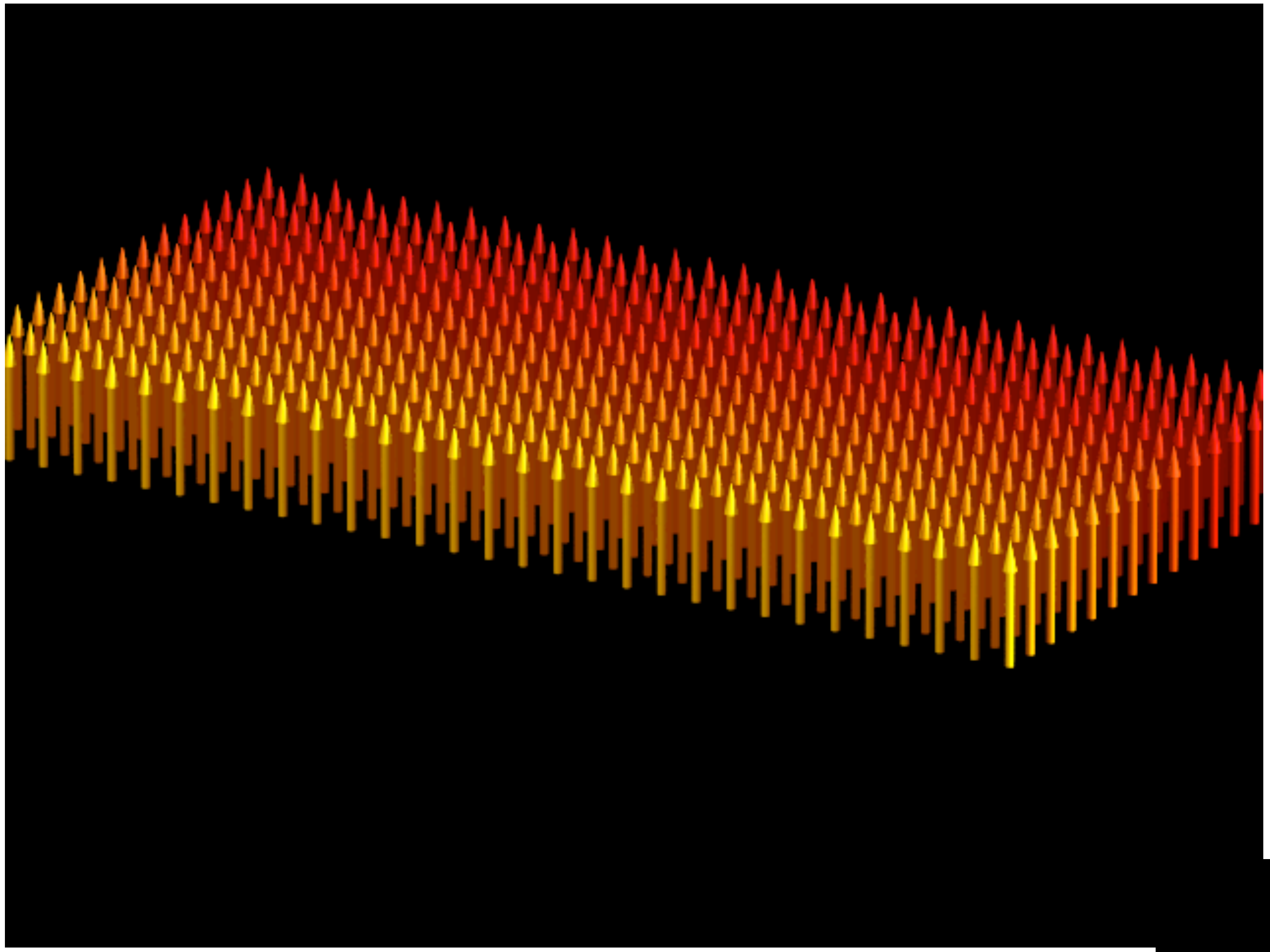


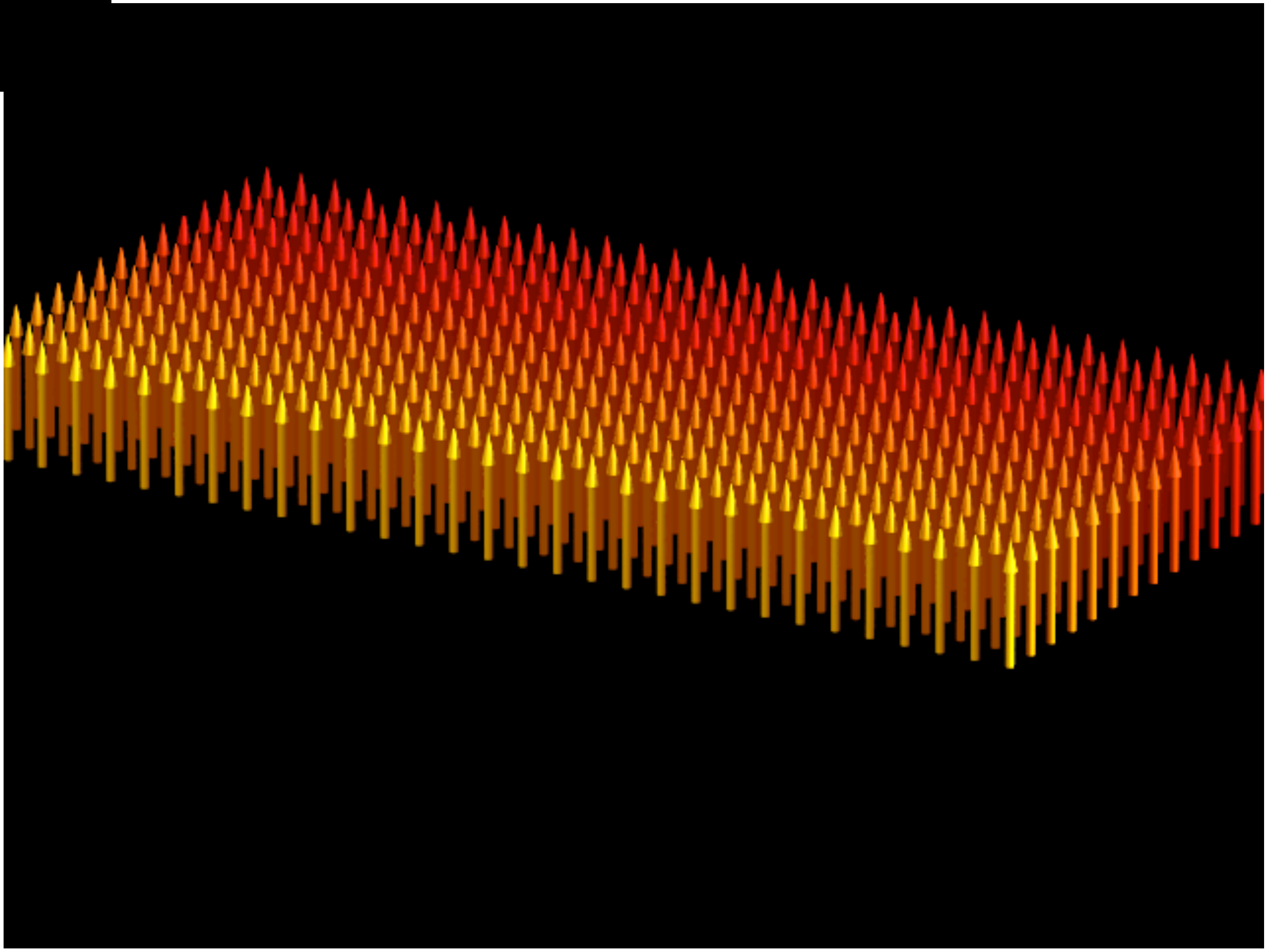


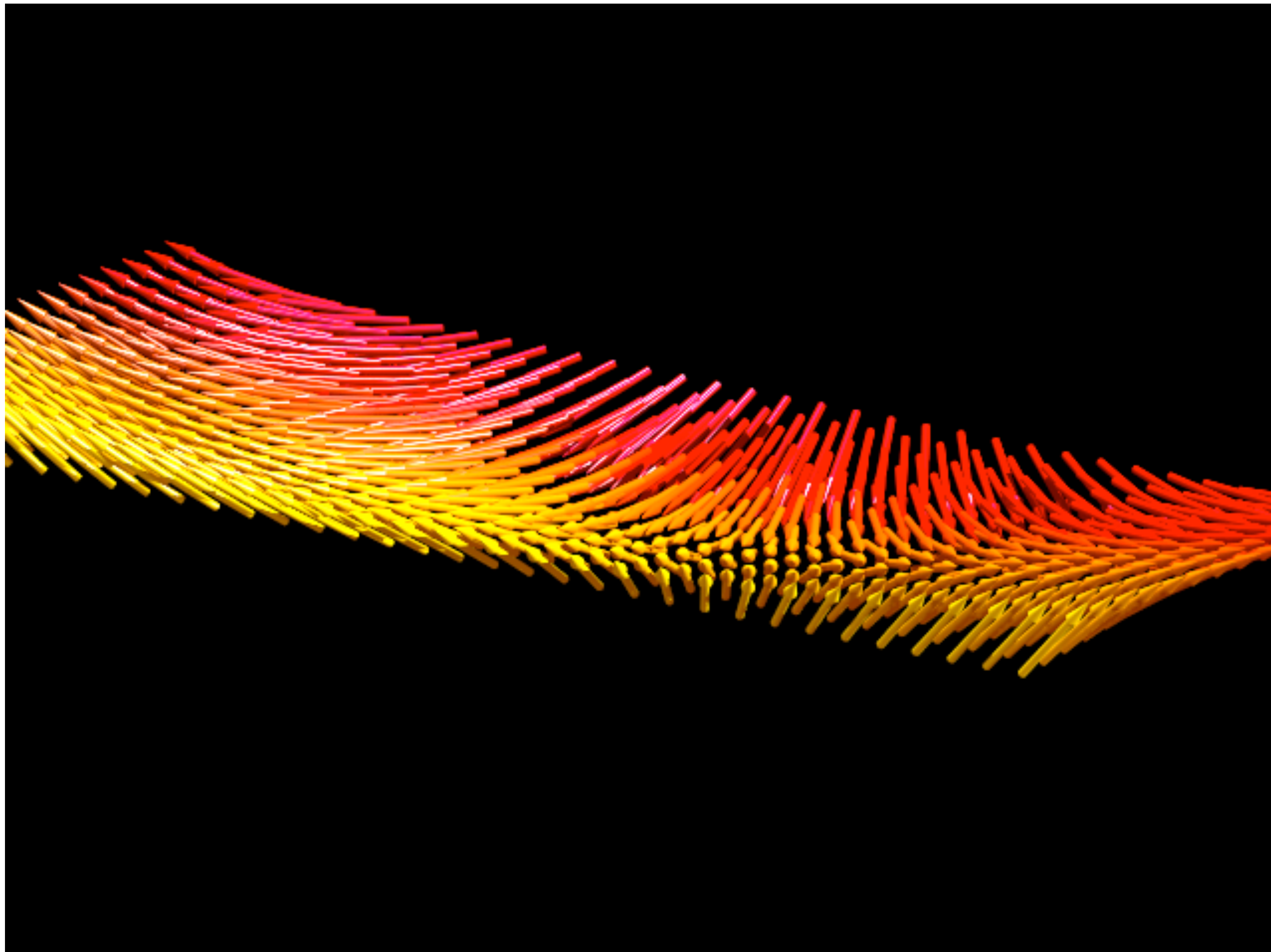
