INSTITUT FÜR
ORGANISCHE CHEMIE
UNIVERSITÄT REGENSBURG

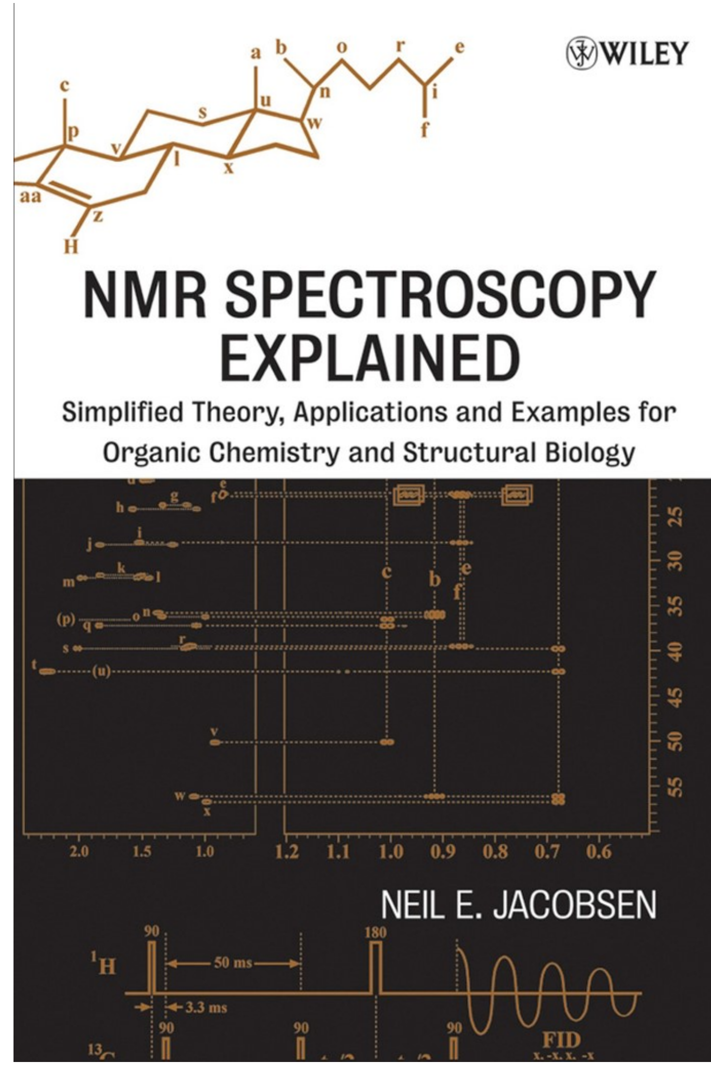
THREE CUPS OF "MODERN NMR SPECTROSCOPY" ESPRESSO

Ilya G. Shenderovich

http://homepages.uni-regensburg.de/~shi56087/

Physical background of NMR	NMR in practice	A research lecture
1. Classical and quantum-mechanical descriptions 2. T_1 and T_2 Relaxations 3. Chemical shift 4. Spin-spin scalar coupling 5. Spin systems of the first and the second orders 6. Chemical exchange 7. Two-dimensional NMR	1. NMR in solution 1.1 From spectrum to structure 1.2. Typical protocol for structure elucidation 2. NMR in the solid state 2.1 Orientation-dependent interactions 2.1 Measurements of internuclear distances 2.3 NMR of surfaces and amorphous solids	NMR Study of Hydrogen Bonding in Solution Down to 100 K

Physical background of NMR



University of California, Irvine
Understanding NMR Spectroscopy
James Keeler, *University of Cambridge*
http://www-keeler.ch.cam.ac.uk/lectures/Irvine/

Sir Paul Callaghan (1947 – 2012)

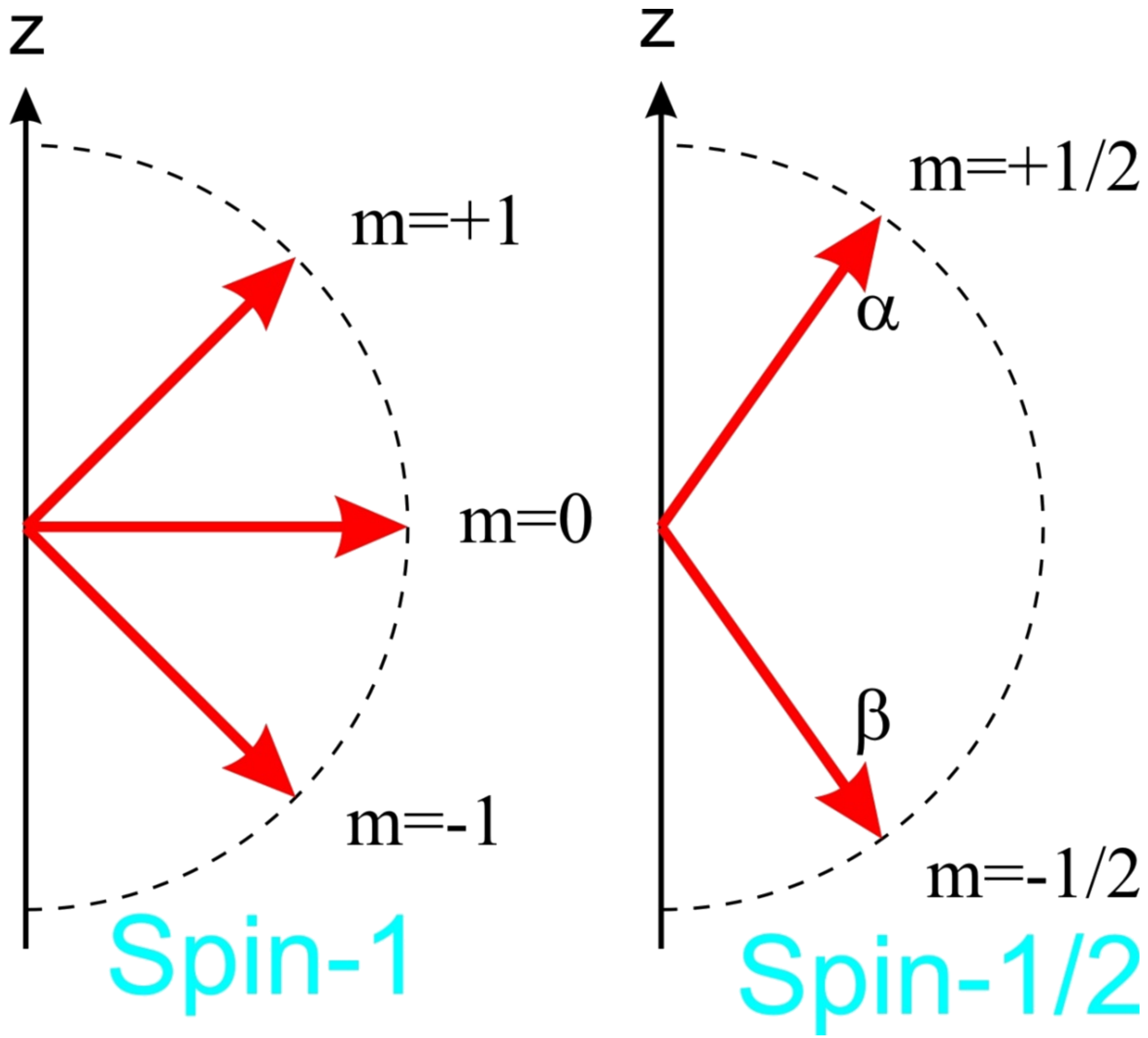
Introductory NMR & MRI

https://www.youtube.com/watch?v=7aRKAXD4dAg&list=PLD14D78BC61685BD7

Nuclear magnetic moment

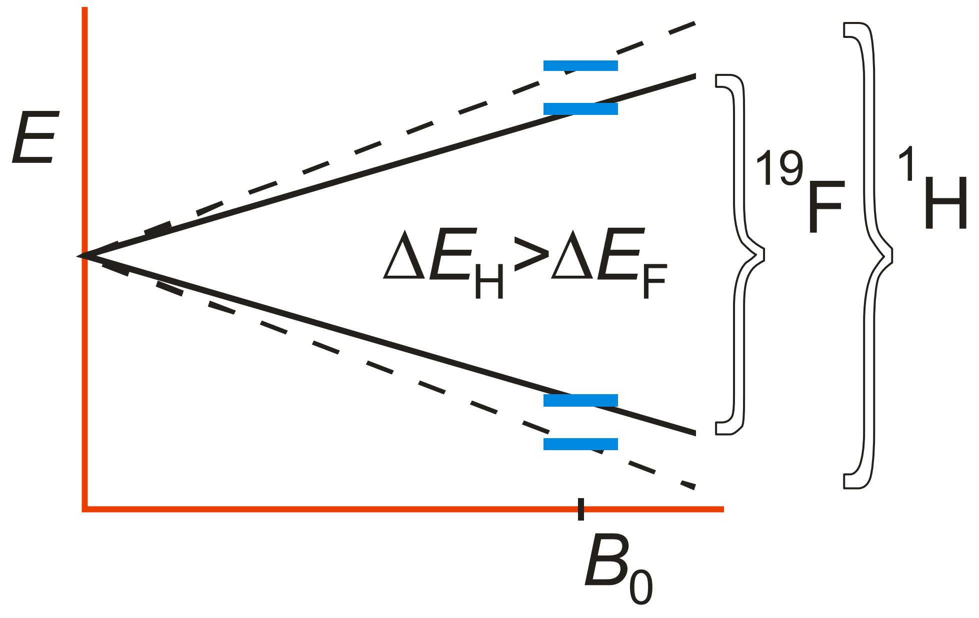
Particle	Mass	Charge	Spin (angular momentum)	Magnetic dipole moment
Electron	√	√	√	√
Proton	√	√	√	√
Neutron	√	×	√	√
Neutrino	√	×	√	×
Photon	×	×	√	×
Graviton (?)	×	×	√	×
Carbon-12	√	√	×	×

