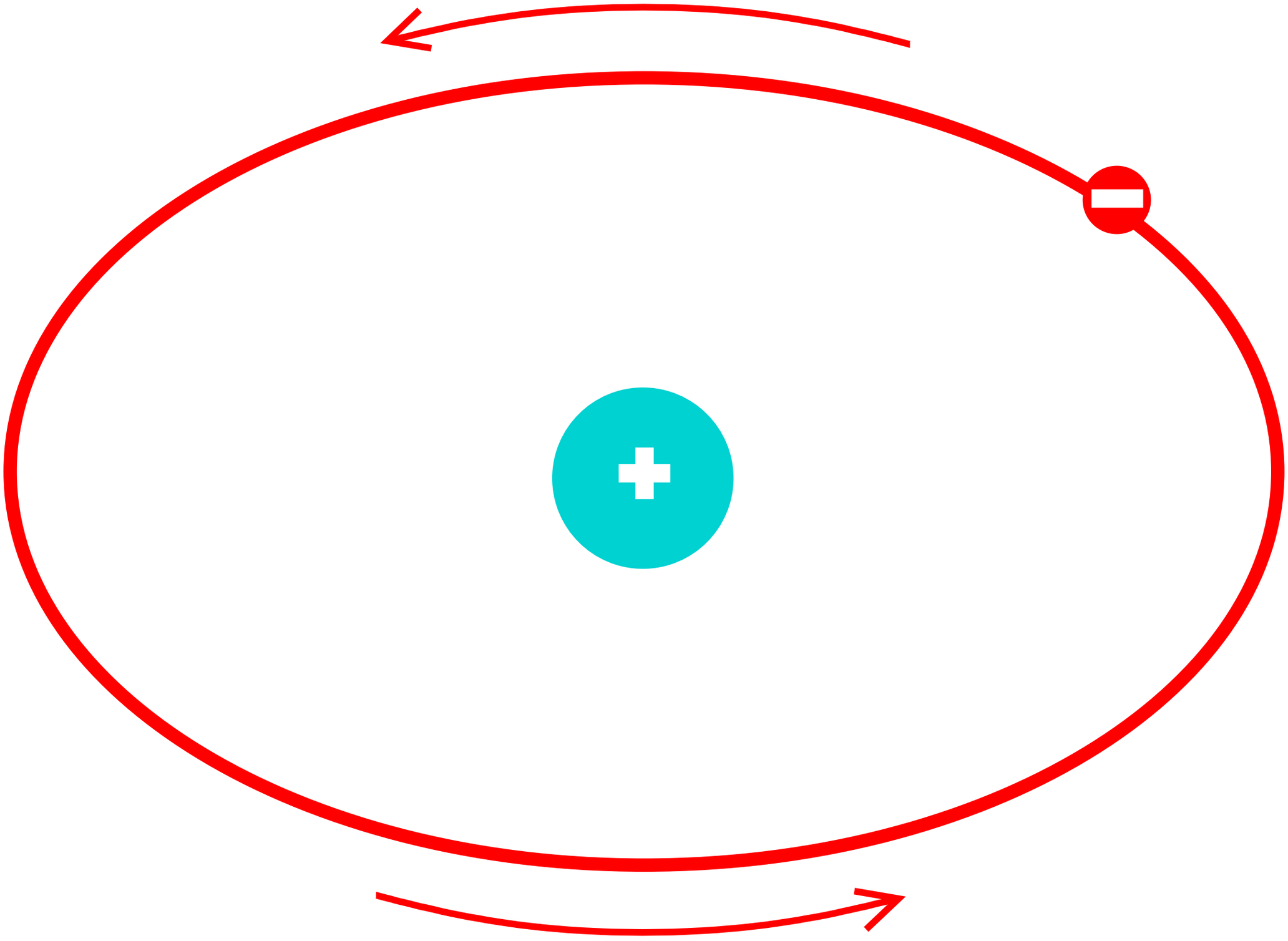
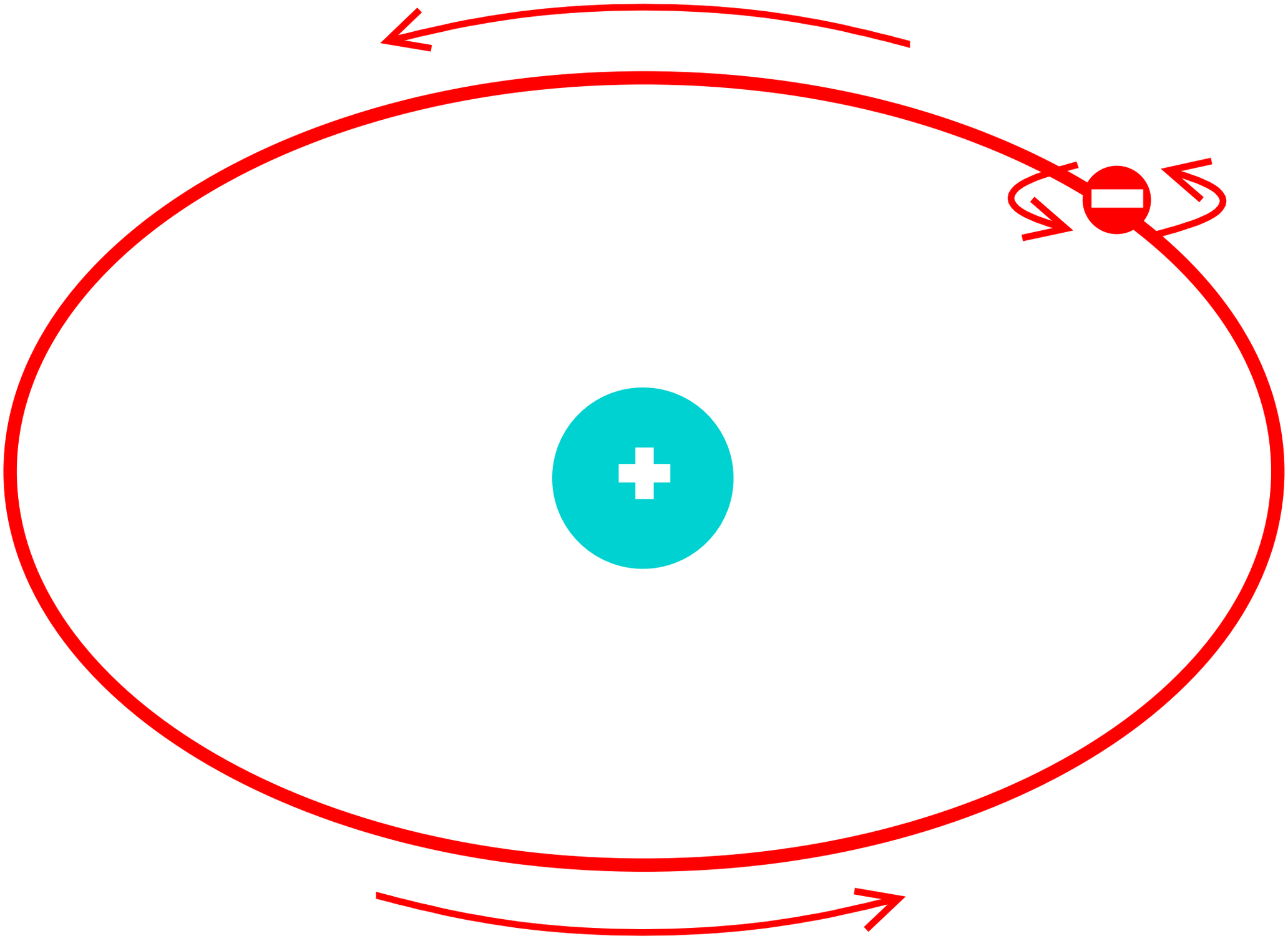
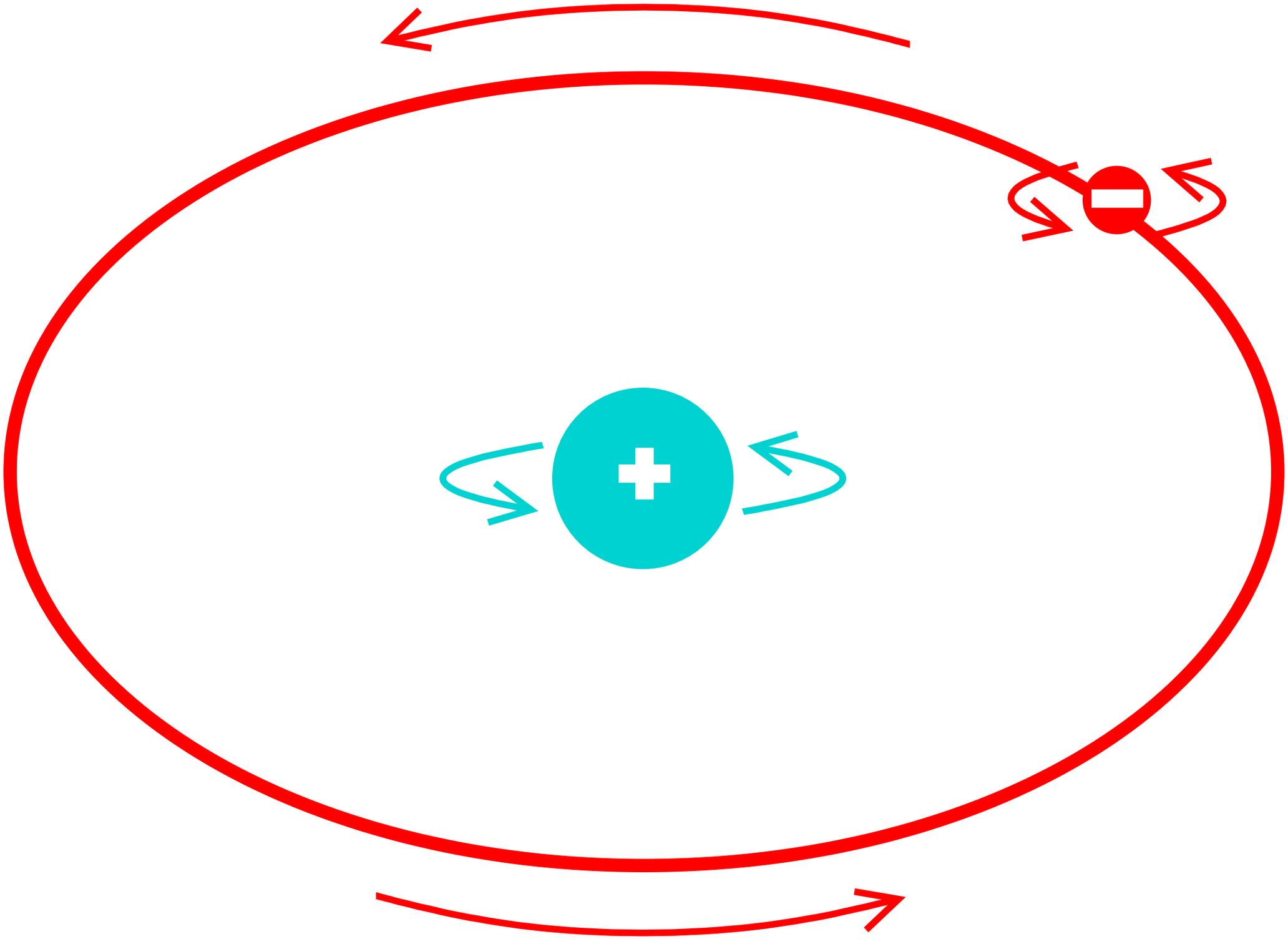
NUCLEAR MAGNETIC RESONANCE







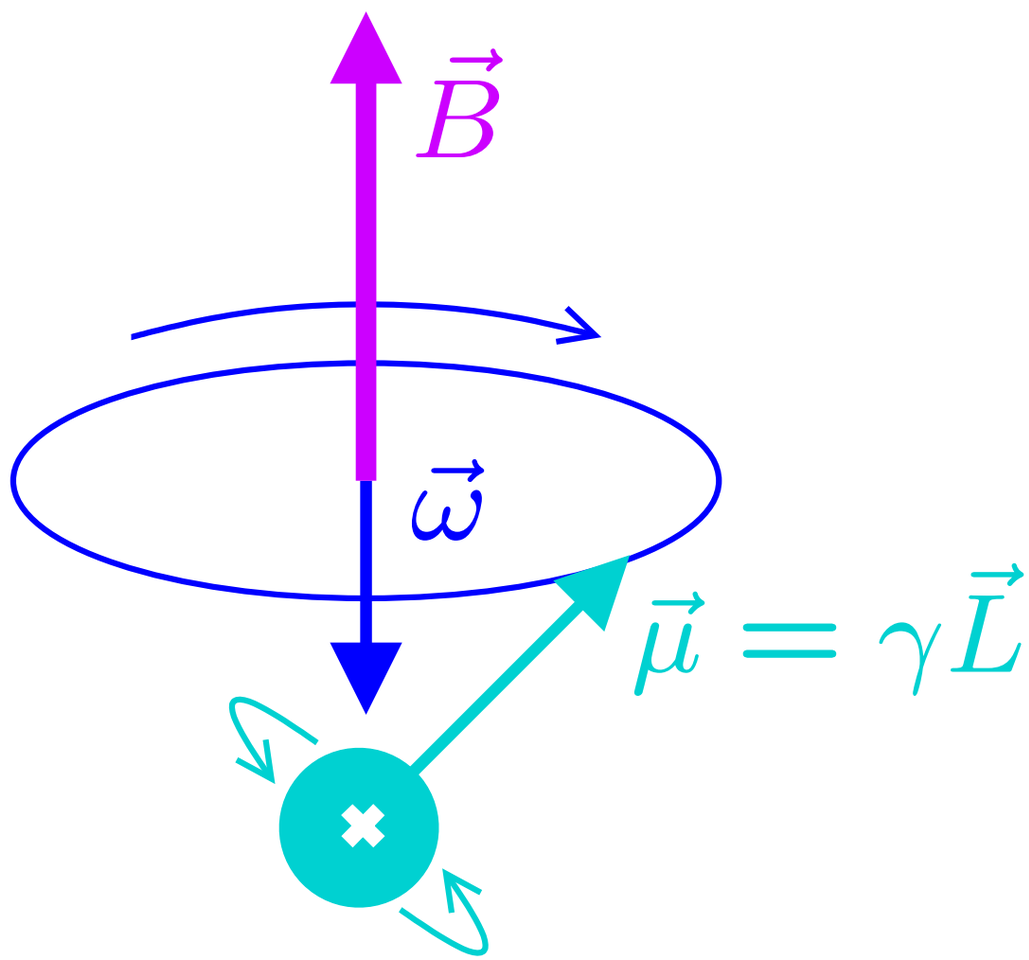
	S	$\frac{10^{-9}\gamma}{\mathrm{rad\,s^{-1}T^{-1}}}$	% v přírodě
e^-	1/2	−182,000	100
^{1}H	1/2	0,277	99,98
^{13}C	1/2	0,067	1,1
^{14}N	1	0,019	99,6
^{15}N	1/2	−0,027	0,4
^{17}O	5/2	−0,036	0,04
^{19}F	1/2	0,252	100
^{31}P	1/2	0,108	100
^{129}Xe	1/2	−0,075	24,4

Počet stacionárních stavů $= 2S + 1$

kvadrupolární jádra (příliš rychle se vrací do rovnováhy)

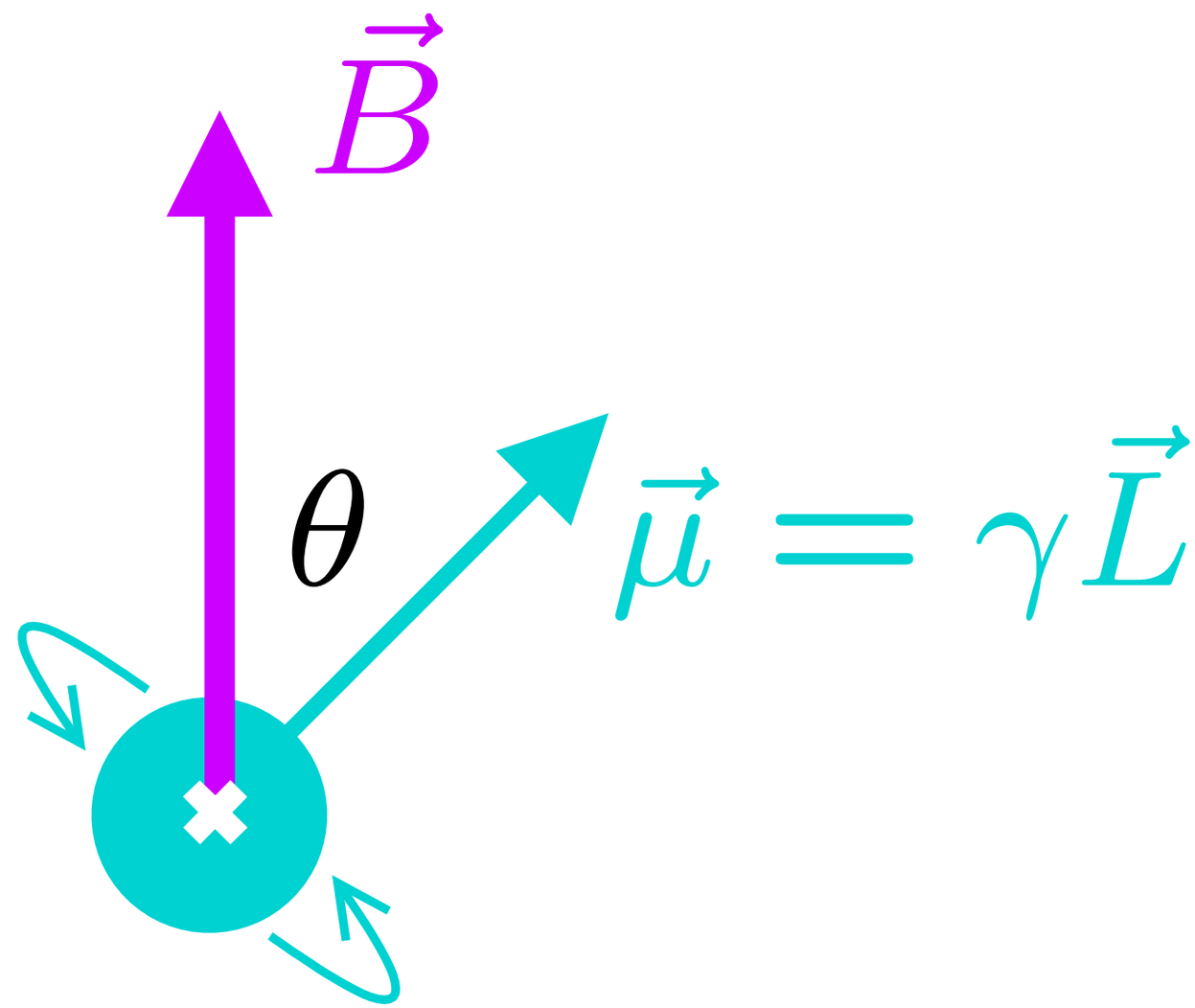
vzácné izotopy (vyžadují obohacení proteinů během exprese)

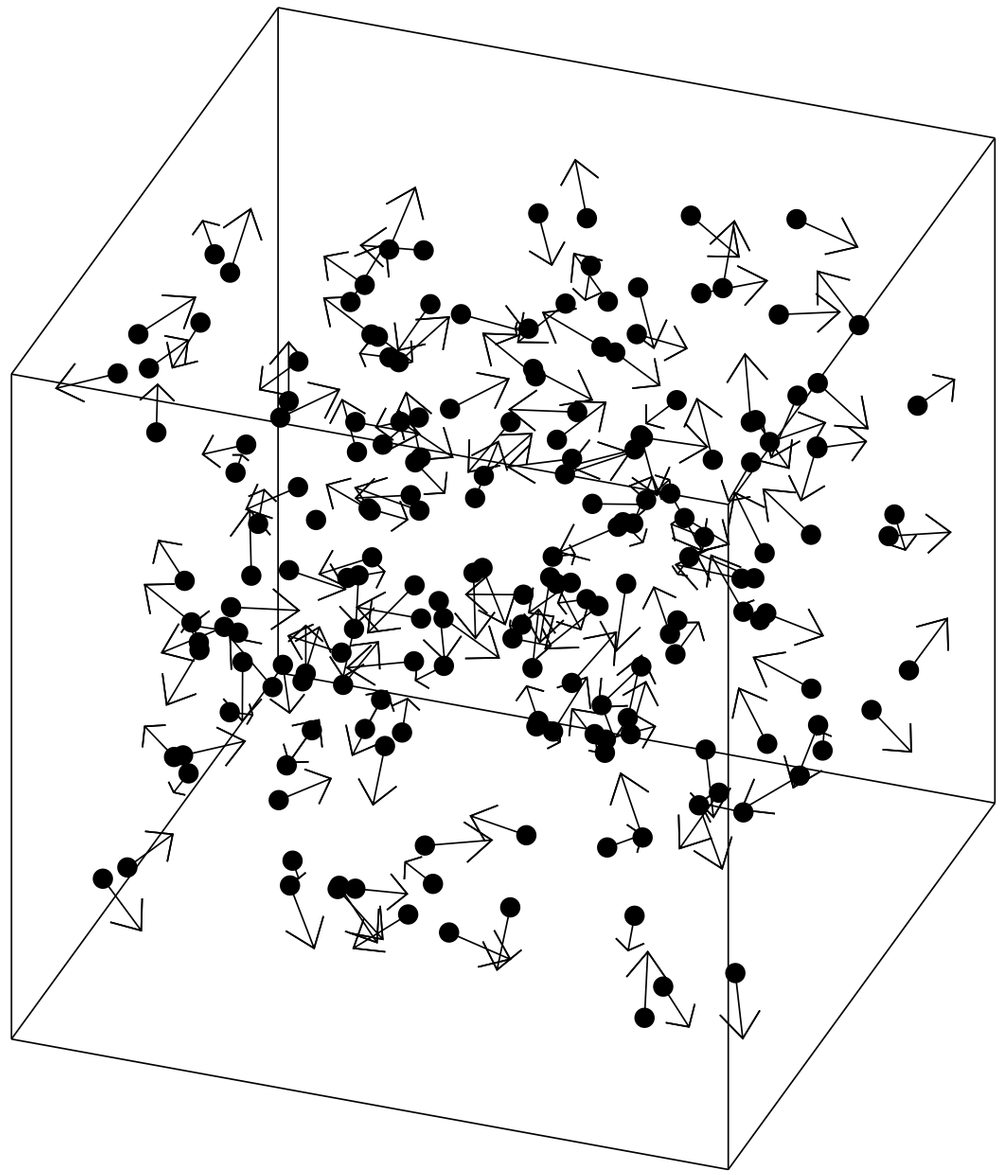
Úhlová rychlost precese $\vec{\omega} = -\gamma \vec{B}$



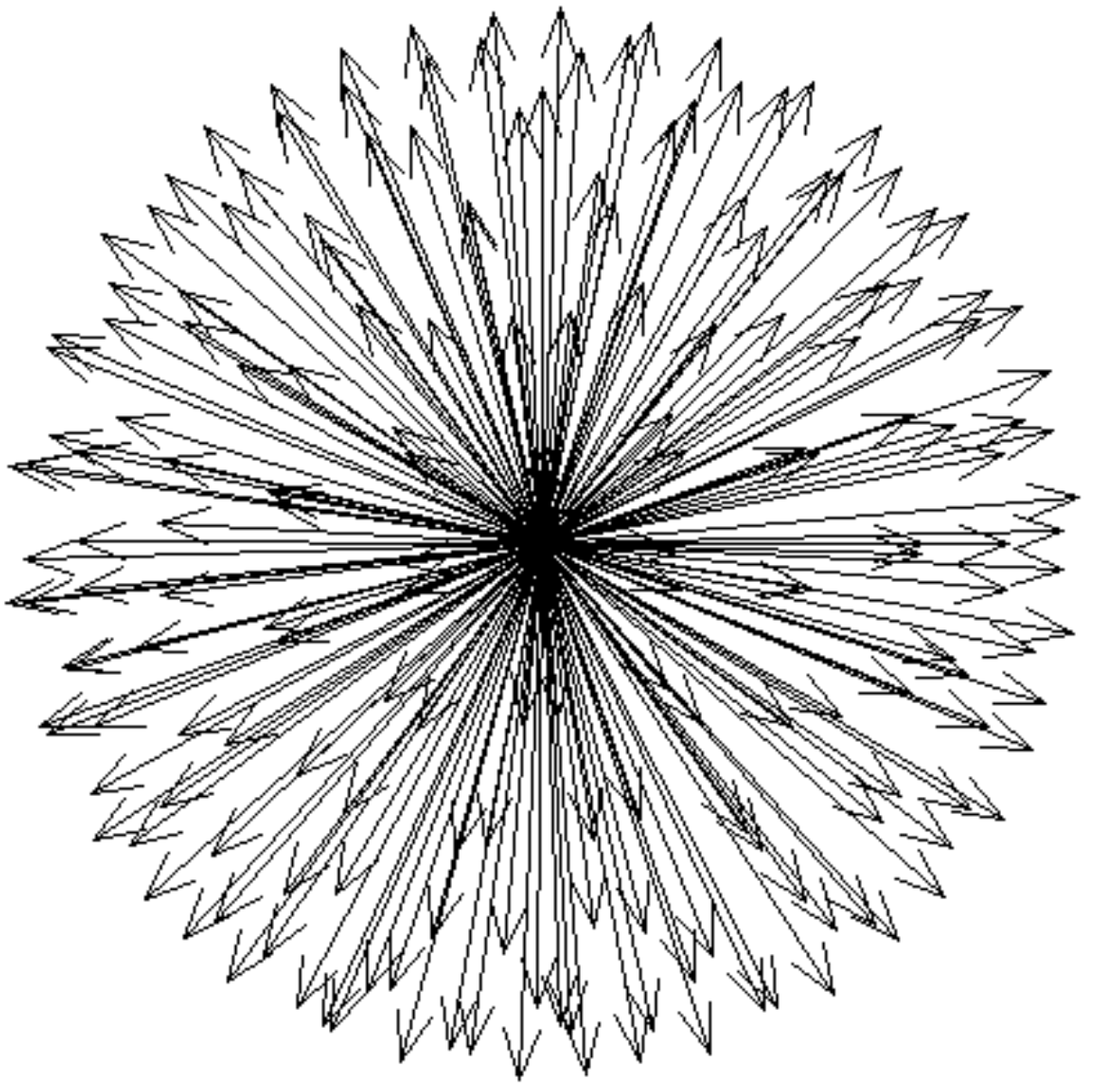
Energie magnetického momentu v poli

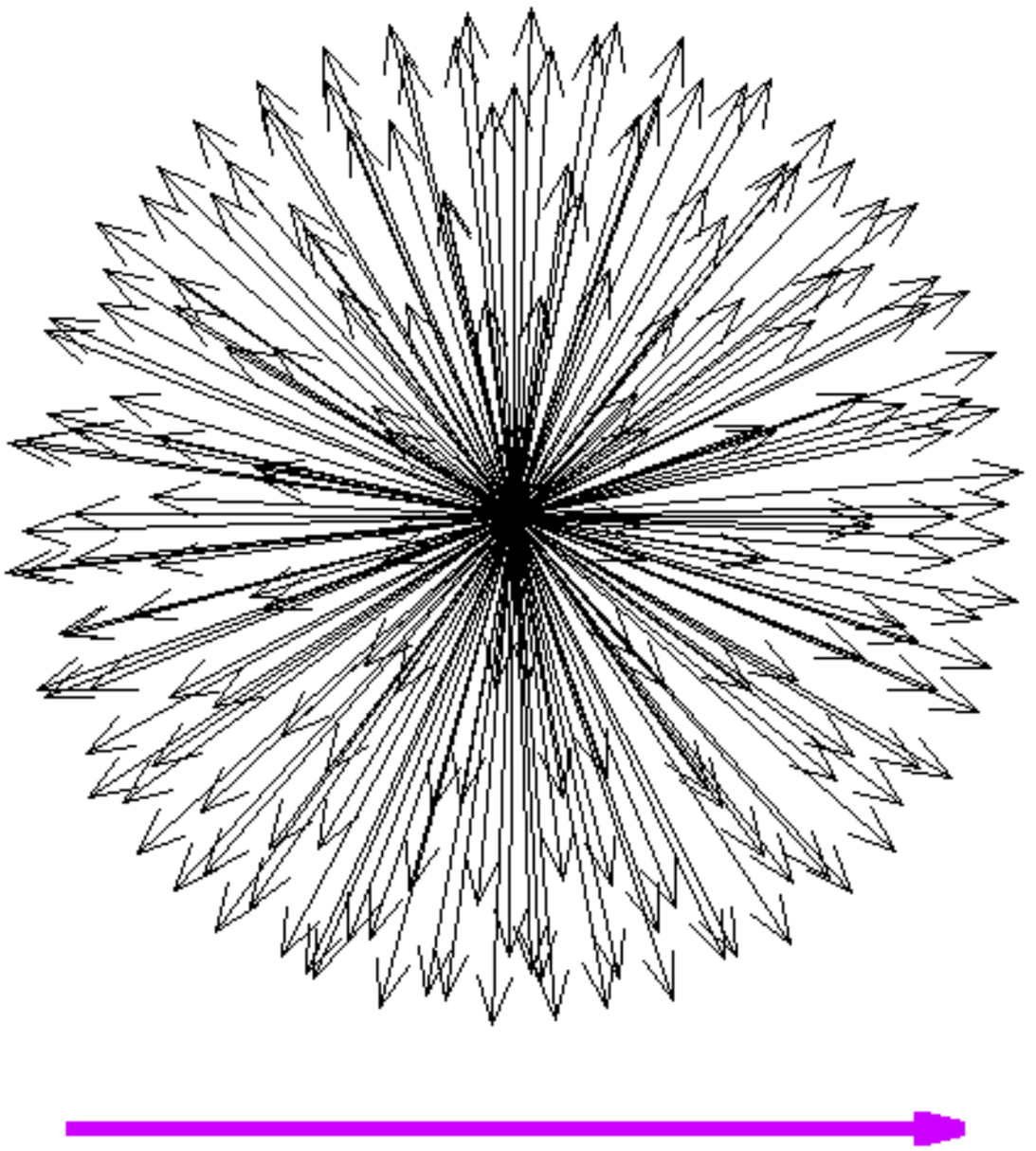
$$U = -\vec{\mu} \cdot \vec{B} = -|\mu||B| \cos\theta$$