bandwidth: 50 kHz

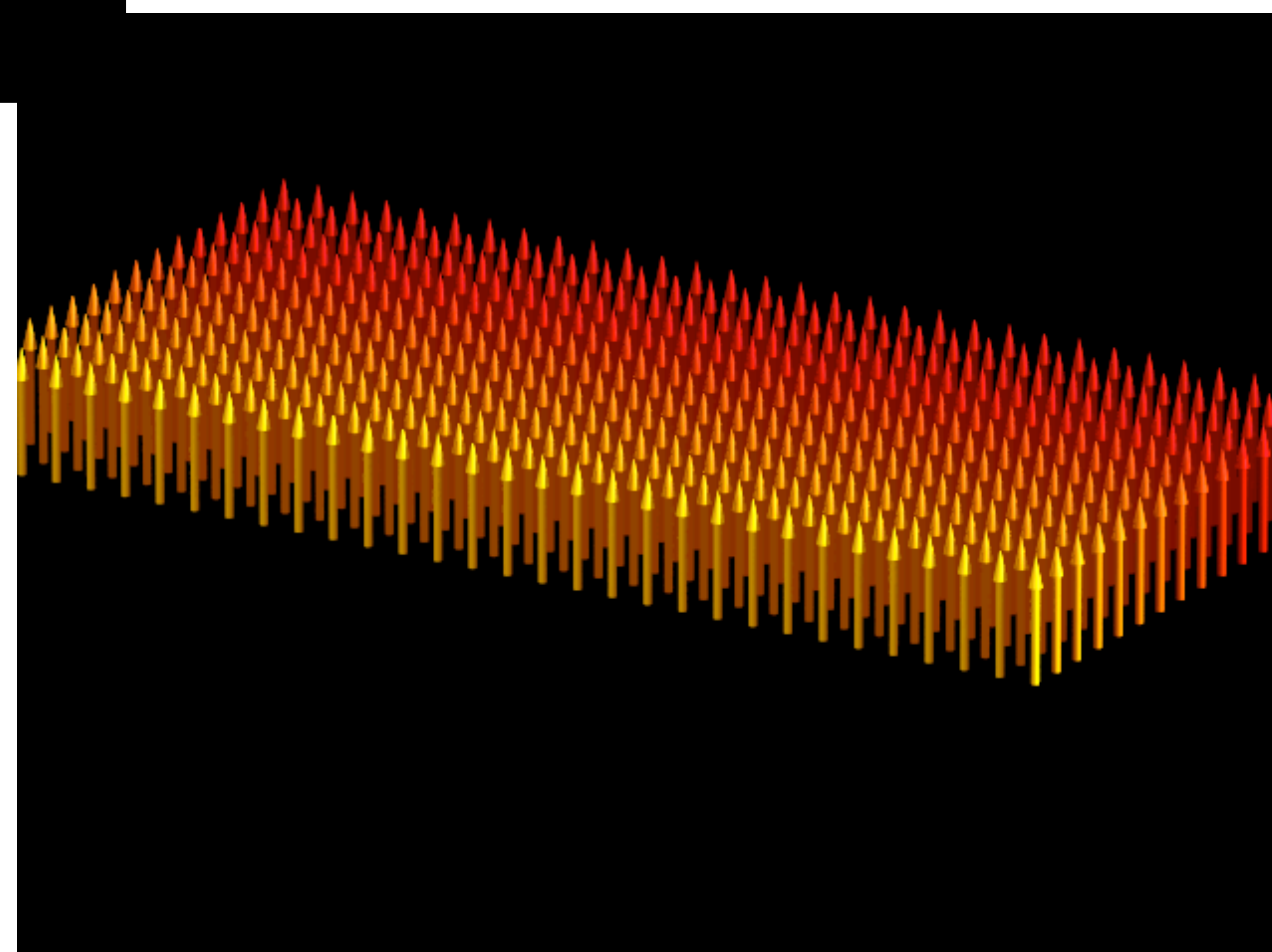
rf amplitude: 15 kHz

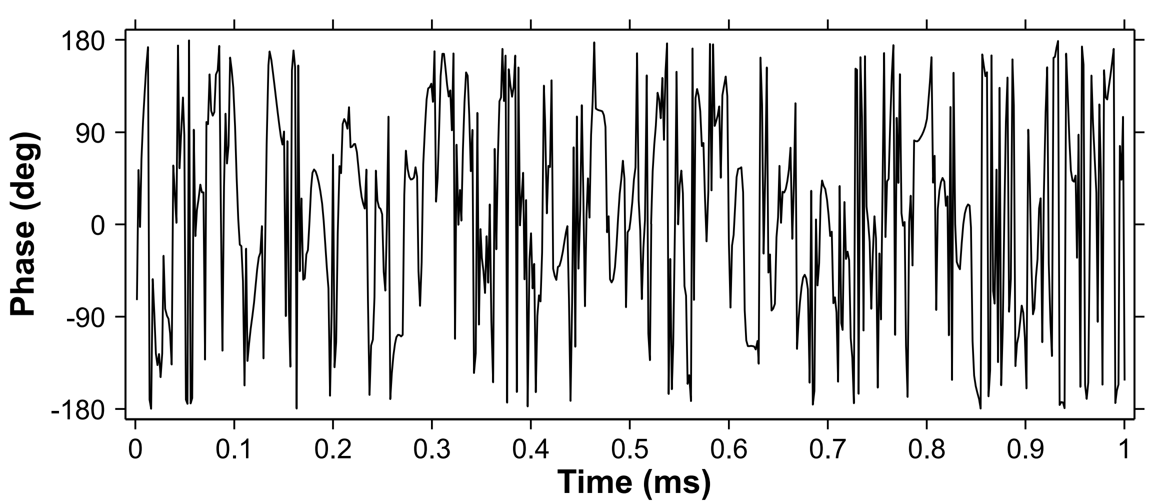
Skinner et al. (2006)