Angular momentum

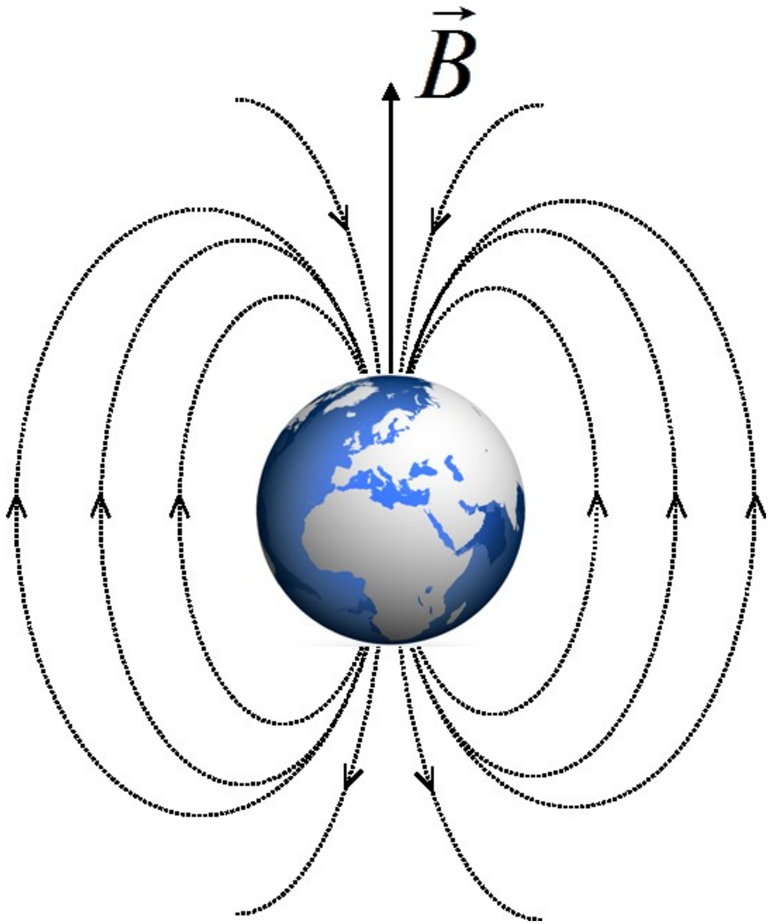


Magnetic dipole moment

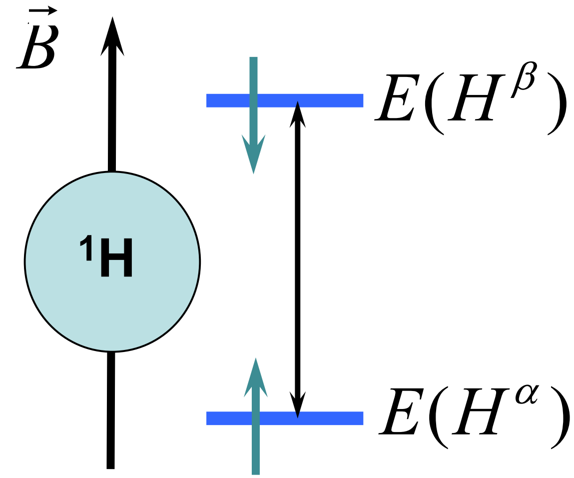
$\Delta E \sim \gamma$



Nuclear magnetic resonance spectroscopy



$$\vec{B} = 5 \cdot 10^{-5}\,T$$



$$\Delta E = 2 \cdot \mu \cdot \vec{B}$$

$$\Delta E = h \cdot \Delta \nu$$

$$\Delta \nu = \frac{2 \cdot \mu \cdot \vec{B}}{h} \approx 2000\ Hz$$

Boltzmann distribution

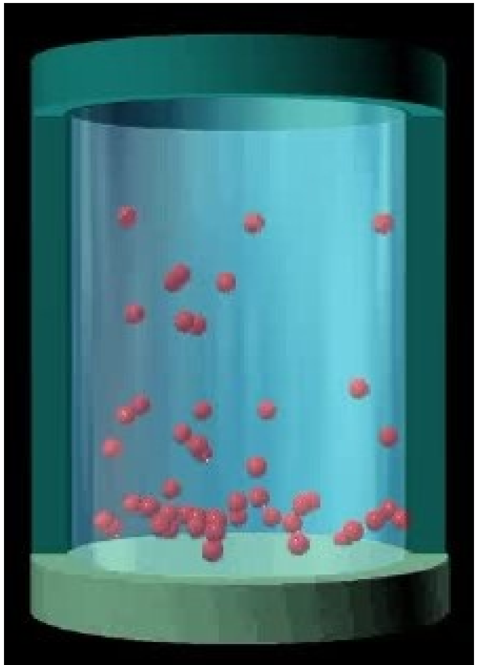
The potential energy of a molecule : $E(h) = m \cdot g \cdot h,$

The pressure of the idealize gass: $P = n \cdot k \cdot T,$

Let's assume for simplicity that T does not depend on h, then: $\frac{dP}{dh} = \frac{dn}{dh} \cdot k \cdot T.$

The pressure of a gas column of the height h on unit area is:

$P = P_0 - m \cdot g \cdot n \cdot h$ we have $dP = -m \cdot g \cdot n \cdot dh.$



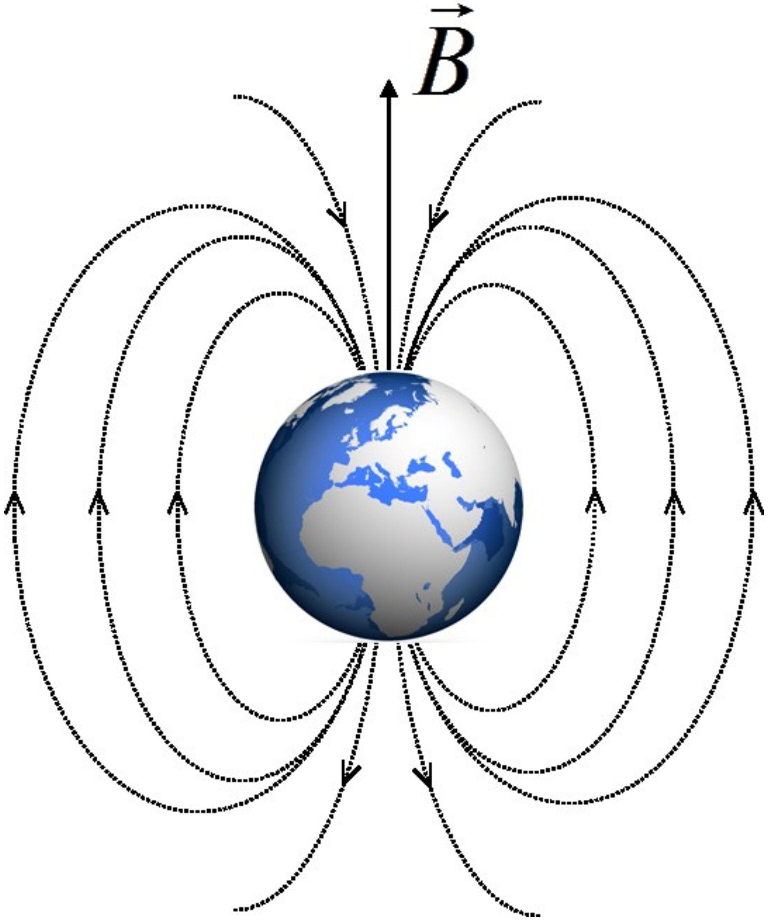
$$\frac{dP}{dh} = \frac{dn}{dh} \cdot k \cdot T = -m \cdot g \cdot n \quad \Rightarrow \quad n \propto \exp(-\frac{m \cdot g \cdot h}{k \cdot T}) = \exp(-\frac{E}{k \cdot T})$$

$$n(h_1) = A \cdot \exp(-\frac{E_1}{k \cdot T}) \quad \text{and} \quad n(h_2) = A \cdot \exp(-\frac{E_2}{k \cdot T}) \quad \Rightarrow$$

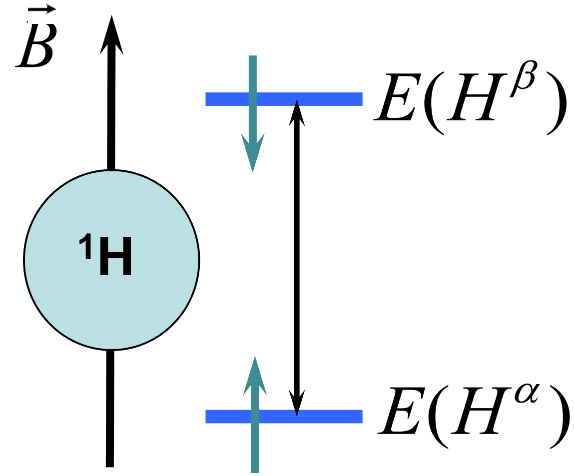
$$\frac{n(h_1)}{n(h_2)} = \exp(-\frac{E_1 - E_2}{k \cdot T})$$

$$n = n_0 \cdot \exp(-\frac{\Delta E}{k \cdot T})$$

Boltzmann distribution



$$\vec{B} = 5\cdot10^{-5}\,T$$

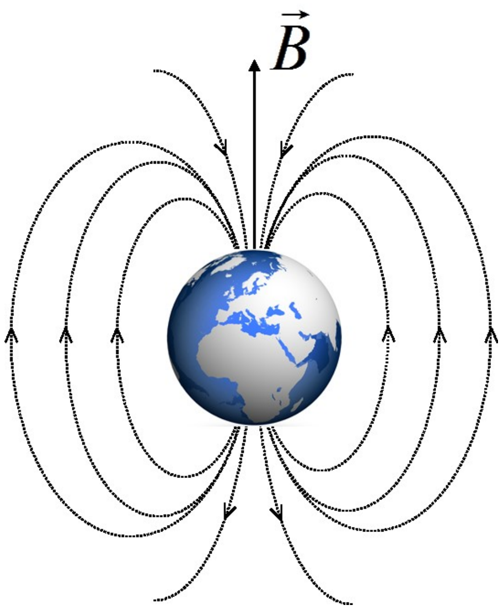


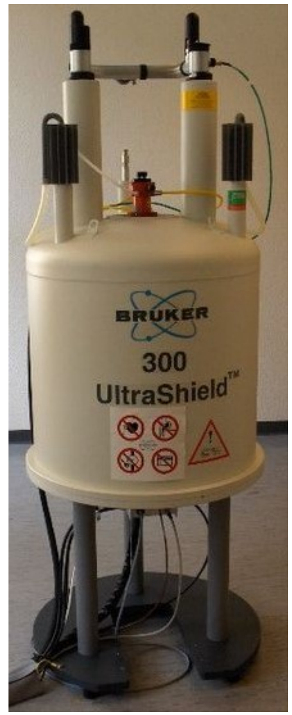
$$\frac{N_\beta}{N_\alpha} = e^{\frac{-\Delta E}{k_B T}} \approx 1 - \frac{-\Delta E}{k_B T} = 1 - \frac{\gamma\hbar B_0}{k_B T}$$

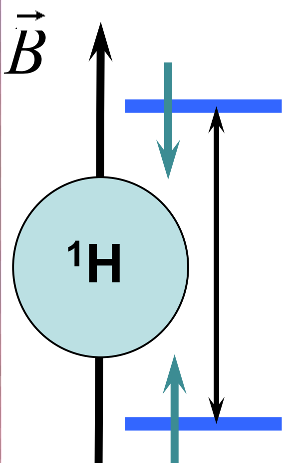
$$\vec{B} = 5\cdot10^{-5}\,T \quad und \quad T = 300\ K$$