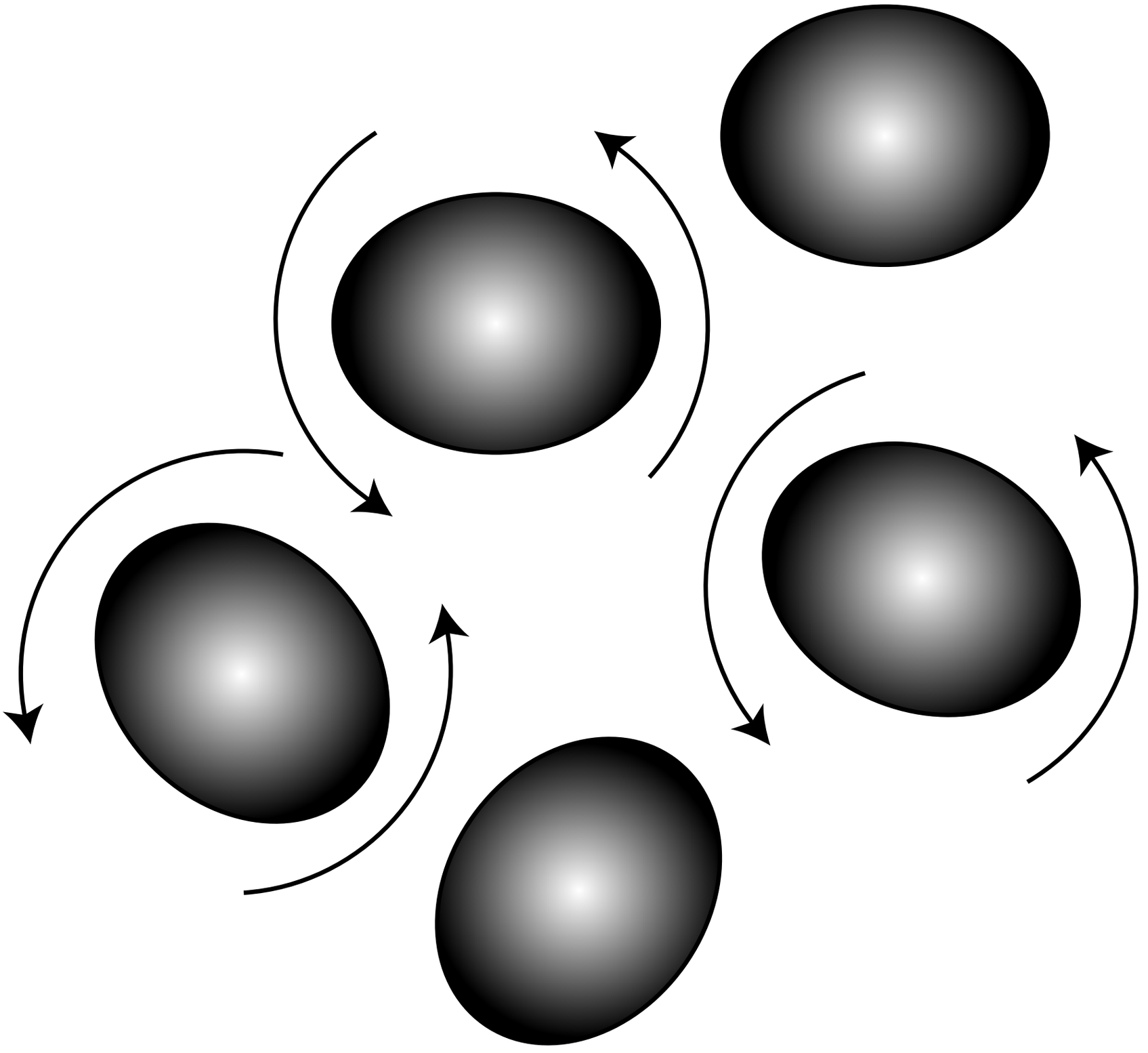


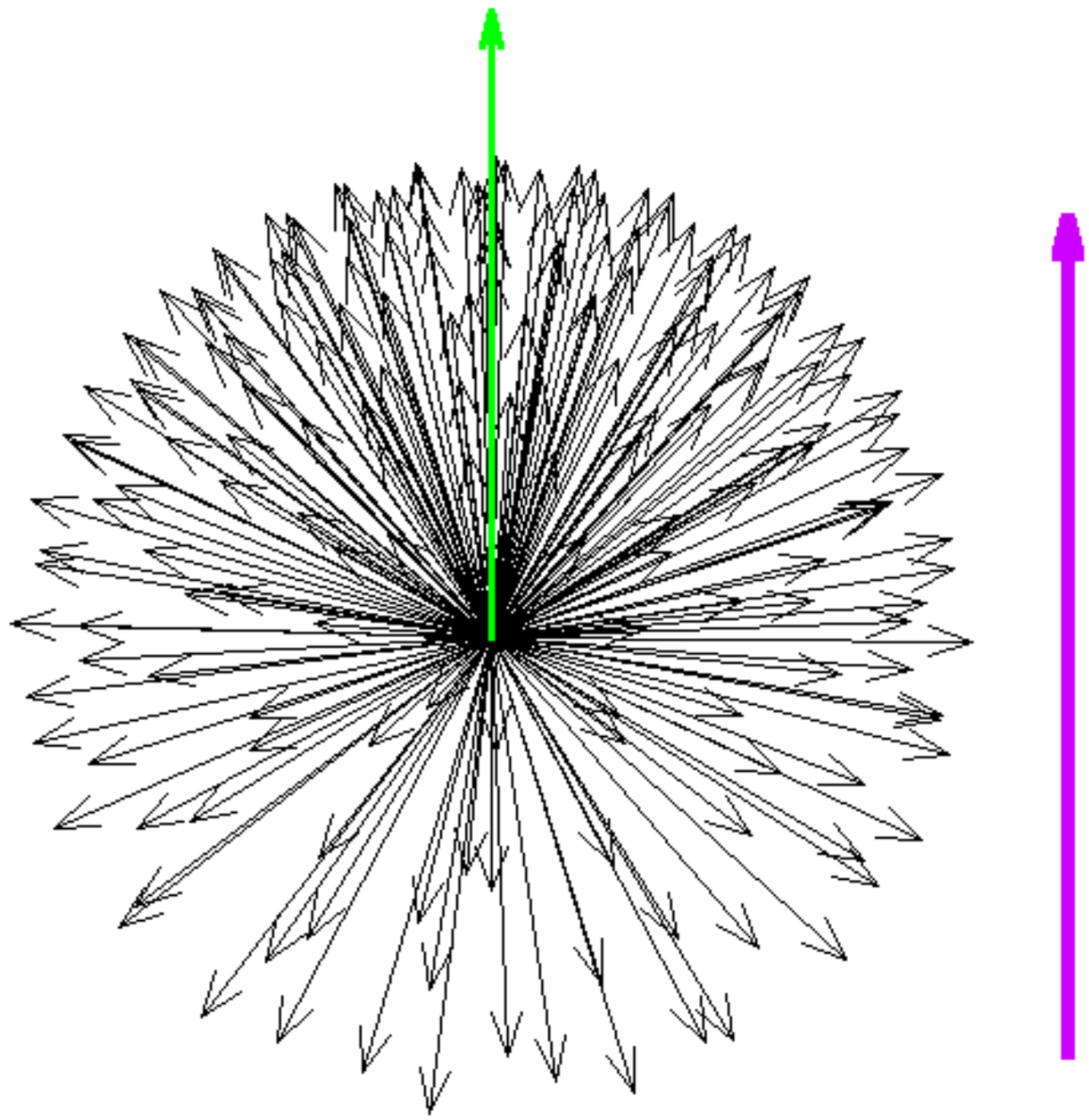
$$\vec{M} = (\vec{\mu}_1 + \vec{\mu}_2 + \vec{\mu}_3 + \vec{\mu}_4 + \vec{\mu}_5 + \vec{\mu}_6 + \cdots)/V$$ Magnetizace



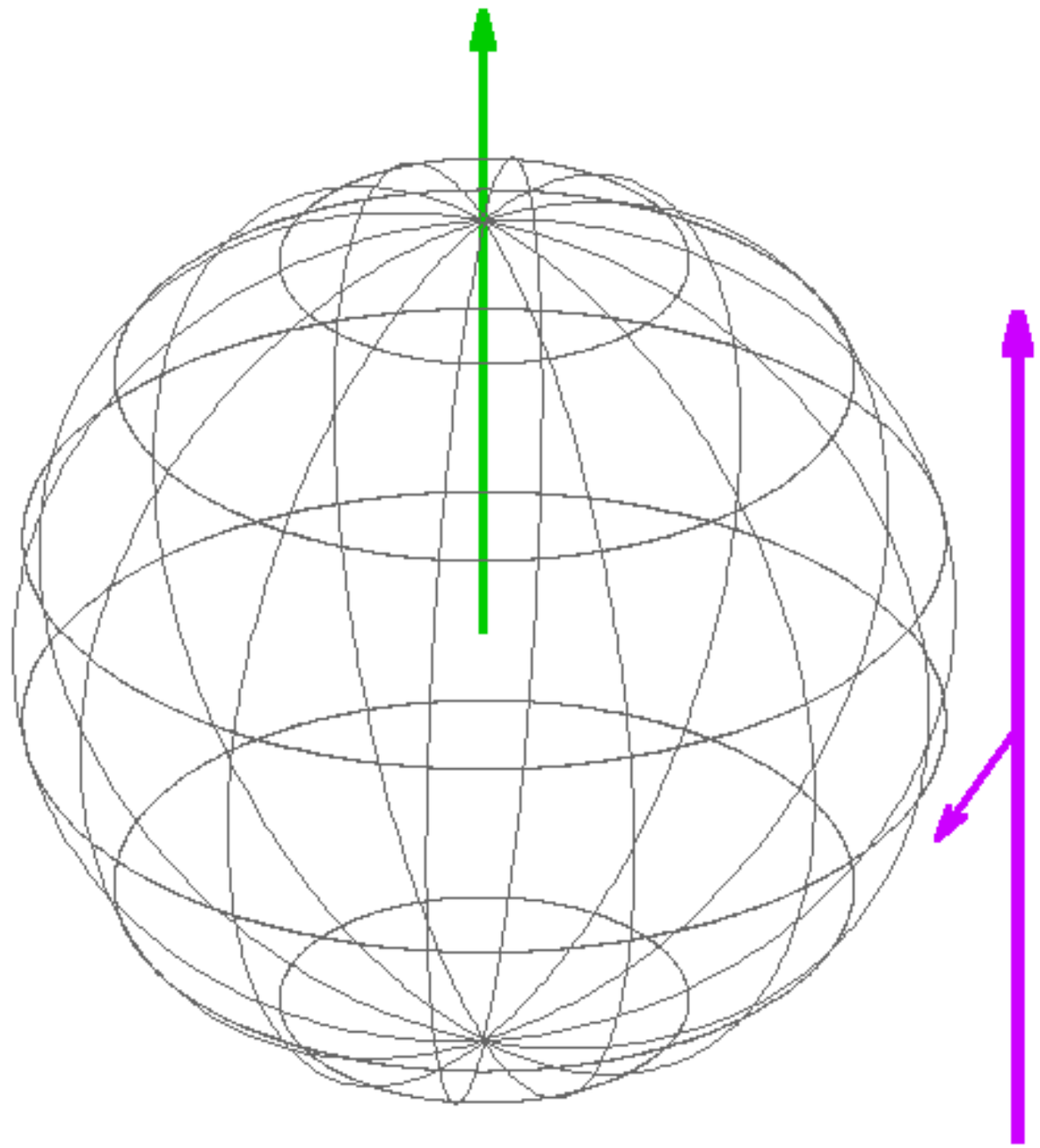


Magnetické momenty v magnetickém poli

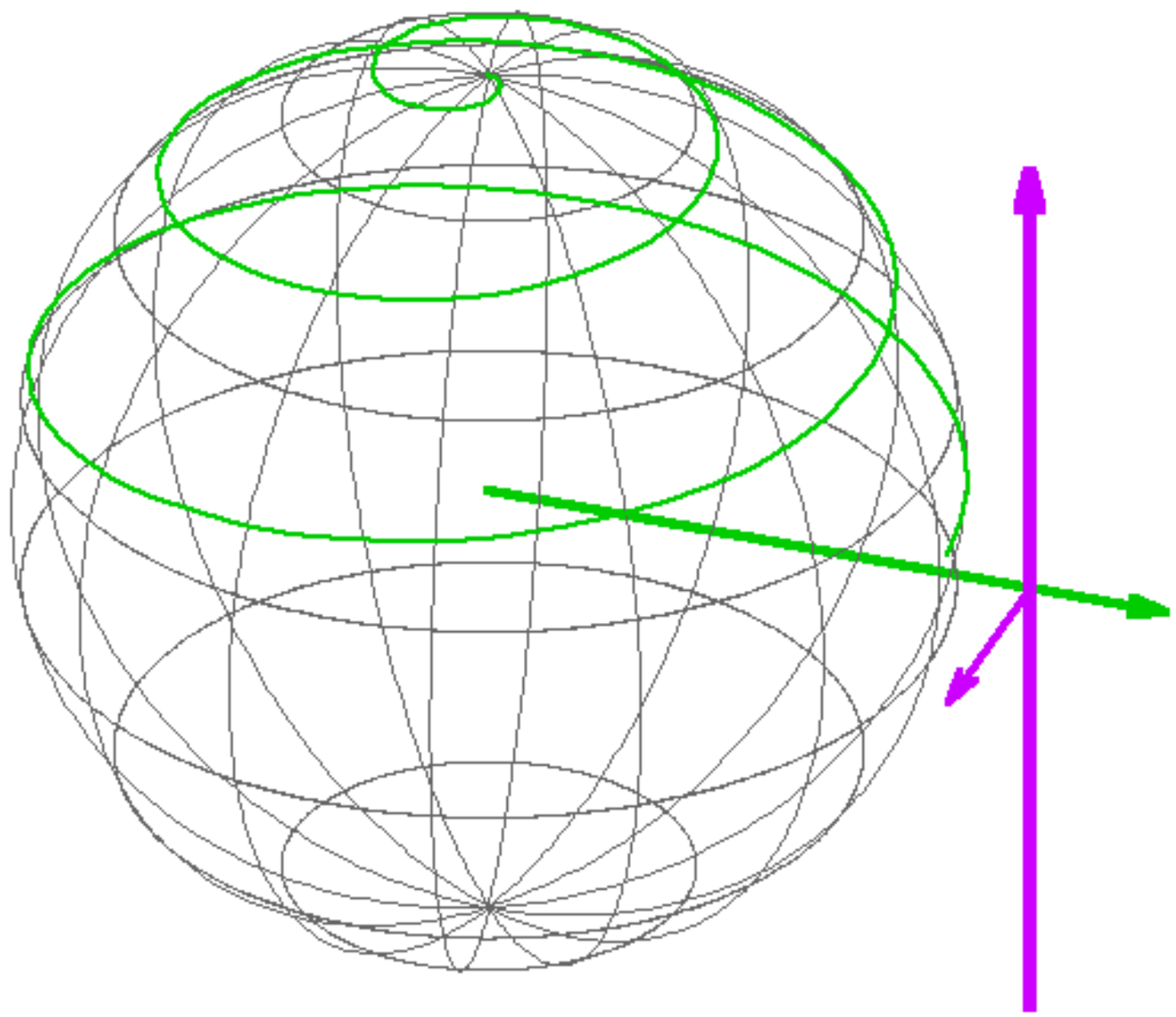


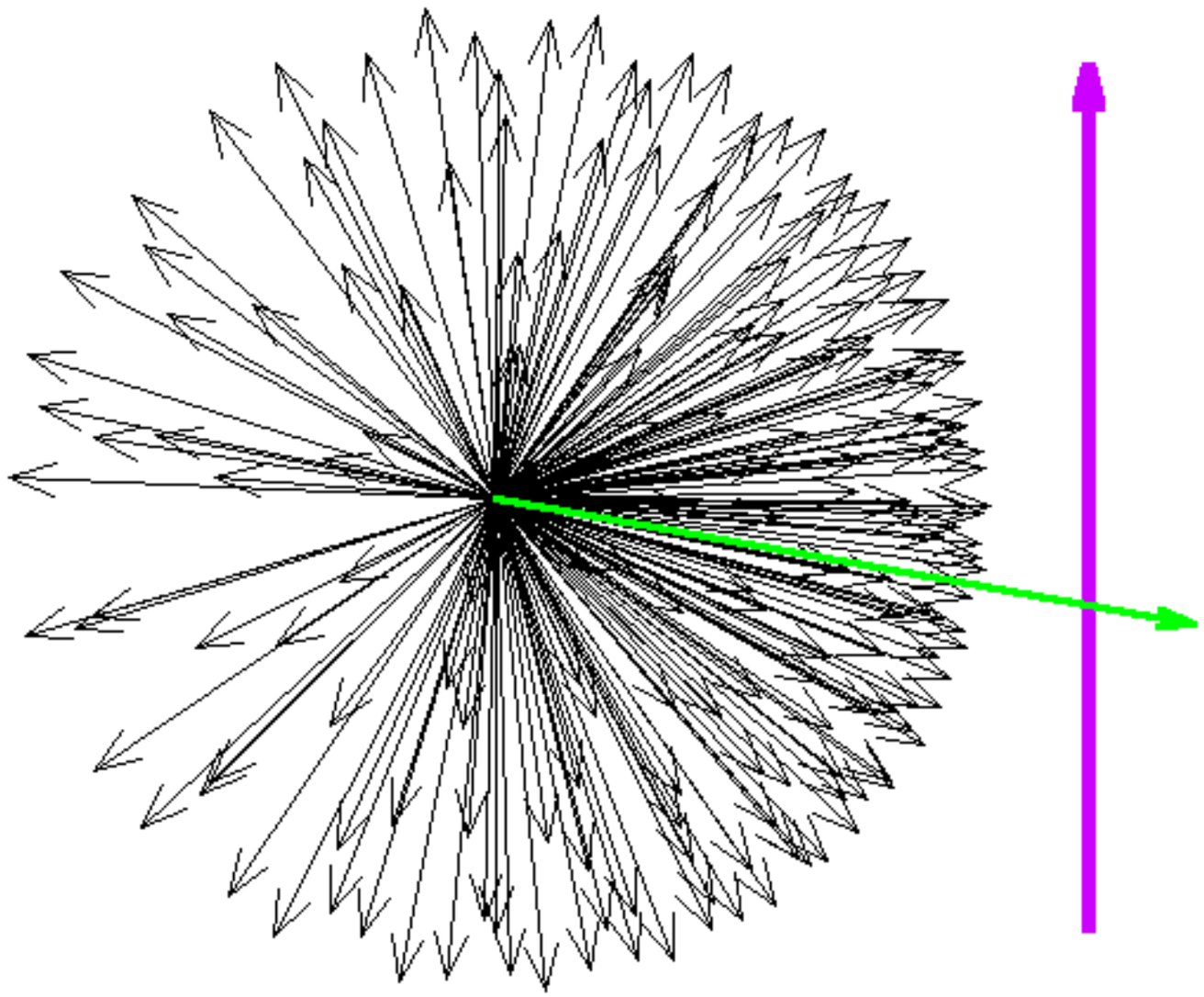


Vertikálně polarizované magnetické momenty ve vertikálním magnetickém poli

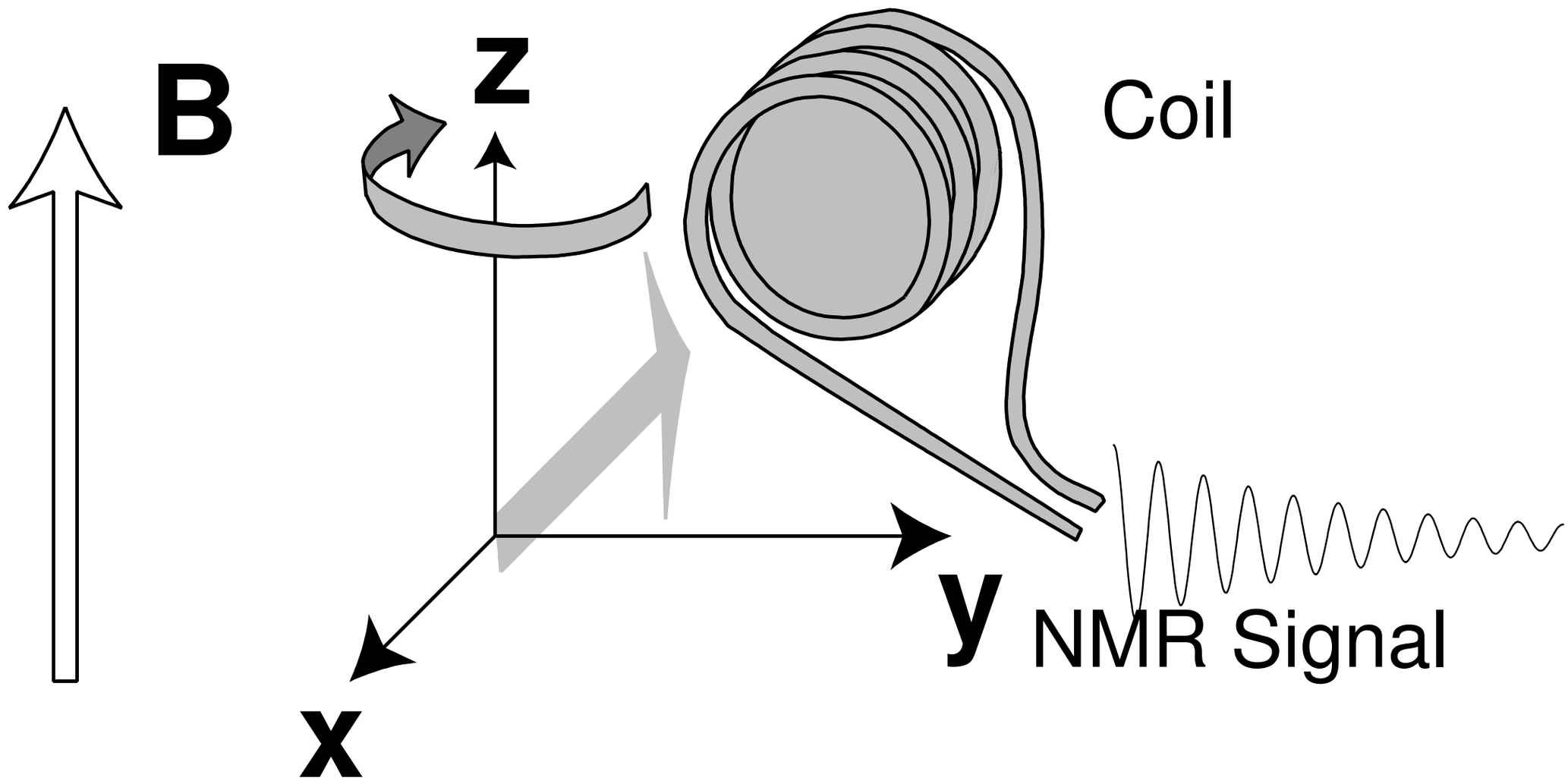


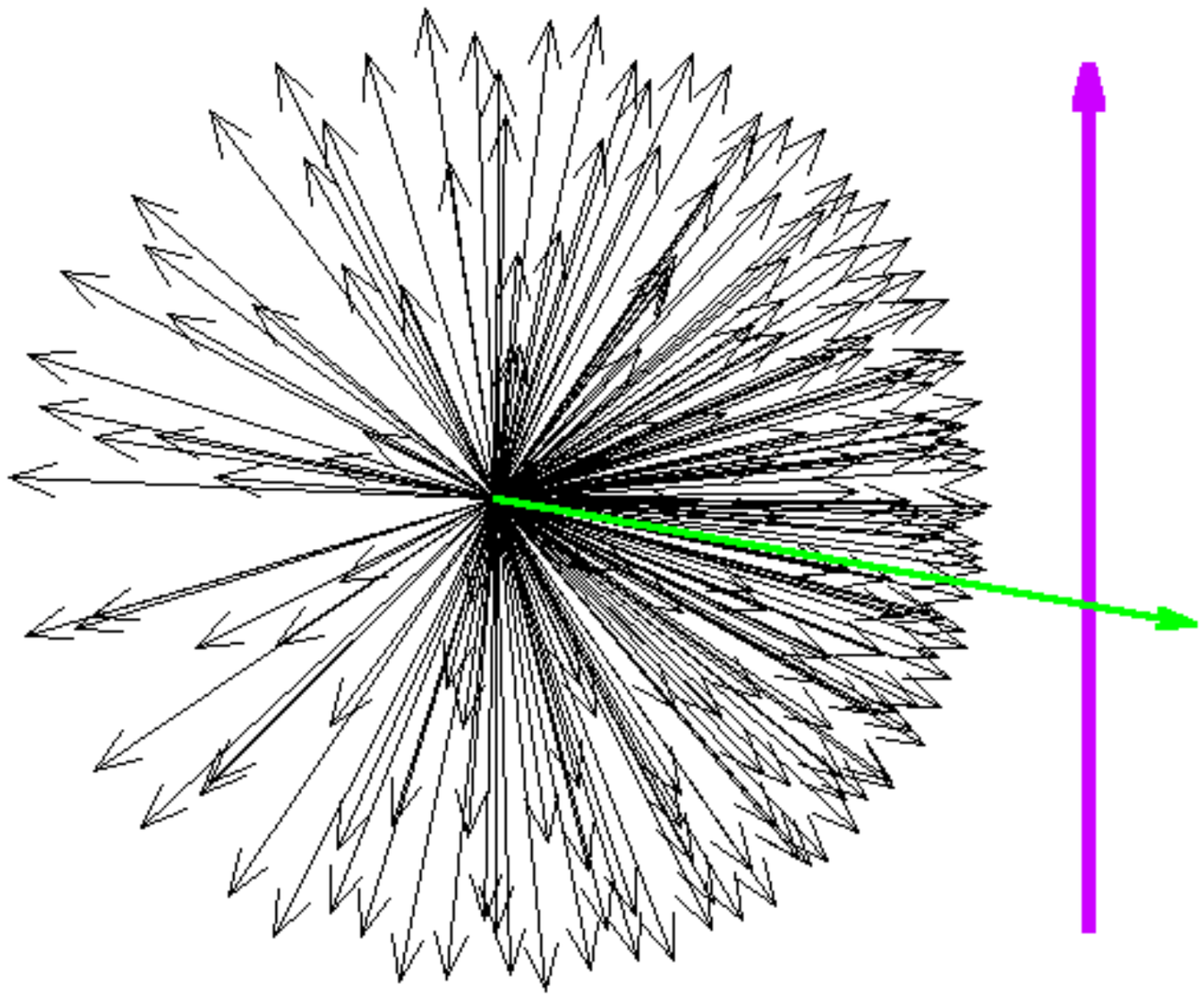
Sklopení vektoru magnetizace

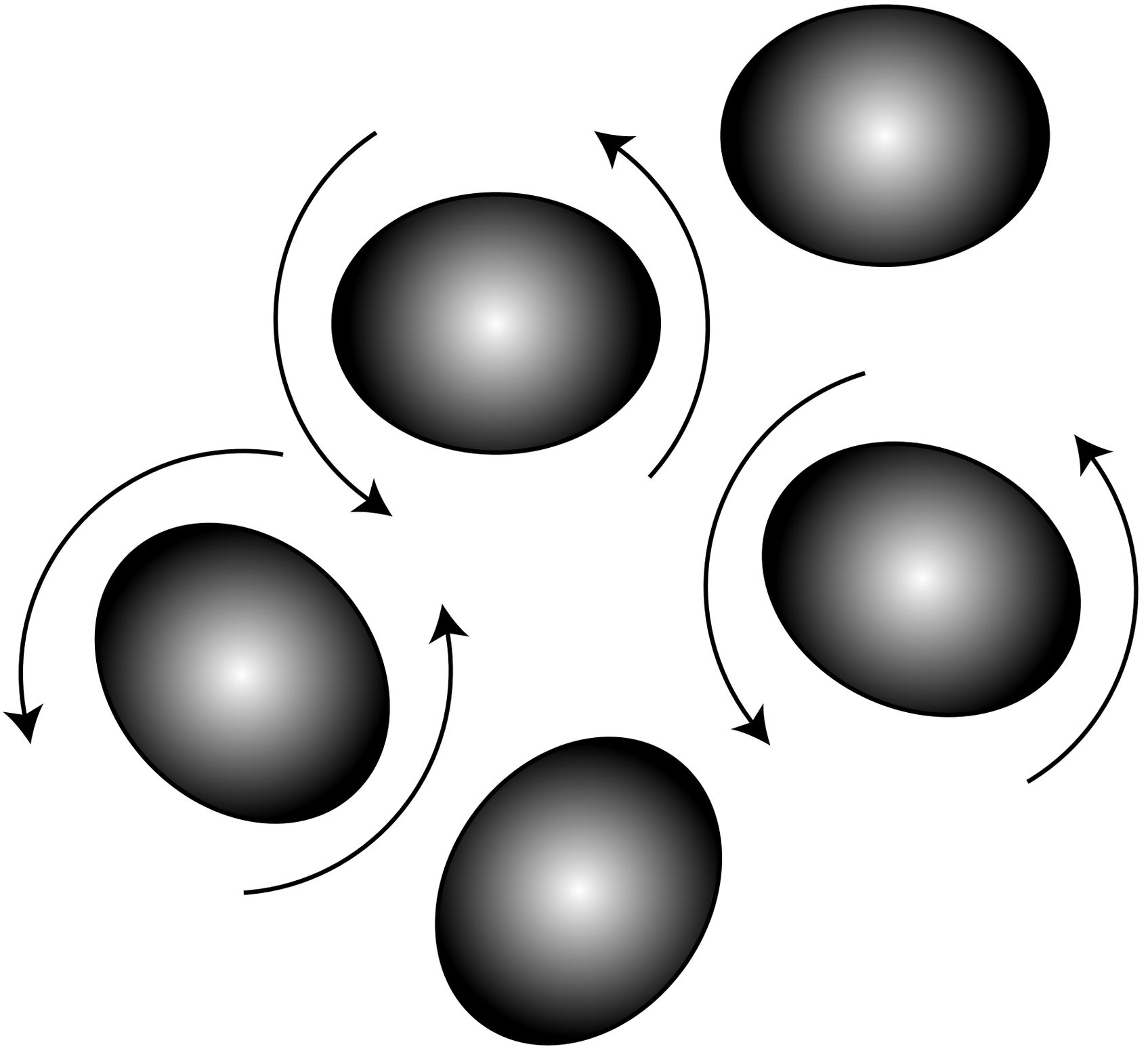


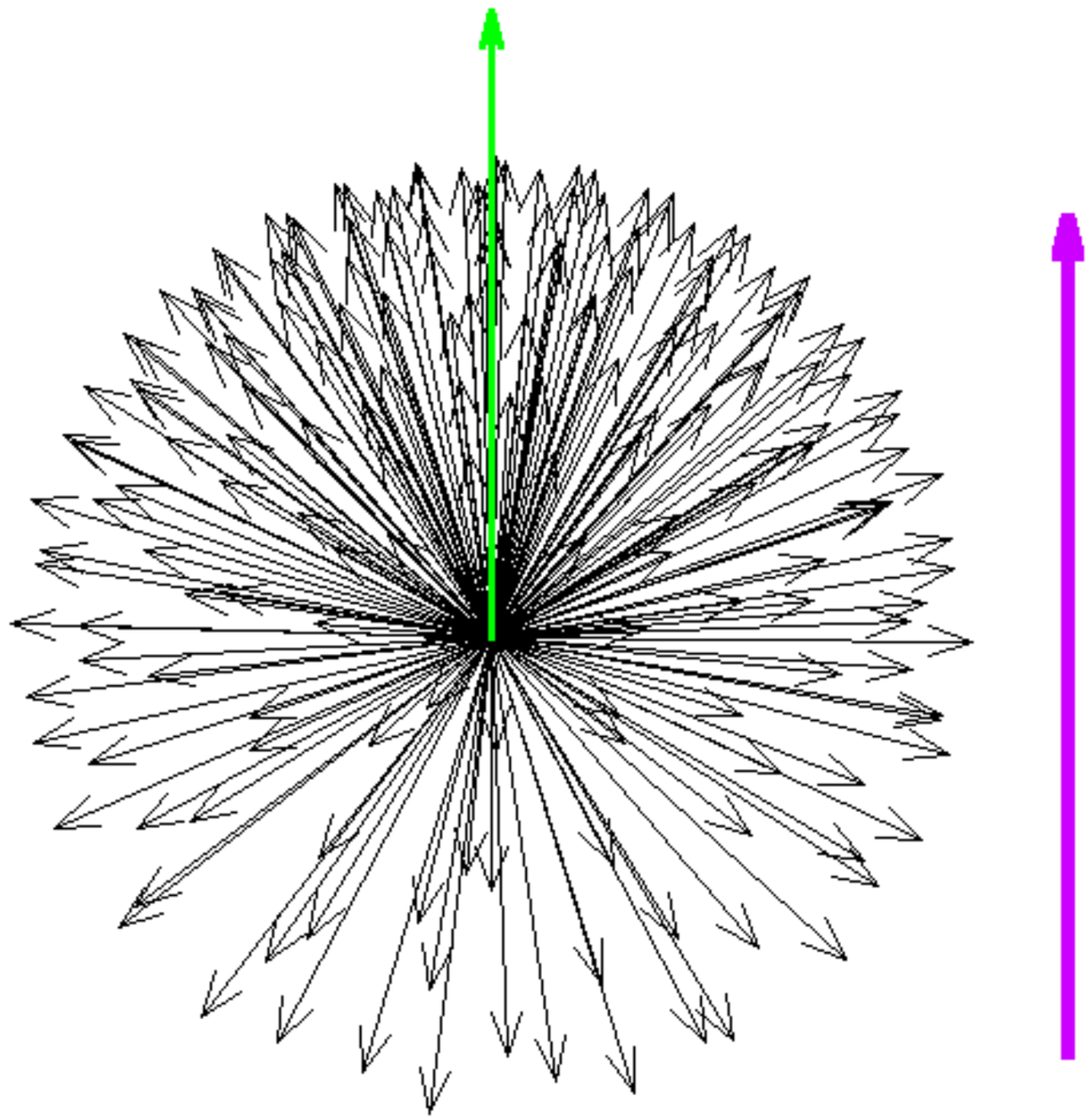


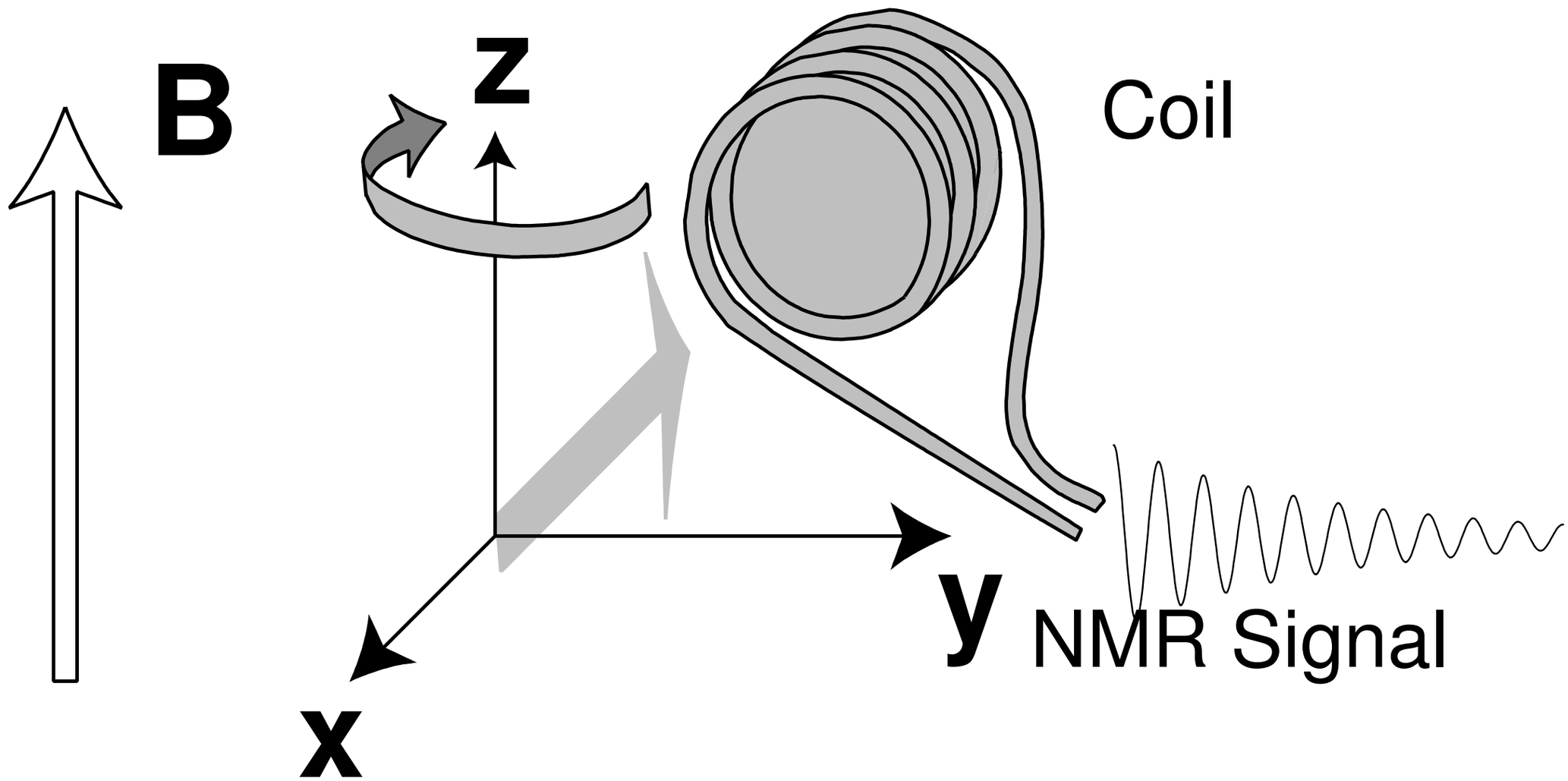
Horizontálně polarizované koherentní magnetické momenty ve vertikálním magnetickém poli