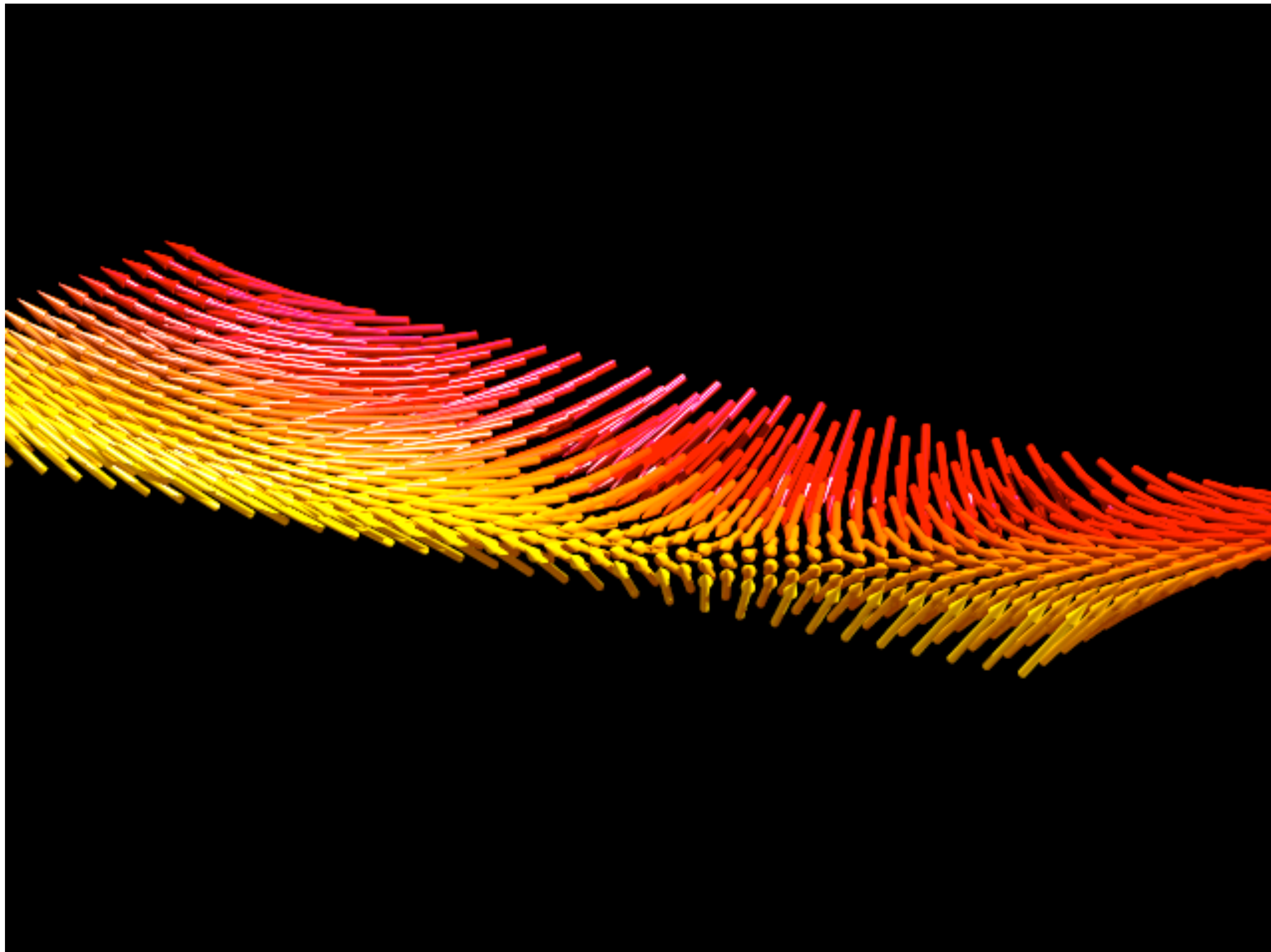


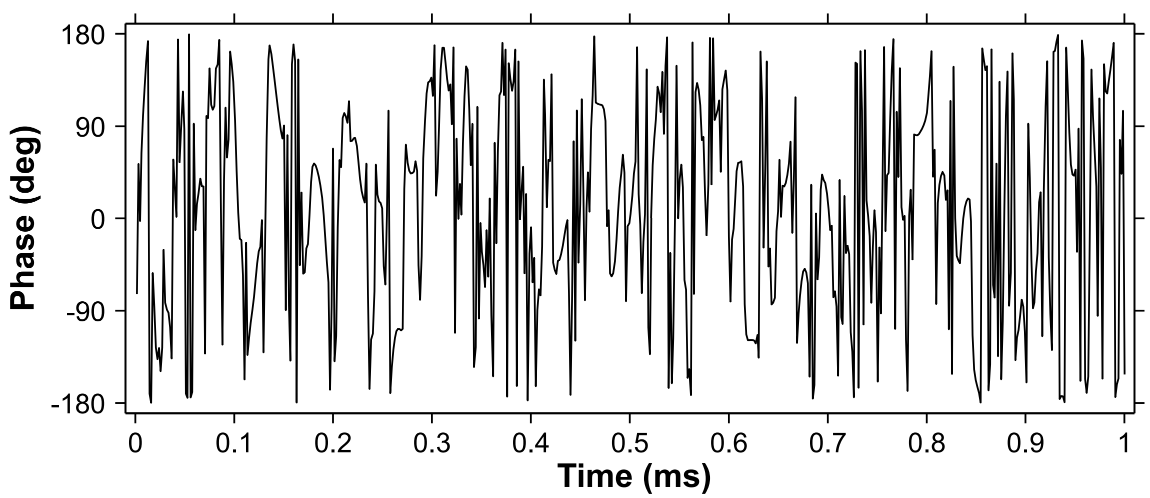




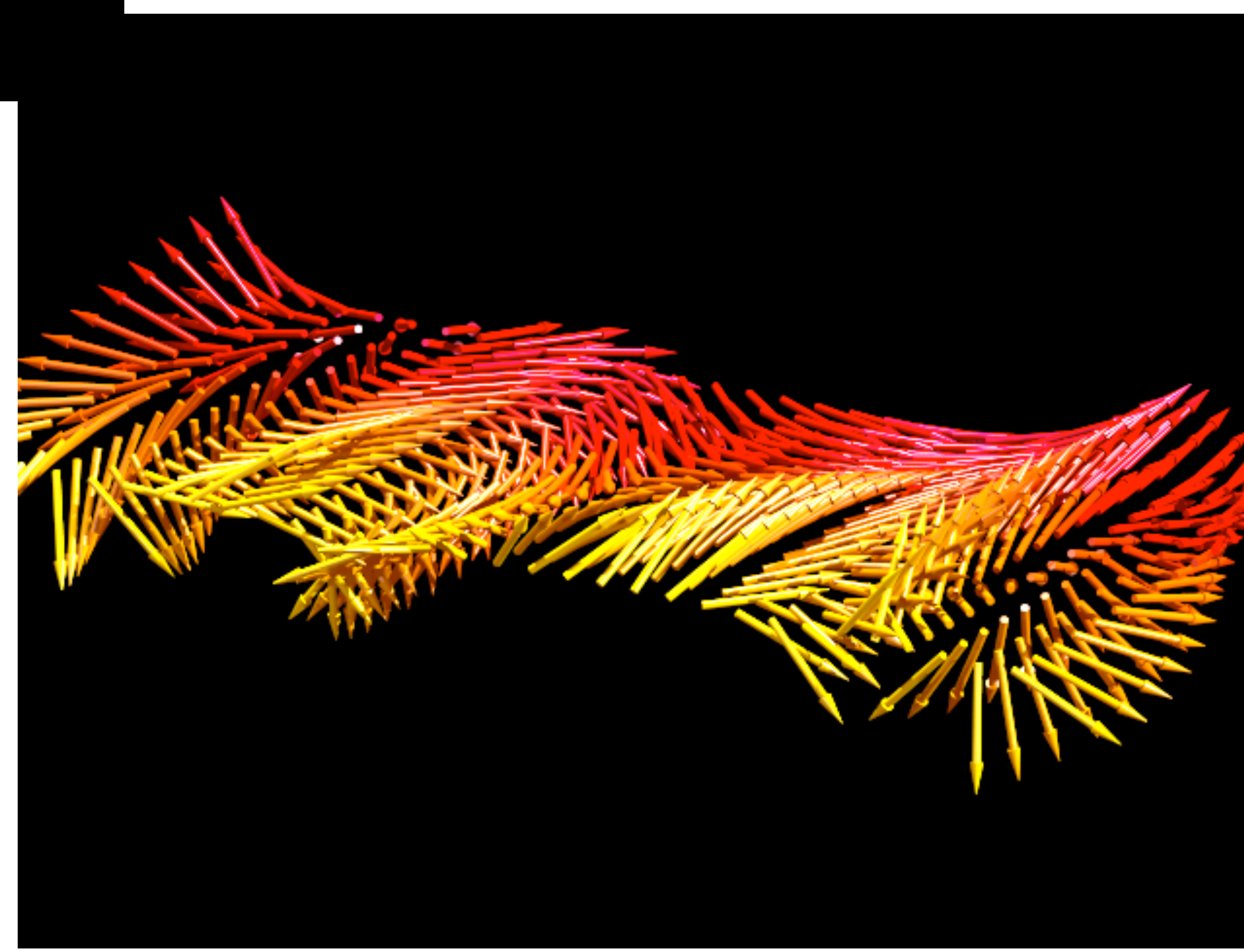


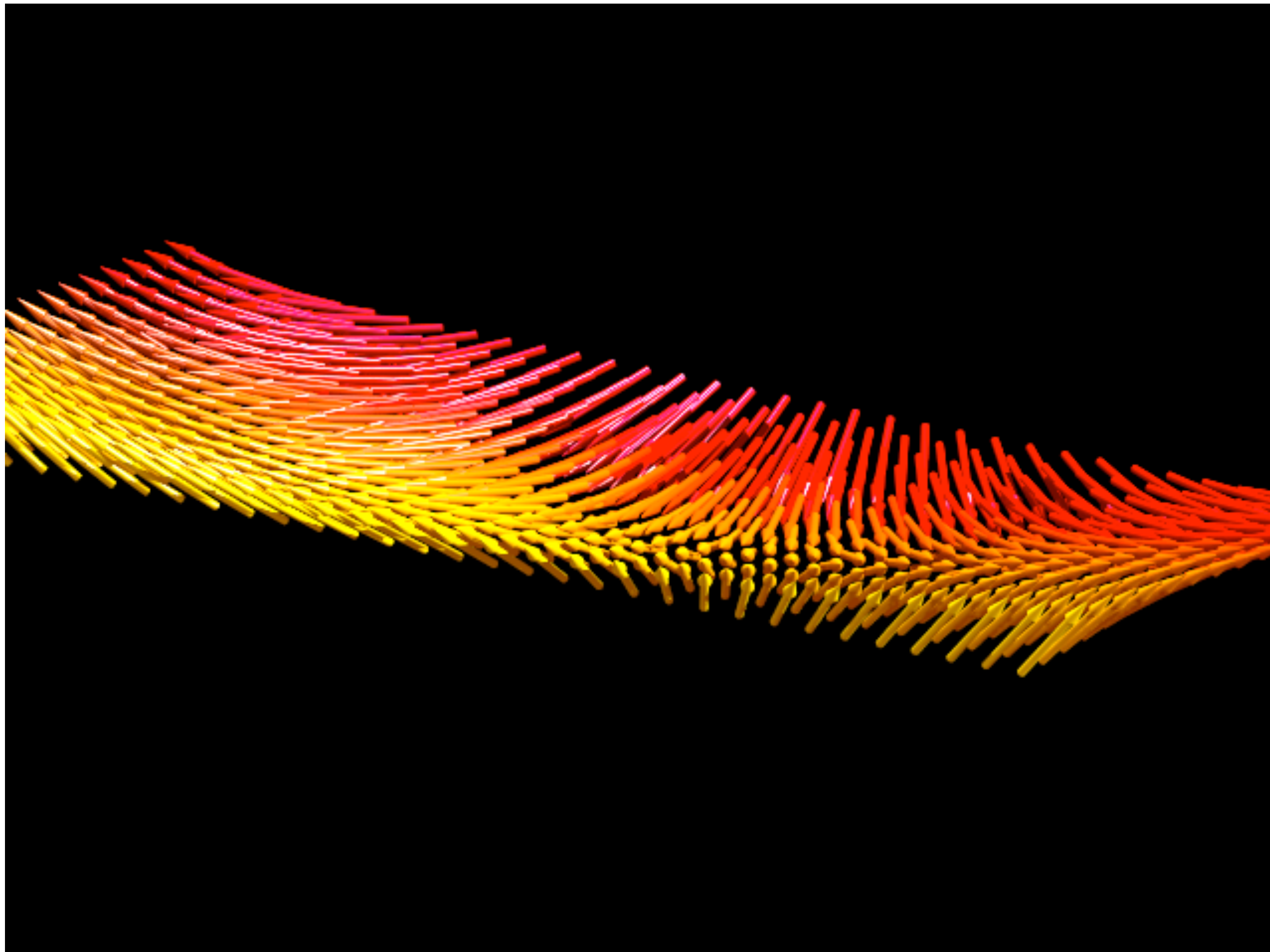

180
90
0
-90
-180
Phase (deg)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
Time (ms)