$$\frac{N_\beta}{N_\alpha} \approx 3.5\cdot10^{-10}$$

NMR spectrometer

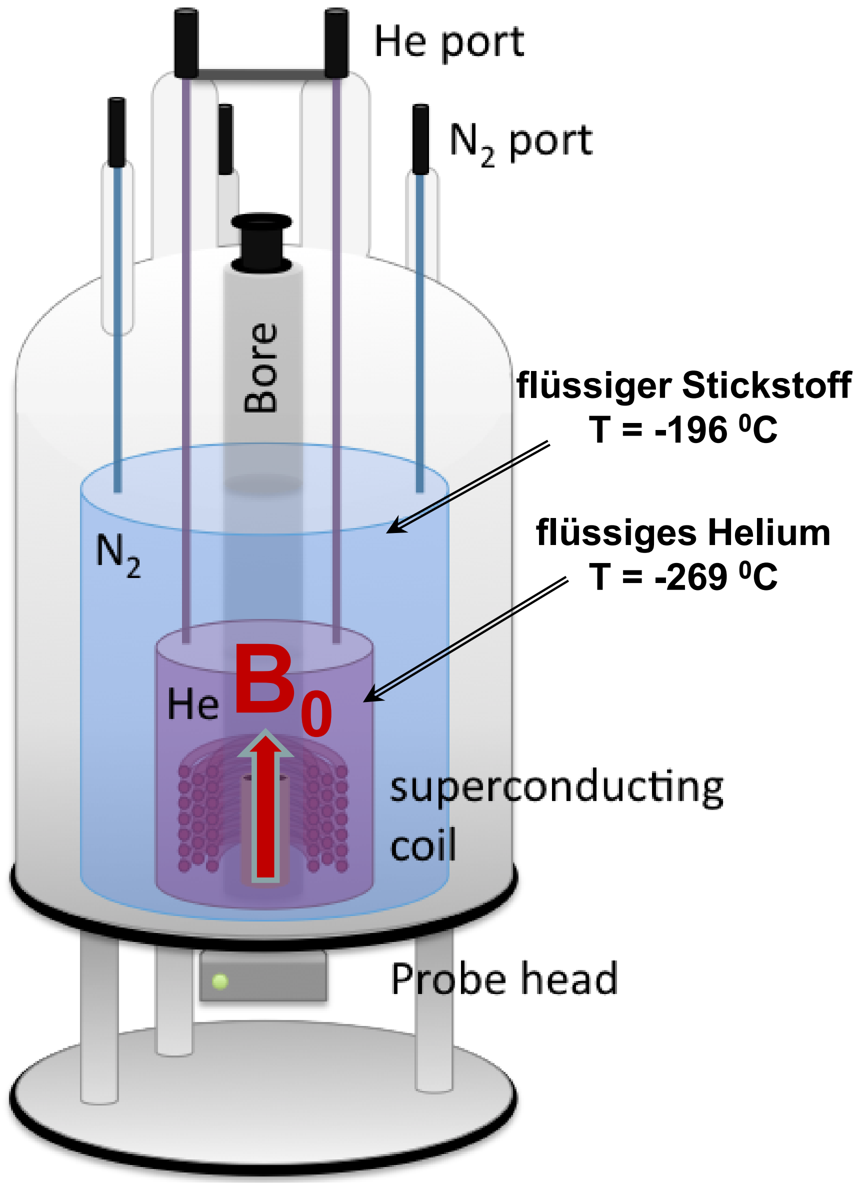




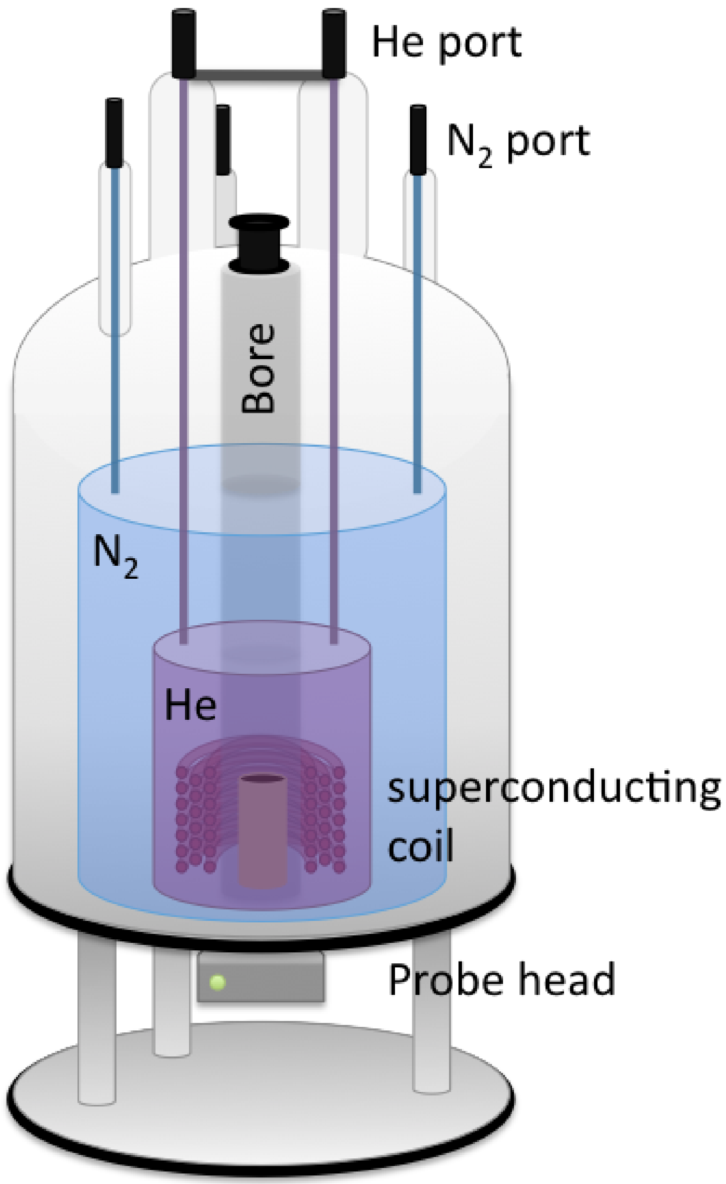


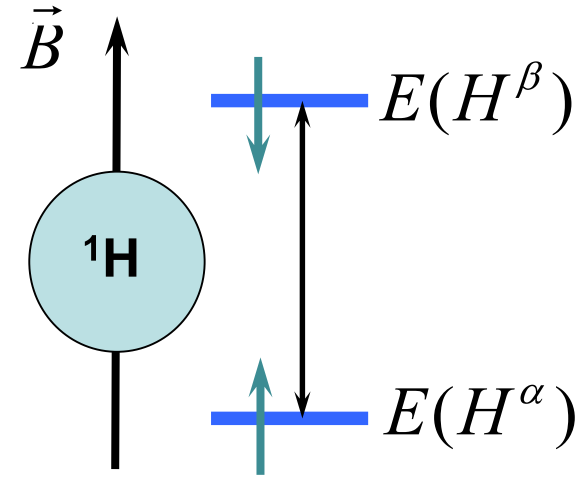
$\vec{B} = 5\cdot 10^{-5}\, T$	$7\, T$	$14\, T$	$24\, T$
$\Delta\nu_{^1H} = 0.002\ MHz$	$300\ MHz$	$600\ MHz$	$1000\ MHz$