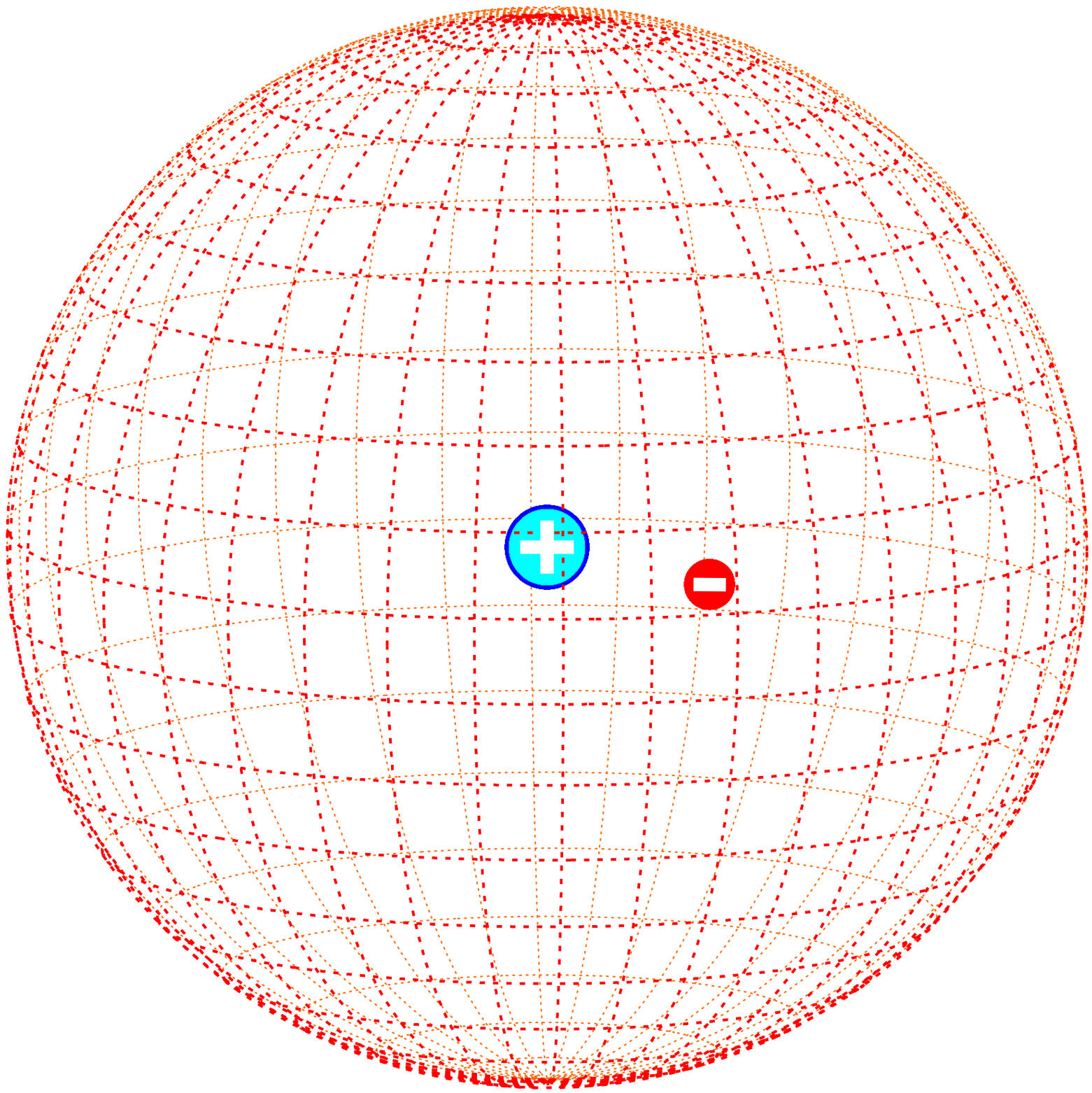

B
z
Coil
y
NMR Signal
x

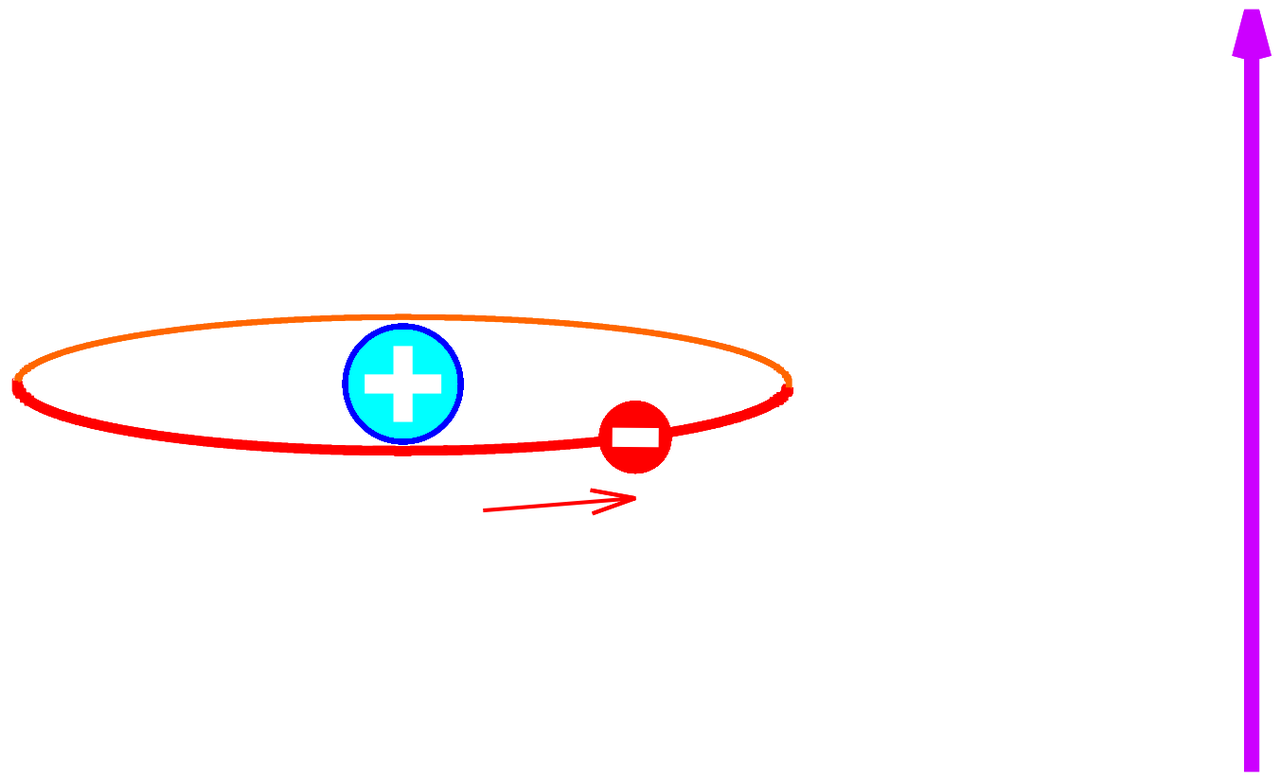


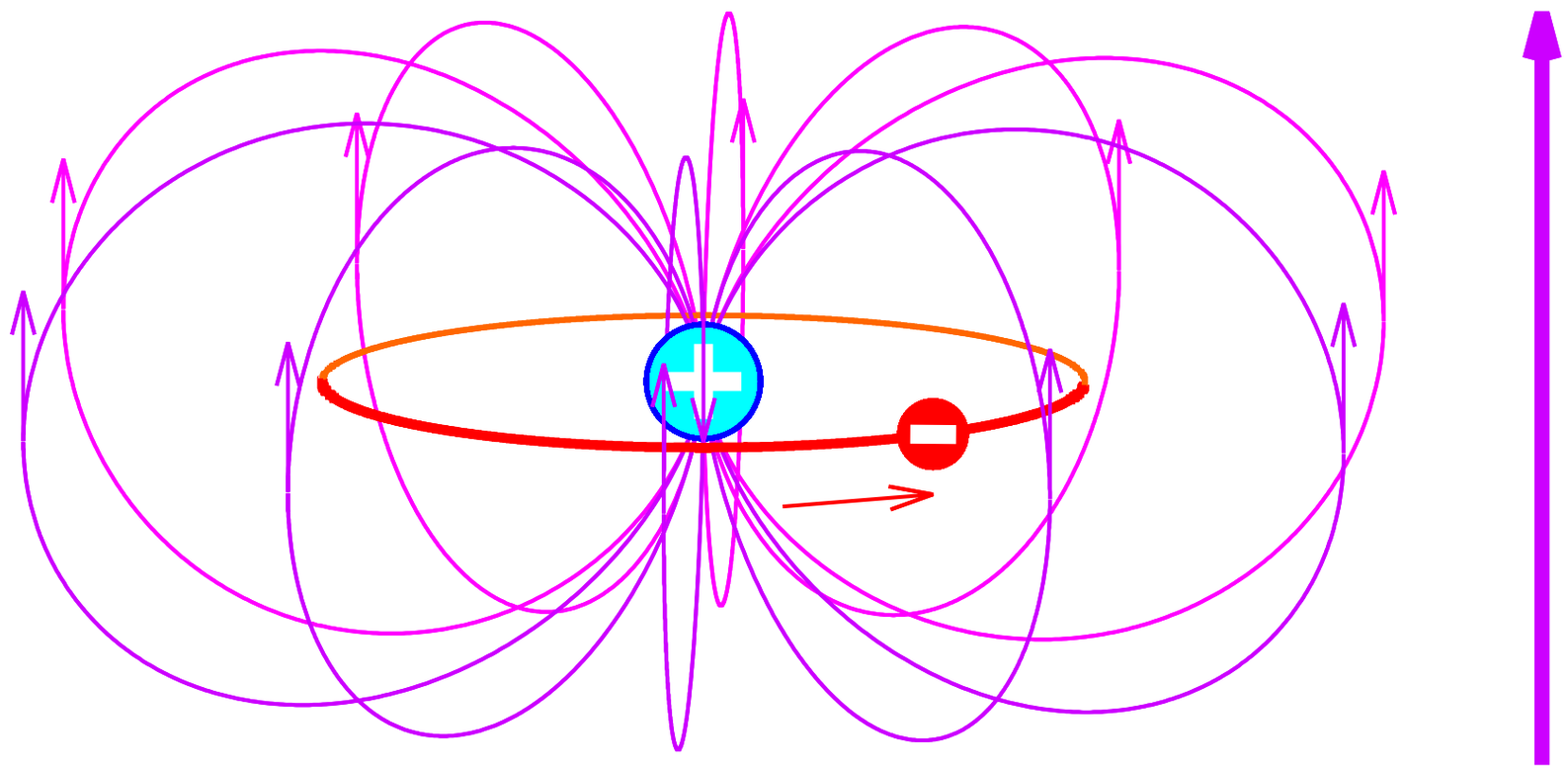


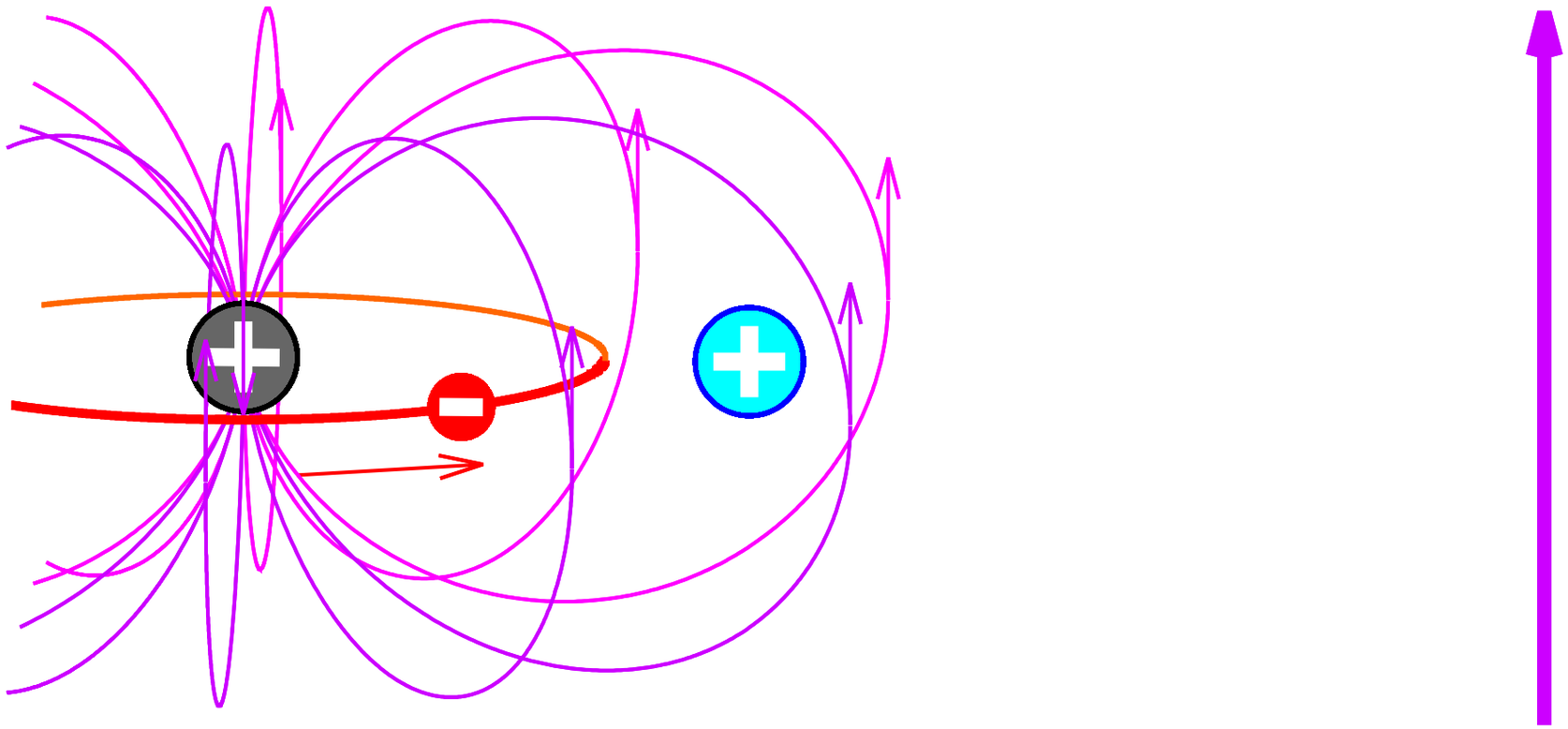


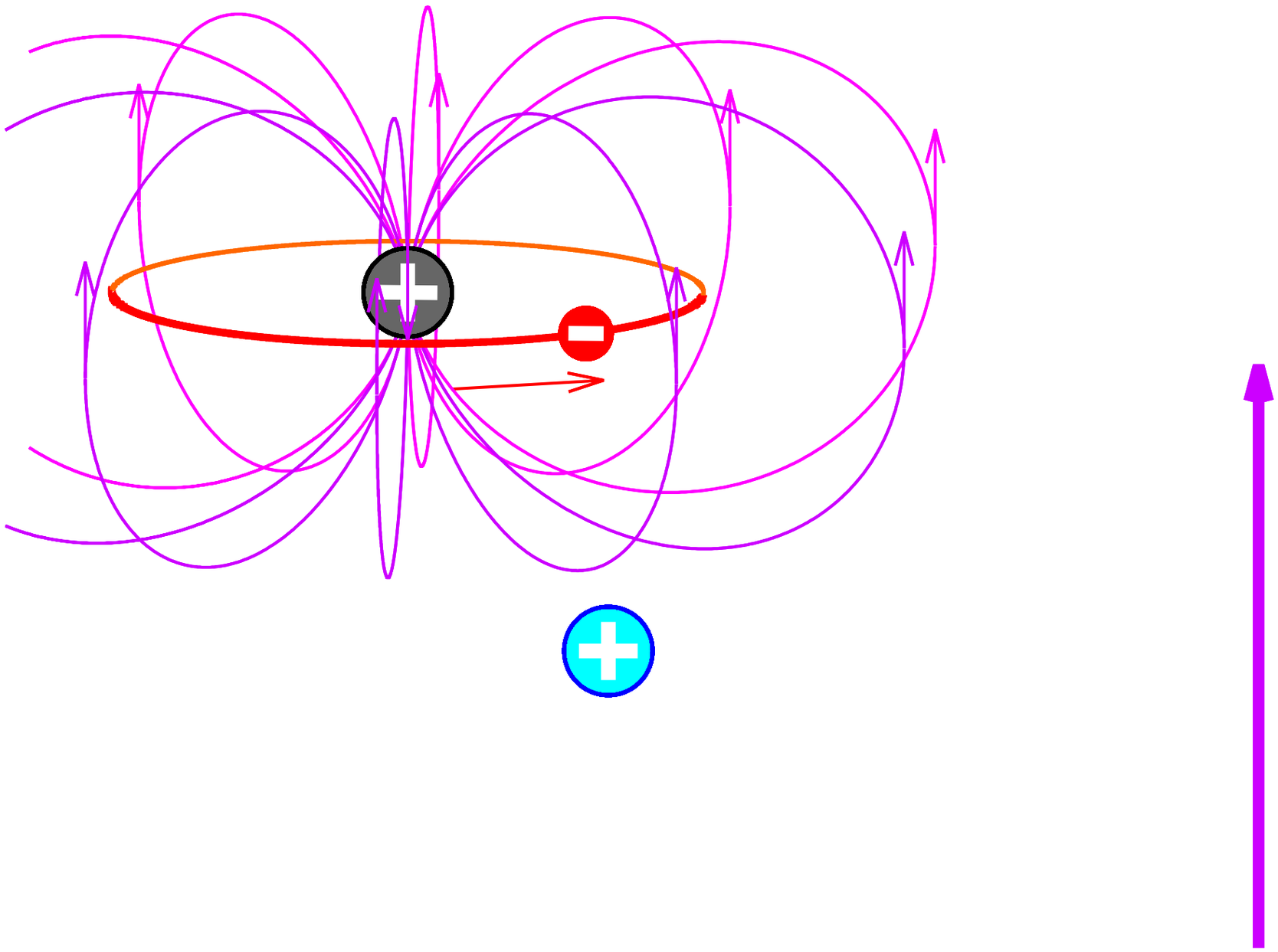

B
z
Coil
y
NMR Signal
x

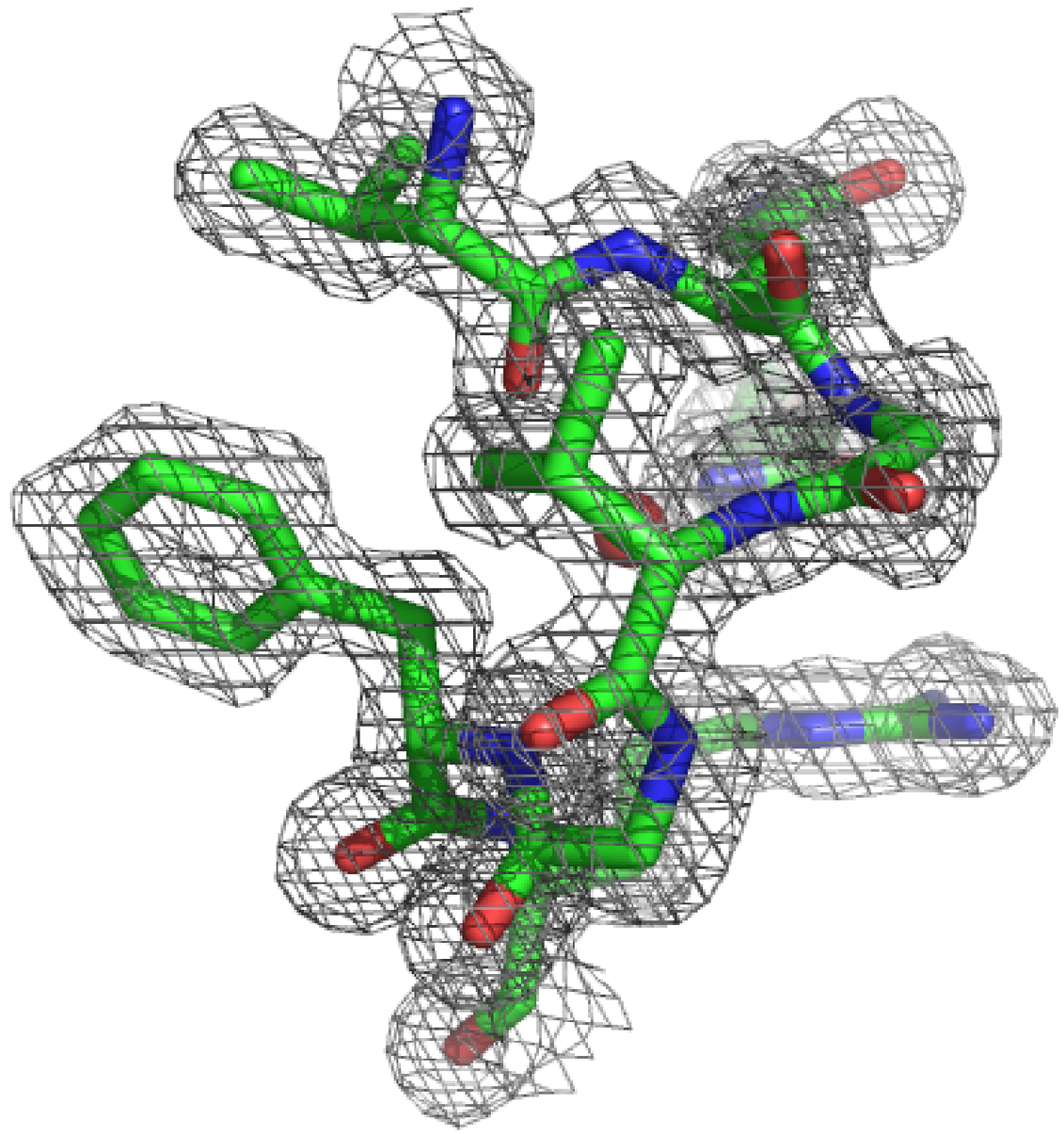


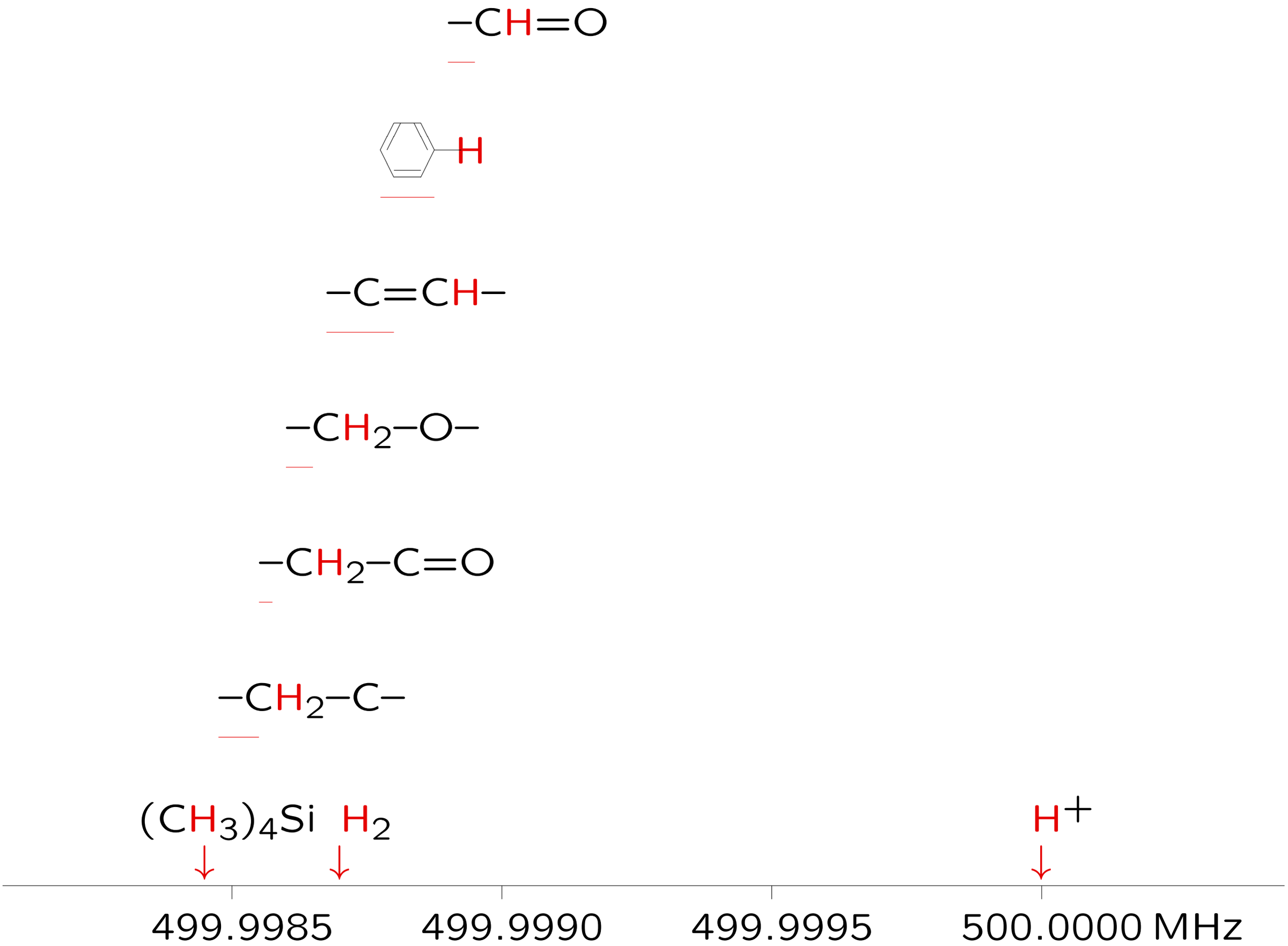


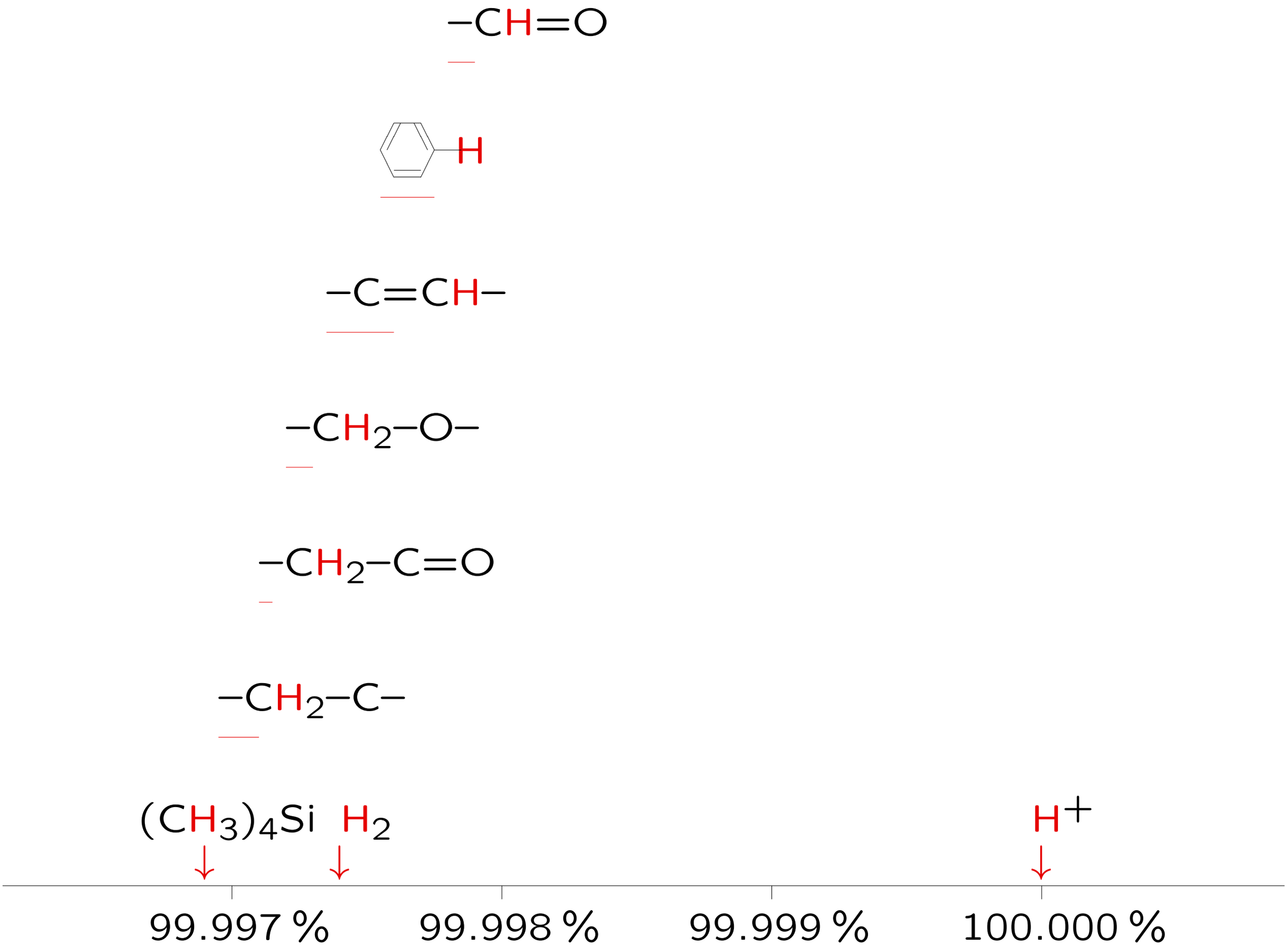


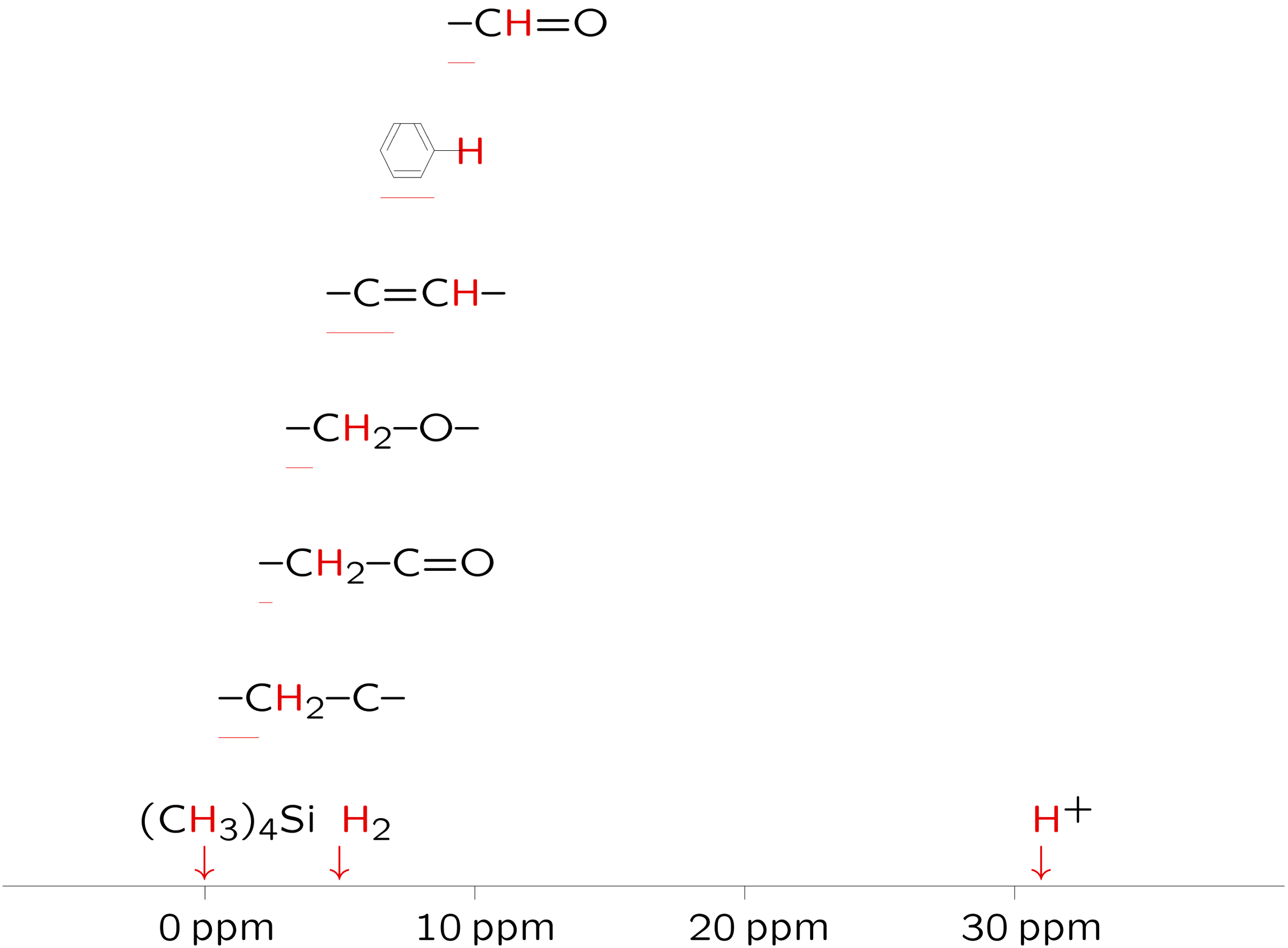


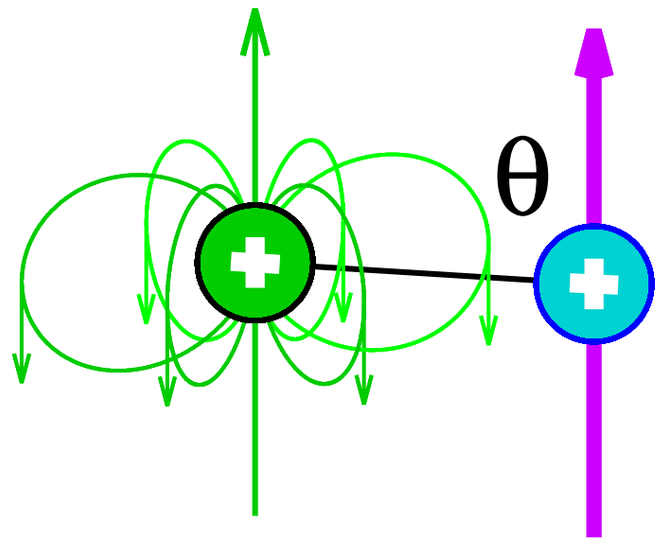


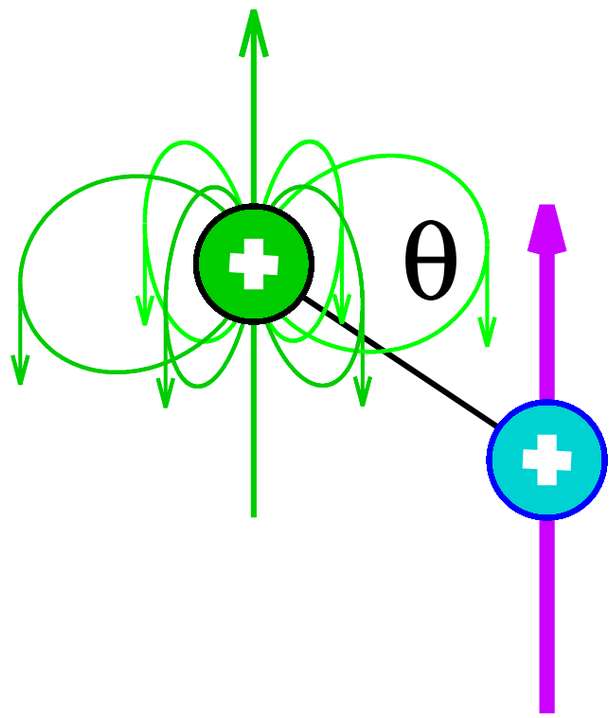


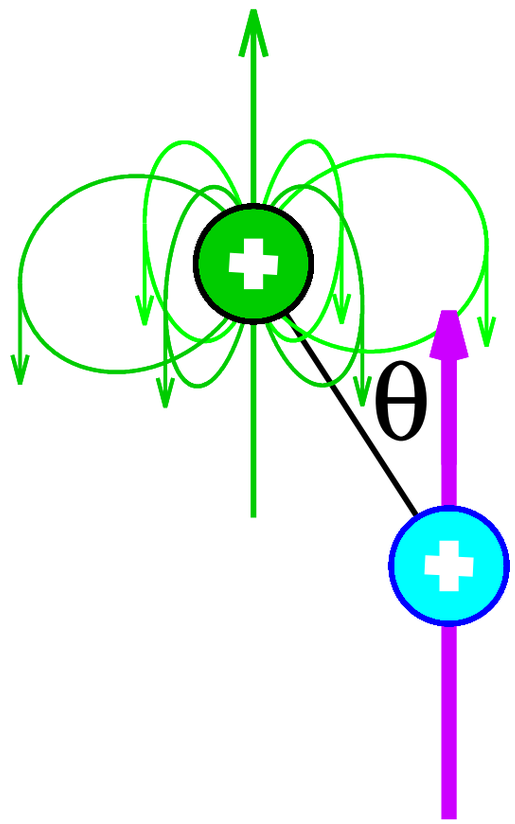

−CH=O
H
−C=CH−
−CH2−O−
−CH2−C=O
−CH2−C−
(CH3)4Si
H2
H+
499.9985
499.9990
499.9995
500.0000 MHz

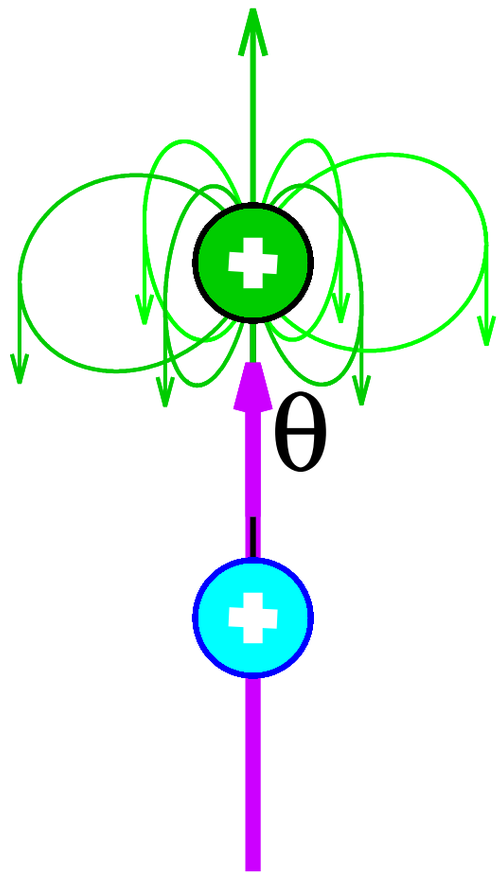

–CH=O
H
–C=CH–