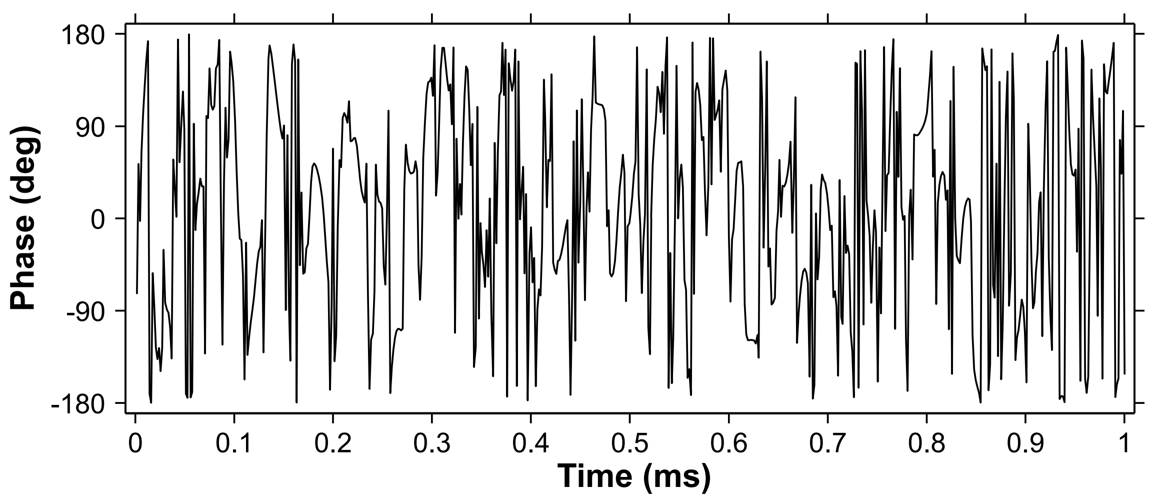




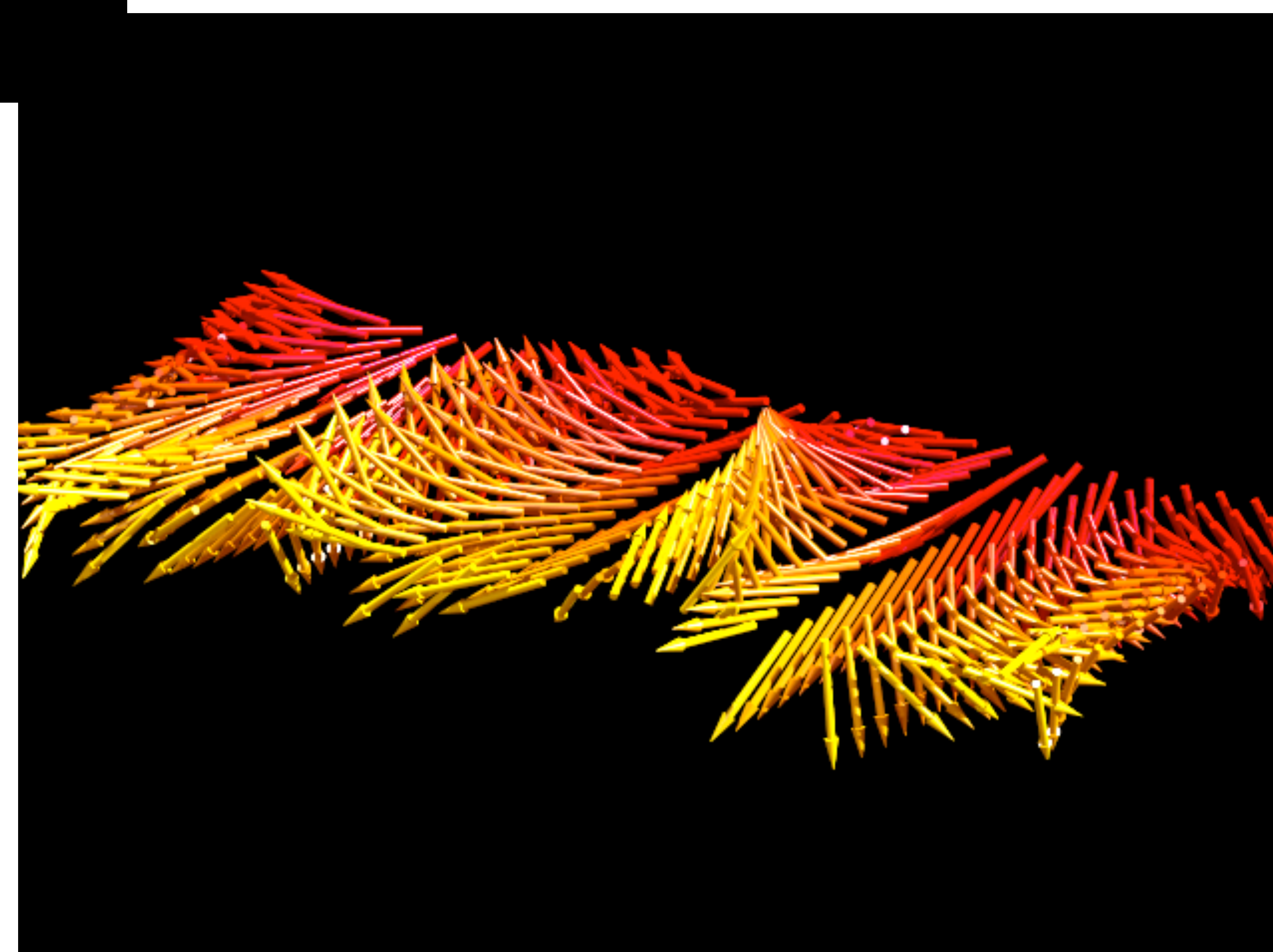
180
90
0
-90
-180
Phase (deg)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
Time (ms)