Superconducting magnet

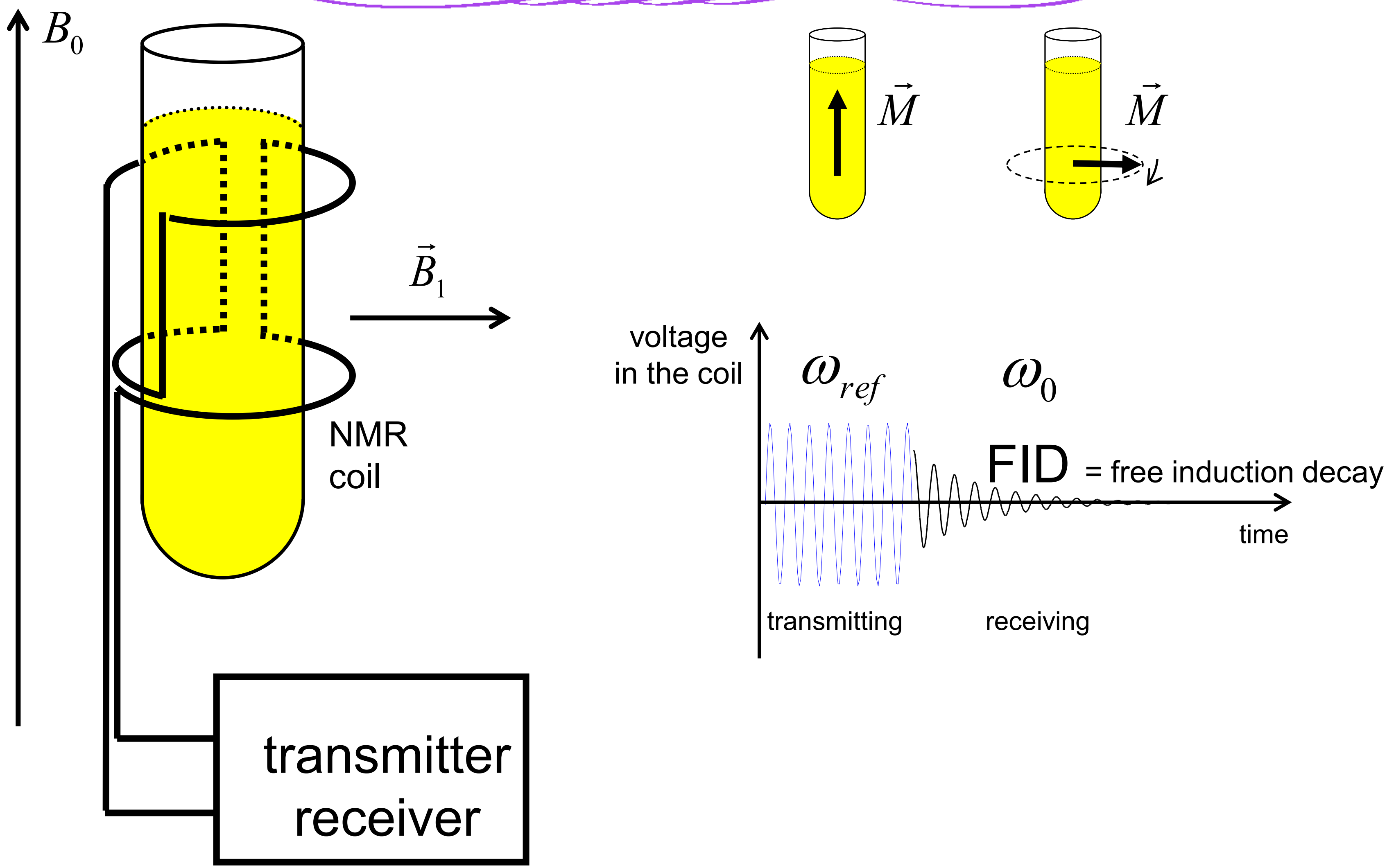


Nuclear magnetic resonance spectroscopy





NMR spectrometer



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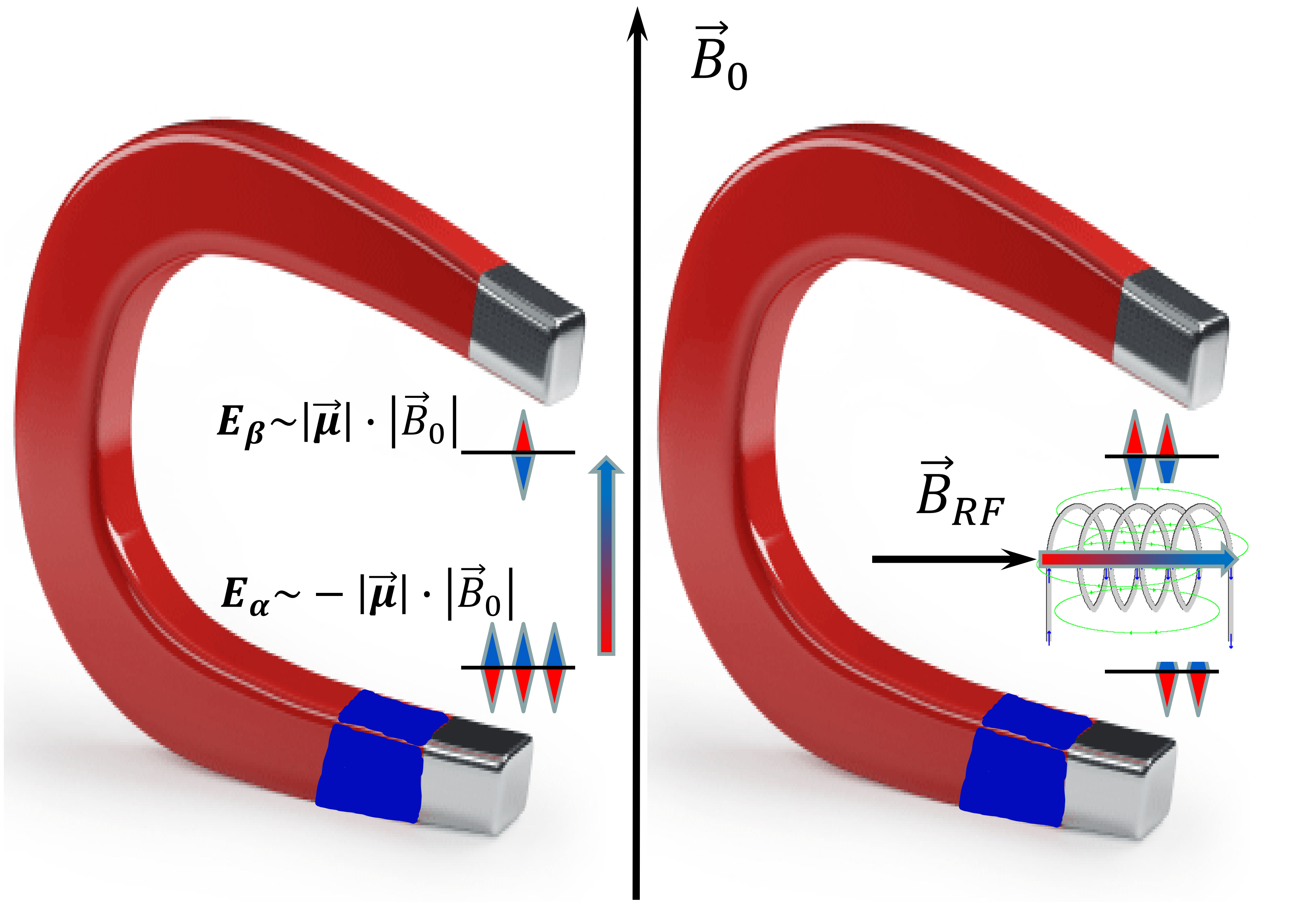
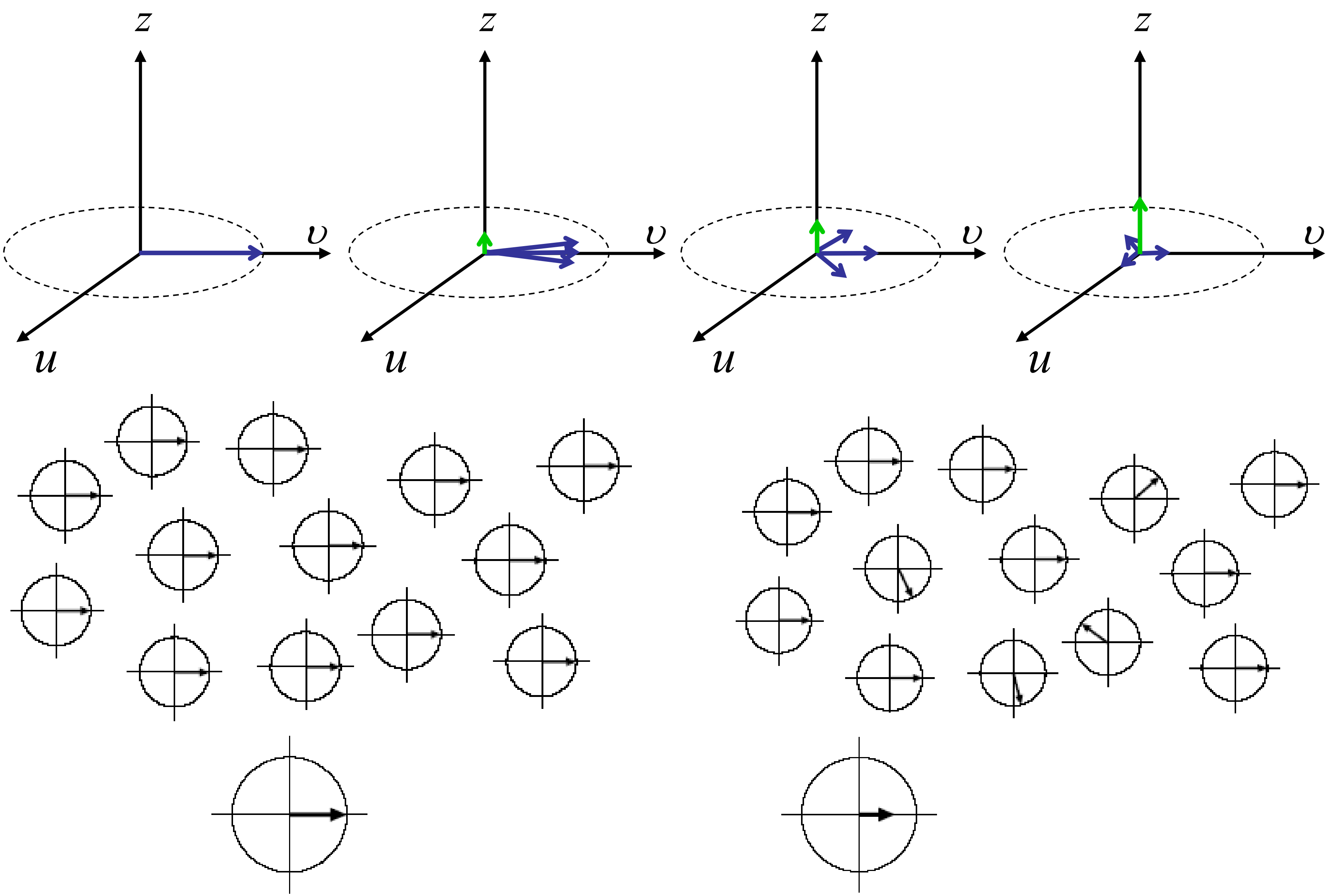
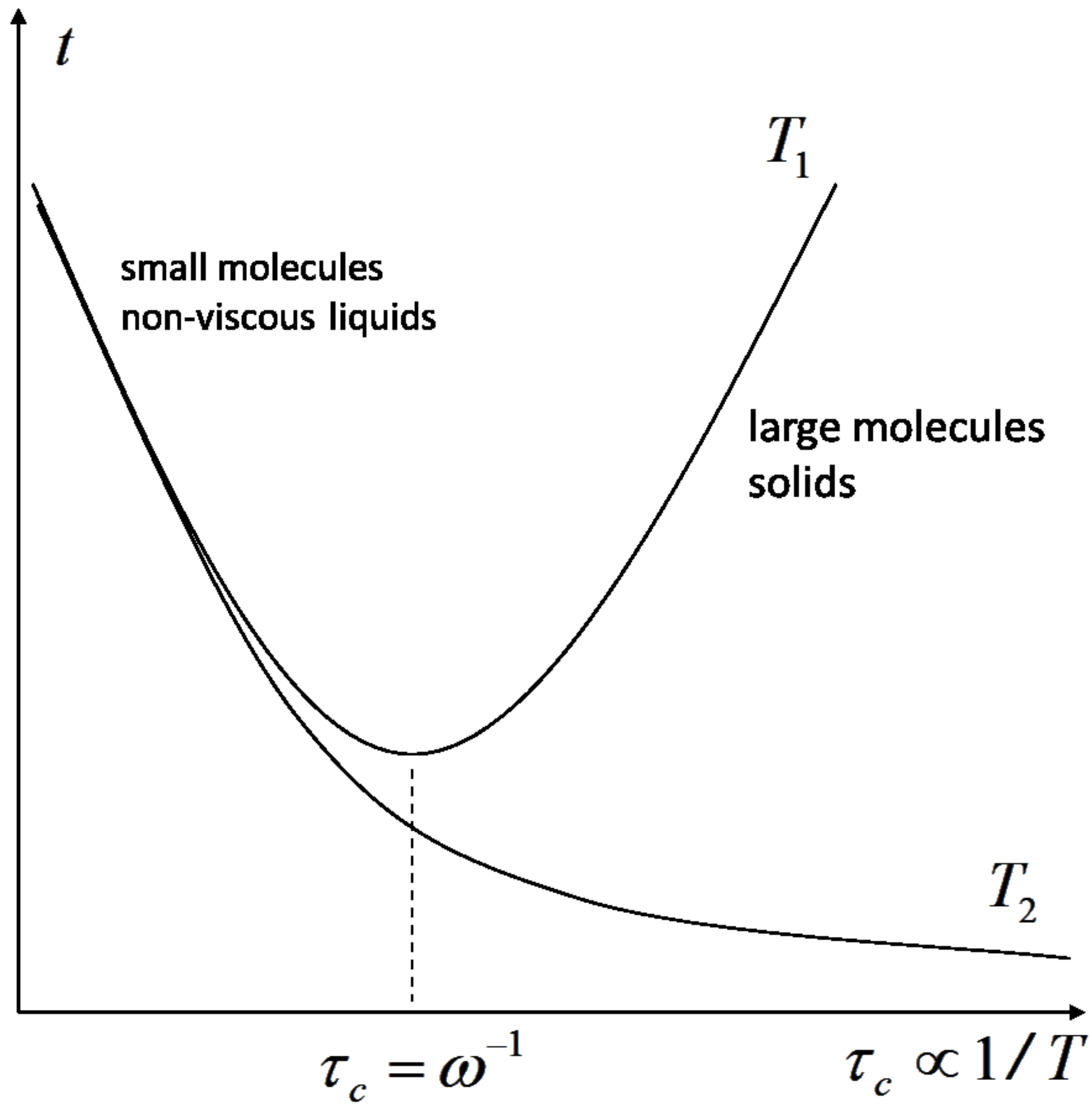


$\vec{B}_0$
$\boldsymbol{E_\beta} \sim |\vec{\boldsymbol{\mu}}| \cdot |\vec{B}_0|$
$\boldsymbol{E_\alpha} \sim -|\vec{\boldsymbol{\mu}}| \cdot |\vec{B}_0|$
$\vec{B}_{RF}$

Longitudinal and transverse relaxation



Longitudinal and transverse relaxation



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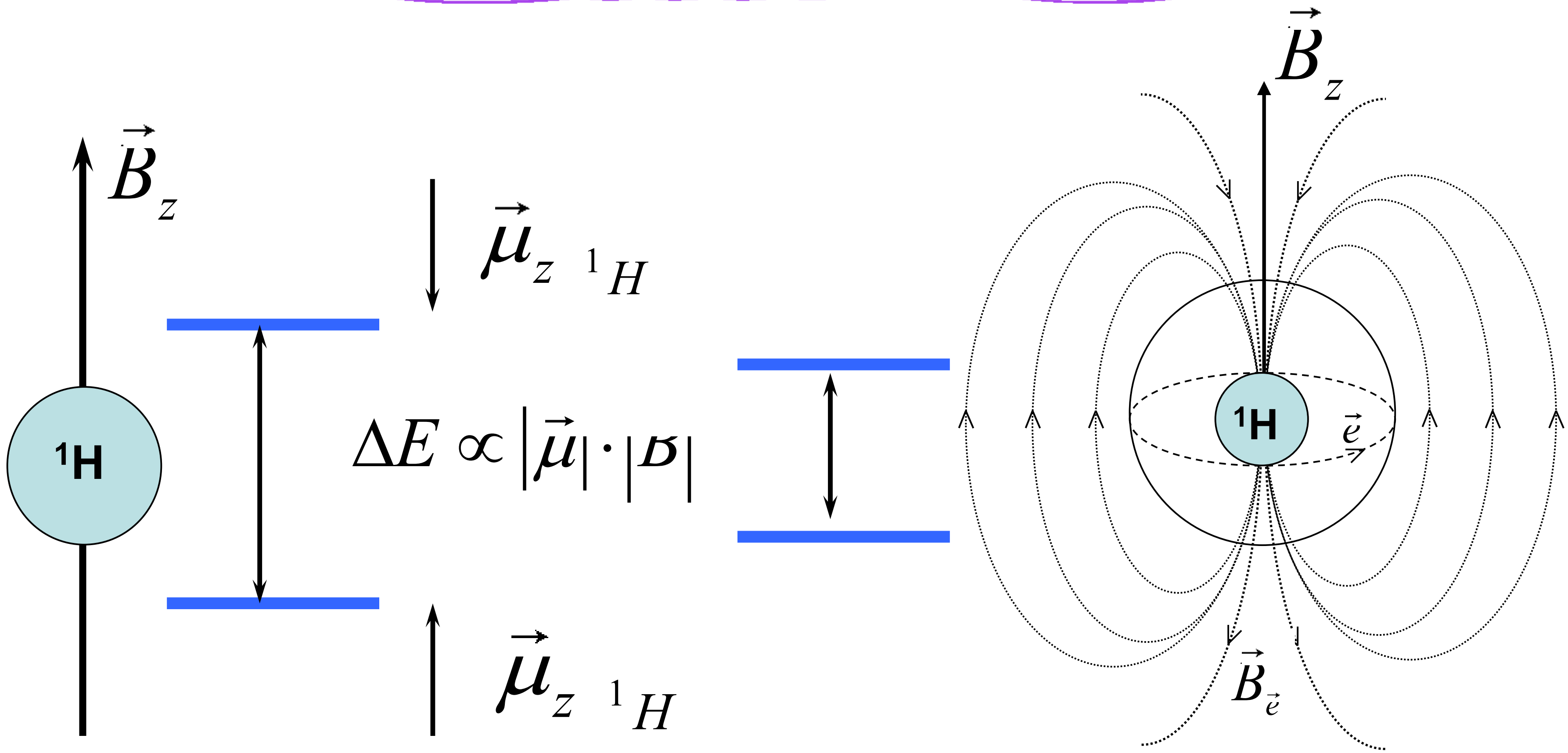
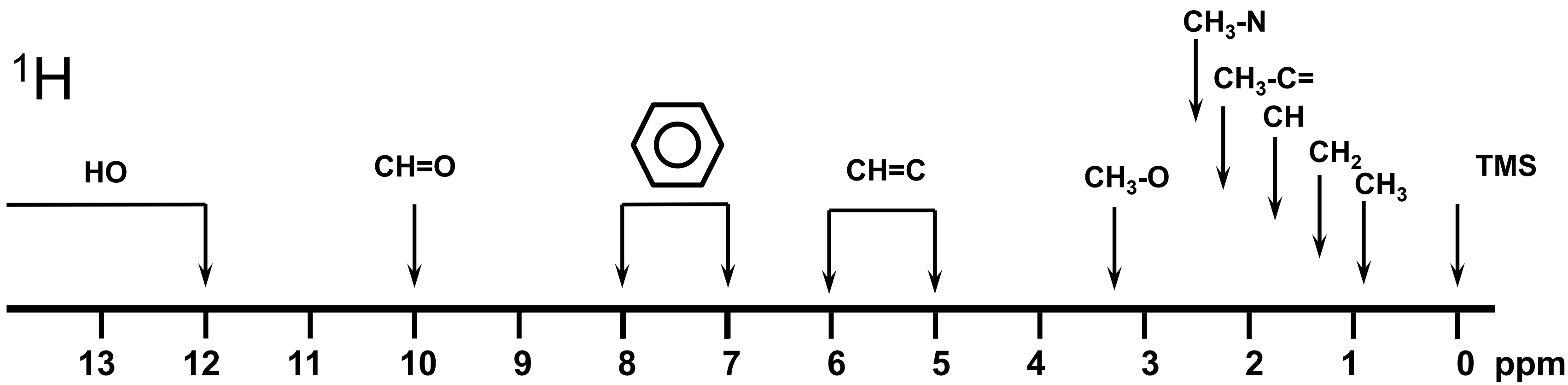
Chemical shift