–CH2–O–
–CH2–C=O
–CH2–C–
(CH3)4Si
H2
H+
99.997 %
99.998 %
99.999 %
100.000 %

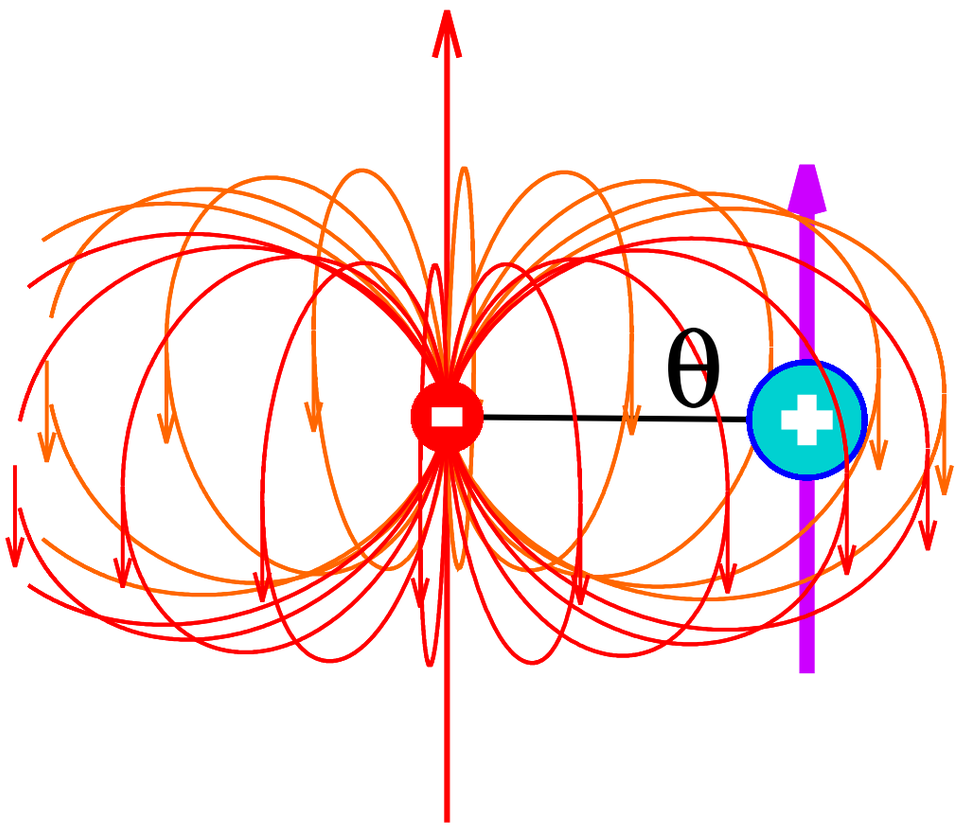

–CH=O
H
–C=CH–
–CH2–O–
–CH2–C=O
–CH2–C–
(CH3)4Si
H2
H+
0 ppm
10 ppm
20 ppm
30 ppm

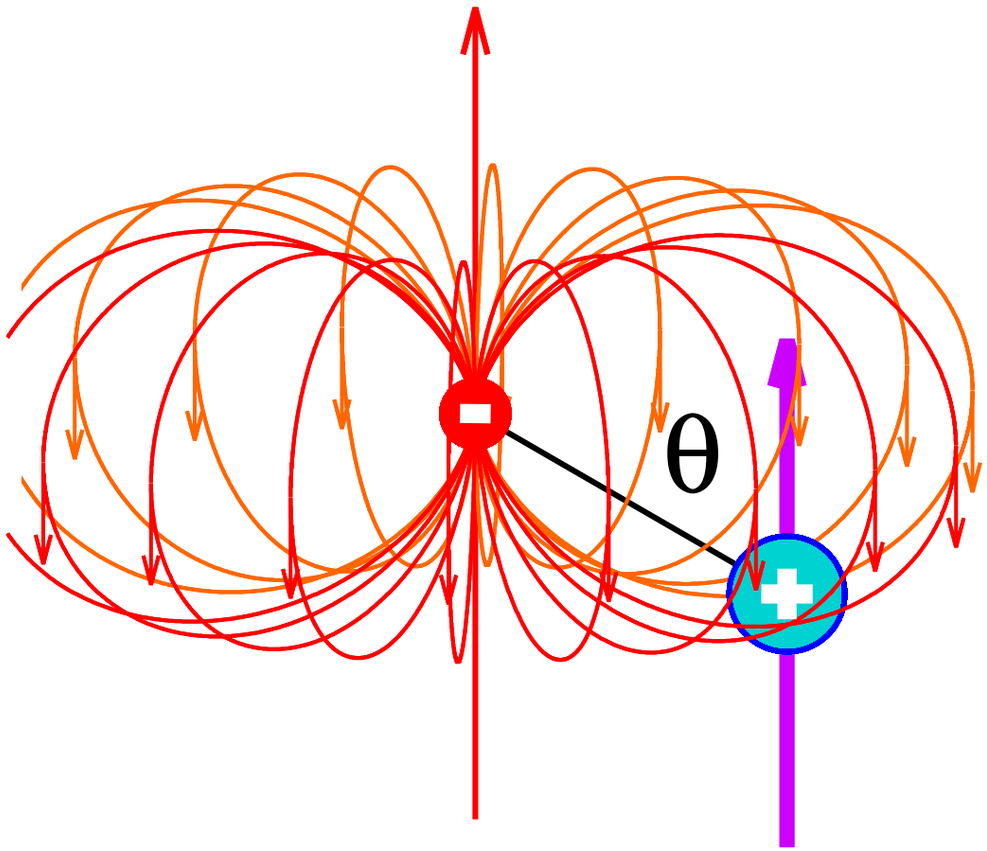

θ

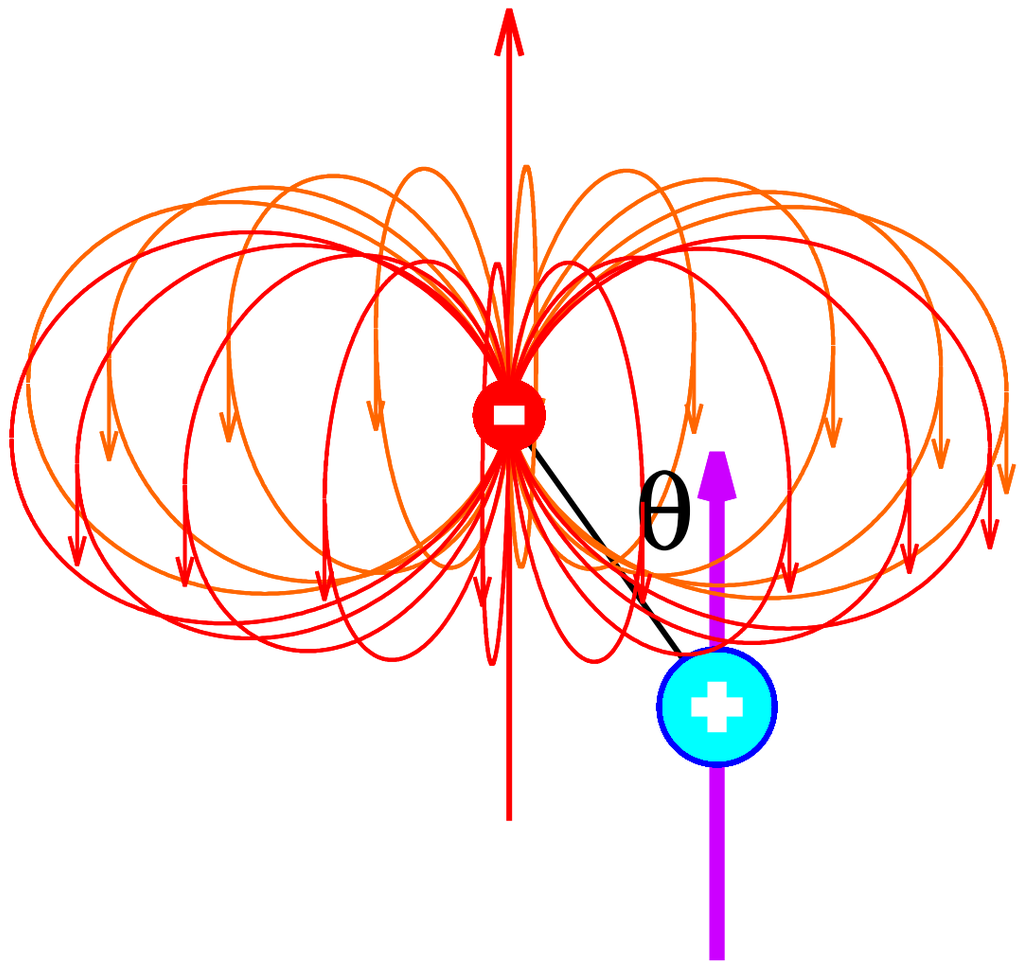

θ

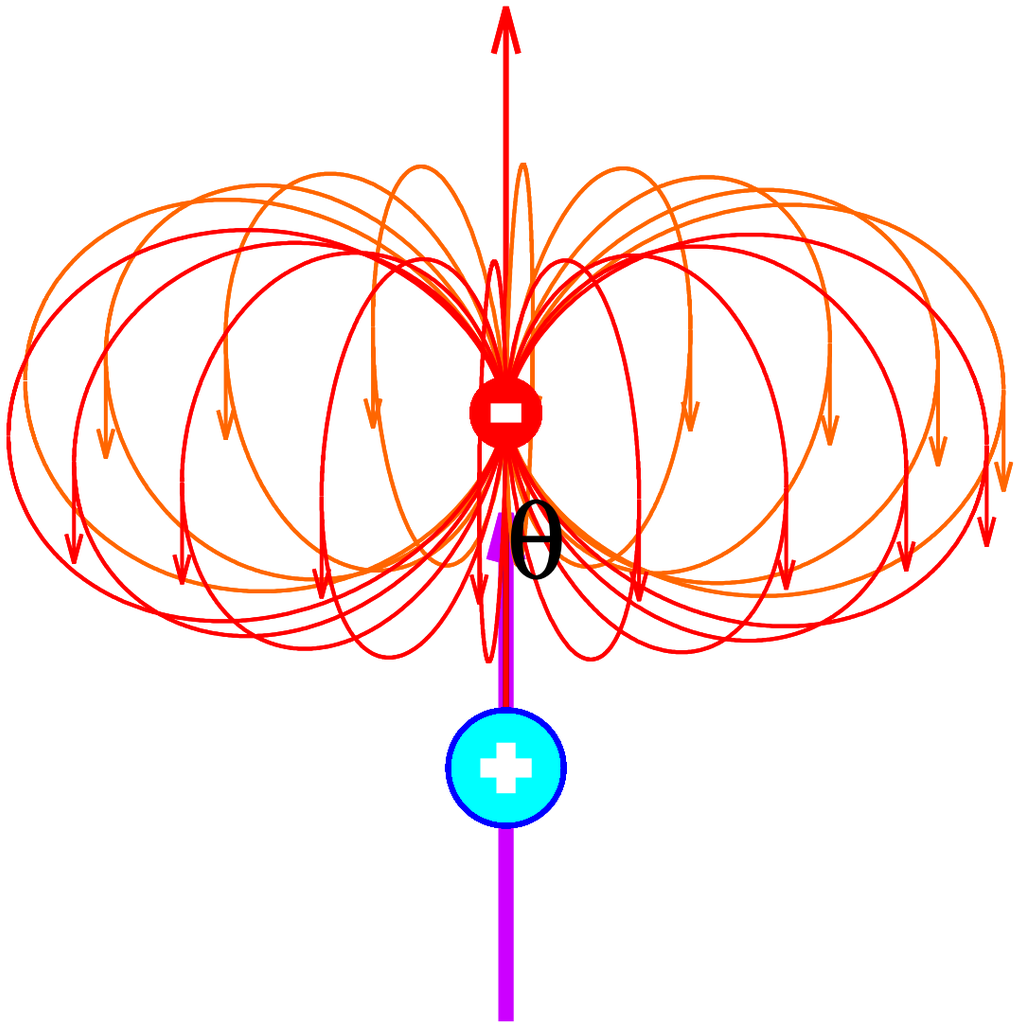

θ

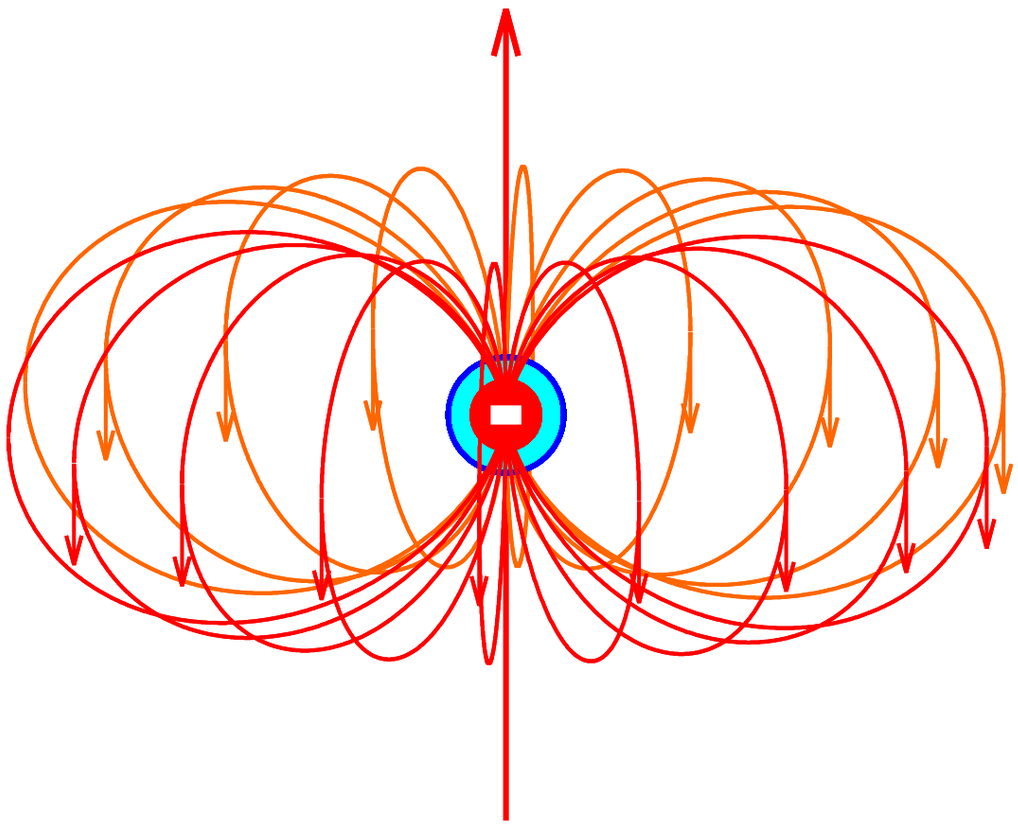

θ


θ

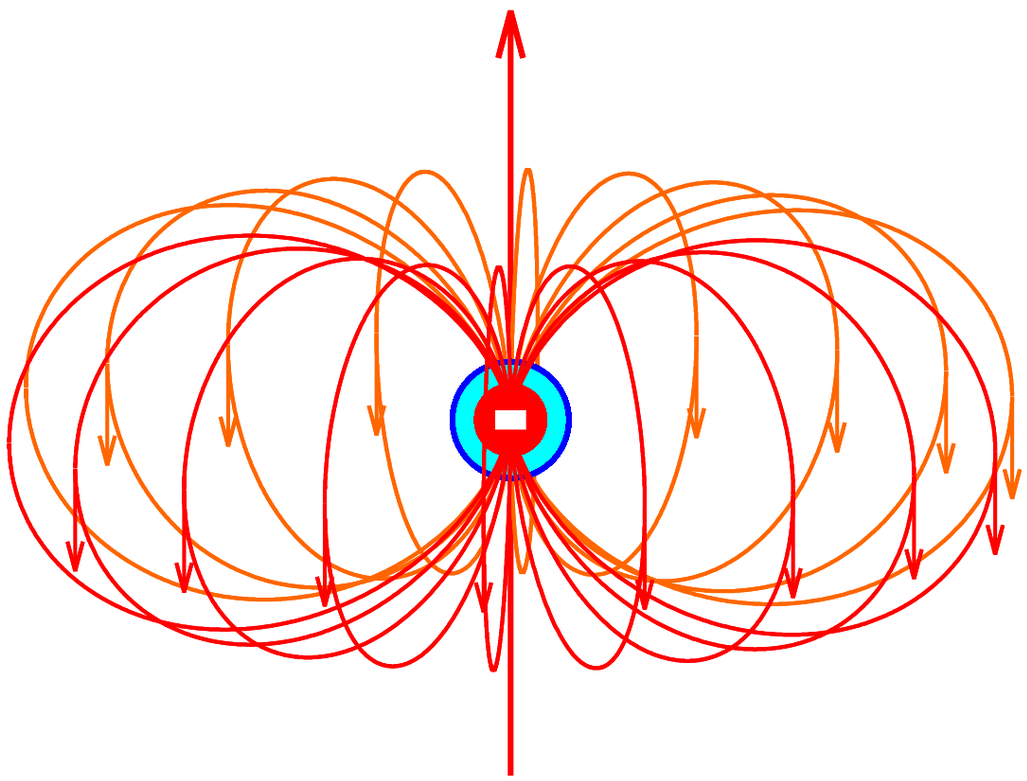

θ

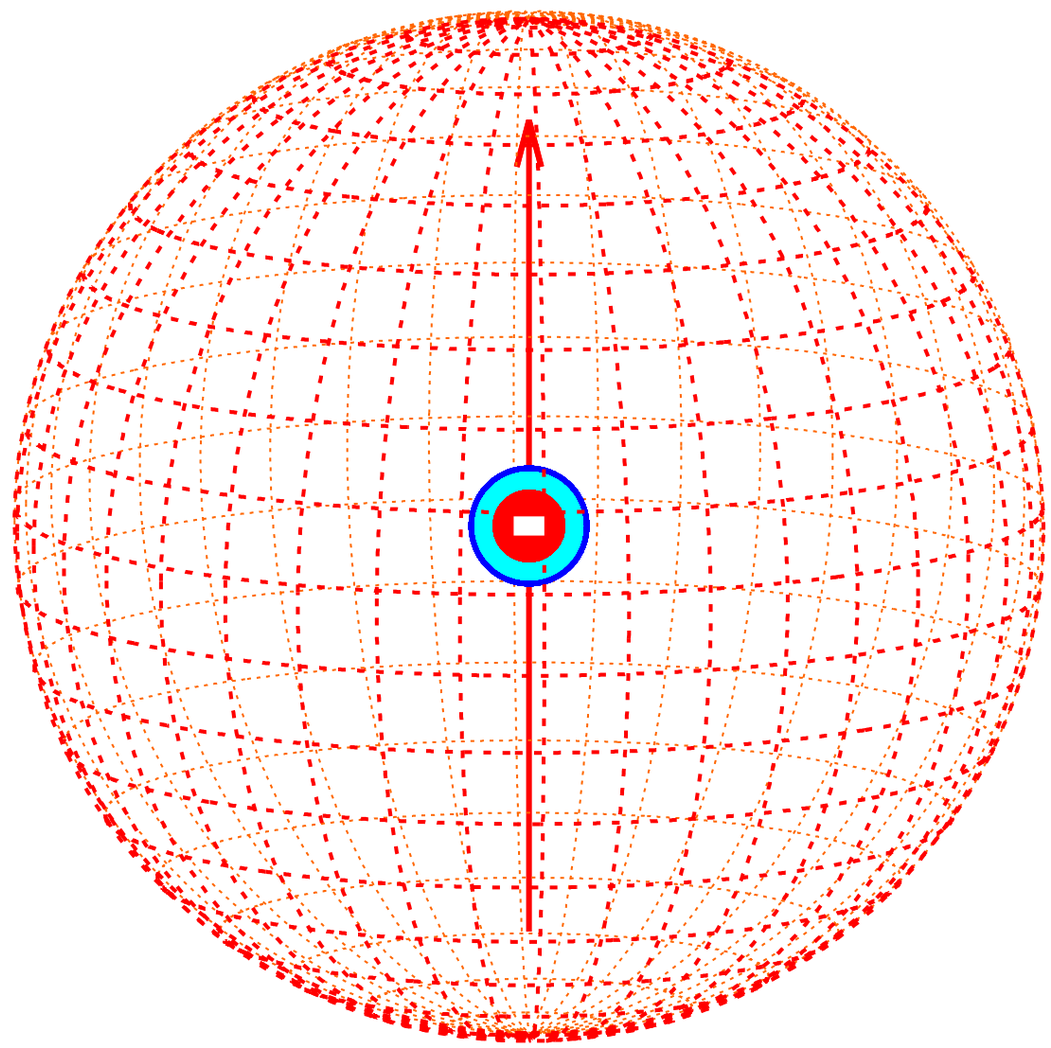

θ

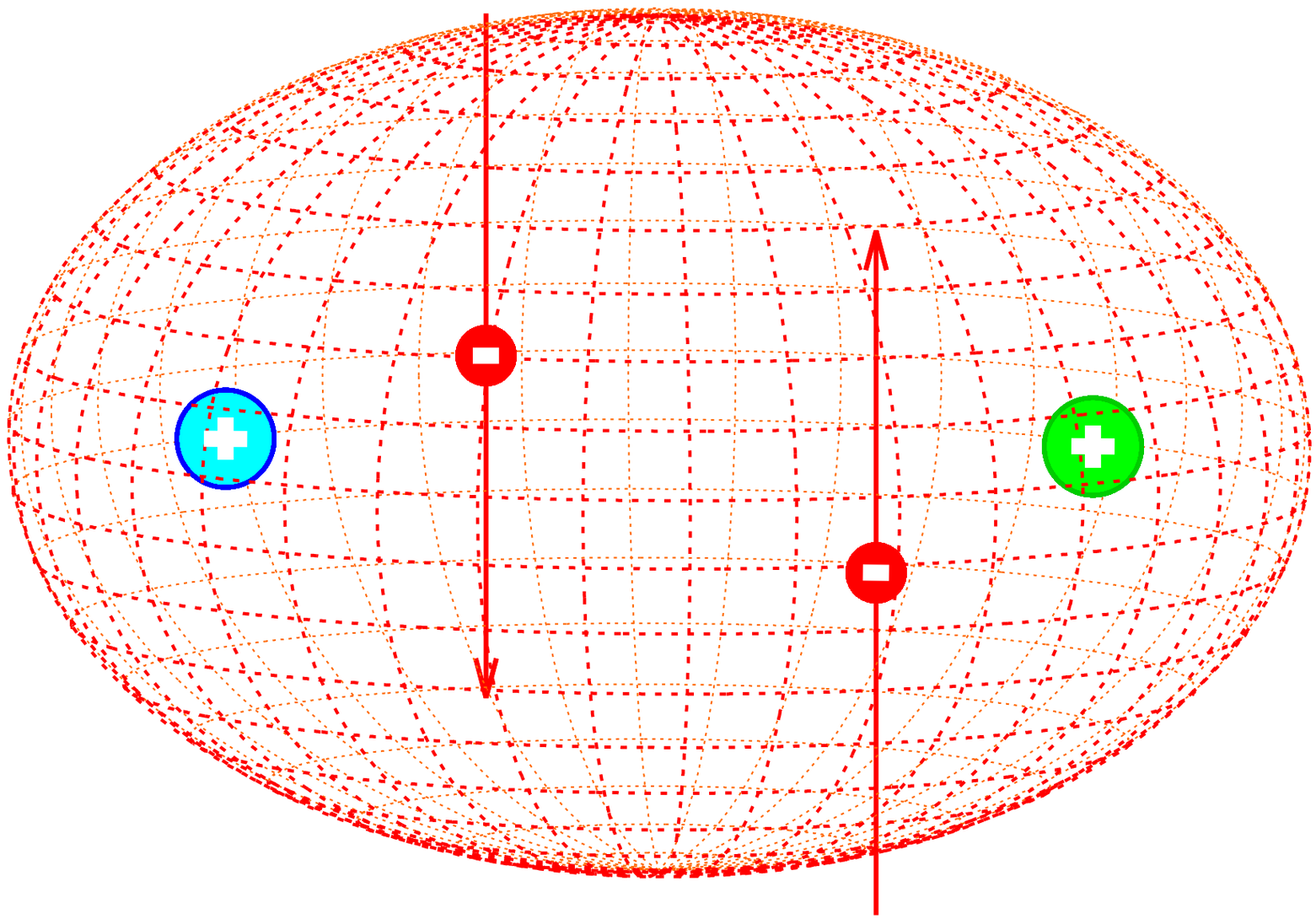

θ

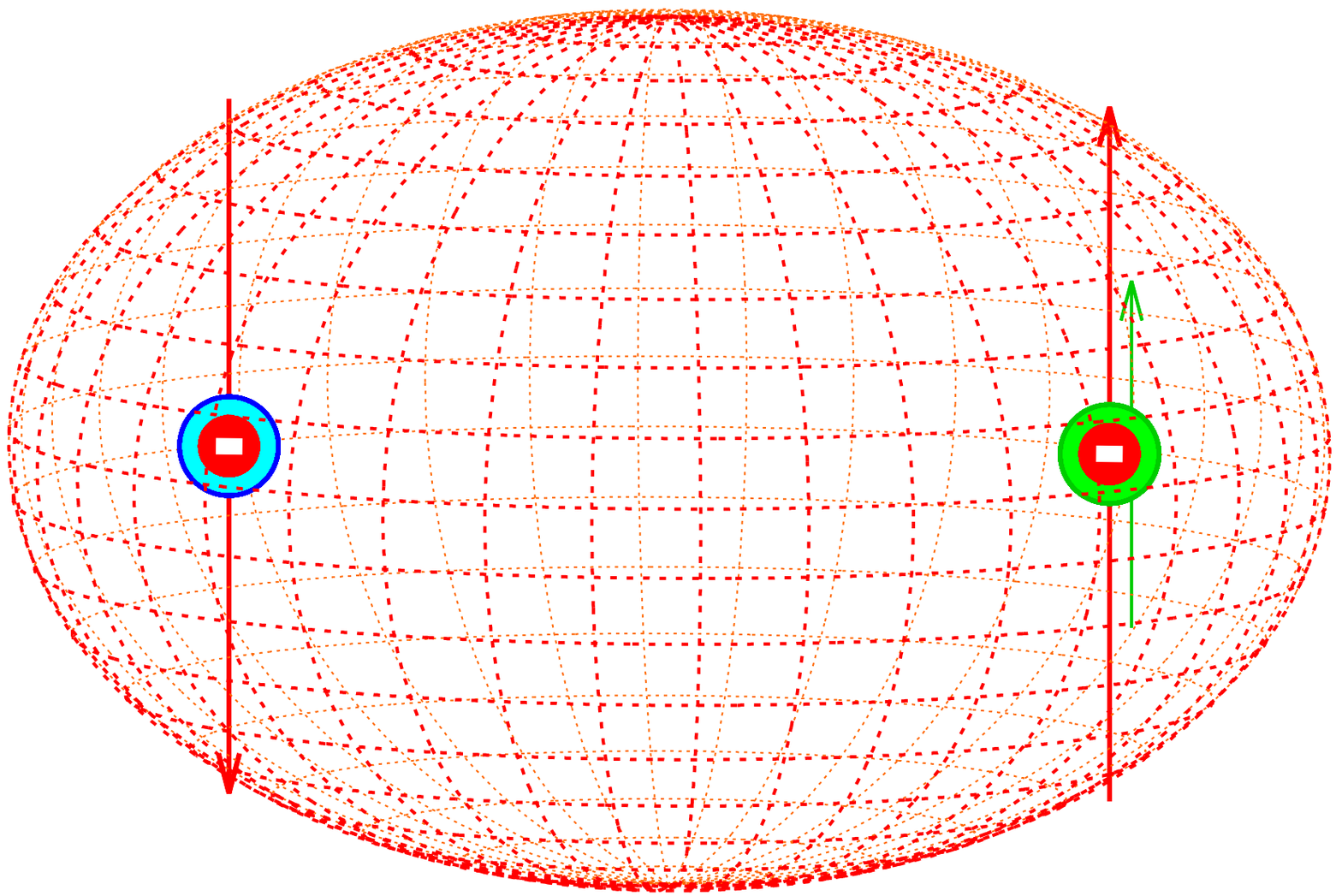


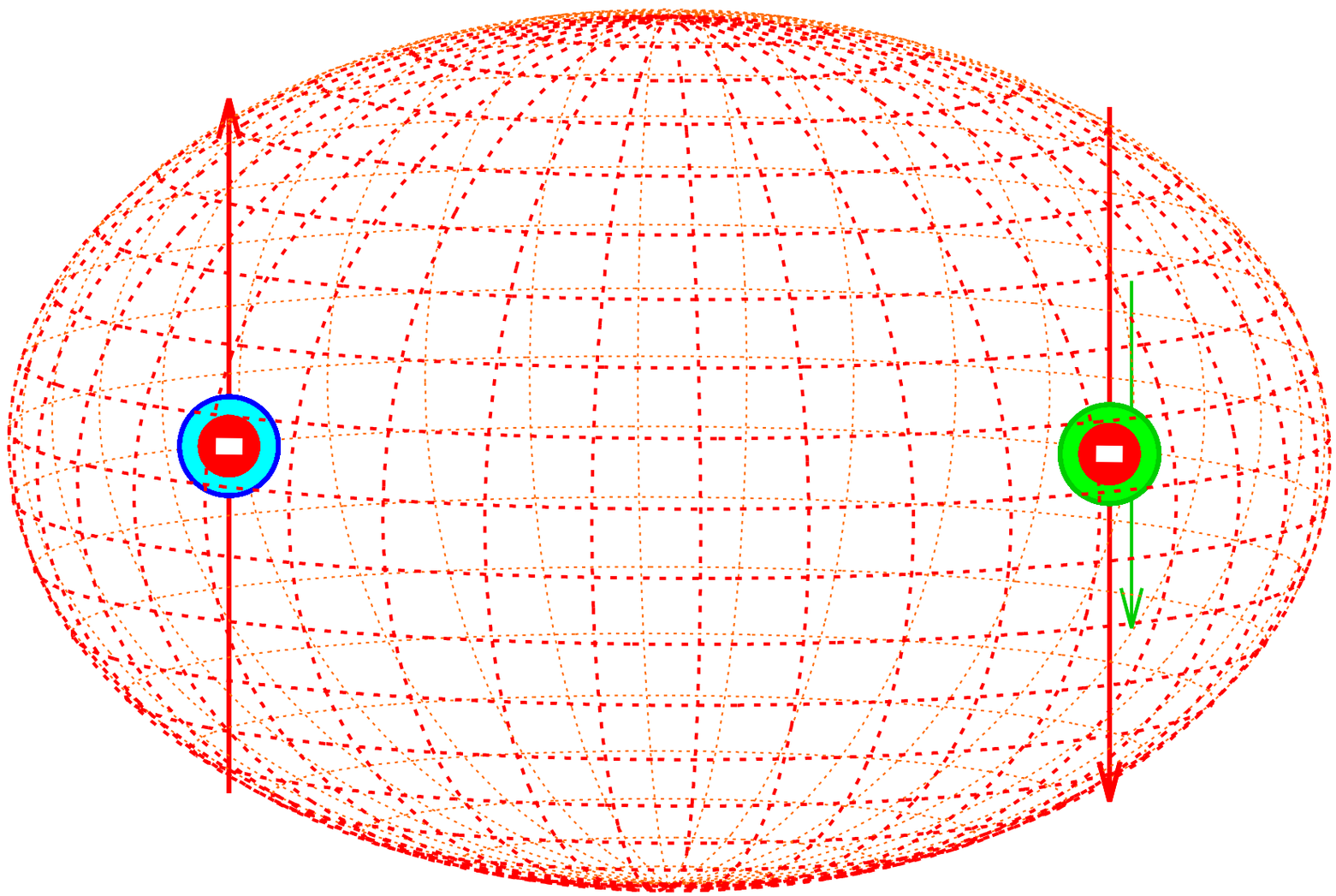
$$E = -\vec{\mu}_{\text{elektron}} \cdot \vec{\mu}_{\text{jádro}} \cdot P(\text{elektron v jádře})$$