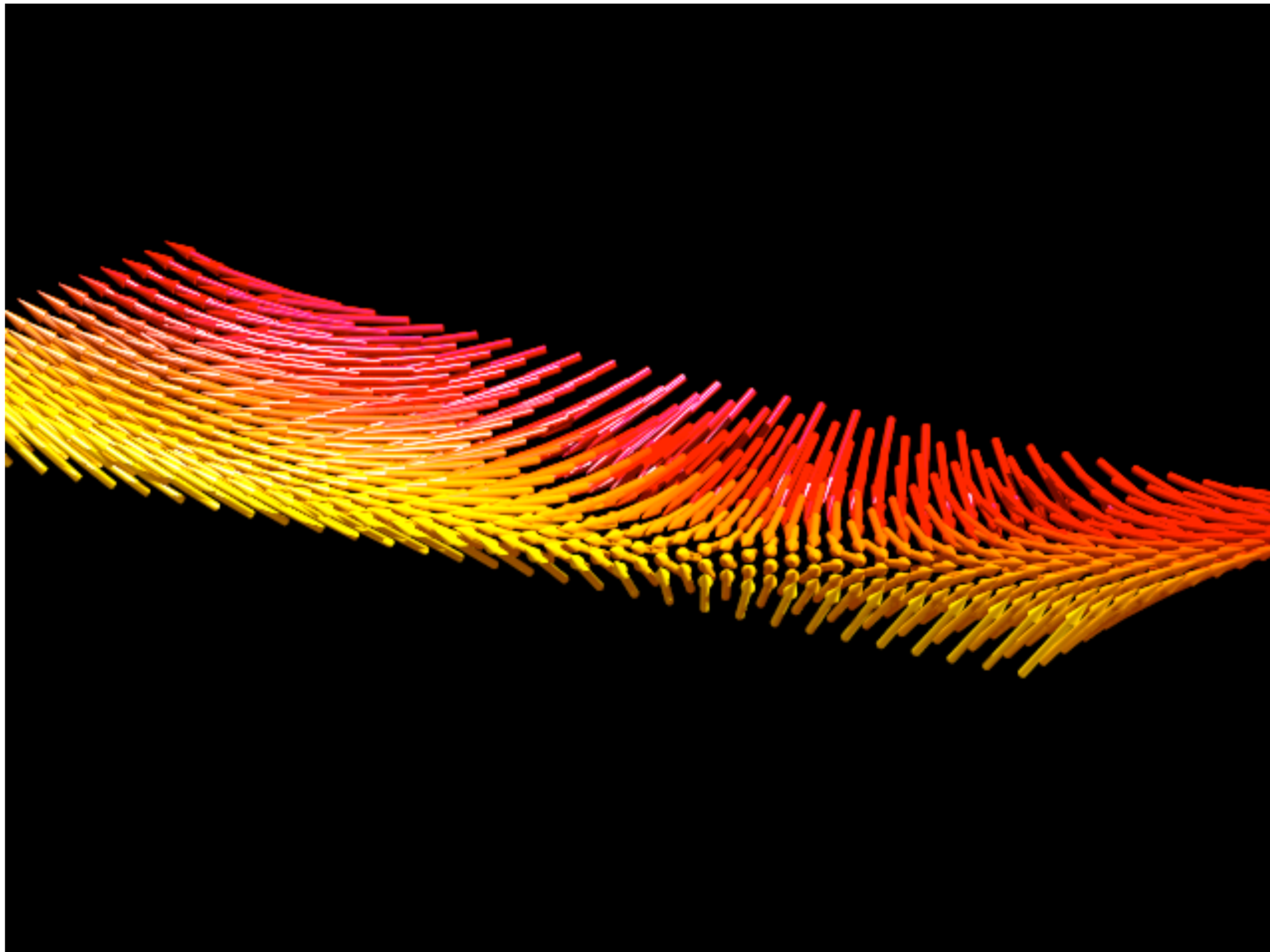


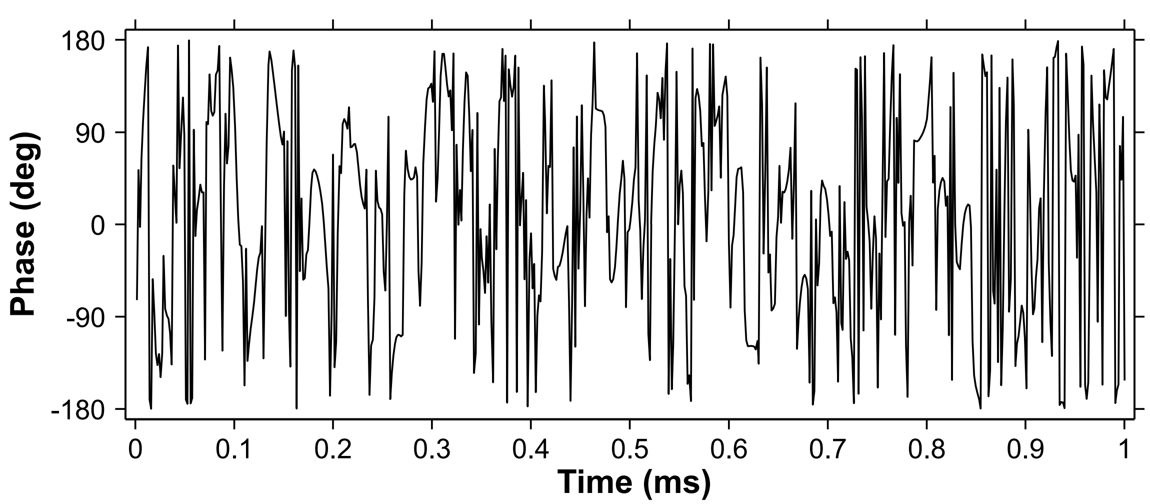




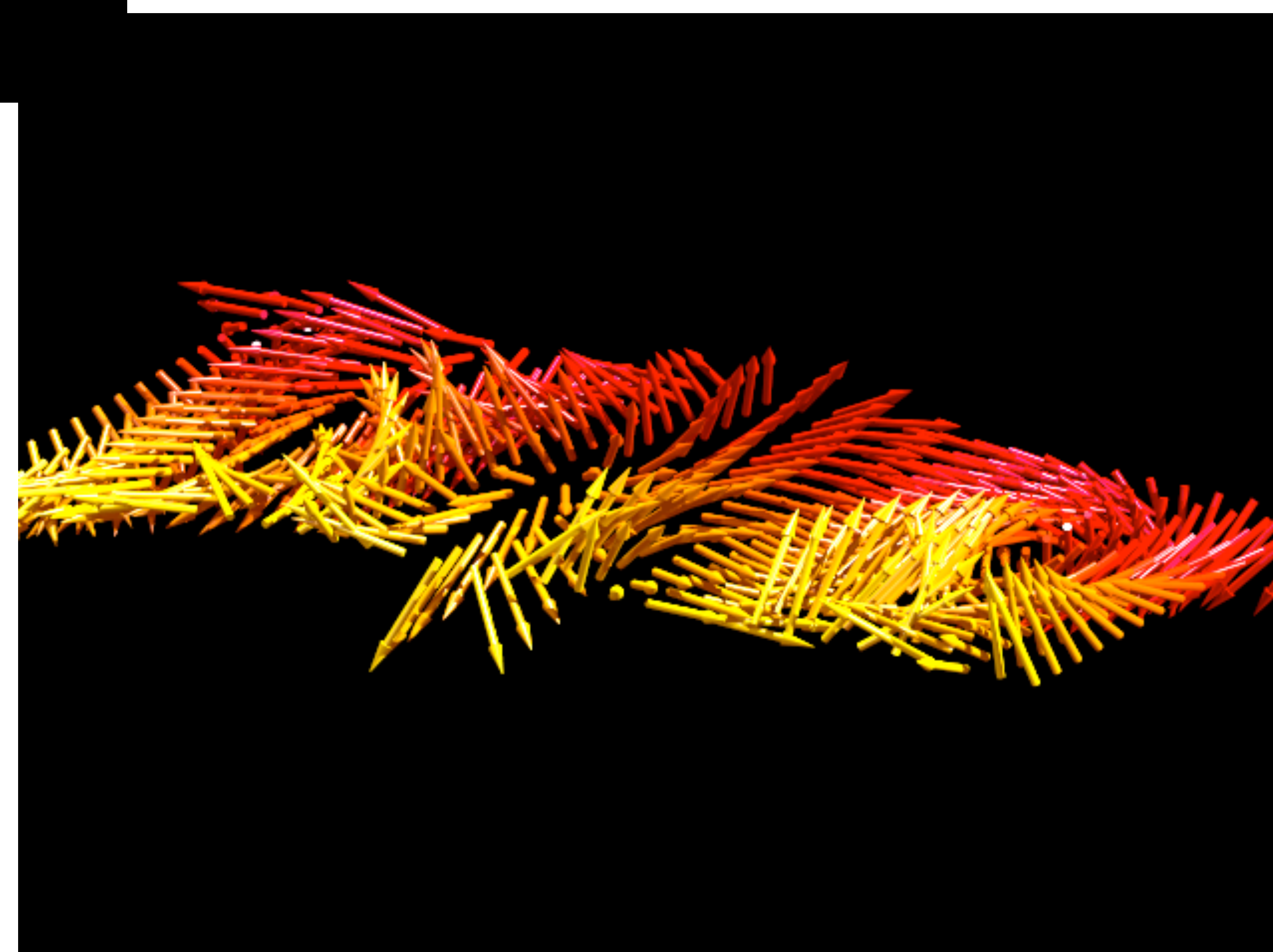
180
90
0
-90
-180
Phase (deg)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
Time (ms)