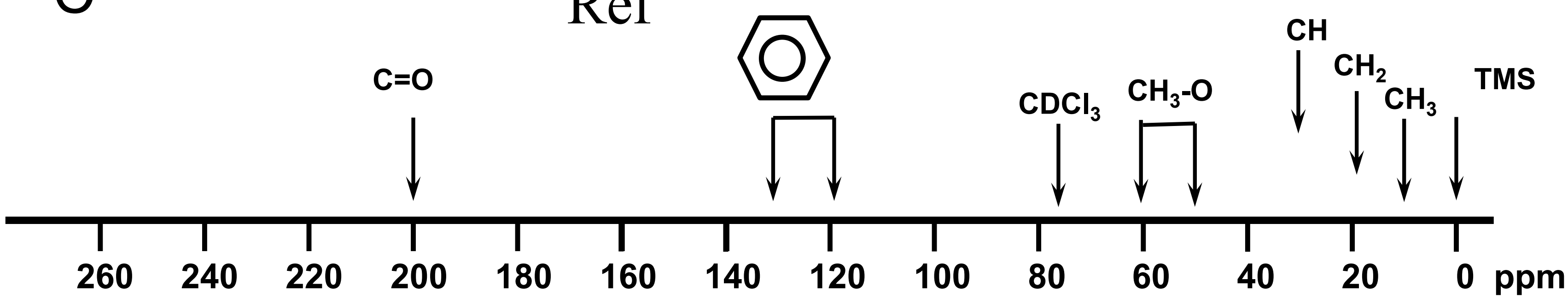
Chemical shift

^{1}H



$$\delta = \frac{\nu_{\mathrm{Probe}} - \nu_{\mathrm{Ref}}}{\nu_{\mathrm{Ref}}}$$

^{13}C



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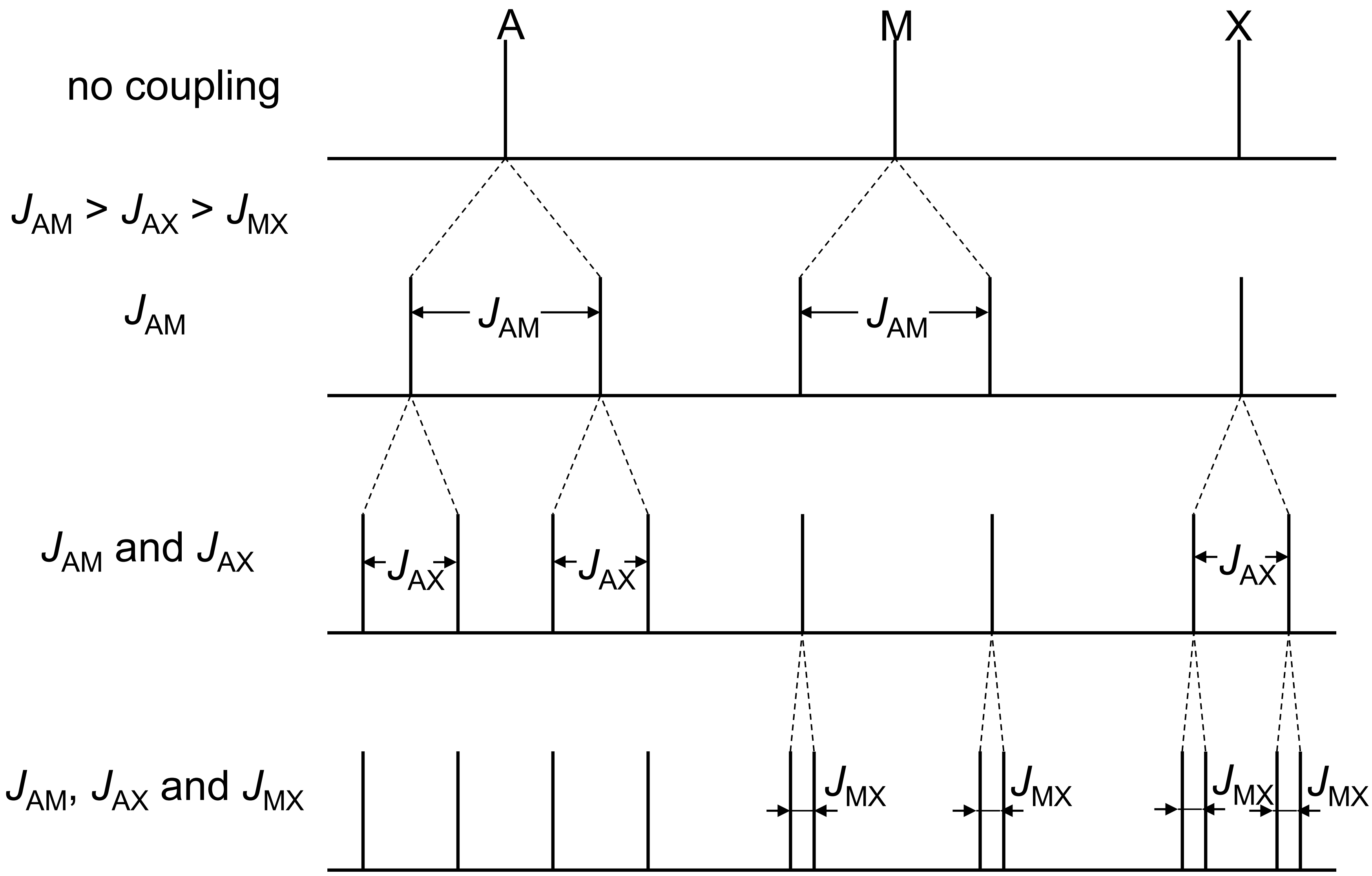
Scalar spin-spin coupling



Scalar spin-spin coupling

Coupling with spins 1/2

A	1
AX	1 1
AX_2	1 2 1
AX_3	1 3 3 1
AX_4	1 4 6 4 1

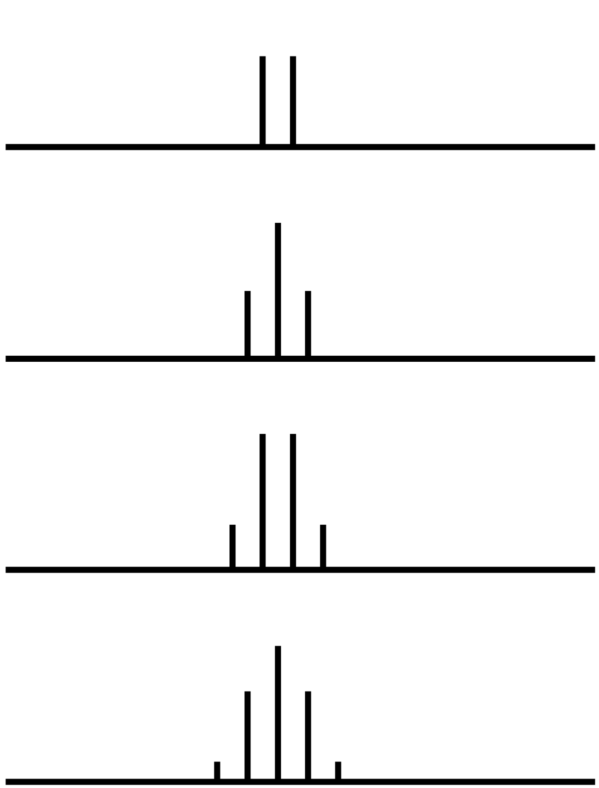
No.

1

2

3

4



Coupling with spins 1

A	1
AX	1 1 1
AX_2	1 2 3 2 1
AX_3	1 3 6 7 6 3 1
AX_4	1 4 10 16 19 16 10 4 1

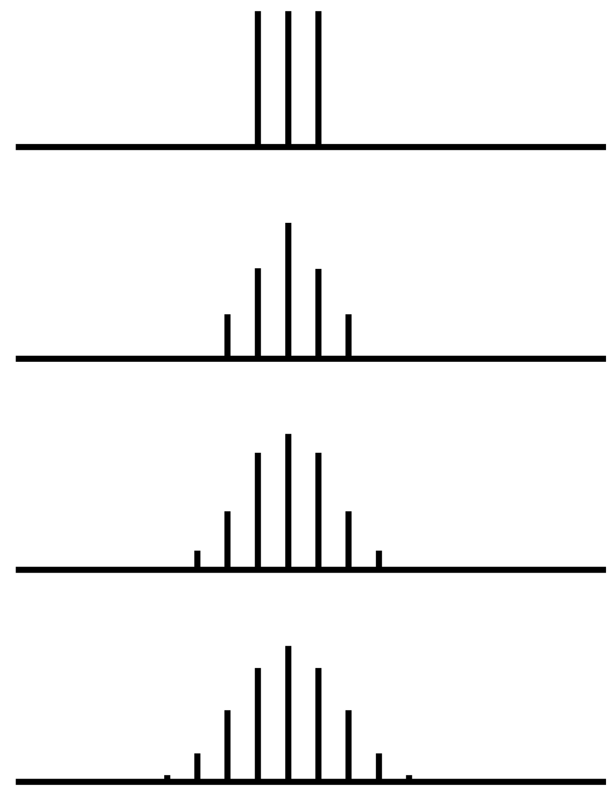
No.

1

2

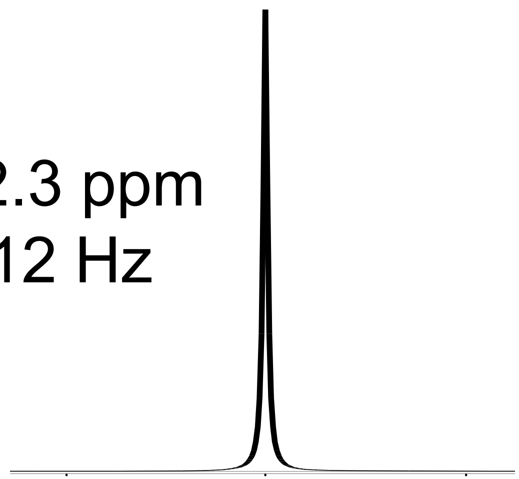
3

4

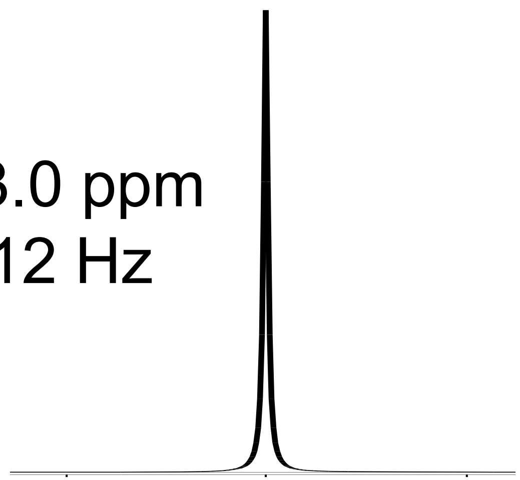


Scalar spin-spin coupling

CH_4
$\delta(^1H) \approx 2.3$ ppm
$^2J_{HH} \approx -12$ Hz



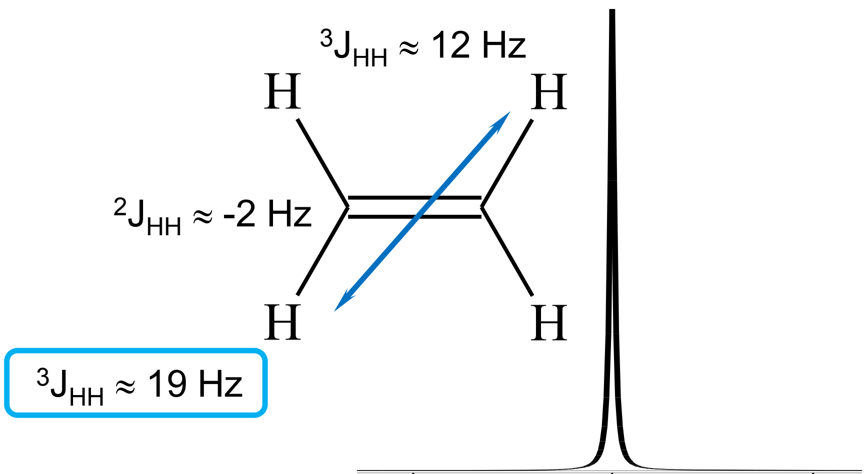
$ClCH_3$
$\delta(^1H) \approx 3.0$ ppm
$^2J_{HH} \approx -12$ Hz