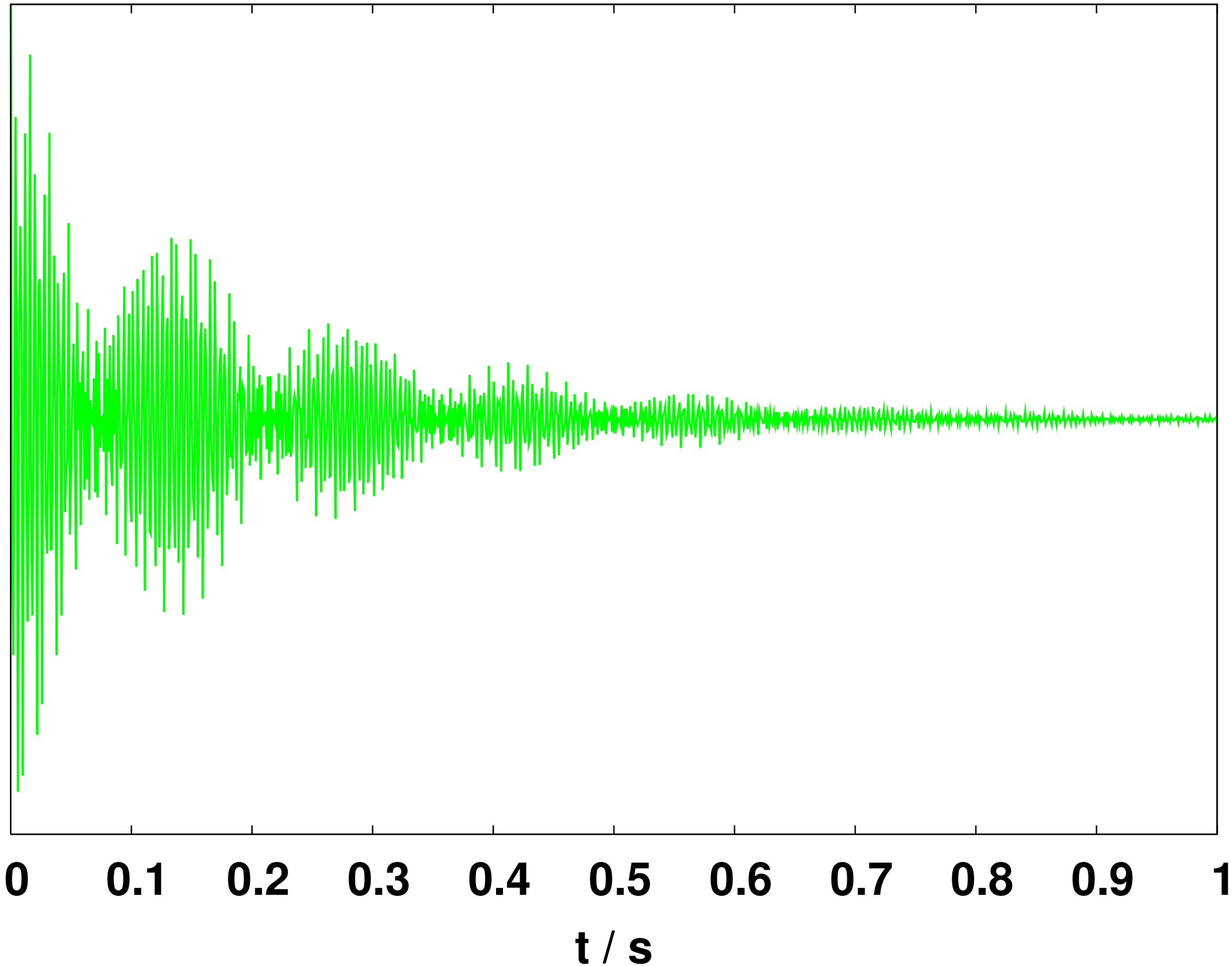


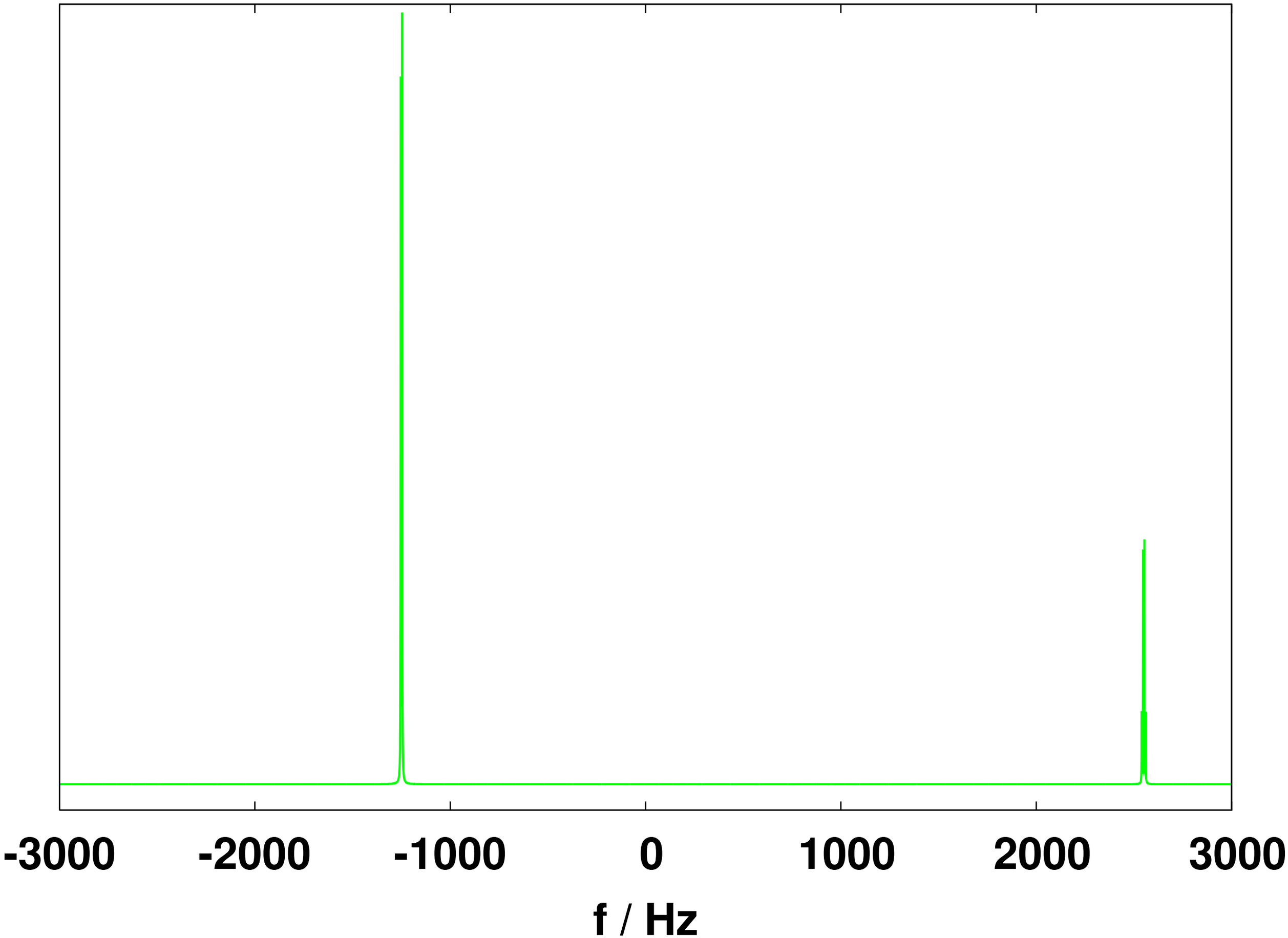


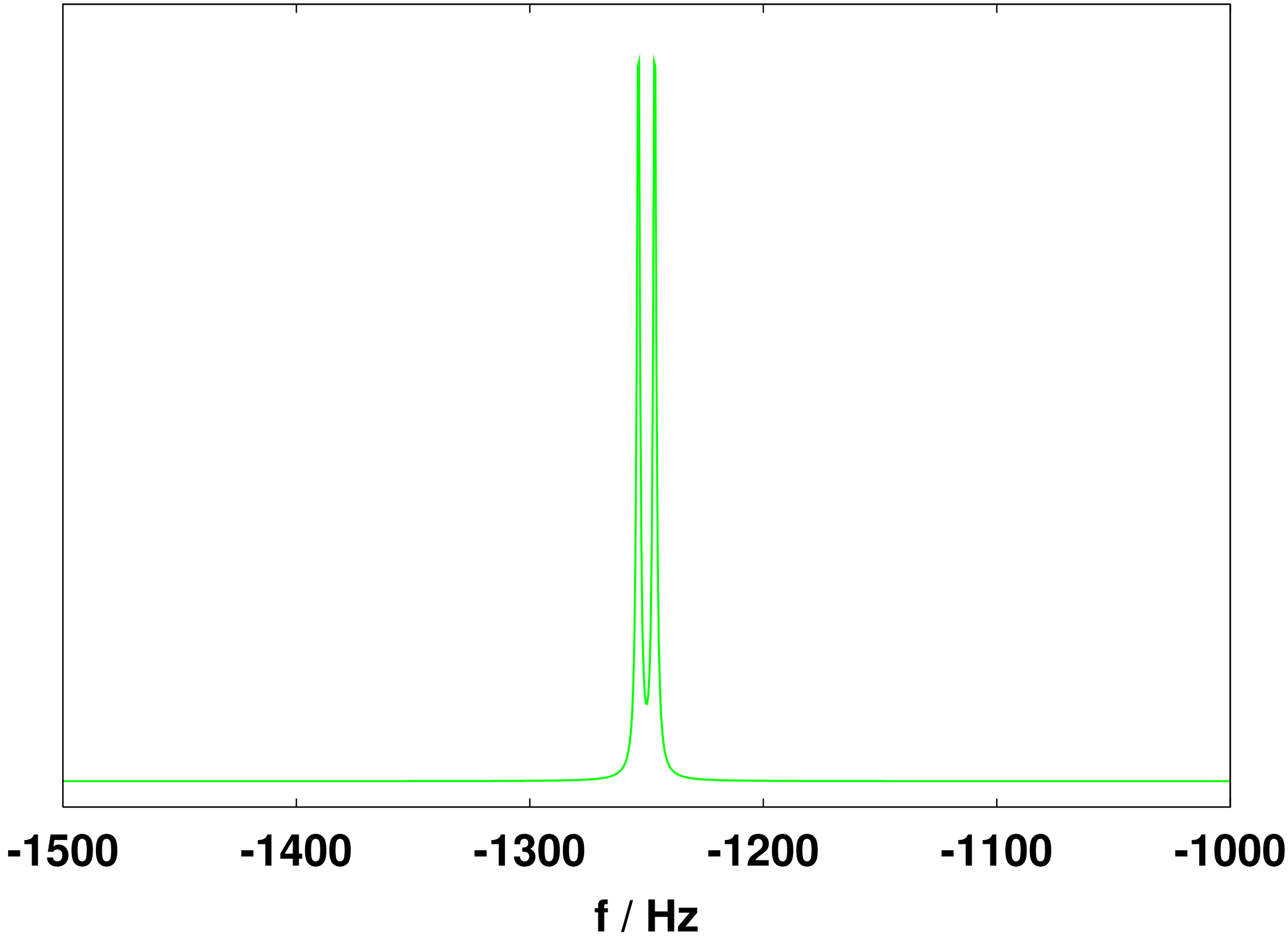


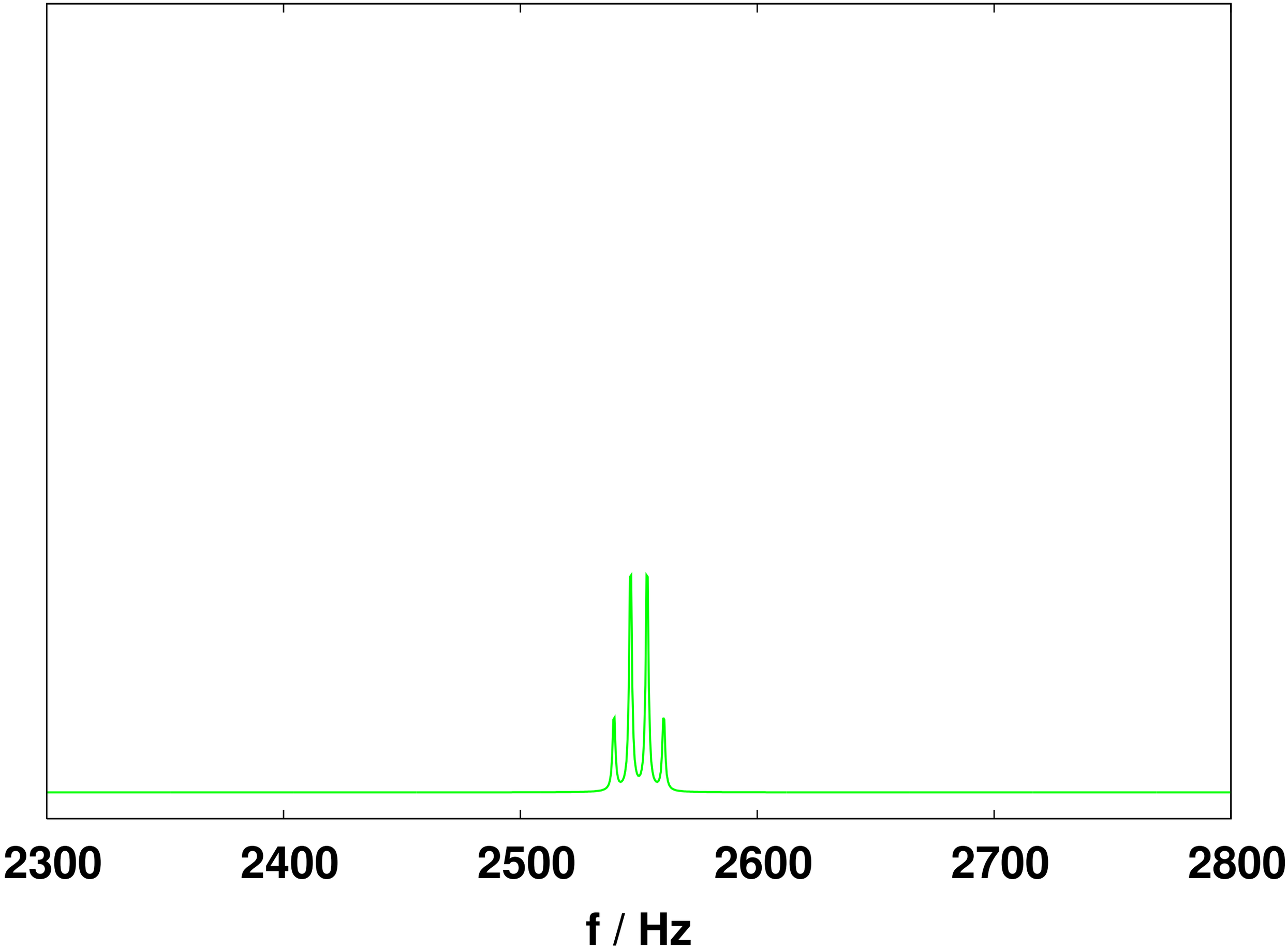


J (C–H)	130–230 Hz	
J (N–H)	90 Hz	
J (C–C)	35–55 Hz	
J (N–C)	10–15 Hz	
J (H–C–H)	14 Hz	
J (H–C–C–H)	0–14 Hz	závisí na torzním úhlu


0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
t / s


-3000
-2000
-1000
0
1000
2000
3000
f / Hz


-1500
-1400
-1300
-1200
-1100
-1000
f / Hz

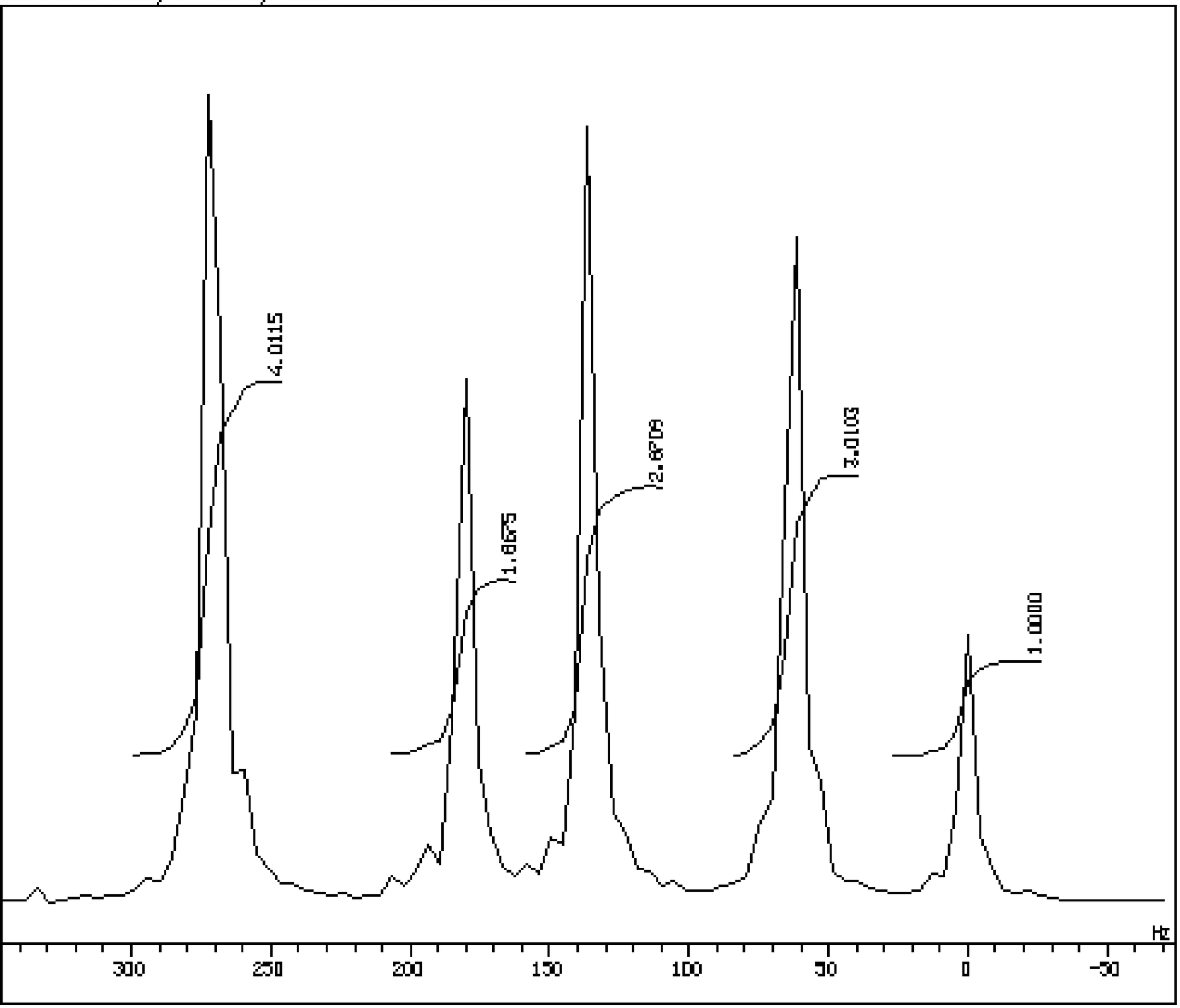

2300
2400
2500
2600
2700
2800
f / Hz

Acetaldehyd

Methyl acetaldehydu

Hänschen klein

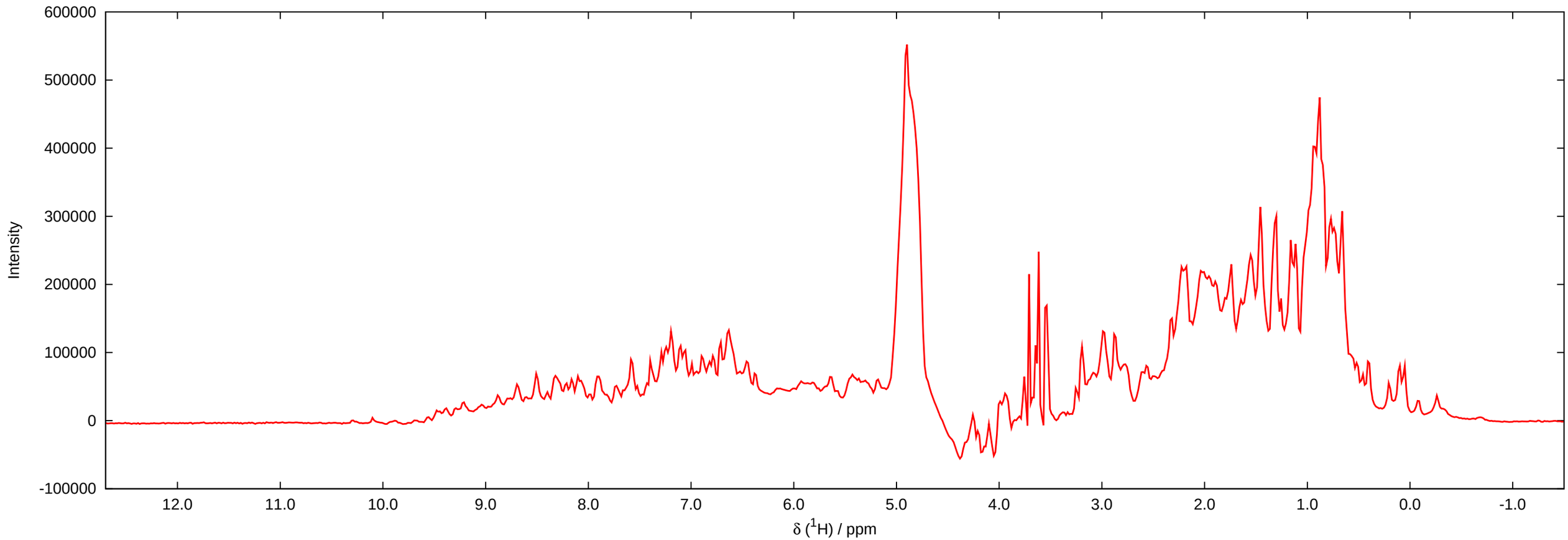
ACETONE IN C6D6, 1H H500FG, MELODY "HAENSCHEN KLEIN"