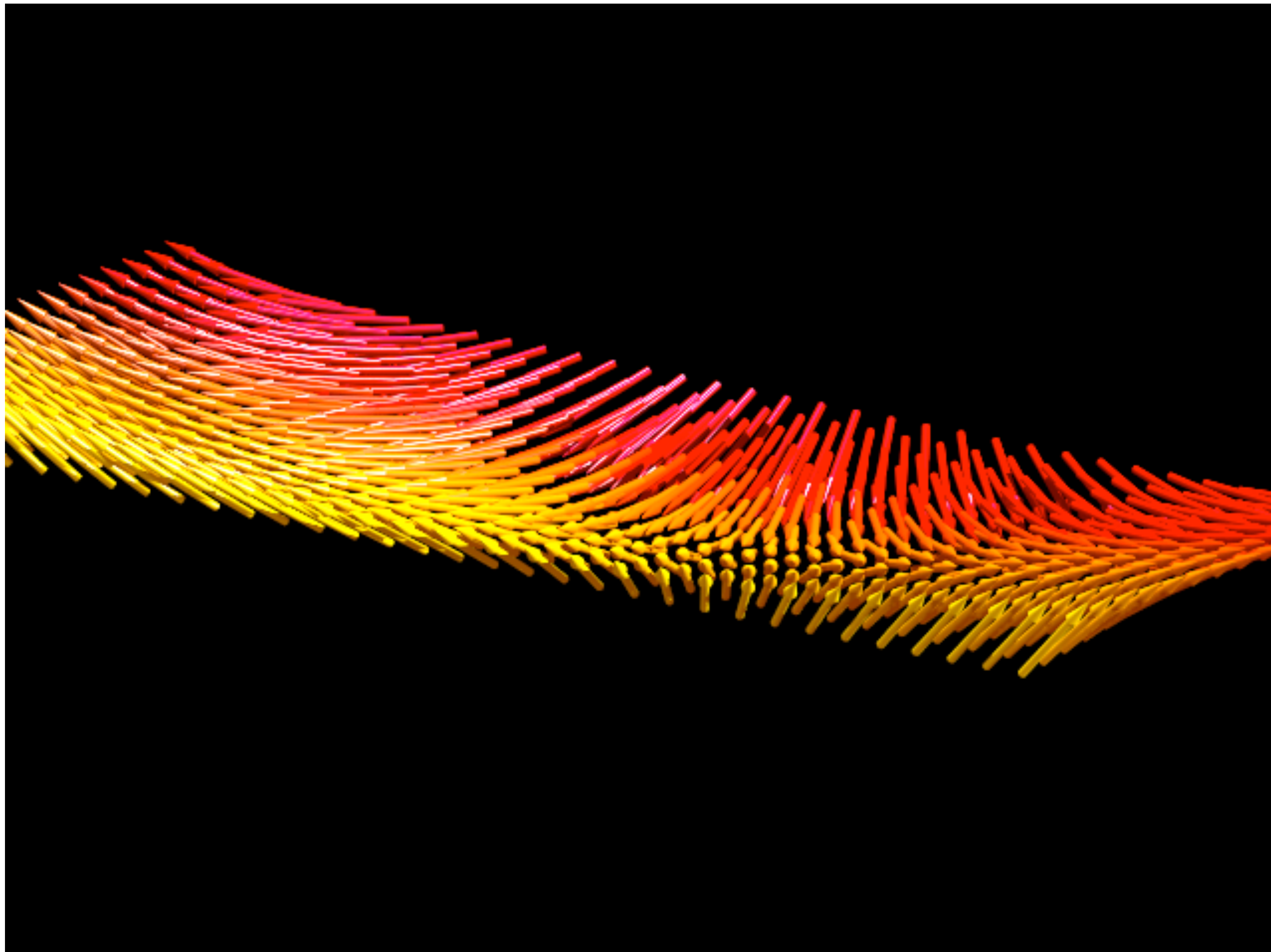


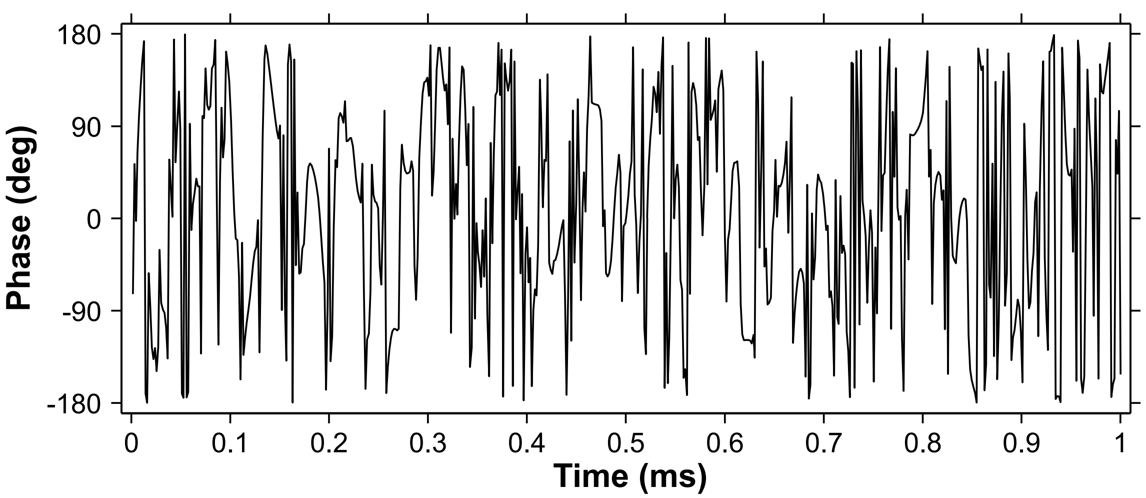




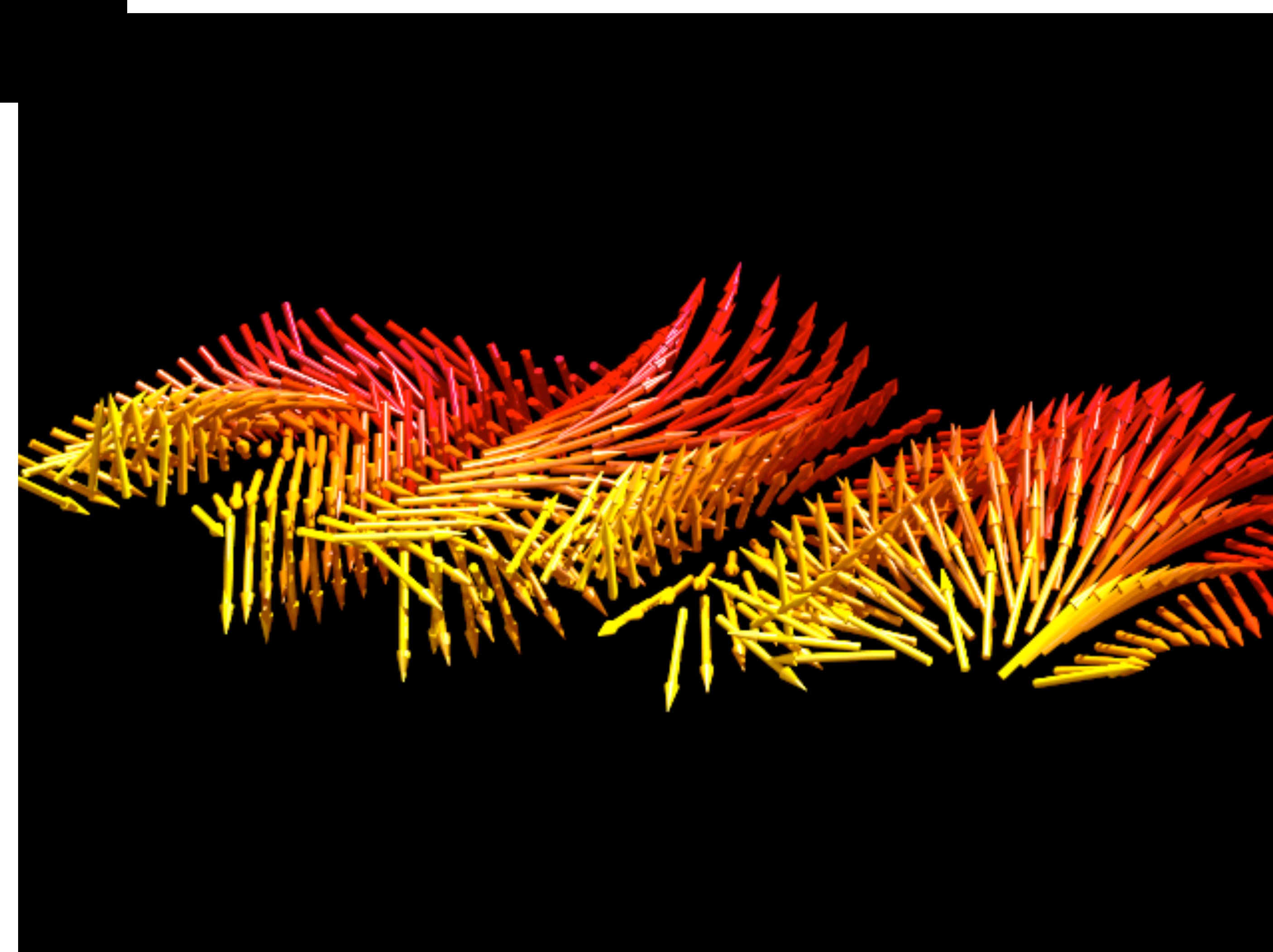
180
90
0
-90
-180
Phase (deg)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
Time (ms)