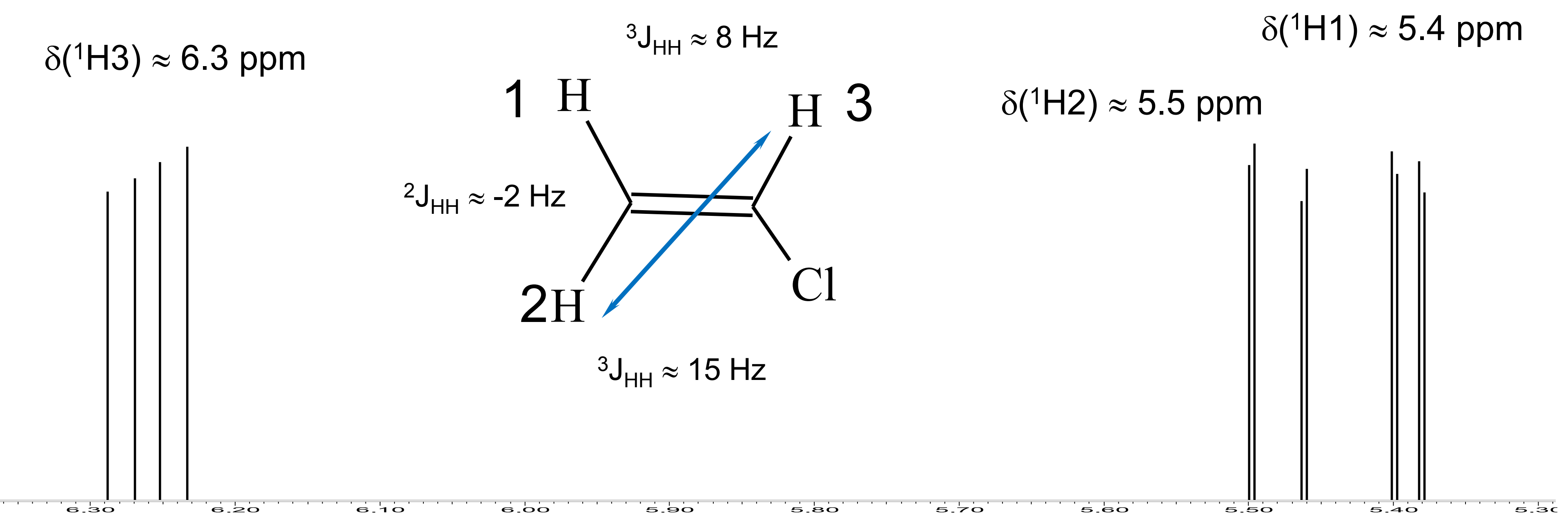


Scalar spin-spin coupling

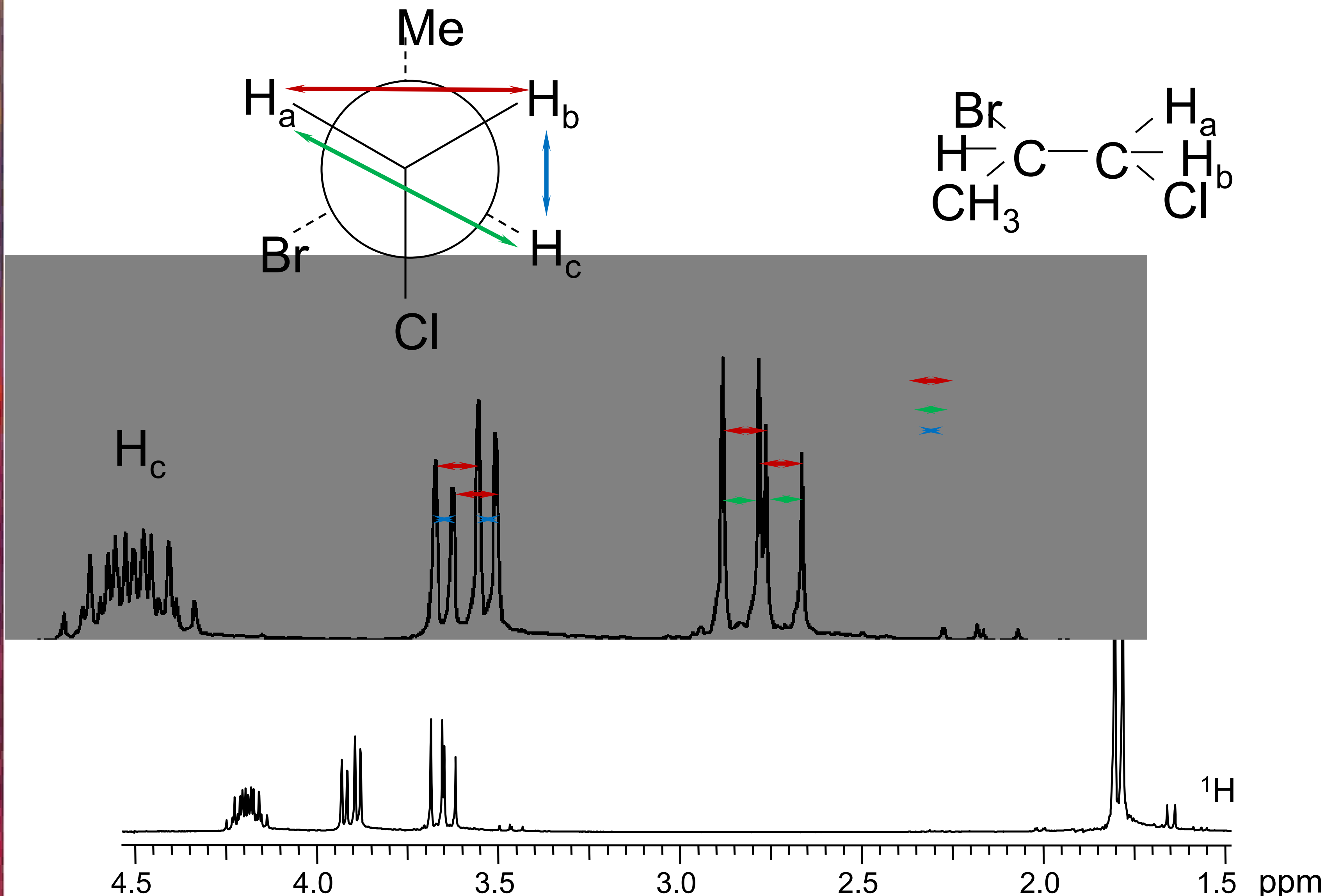
$H_2C=CH_2$

$\delta(^1H) \approx 5.3$ ppm





Scalar spin-spin coupling



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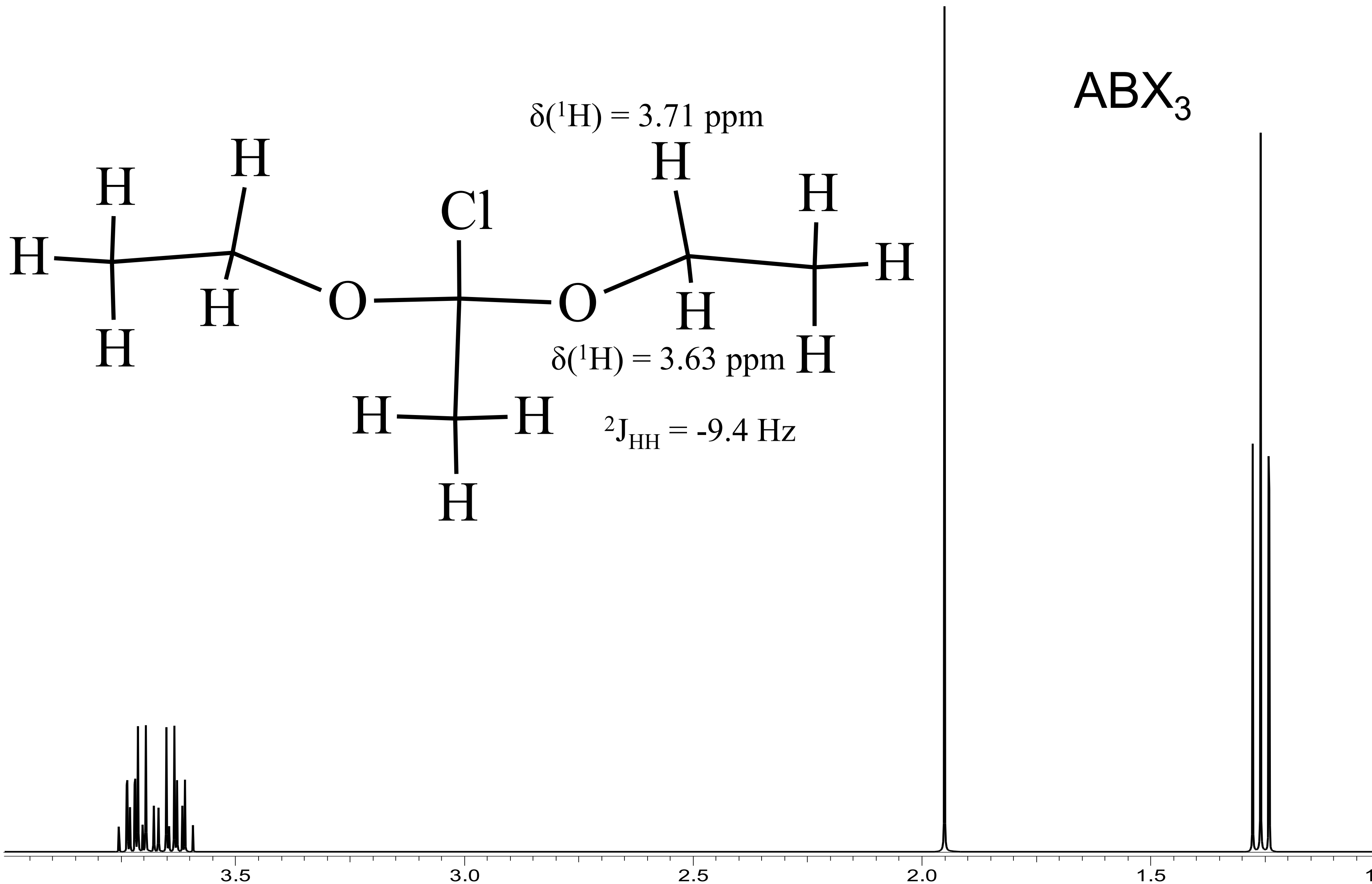
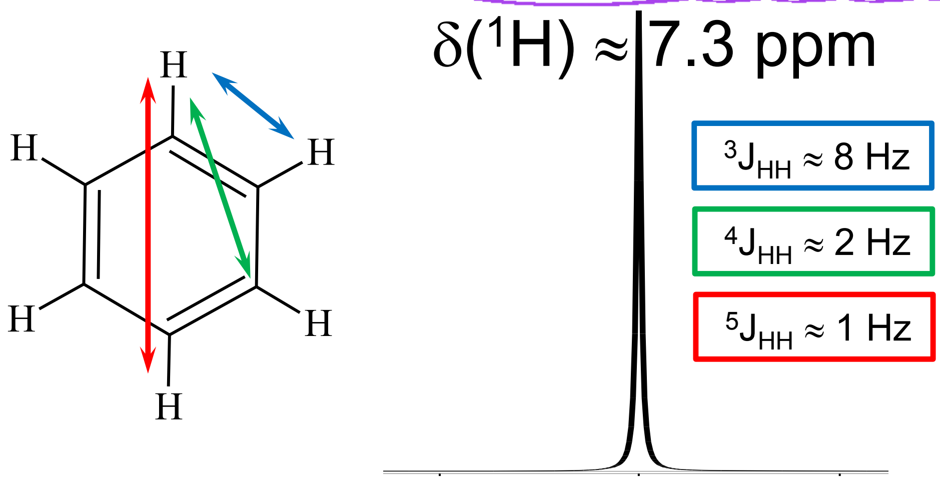
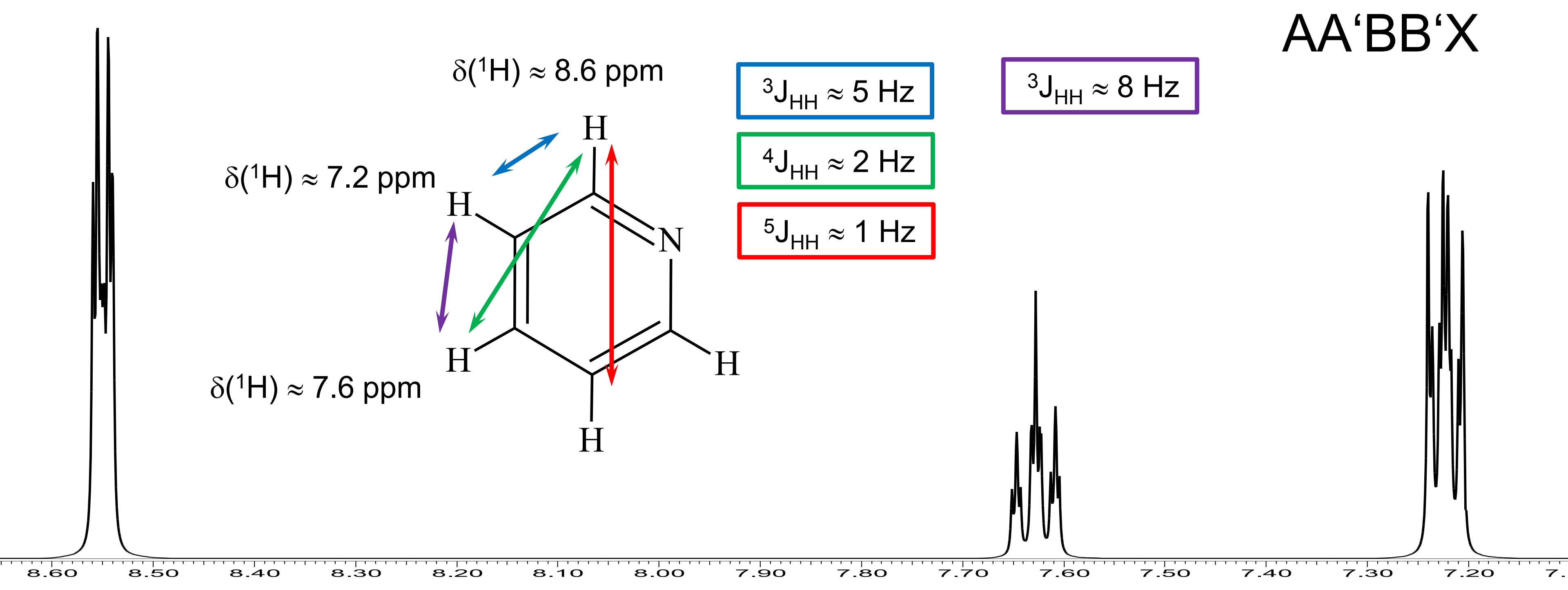
Pople nomenclature