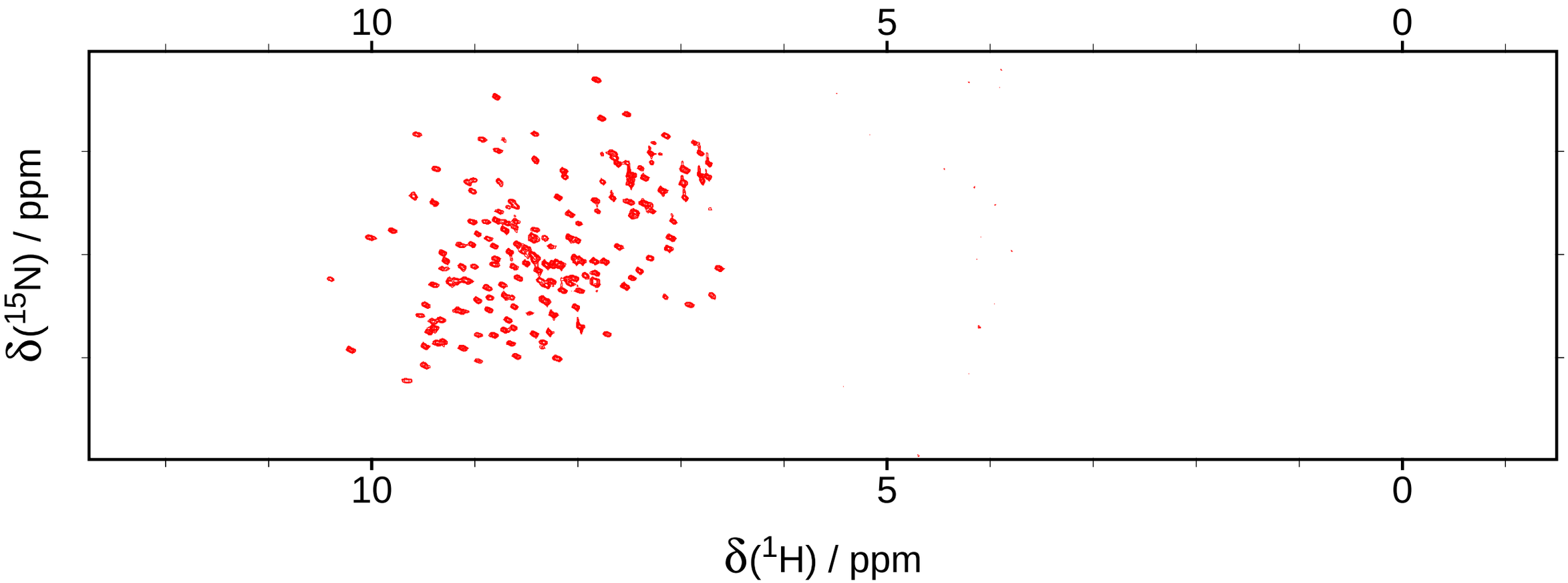


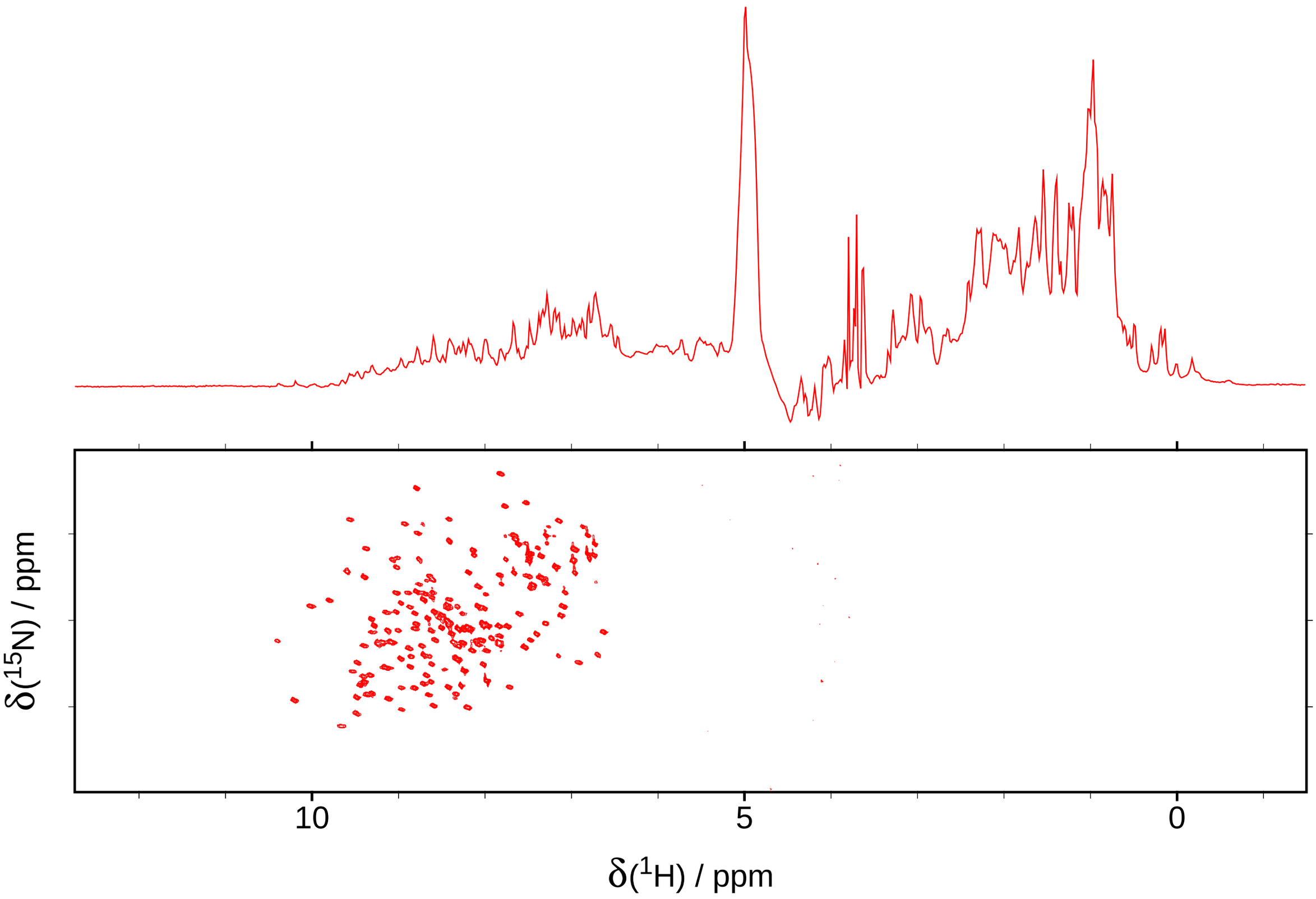
JEOL

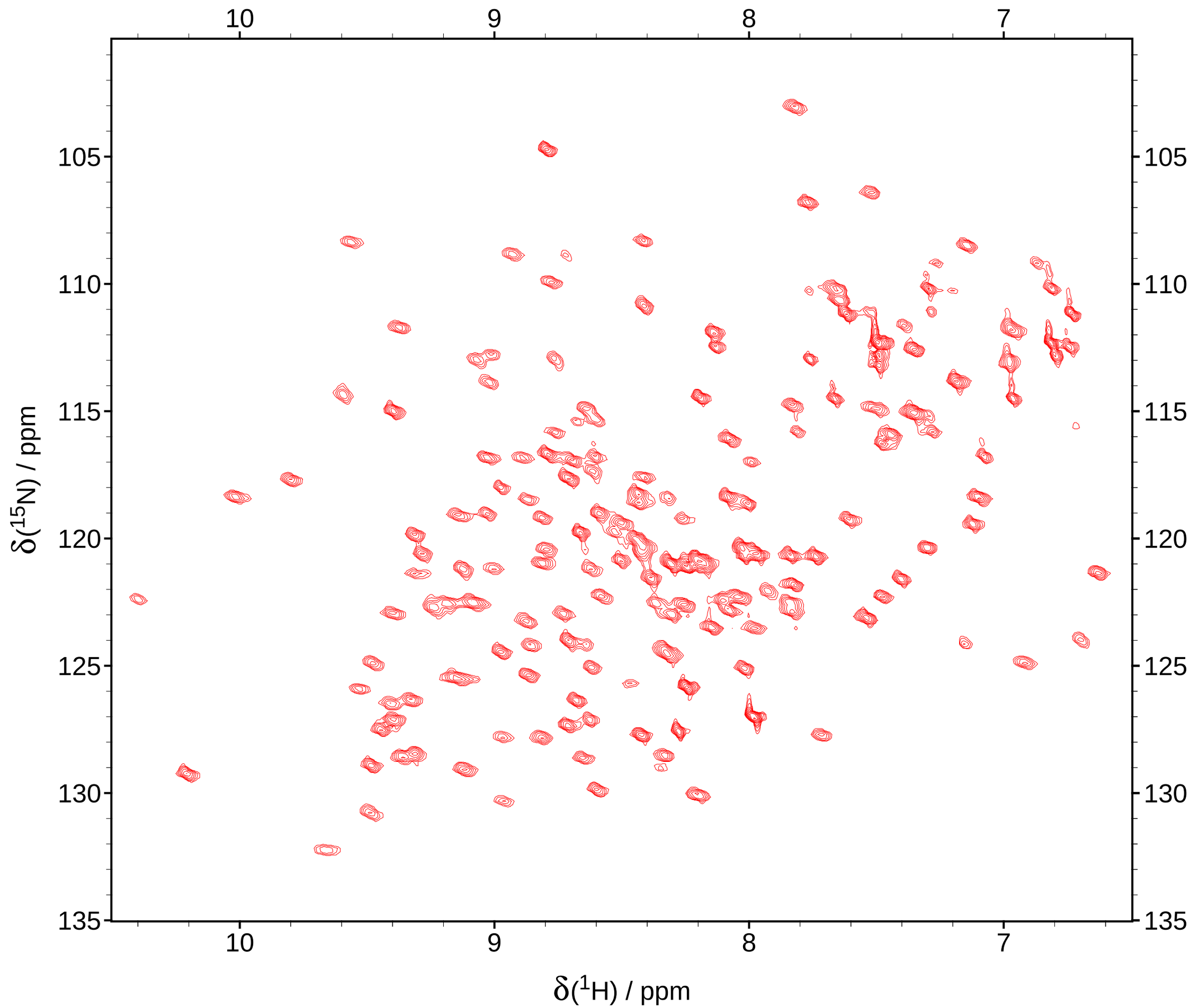
12-AUG-1996 19:16:29.54

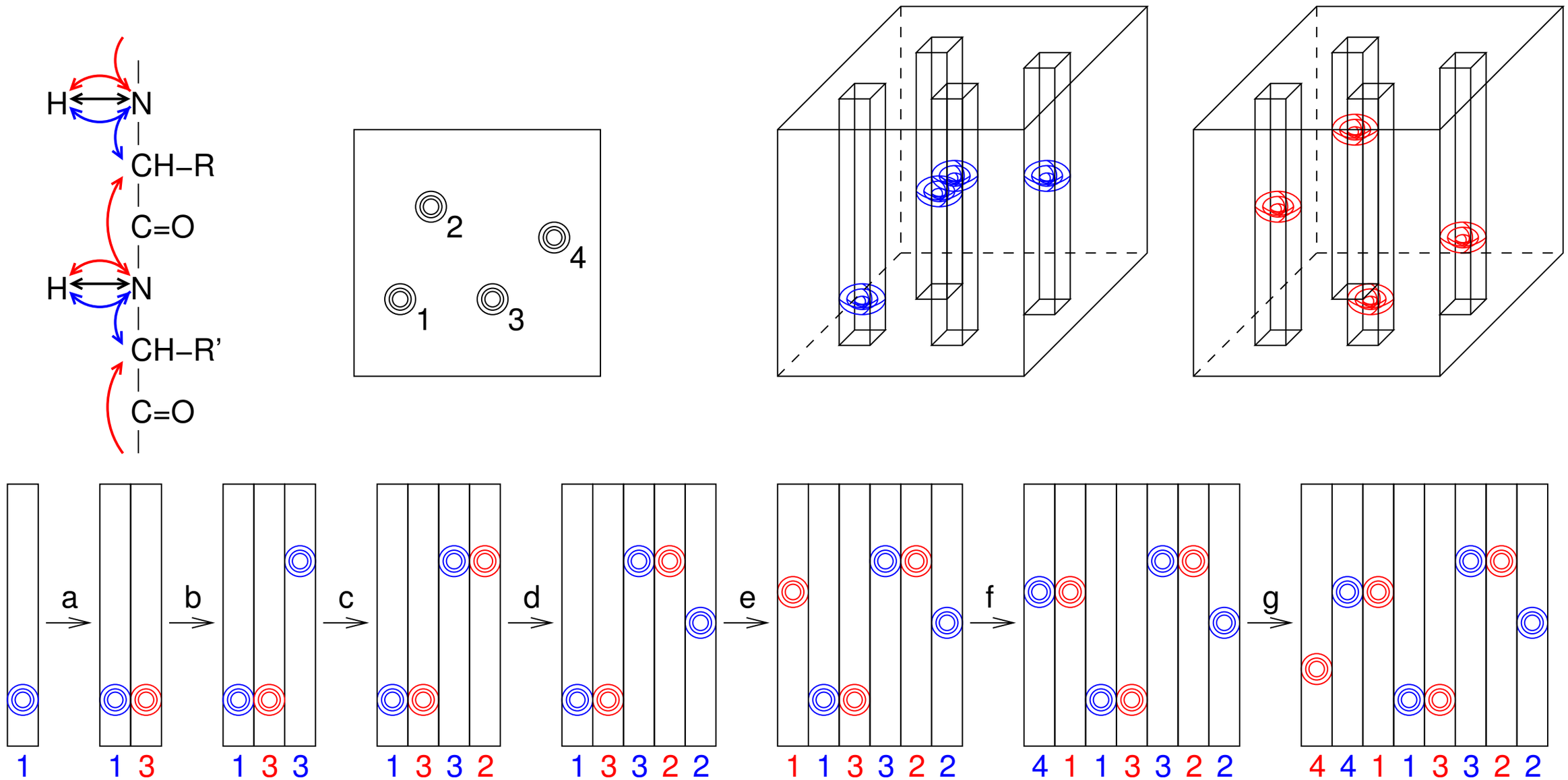
SFILE	:HANS
EXMOD	:HANS
IRMOD	:NON
POINT	: 2048
SAMPO	: 2048
FREQU	: 9000.90 Hz
FILTR	: 4500 Hz
SCANS	: 1
DUMMY	: 0
ACQTM	: 0.2275 sec
PD	: 2.7222 sec
RGAIN	: 10
PW1	: 1.00 usec
OBNUC	:1H
OBFRQ	: 500.00 MHz
OBSET	:160200.00 Hz
IRNUC	:13C
IRFRQ	: 125.65 MHz
IRSET	:127958.00 Hz
IRATN	: 511
IRPW1	: 50.0 usec
IRBP1	: 50
IRBP2	: 6
IRRNS	: 0
TRNUC	:1H
TRFRQ	: 500.00 MHz
TRSET	:162410.00 Hz
TRATN	: 511
TRPW1	: 50.0 usec
TRBP1	: 30
TRBP2	: 6
TRRNS	: 0
CTEMP	: 24.1 c
CSPED	: 11 Hz
SLVNT	:C6D6
RESOL	: 4.39 Hz
NNOMD	: 8
BF	: 0.10 Hz
GF	: 0.00 Hz
PP	: 840 cp
ABSPO	: -92.11 deg
ABSP1	: 0.00 deg
T1	: 0.00 s
T2	: 0.00 s
T3	: 90.00 s
T4	: 100.00 s
REFVL	: 0.00 ppm
THSP	: 902
XE	: 421.92 Hz
XS	: -676.83 Hz
YG	: 0.0011

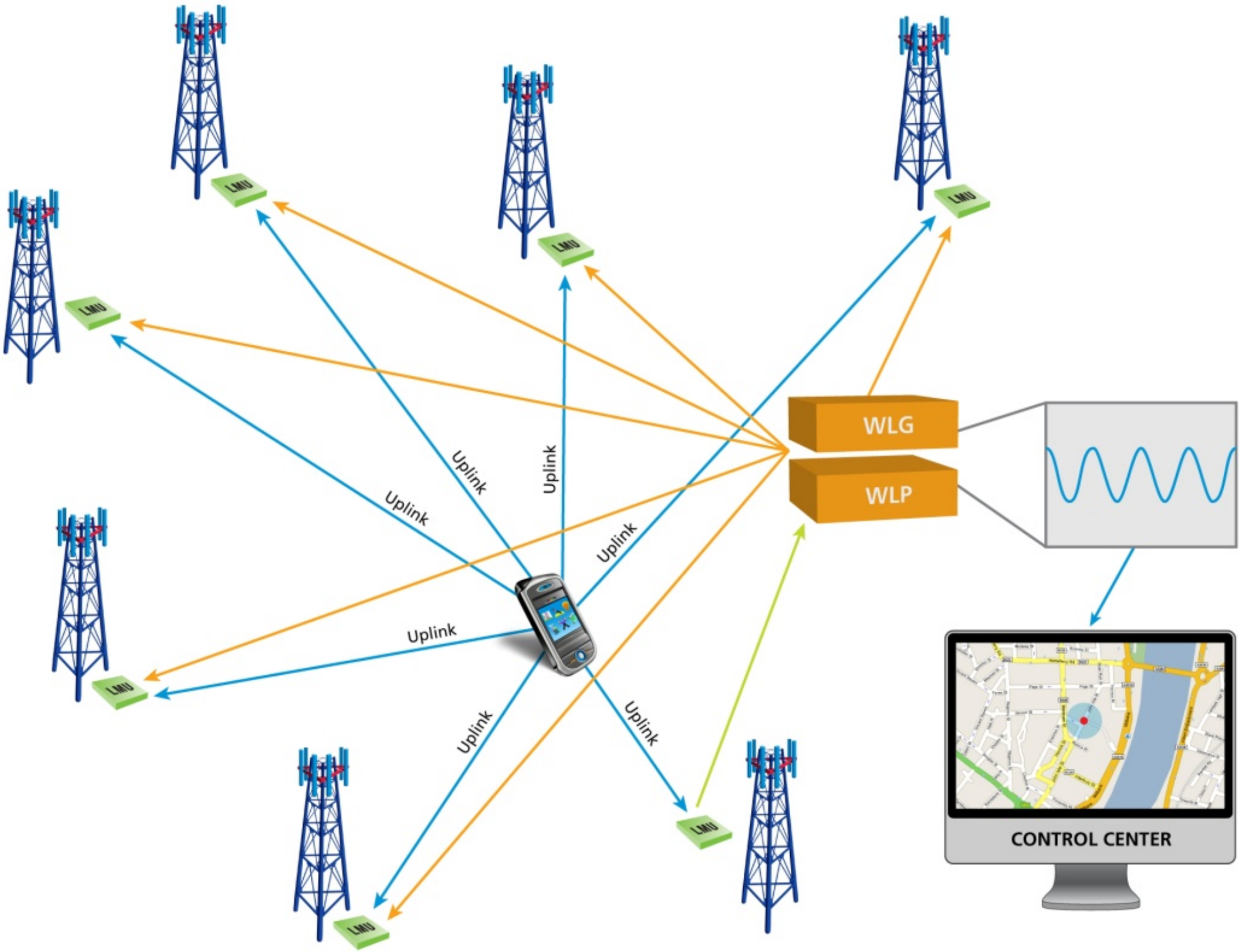

600000
500000
400000
300000
200000
100000
0
-100000
Intensity
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
δ (^{1}H) / ppm

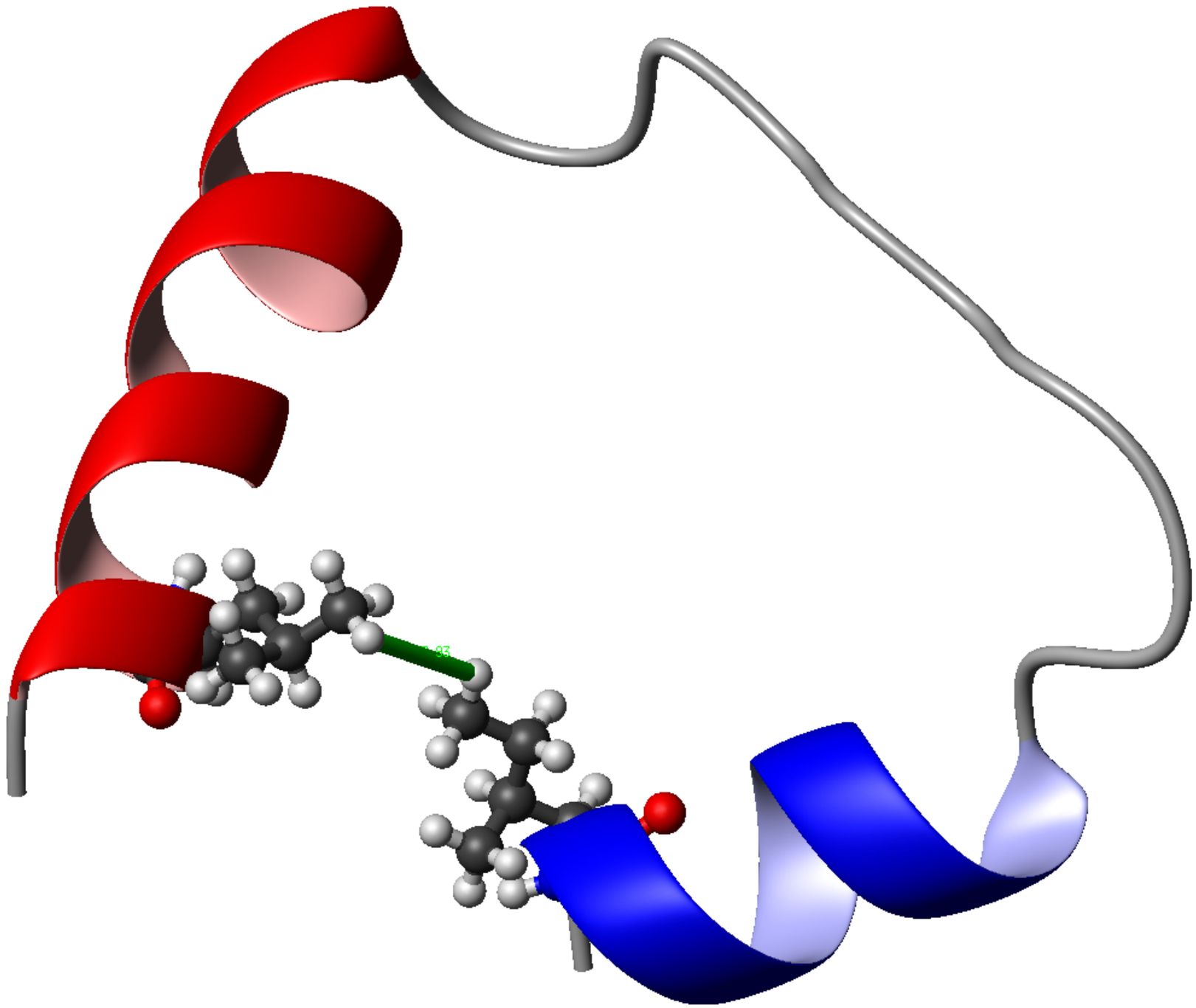

10
5
0
δ(15N) / ppm
10
5
0
δ(1H) / ppm

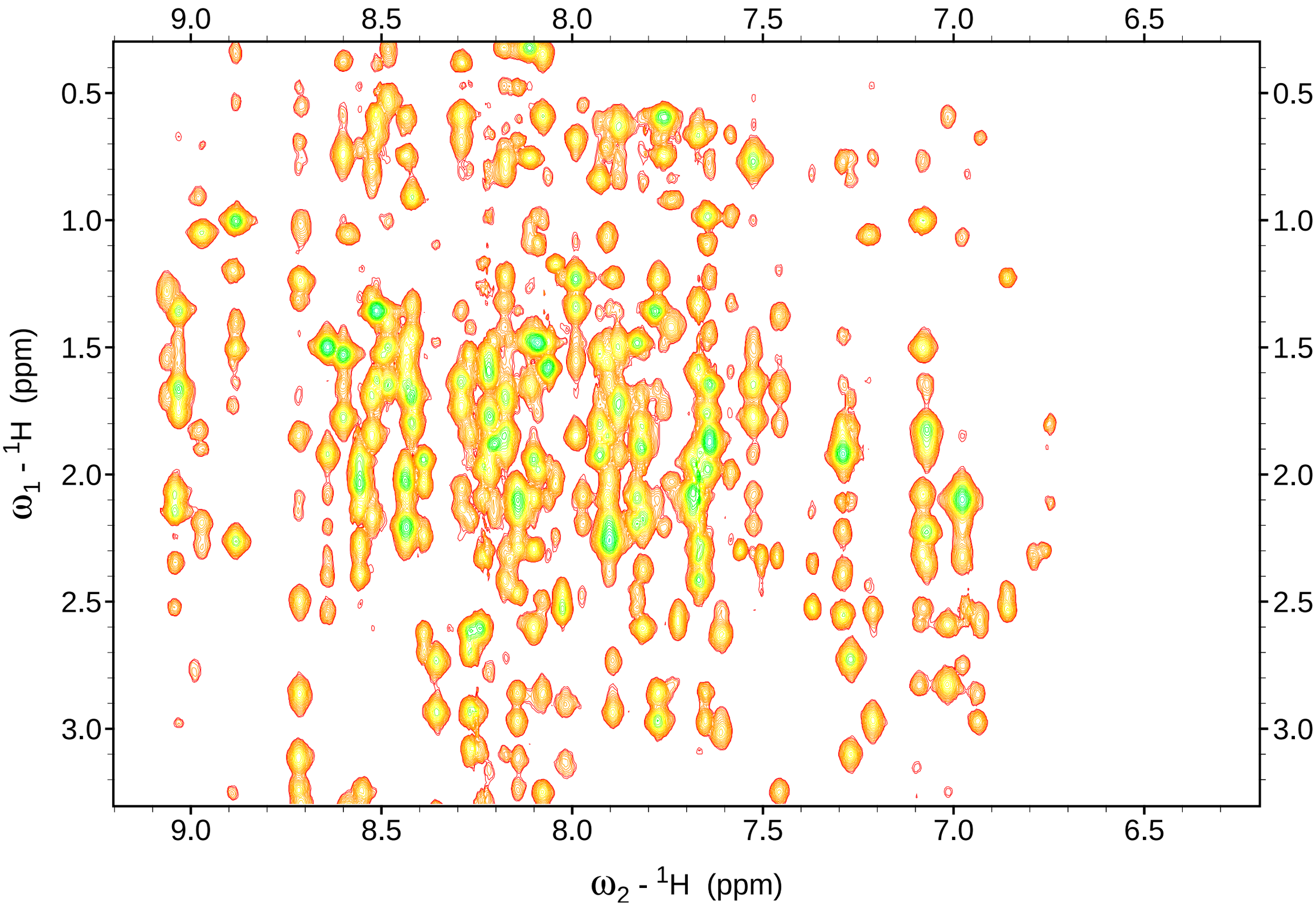

10
5
0
δ(1H) / ppm
δ(15N) / ppm

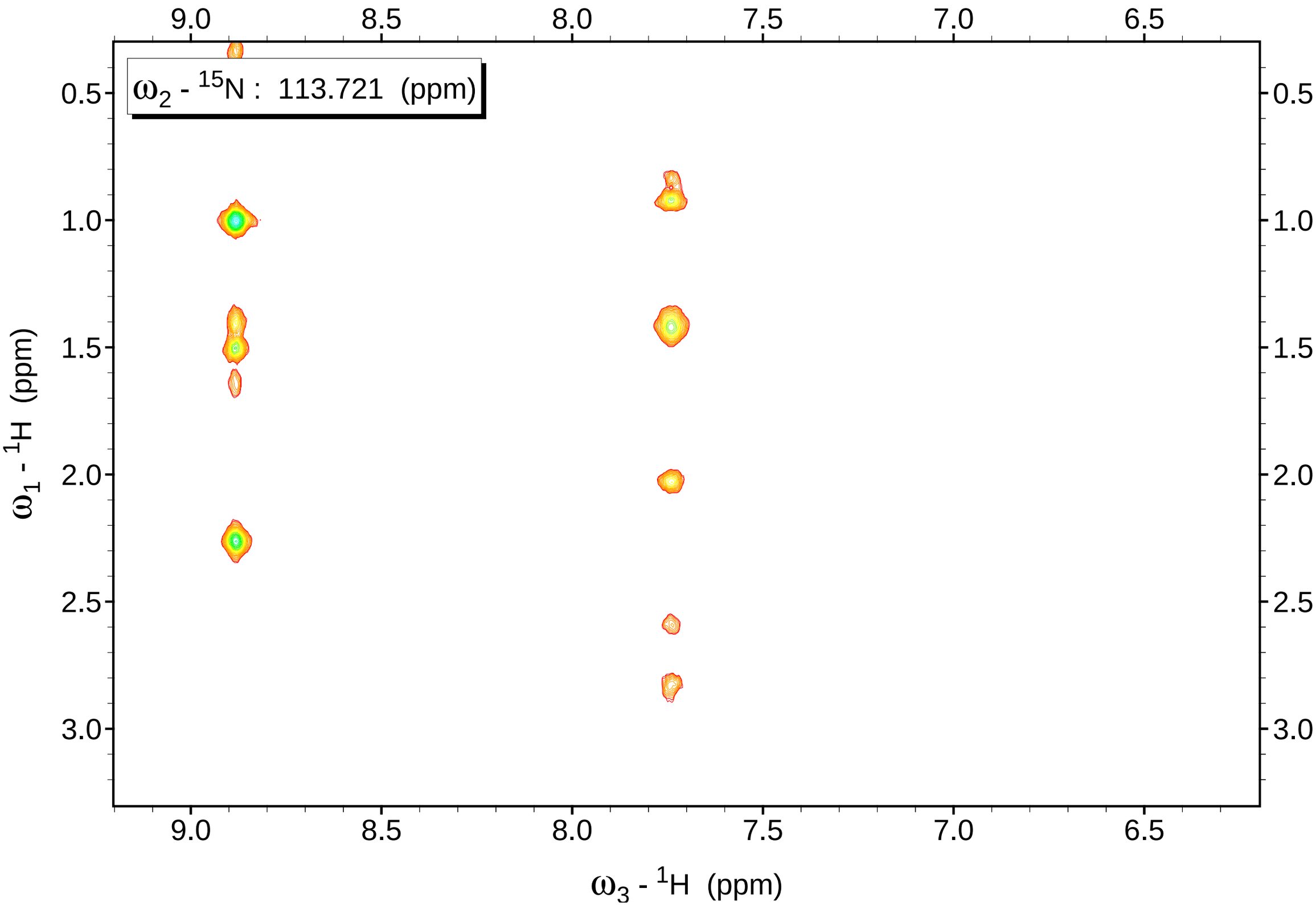

10
9
8
7
105
110
115
120
125
130
135
δ(15N) / ppm
δ(1H) / ppm

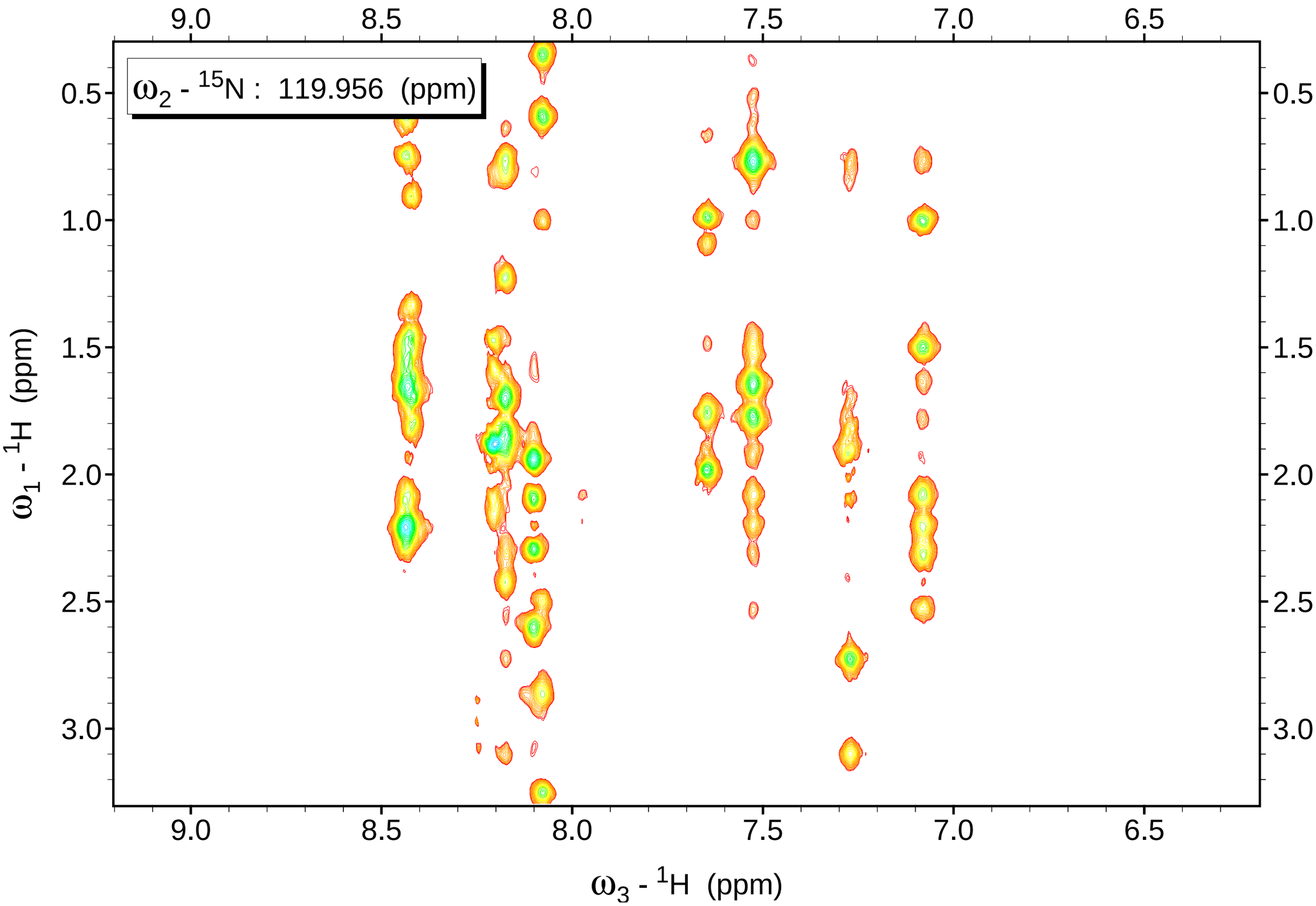

H
N
CH–R
C=O
H
N
CH–R'
C=O
1
2
3
4
a
b
c
d
e
f
g
1
1 3
1 3 3
1 3 3 2
1 3 3 2 2
1 1 3 3 2 2
4 1 1 3 3 2 2
4 4 1 1 3 3 2 2

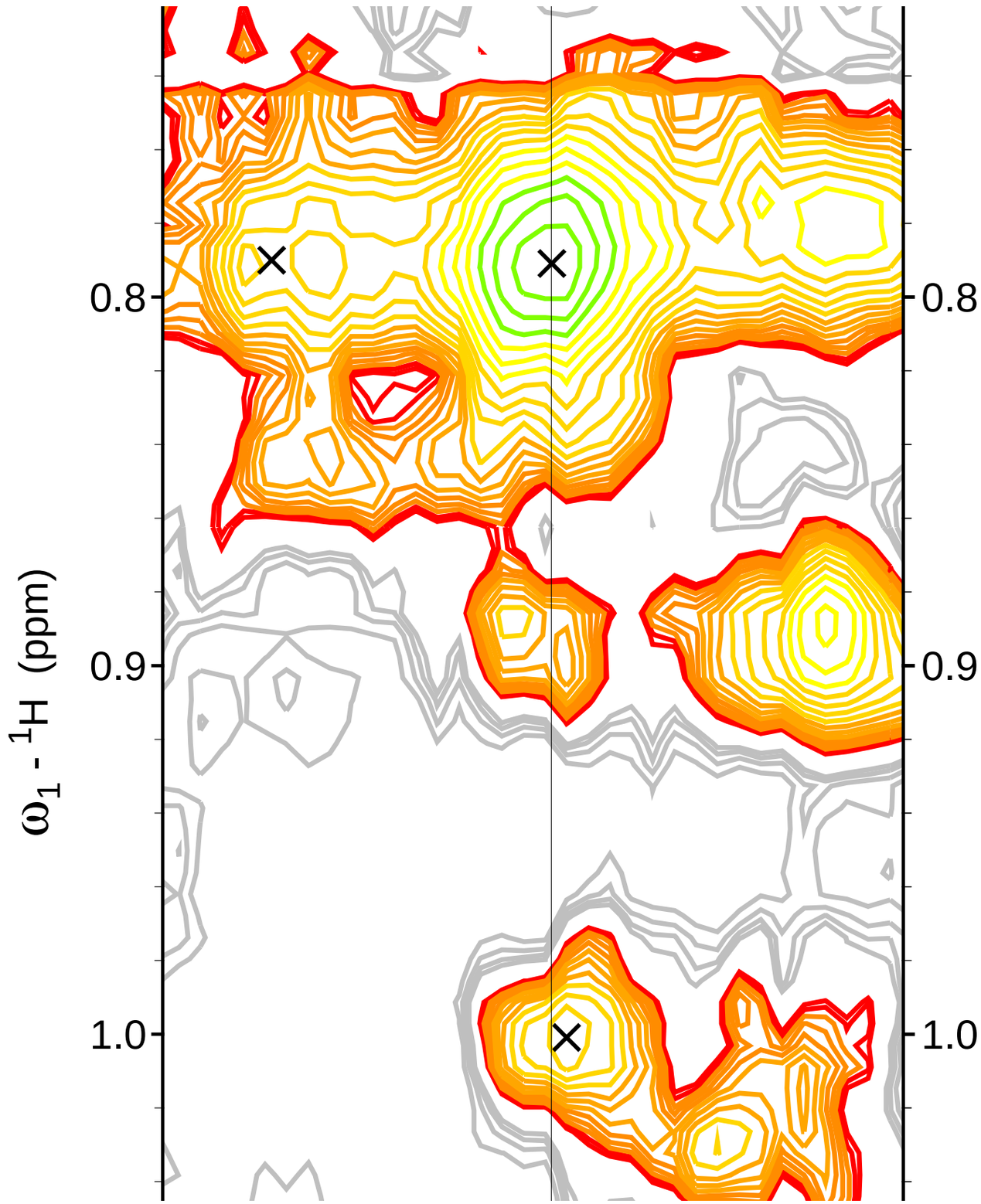

LMU
LMU
LMU
LMU
LMU
LMU
Uplink
Uplink
Uplink
Uplink
Uplink
Uplink
Uplink
WLG
WLP
CONTROL CENTER

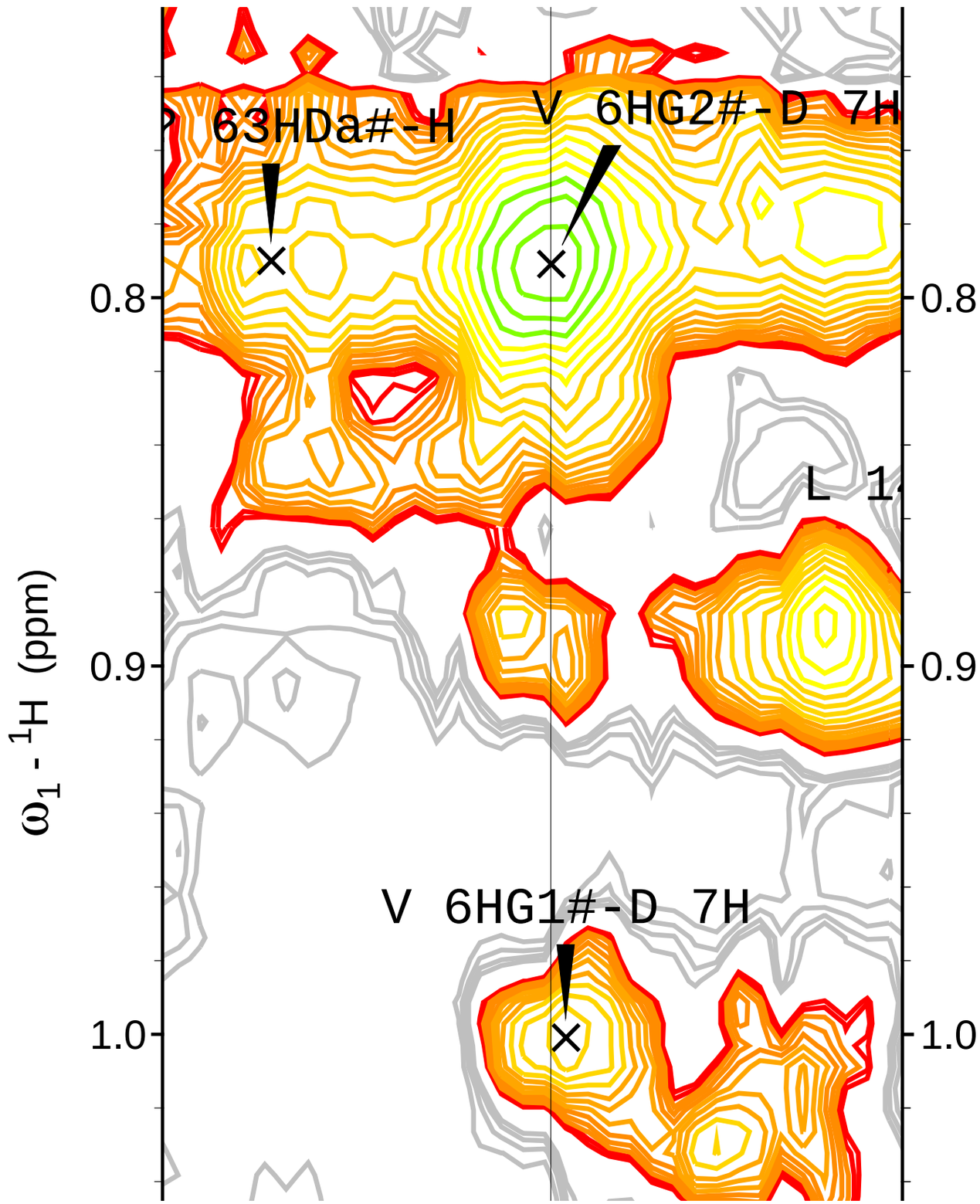



9.0
8.5
8.0
7.5
7.0
6.5
0.5
1.0
1.5
2.0
2.5
3.0
ω_1 - ^{1}H (ppm)
ω_2 - ^{1}H (ppm)