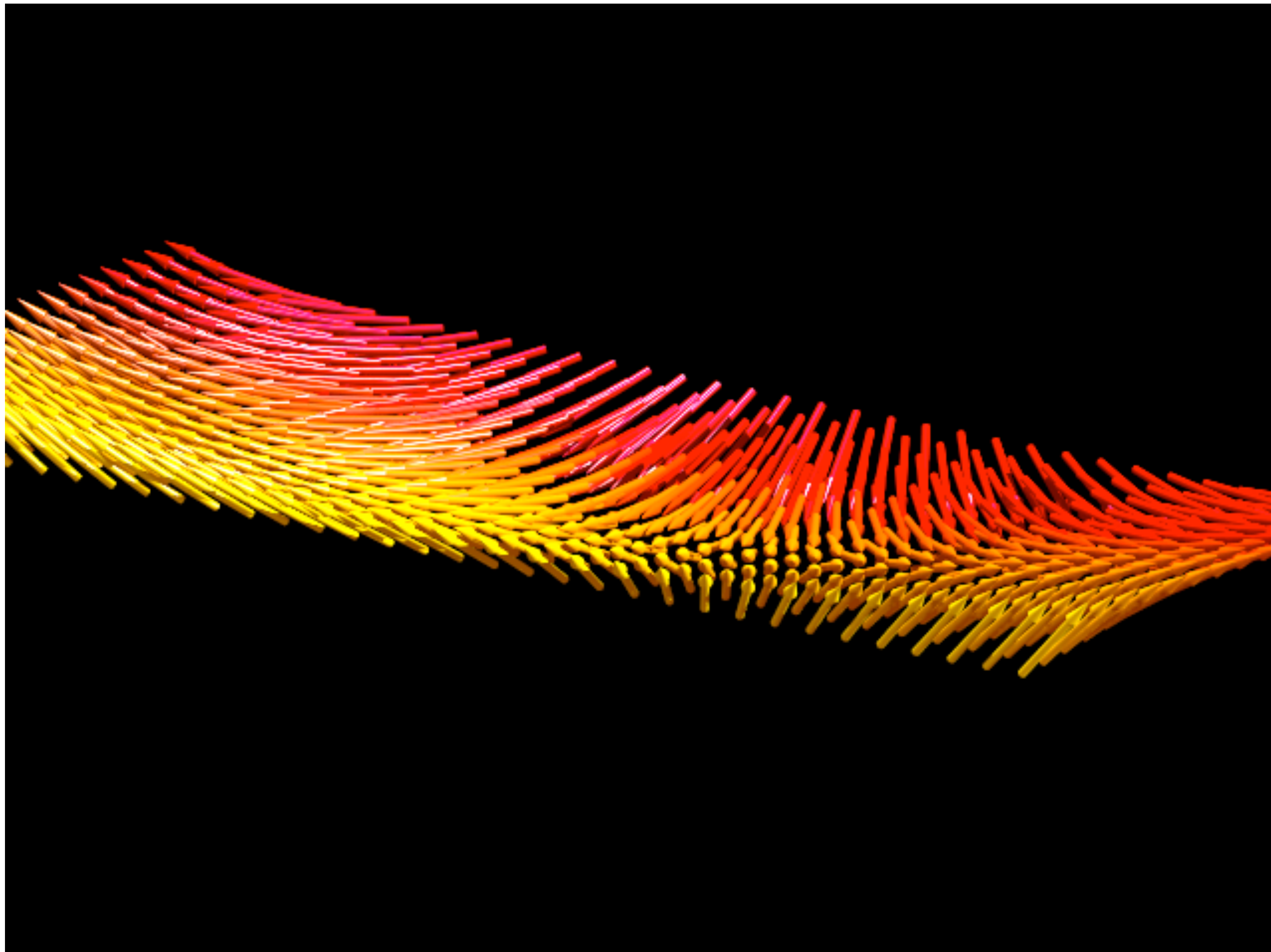


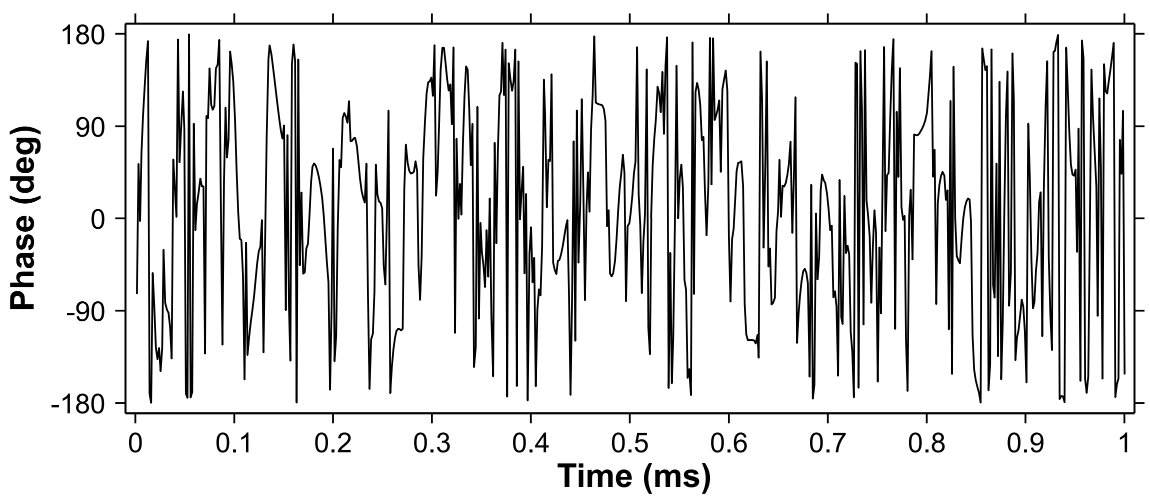


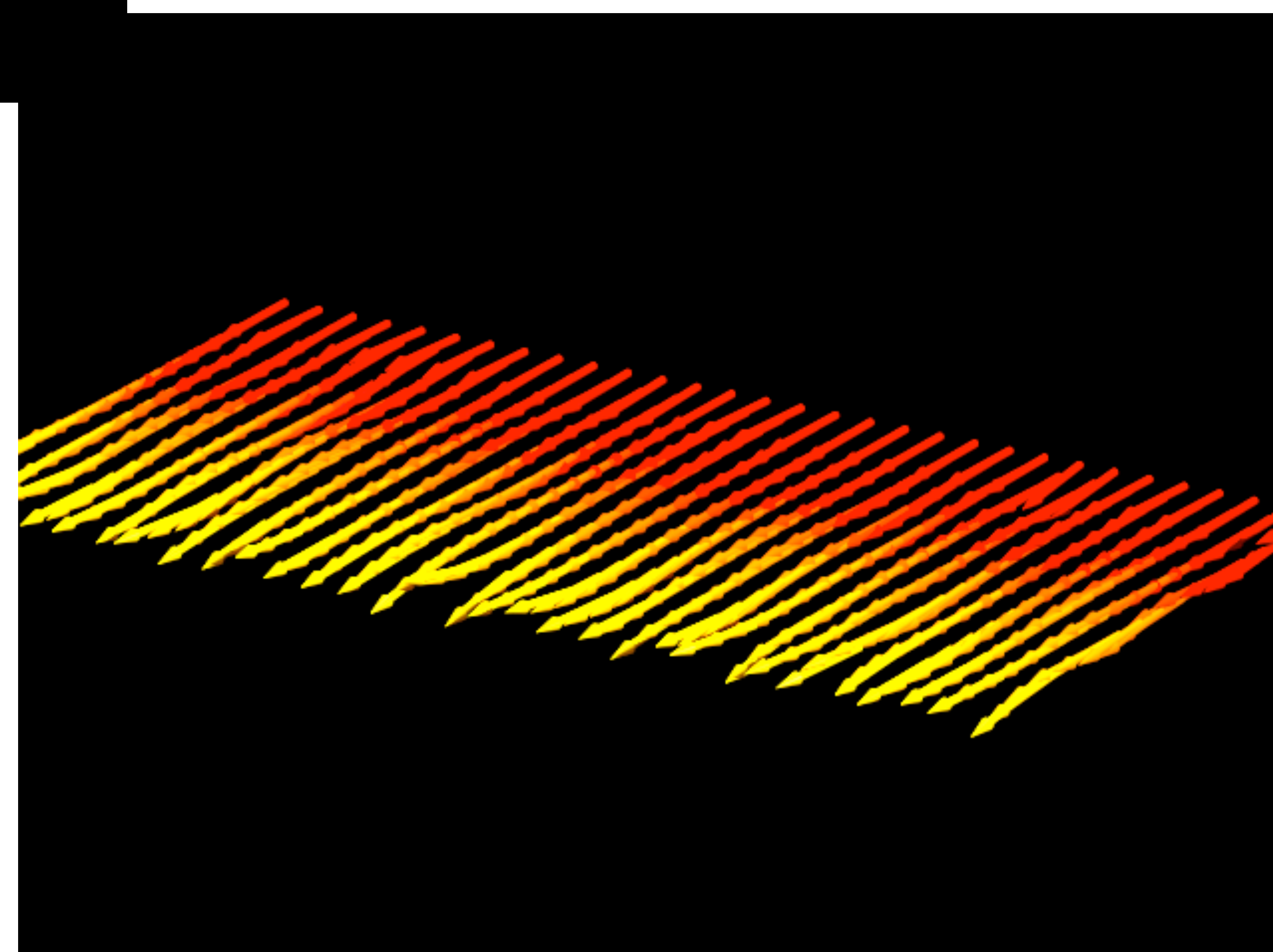


180
90
0
-90
-180
Phase (deg)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
Time (ms)

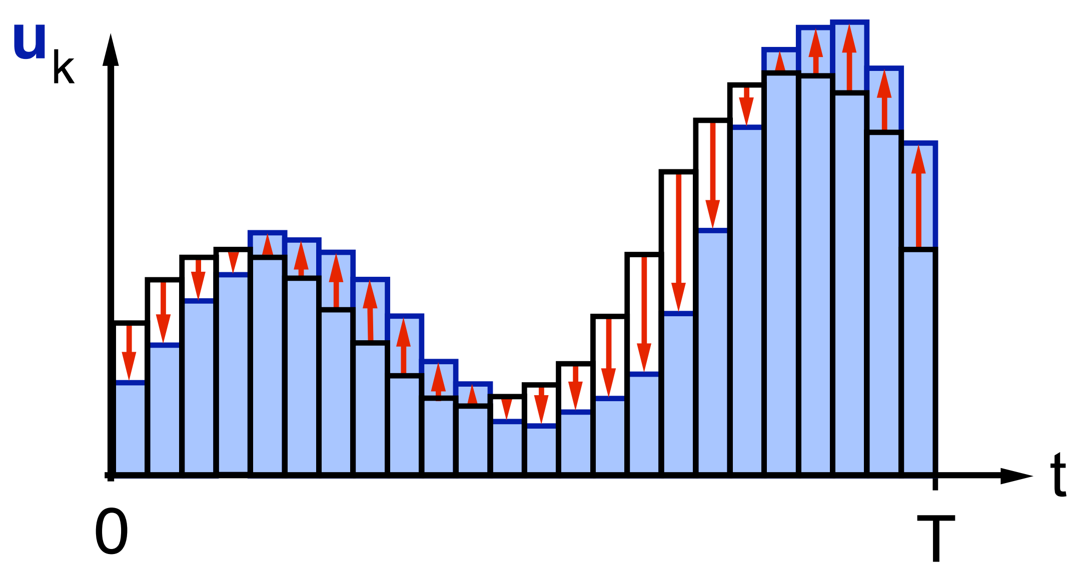





180
90
0
-90
-180
Phase (deg)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
Time (ms)



GRAPE (Gradient Ascent Pulse Engineering)