Second Order Effects in Coupled Systems





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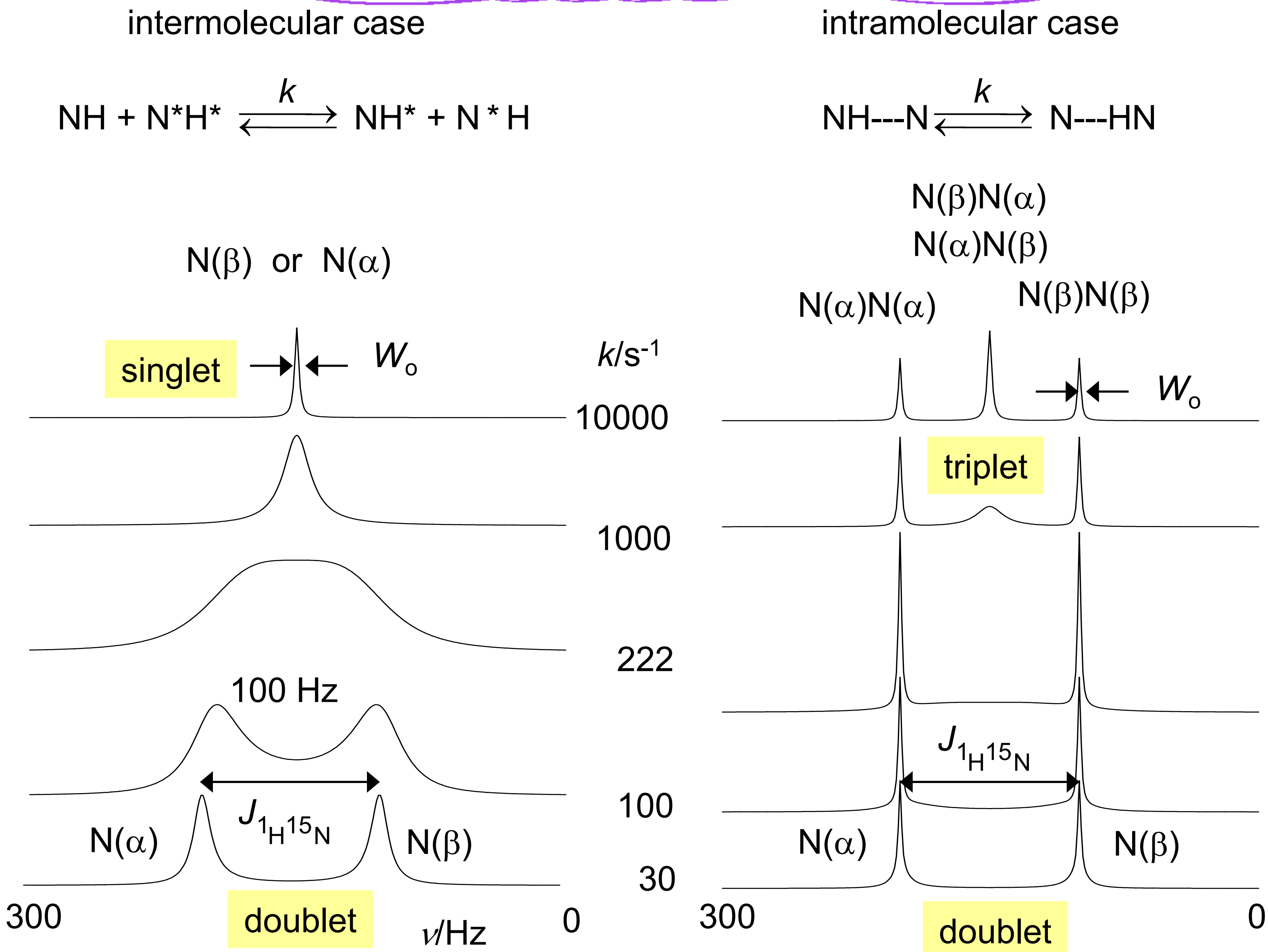
Proton exchange



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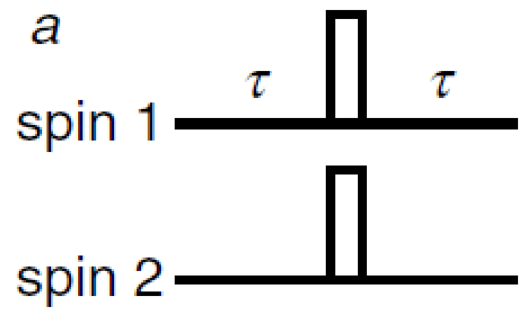
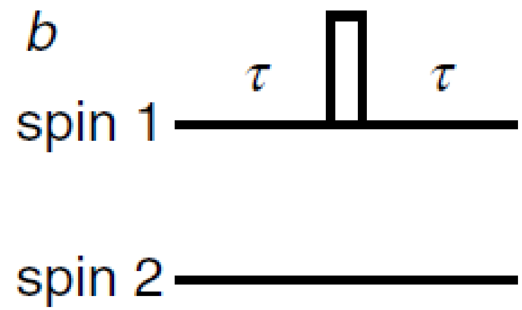
Spin Echoes

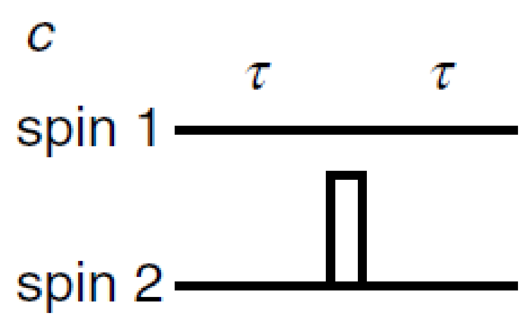
Offset (chemical shift) – refocused
J coupling – evolves for 2τ



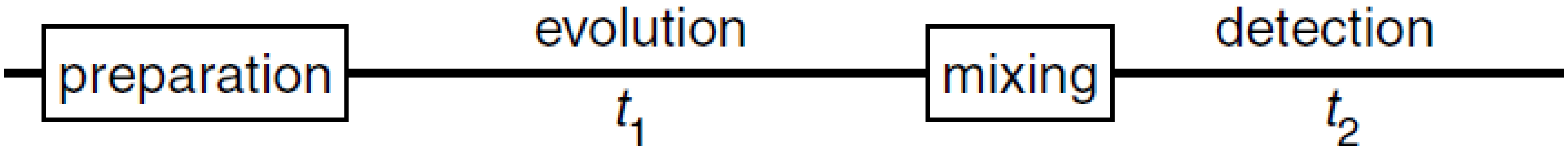
Offset (chemical shift) – refocused
J coupling – refocused



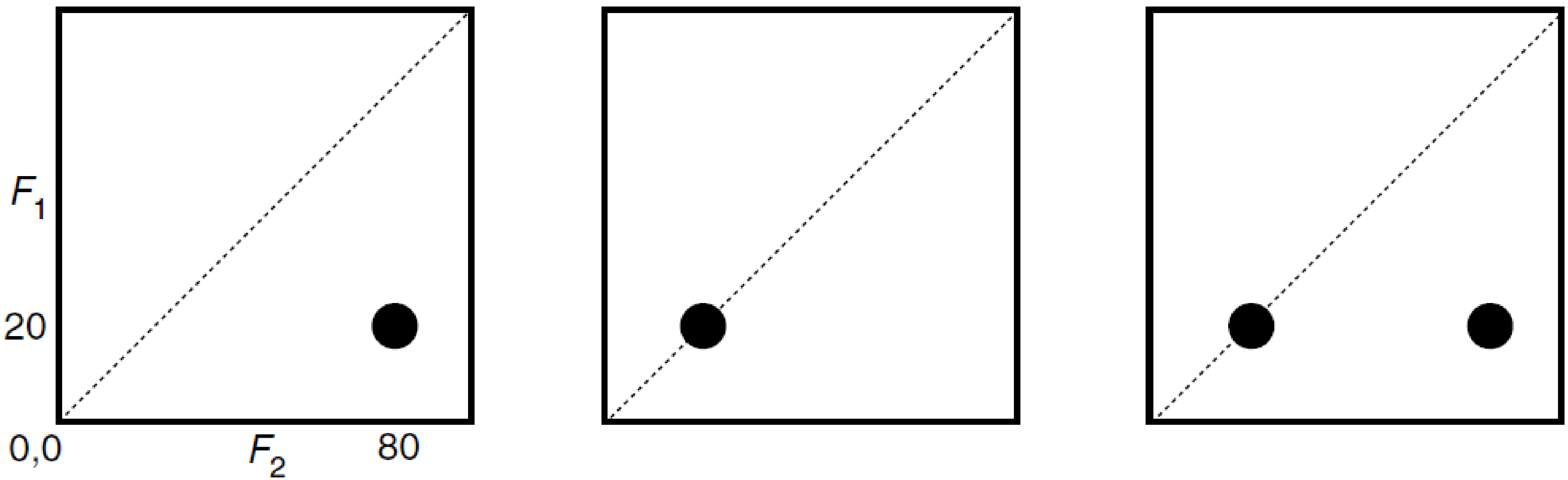
Offset (chemical shift) – evolves for 2τ
J coupling – refocused



2D-NMR



$$t_1 = 0, \Delta_1, 2\Delta_1, 3\Delta_1, \ldots, N\Delta_1 \quad N \approx 100$$



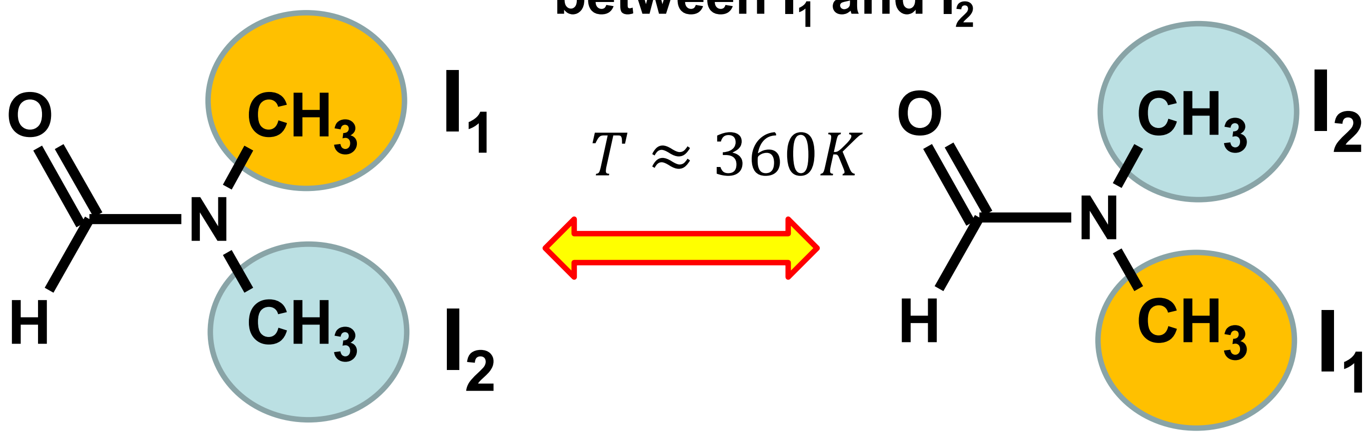
preparation
↓
Ω_1
↓
mixing
↓
Ω_2
Full magnetization transfer