ω2 - 15N : 113.721 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
0.5
1.0
1.5
2.0
2.5
3.0
ω1 - 1H (ppm)
ω3 - 1H (ppm)


ω2 - 15N : 119.956 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
0.5
1.0
1.5
2.0
2.5
3.0
ω1 - 1H (ppm)
ω3 - 1H (ppm)

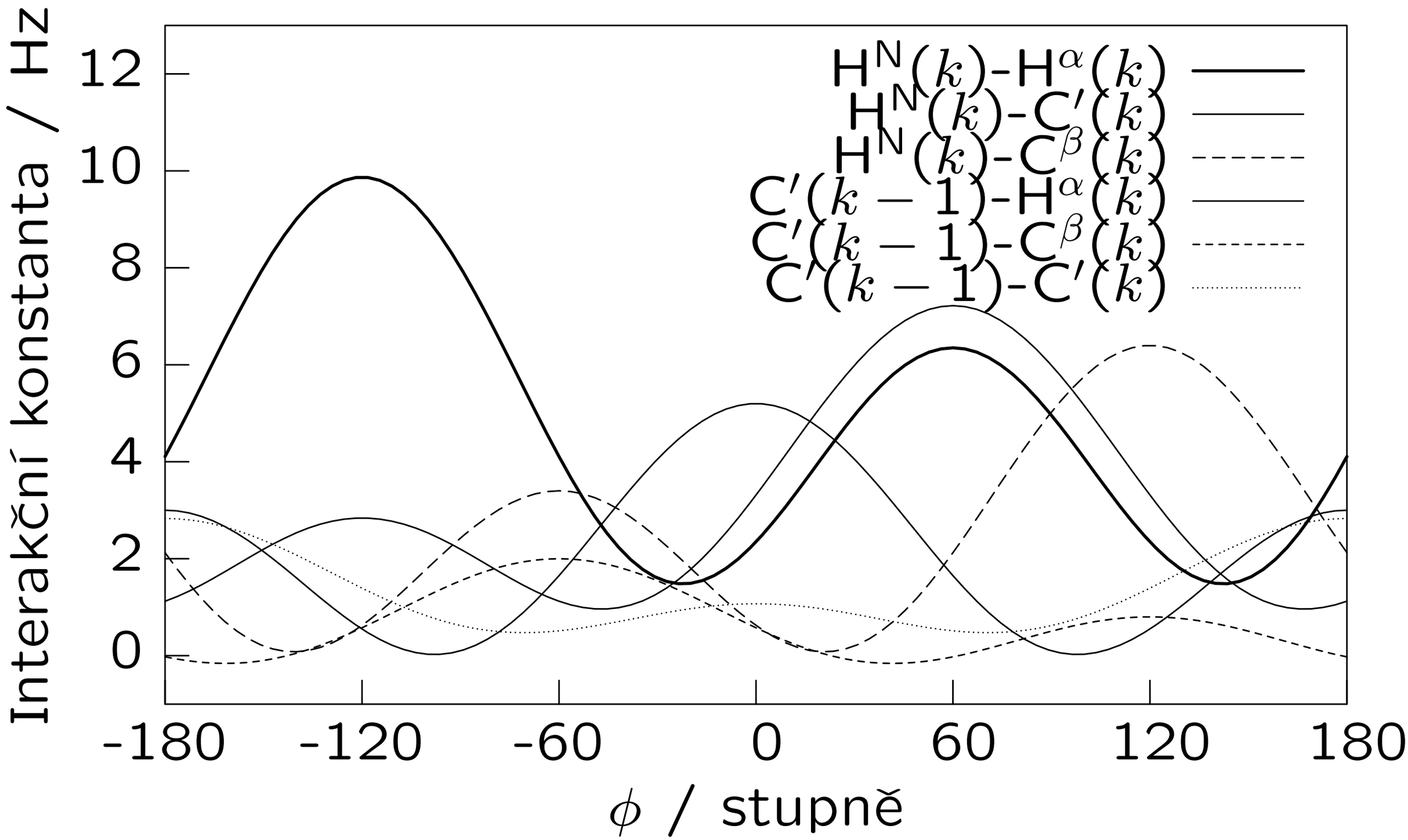

0.8
0.9
1.0
0.8
0.9
1.0
ω_1 - ^{1}H (ppm)


63HDa#-H
V 6HG2#-D 7H
L 1
V 6HG1#-D 7H
0.8
0.9
1.0
ω_1 - ^{1}H (ppm)

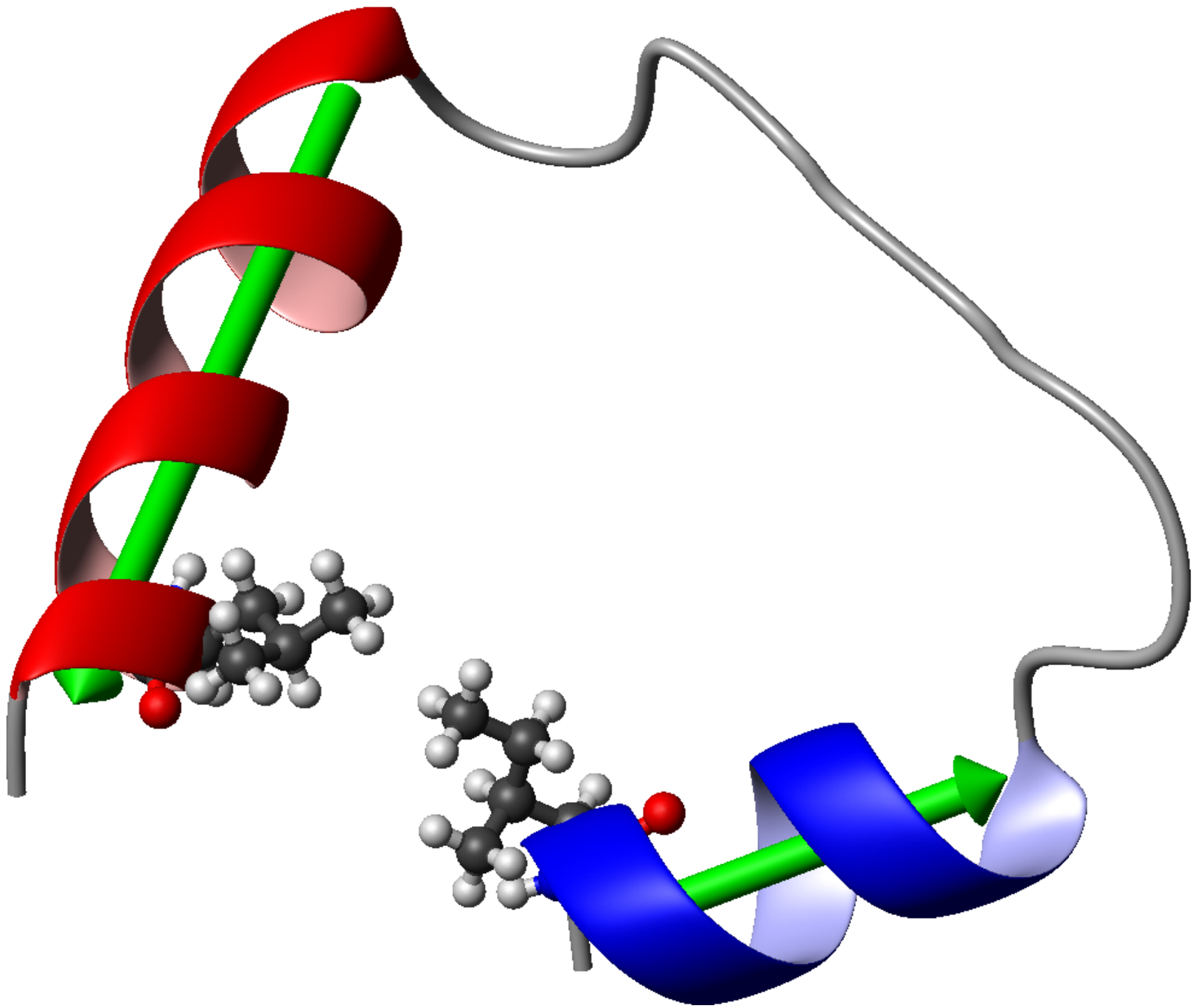
$$\frac{S}{S_{\text{ref}}} = \left(\frac{r_{\text{ref}}}{r}\right)^6 \tag{1}$$

$$r = r_{\text{ref}} \sqrt[6]{\frac{S_{\text{ref}}}{S}} \tag{2}$$

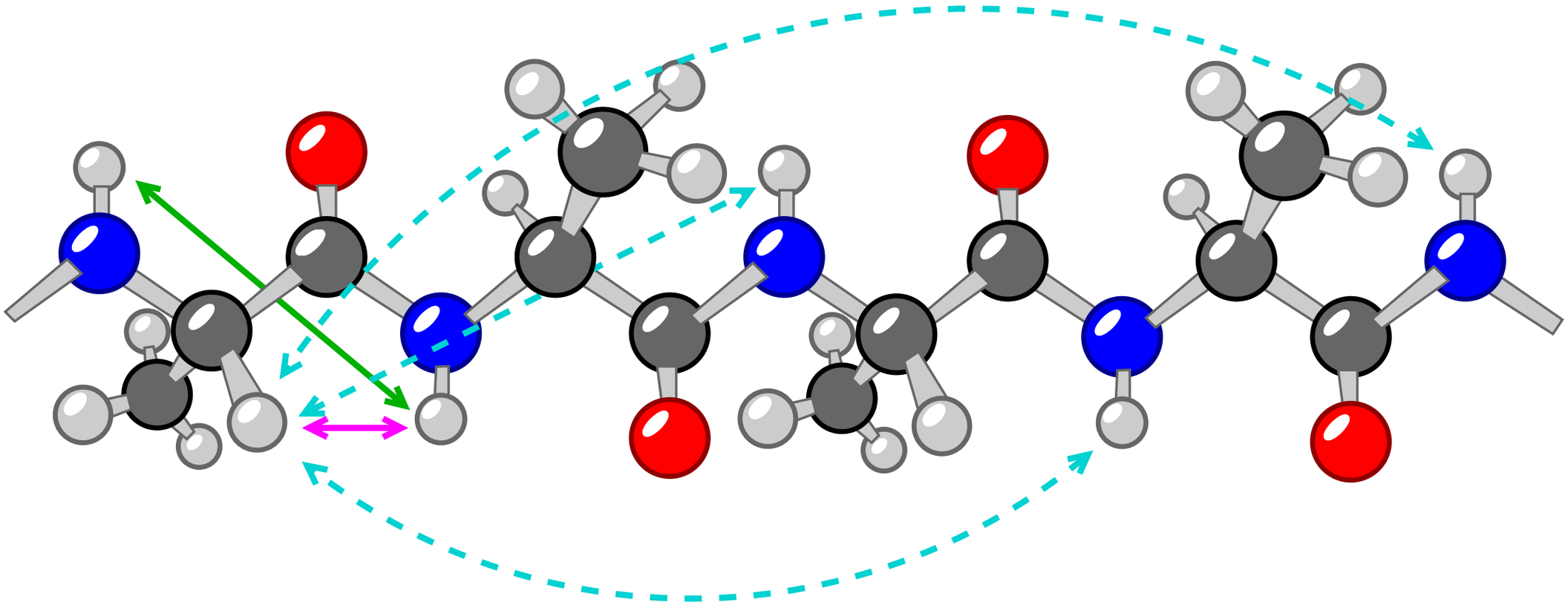
Referenční protony		vzdálenost
geminální v methylenu	H–C–H	0,17 nm
vicinální v aromatickém kruhu	H–C=C–H	0,25 nm
meta v aromatickém kruhu	H–C=CH–C–H	0,42 nm

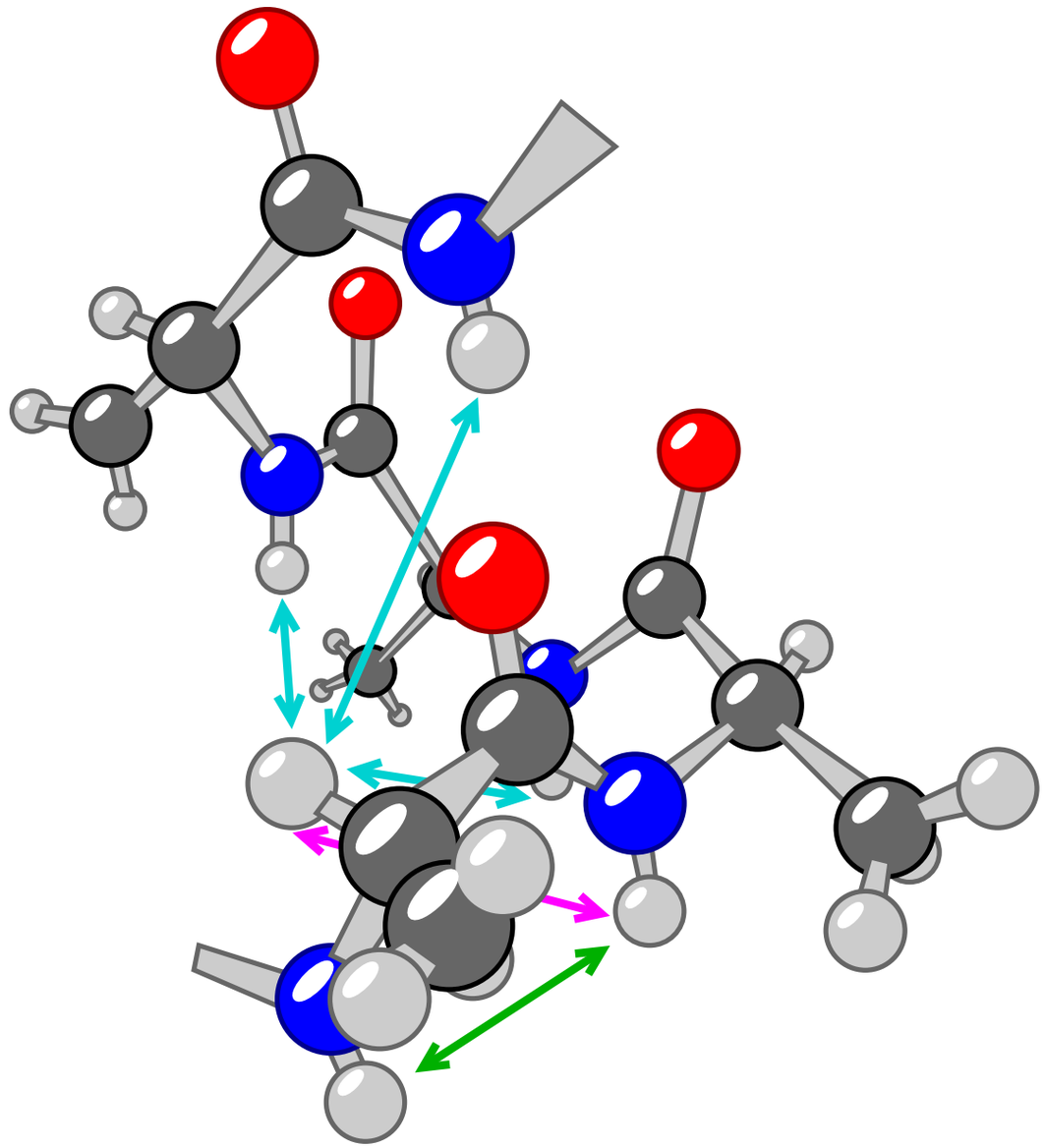

Interakční konstanta / Hz
12
10
8
6
4
2
0
-180
-120
-60
0
60
120
180
ϕ / stupně
$H^N(k)$-$H^\alpha(k)$
$H^N(k)$-$C'(k)$
$H^N(k)$-$C^\beta(k)$
$C'(k-1)$-$H^\alpha(k)$
$C'(k-1)$-$C^\beta(k)$
$C'(k-1)$-$C'(k)$

Zbytkové dipólové interakce $\propto \langle 3\cos^2\theta - 1\rangle \Rightarrow$ orientace



Data	β-list	α-šroubovice
$\delta(\mathrm{C}')$, $\delta(\mathrm{C}^{\alpha})$	$\downarrow$	$\uparrow$
$\delta(\mathrm{C}^{\beta})$, $\delta(\mathrm{H}^{\alpha})$	$\uparrow$	$\downarrow$
$\lvert \mathrm{H}_i^{\alpha}\mathrm{H}_{i+1}^{\mathrm{N}} \rvert$	0,22 nm	0,35 nm
$\lvert \mathrm{H}_i^{\mathrm{N}}\mathrm{H}_{i+1}^{\mathrm{N}} \rvert$	0,40 nm	0,28 nm
$\lvert \mathrm{H}_i^{\alpha}\mathrm{H}_{i+2}^{\mathrm{N}} \rvert$	daleko	0,42 nm
$\lvert \mathrm{H}_i^{\alpha}\mathrm{H}_{i+3}^{\mathrm{N}} \rvert$	daleko	0,34 nm
$\lvert \mathrm{H}_i^{\alpha}\mathrm{H}_{i+4}^{\mathrm{N}} \rvert$	daleko	0,42 nm
${}^3J(\mathrm{H}_i^{\mathrm{N}}\mathrm{H}_i^{\alpha})$	$>$ 8 Hz	$<$ 5 Hz