desired transfer: $A \longrightarrow C$

performance: $\langle C \mid \rho(T) \rangle$

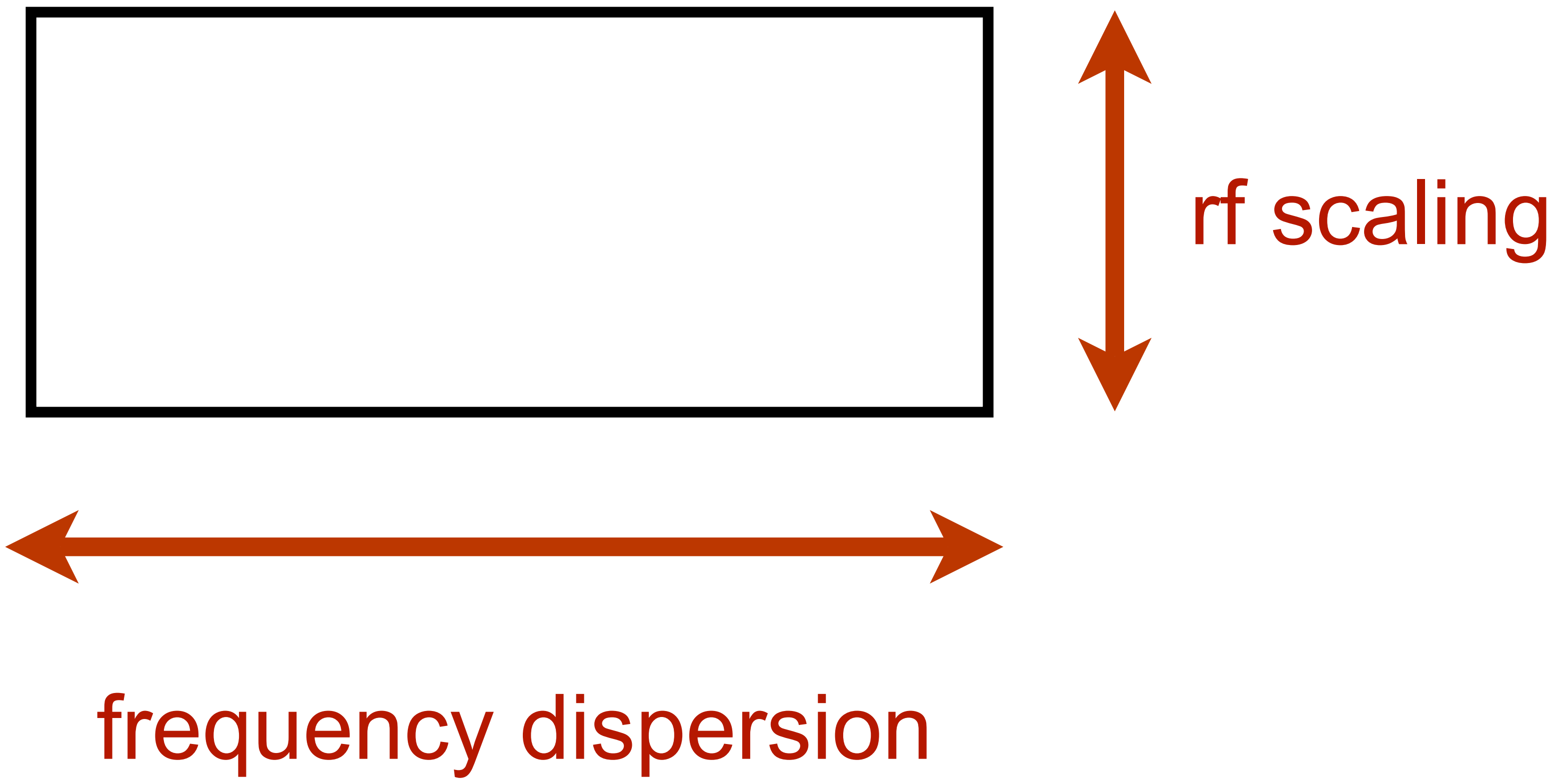
$\rho(0) = A$

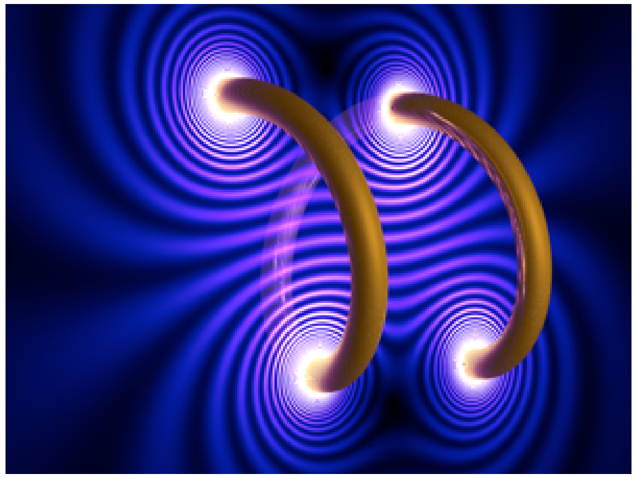
$\lambda(T) = C$

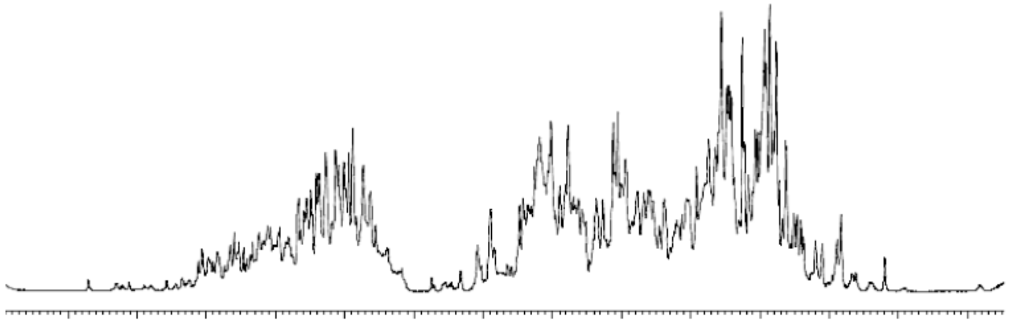
$$\boxed{\mathbf{u}_k(t) \longrightarrow \mathbf{u}_k(t) + \varepsilon \left\langle \lambda(t) \,\middle|\, [-i\, H_k, \rho(t)] \right\rangle}$$

Khaneja, Reiss, Kehlet, Schulte-Herbrüggen, Glaser, J. Magn. Reson. 172, 296-305 (2005)

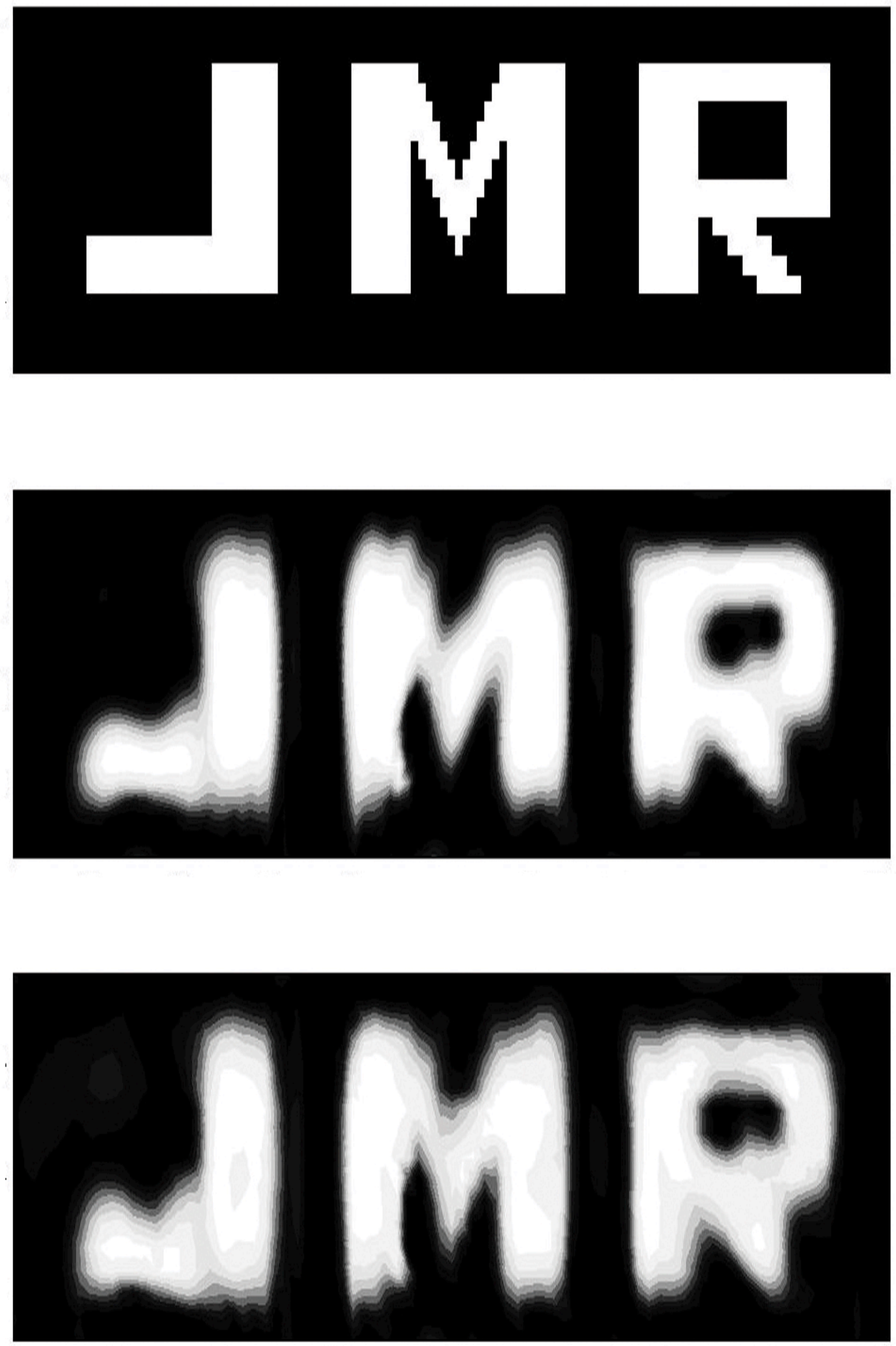
Pattern Pulses



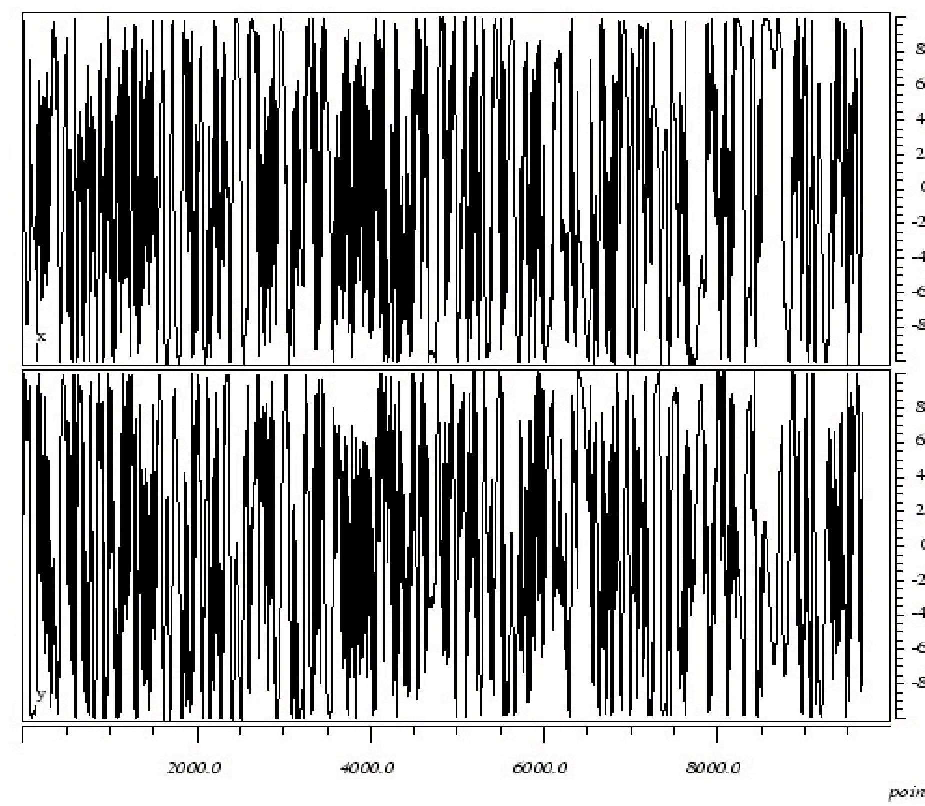




Pattern Pulses



rf amplitude (x)



rf amplitude (y)

Kobzar et al., J. Magn. Reson. (2005)