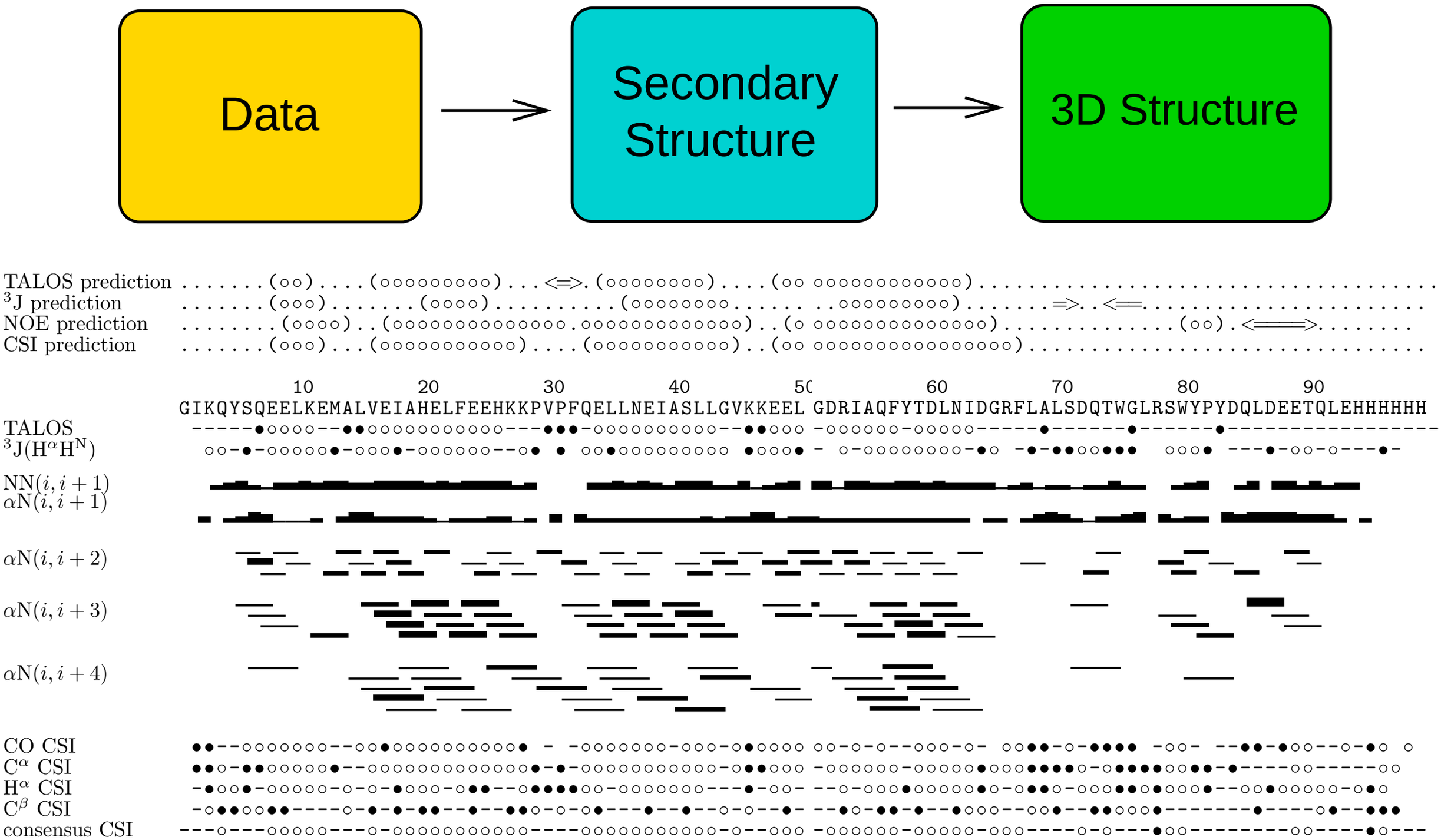


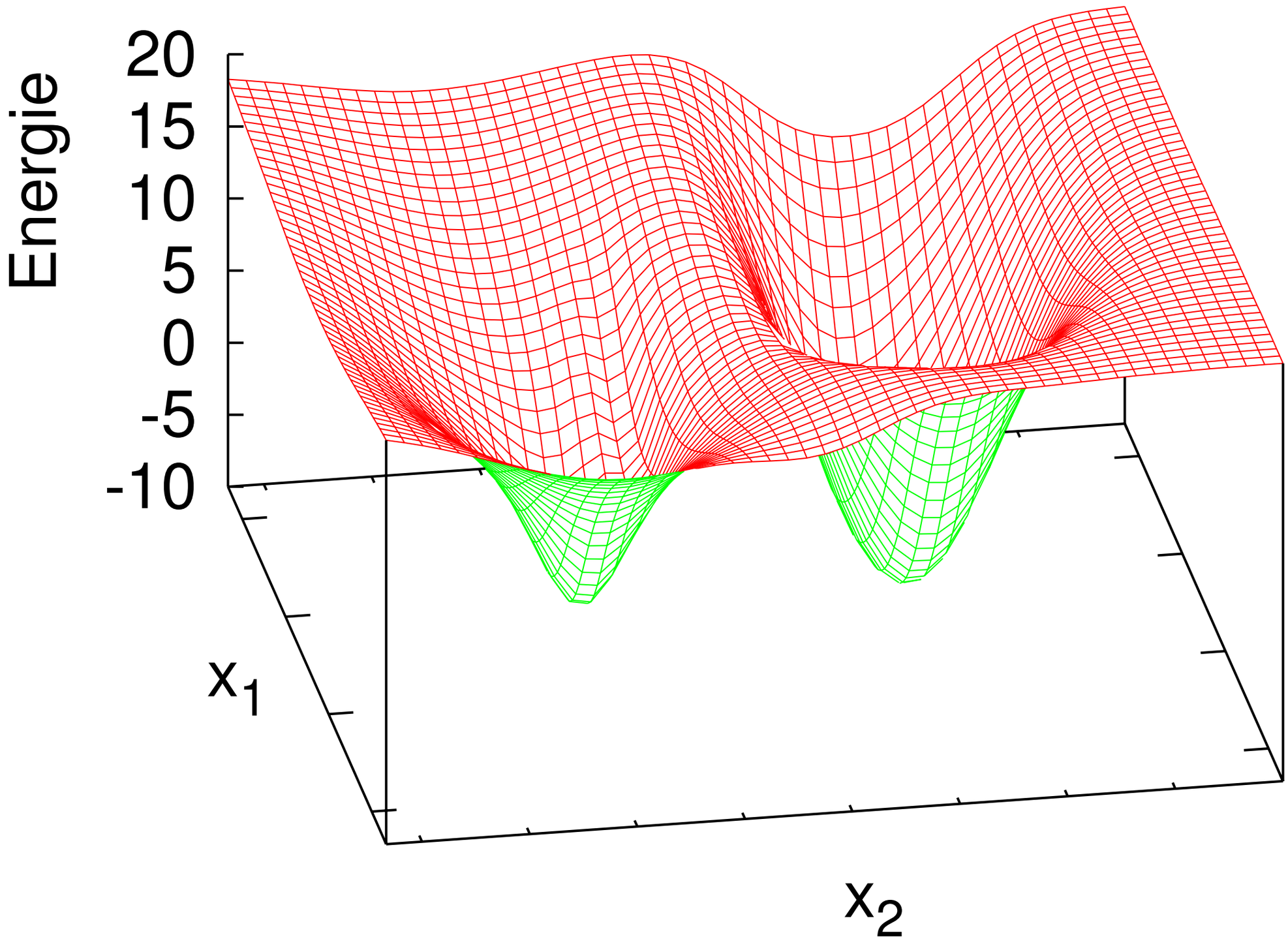
α-helix

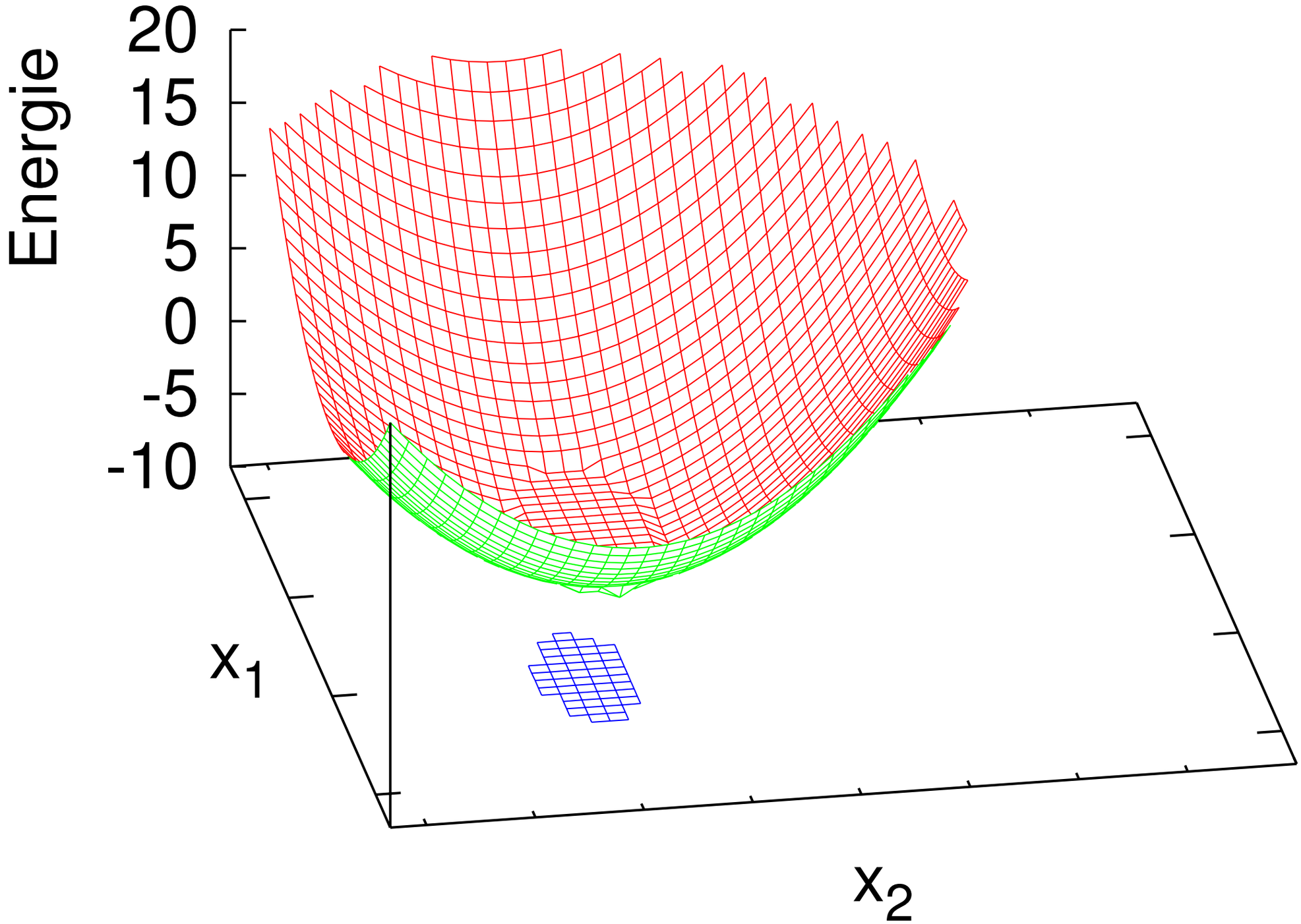
3_{10}-helix

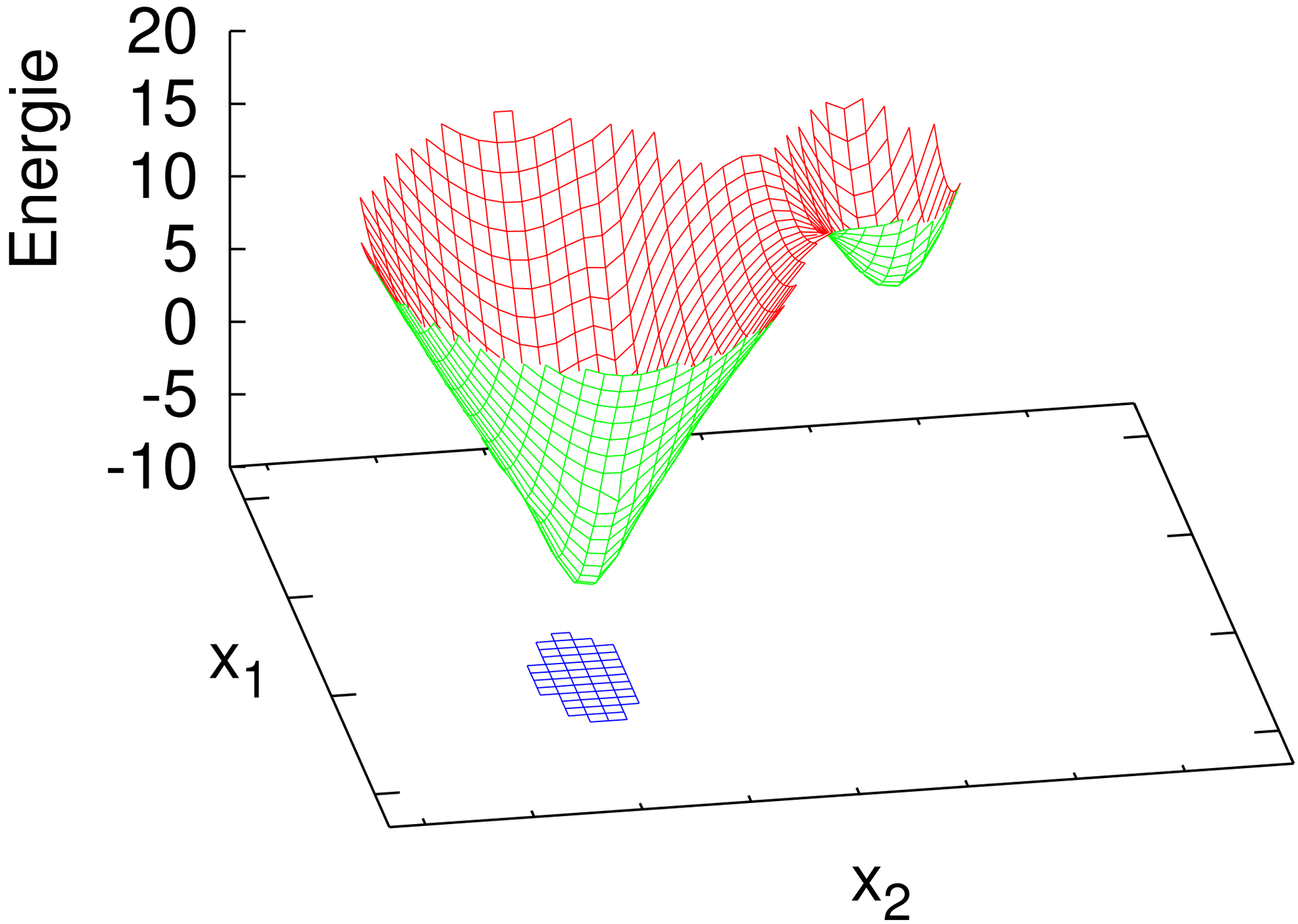
antiparallel β-sheet

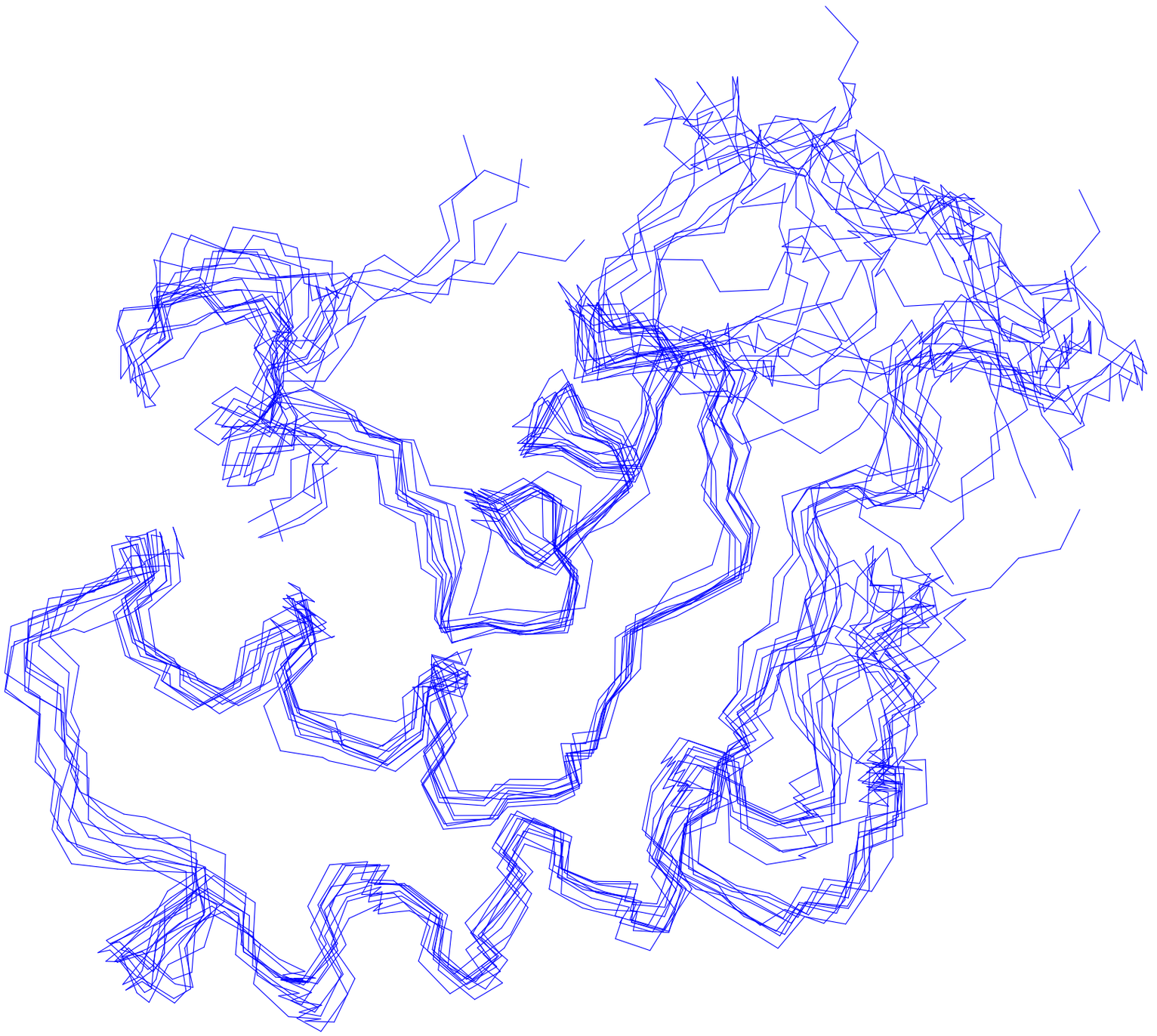
parallel β-sheet

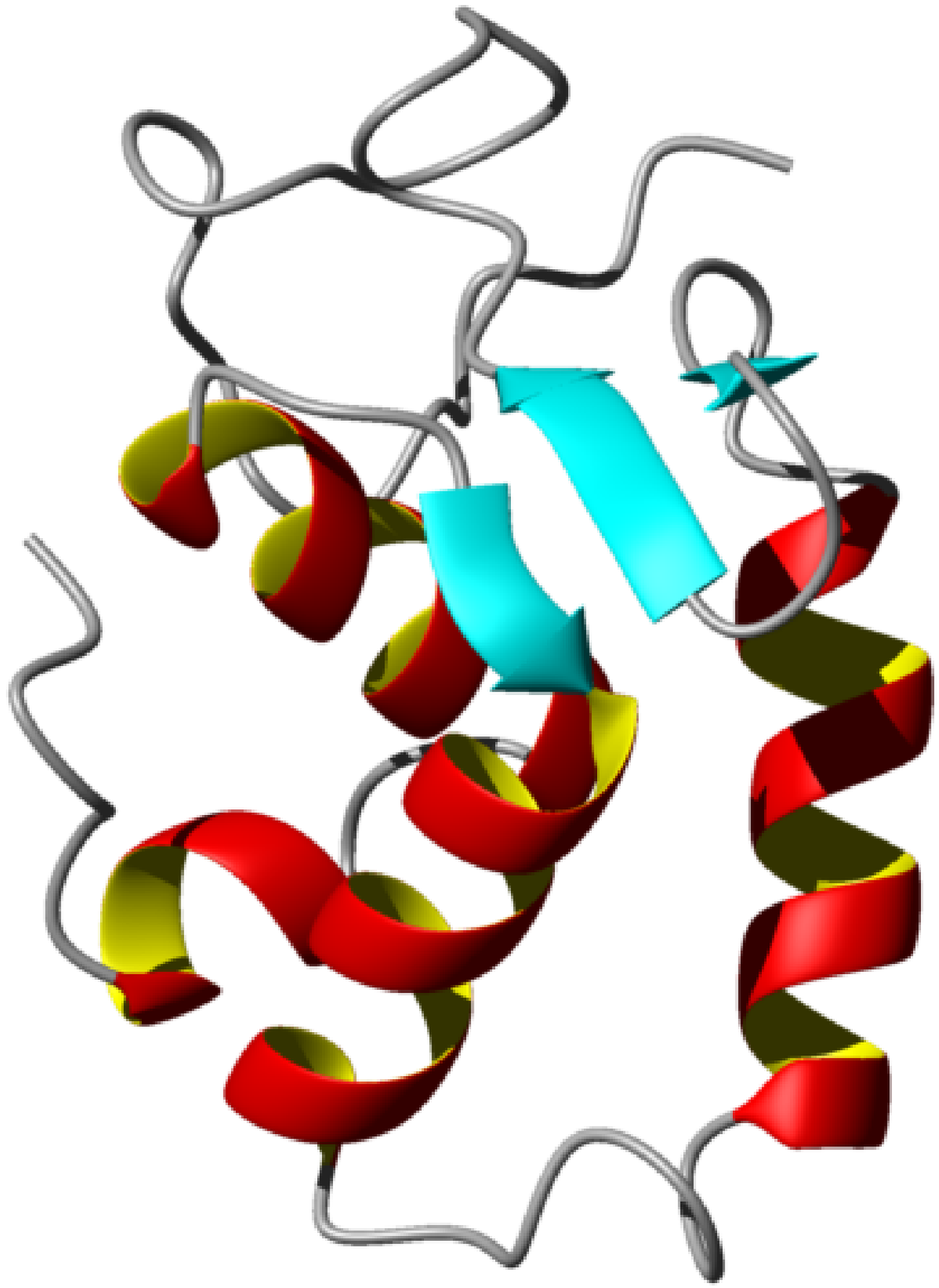

Data
Secondary Structure
3D Structure
TALOS prediction
3J prediction
NOE prediction
CSI prediction
10 20 30 40 50 60 70 80 90
GIKQYSQEELKEMALVEIAHELFEEHKKPVPFQELLNEIASLLGVKKEEL GDRIAQFYTDLNIDGRFLALSDQTWGLRSWYPYDQLDEETQLEHHHHHH
TALOS
3J(HαHN)
NN(i, i + 1)
αN(i, i + 1)
αN(i, i + 2)
αN(i, i + 3)
αN(i, i + 4)
CO CSI
Cα CSI
Hα CSI
Cβ CSI
consensus CSI

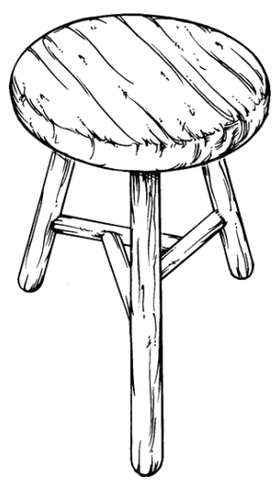

Energie
20
15
10
5
0
-5
-10
x1
x2

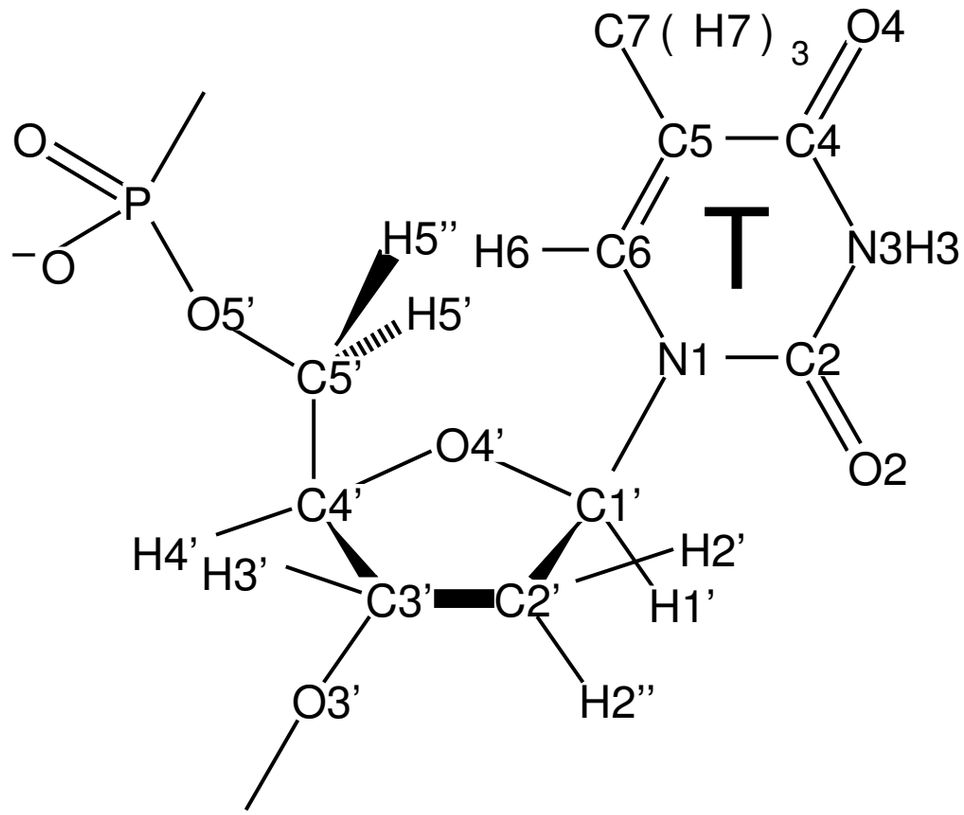

Energie
20
15
10
5
0
-5
-10
x1
x2

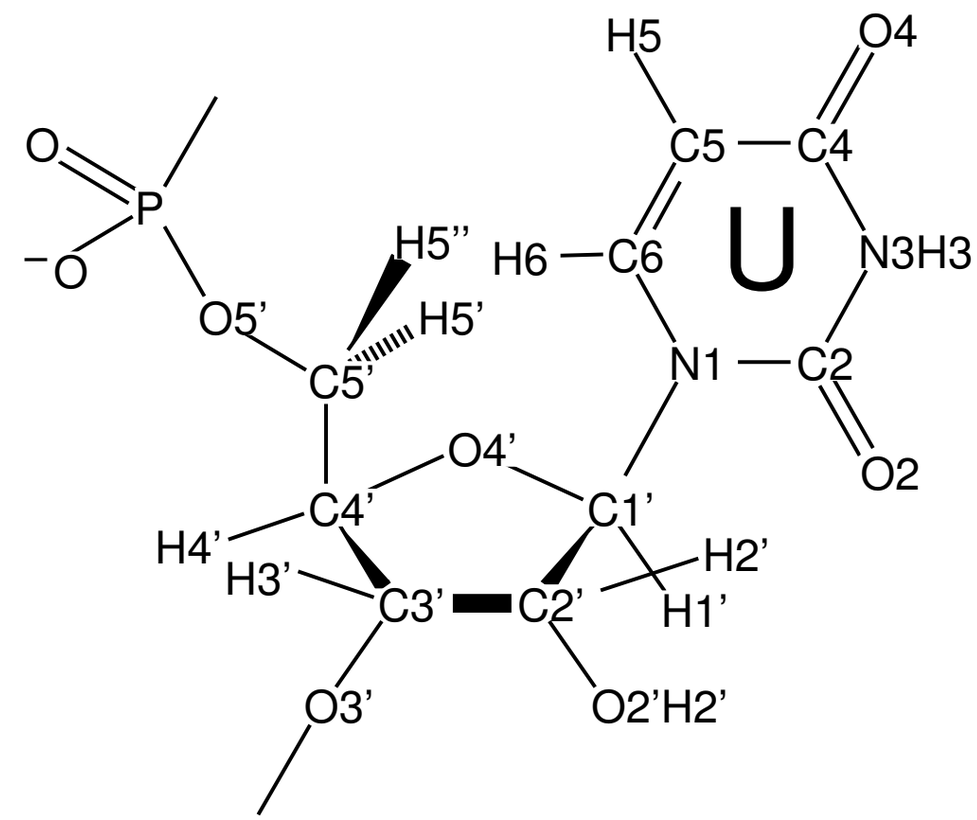

Energie
20
15
10
5
0
-5
-10
x1
x2

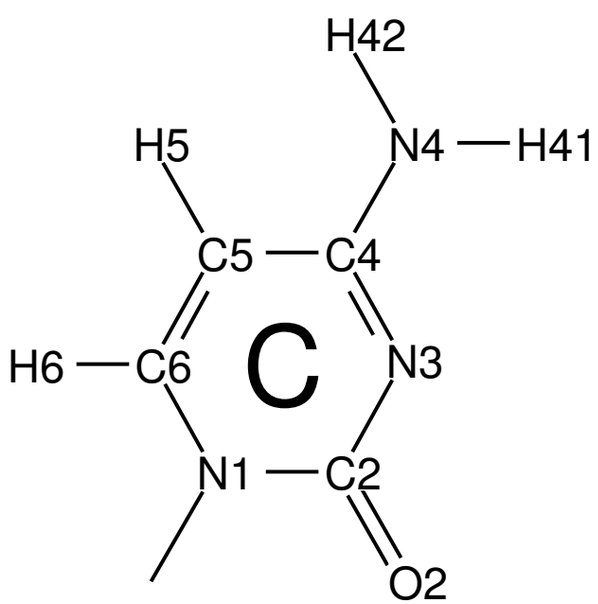


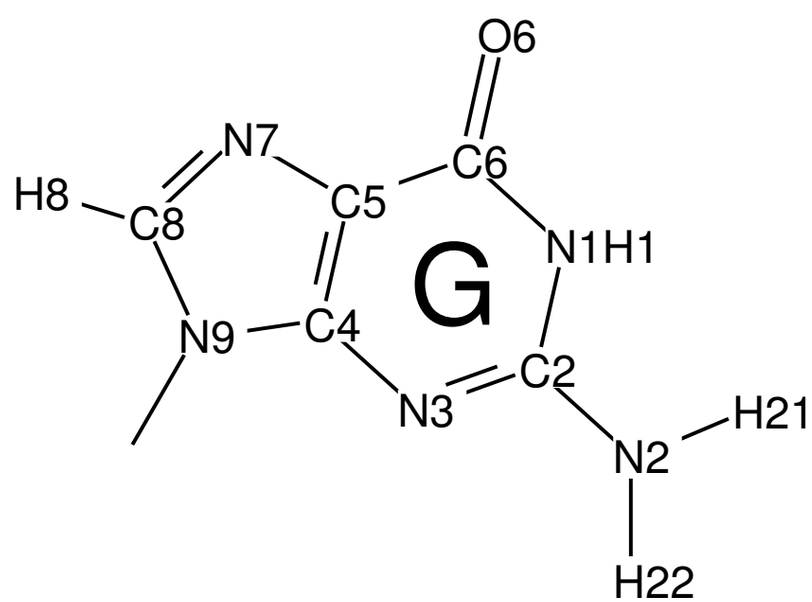


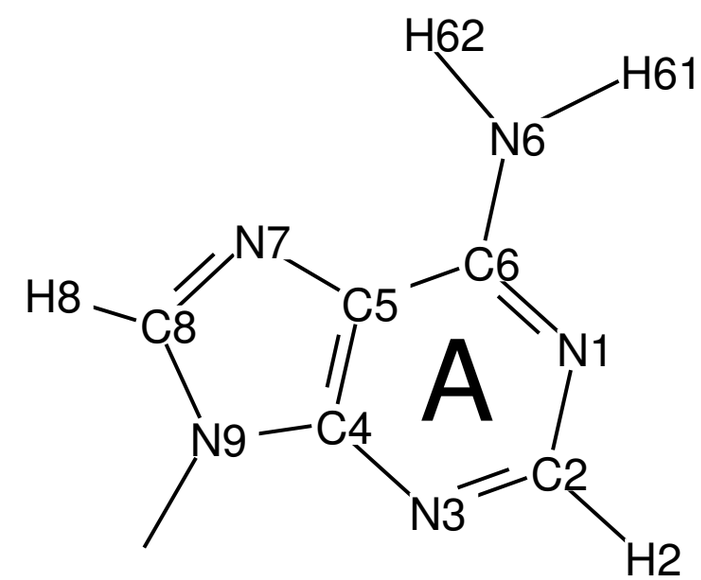



C7 (H7) 3
O4
O
P
− O
C5
C4
H5''
H6
C6
T
N3H3
O5'
H5'
C5'
N1
C2
O4'
O2
C4'
C1'
H4'
H3'
H2'
C3'
C2'
H1'
O3'
H2''


H5
O4
O
P
− O
C5
C4
H5''
H6
C6
U
N3H3
O5'
H5'
C5'
N1
C2
O4'
O2
C4'
C1'
H4'
H3'
H2'
C3'
C2'
H1'
O3'
O2'H2'

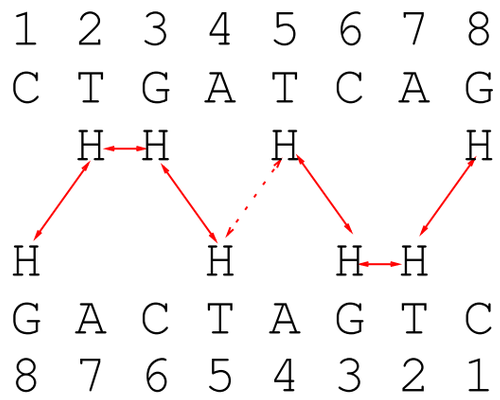

H42
H5
N4
H41
C5
C4
H6
C6
C
N3
N1
C2
O2

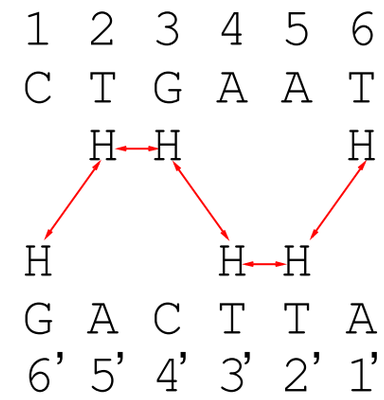

O6
N7
C6
H8
C8
C5
N1H1
G
N9
C4
N3
C2
N2
H21
H22

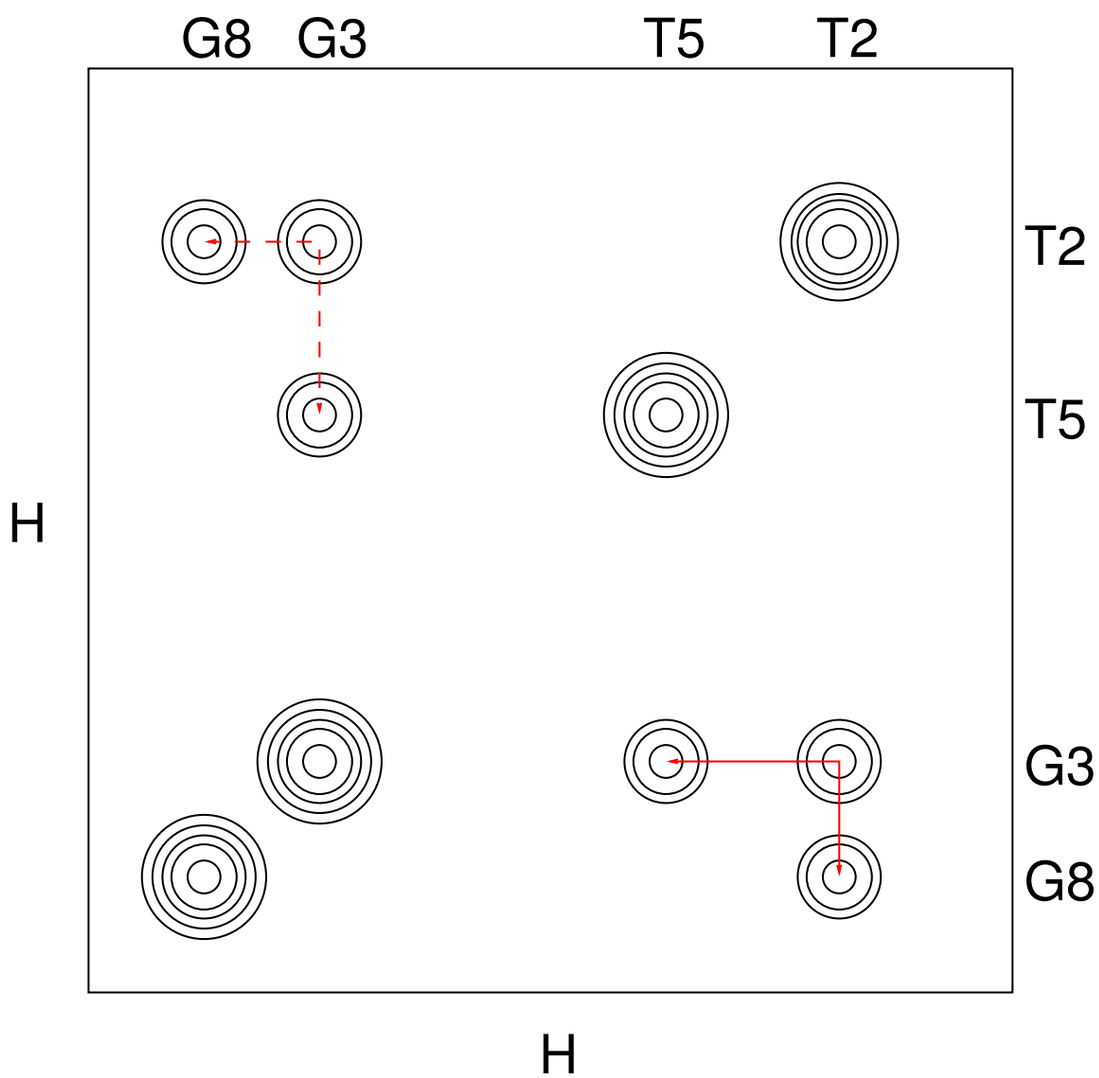

H62
H61
N6
N7
C6
H8
C8
C5
N1
A
N9
C4
N3
C2
H2

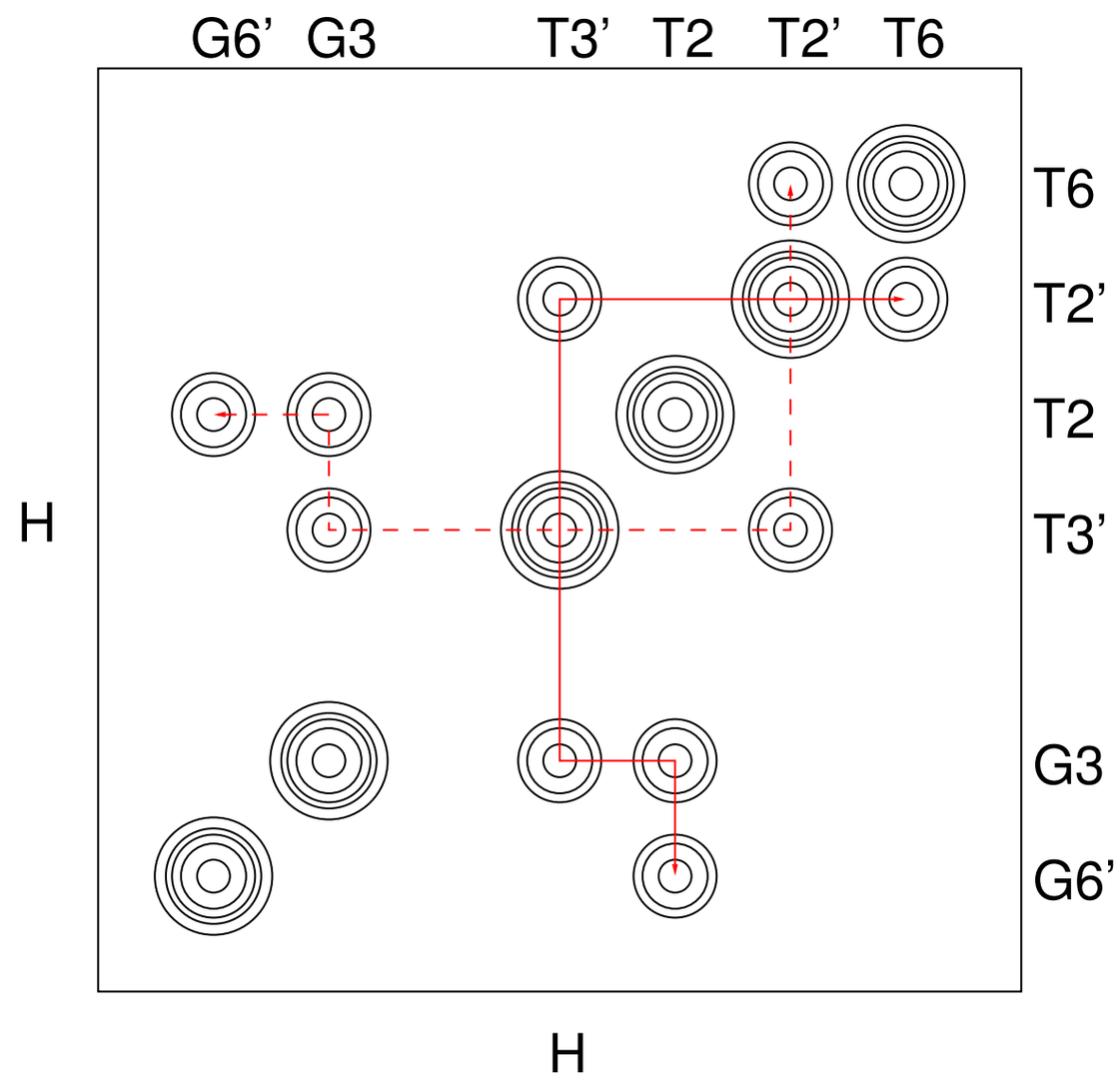
DNA double helix B

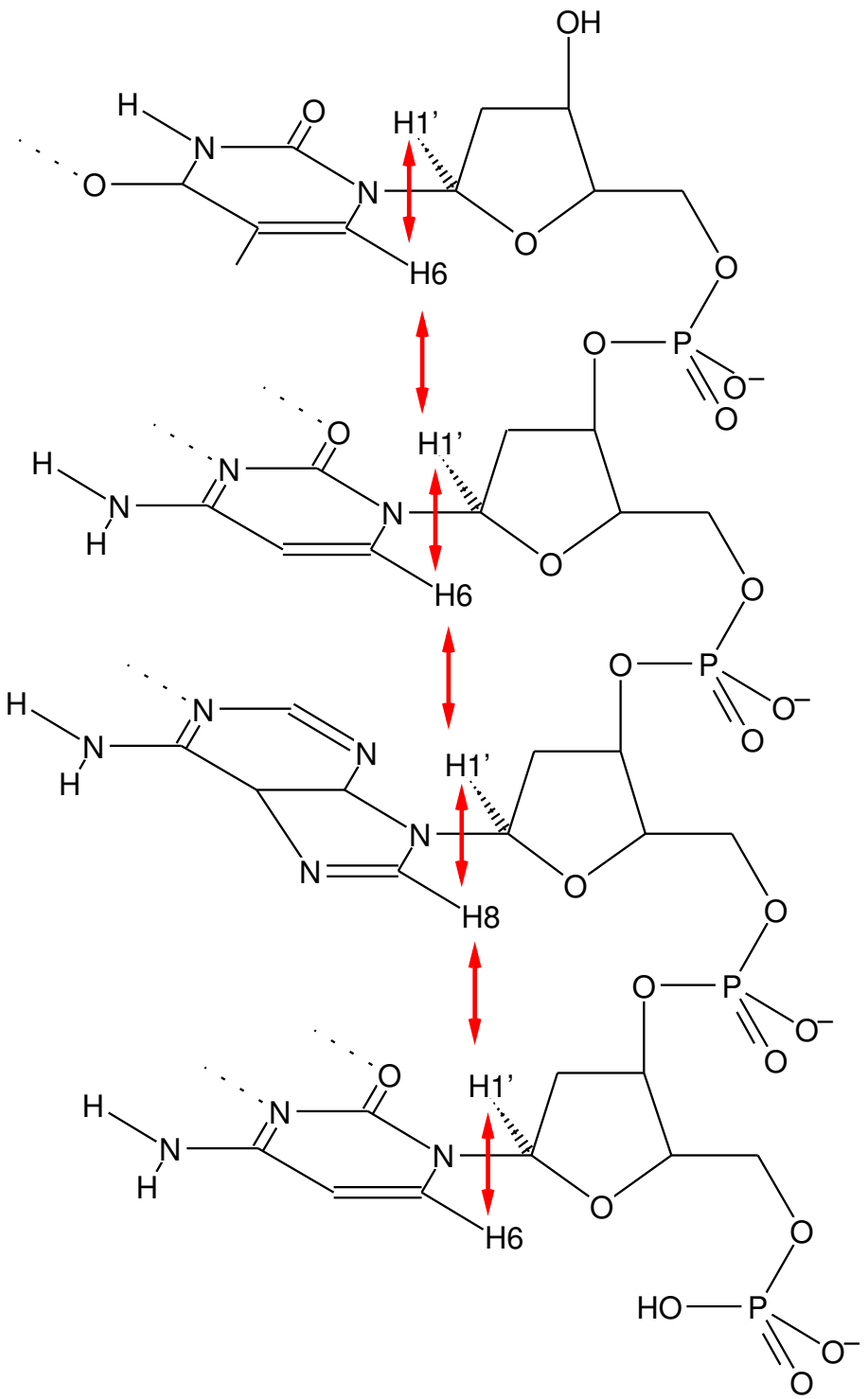
DNA double helix A

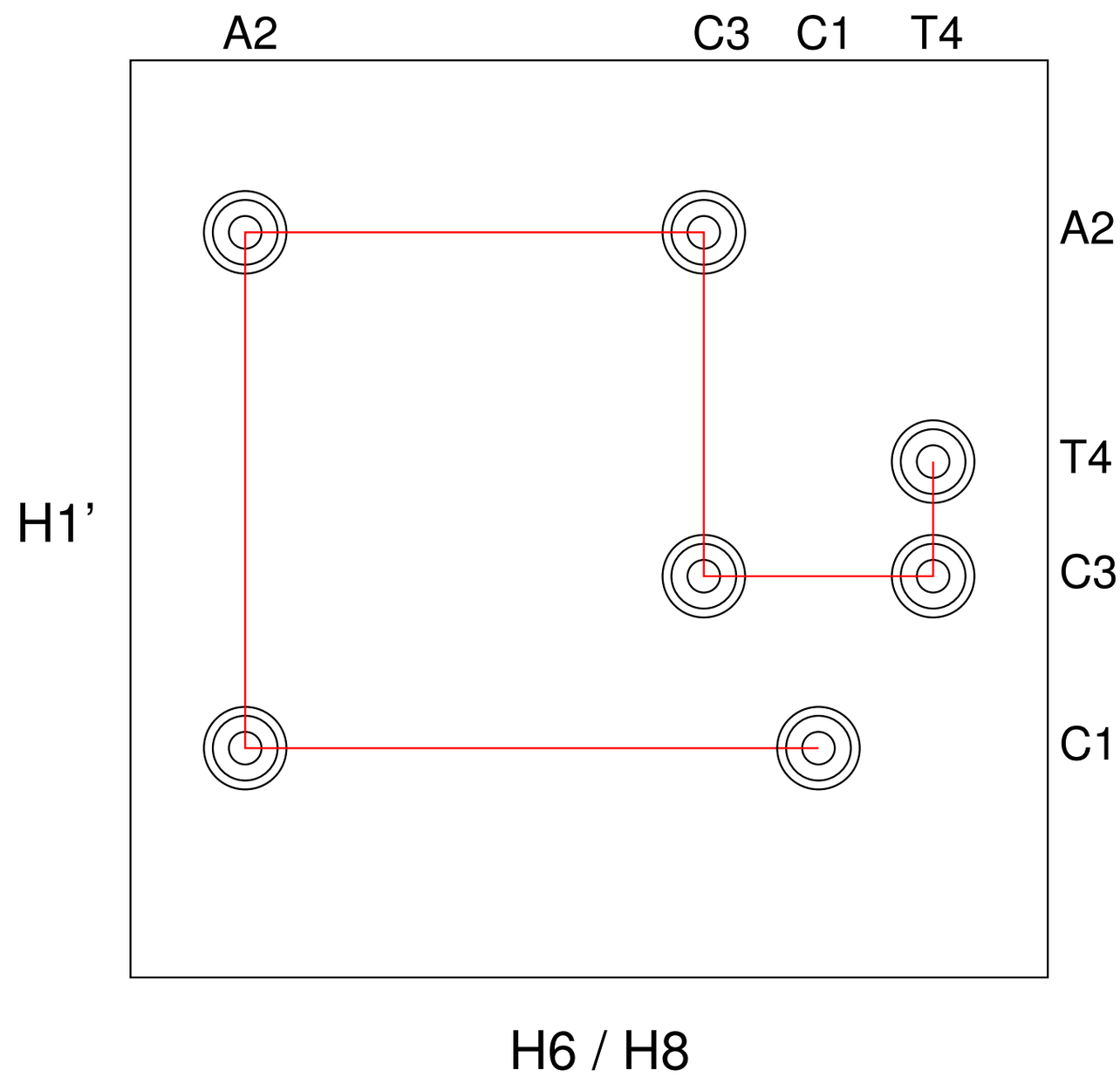

1 2 3 4 5 6 7 8
C T G A T C A G
H H H H
H H H H
G A C T A G T C
8 7 6 5 4 3 2 1


1 2 3 4 5 6
C T G A A T
H H H
H H H
G A C T T A
6' 5' 4' 3' 2' 1'


G8 G3 T5 T2
T2
T5
H
G3
G8
H


G6' G3 T3' T2 T2' T6
T6
T2'
T2
H
T3'
G3
G6'
H


OH
H
O
N
H1'
N
O
H6
O
O
P
O⁻
O
H
N
O
H1'
N
H
N
O
H6
O
O
P
O⁻
O
H
N
N
H
H1'
N
N
N
H8
O
O
P
O⁻
O
H
N
O
H1'
N
H
N
O
H6
O
HO
P
O⁻
O


A2
C3
C1
T4
A2
T4
C3
C1
H1'
H6 / H8