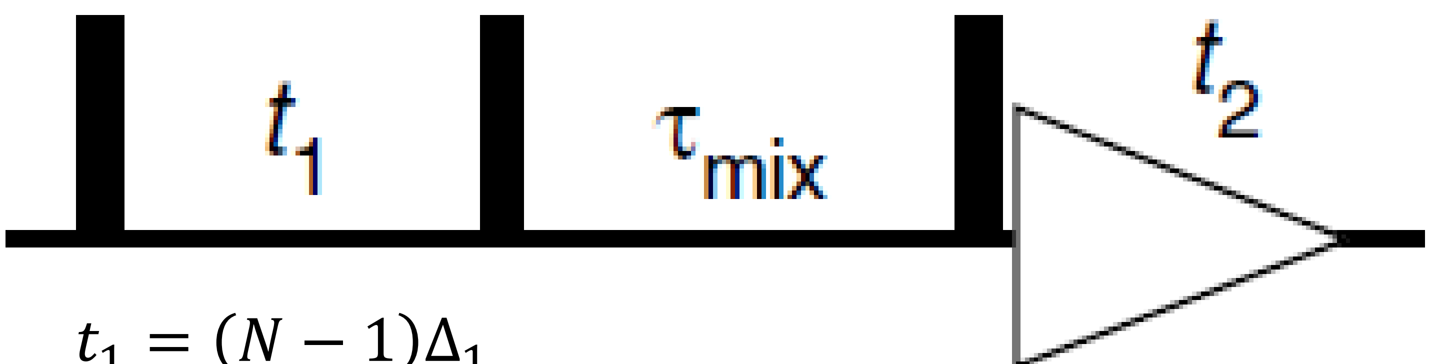
preparation
↓
Ω_1
↓
mixing
↓
Ω_1
No magnetization transfer

preparation
↓
Ω_1
↓
mixing
↓ ↓
Ω_1 Ω_2
Partial magnetization transfer

2D-NMR. EXSY (EXchange SpectroscopY)

Chemical exchange between I_1 and I_2

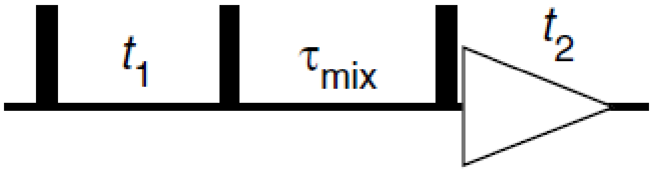




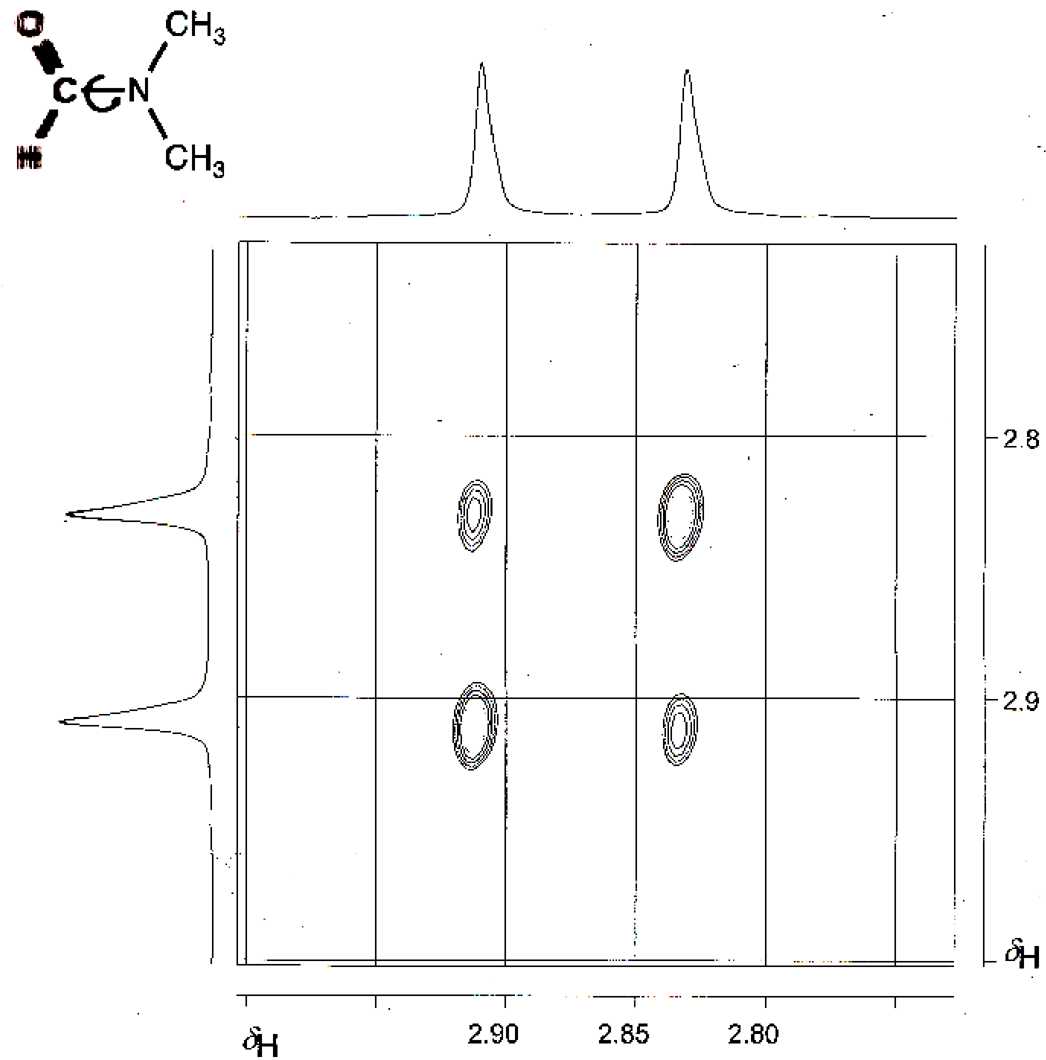
$$t_1 = (N-1)\Delta_1$$
$$\Delta_1 = 1/2sw1 \approx 2ms$$
$$N \approx 32$$

$$\tau \approx 1s$$

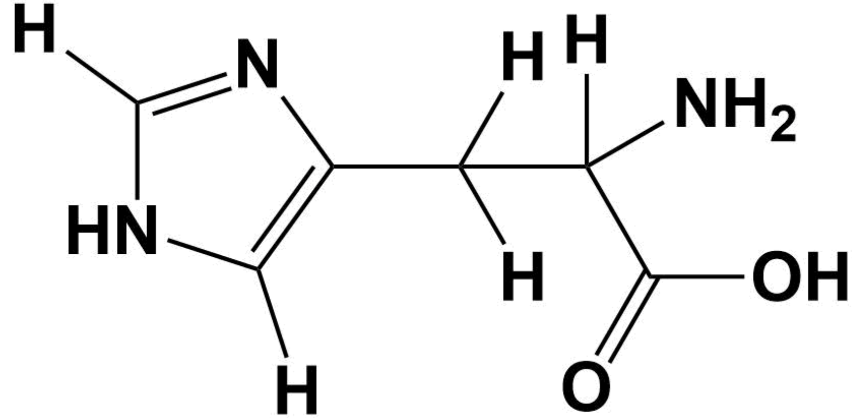
2D-NMR. EXSY (EXchange SpectroscopY)

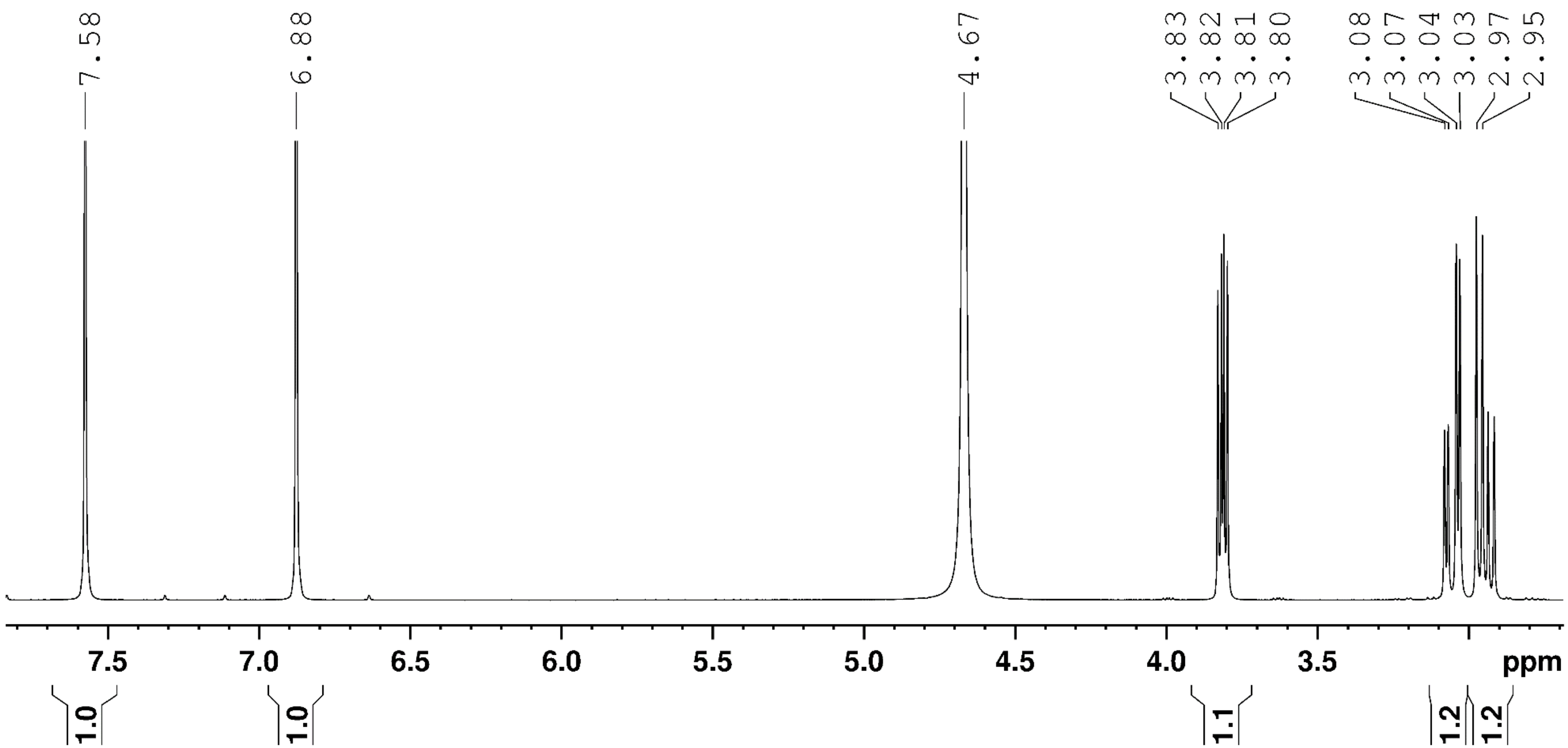


$$\tau_{opt} \approx \frac{1}{T_1^{-1} + k_{AB} + k_{BA}}$$



L-Histidin,
^1H NMR in D_2O





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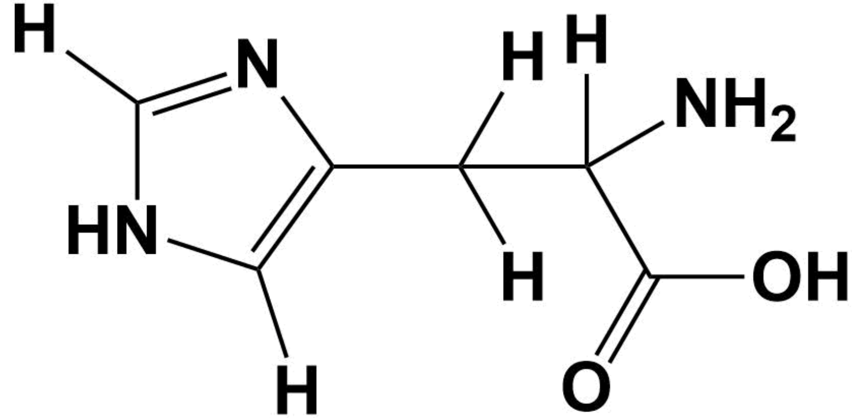
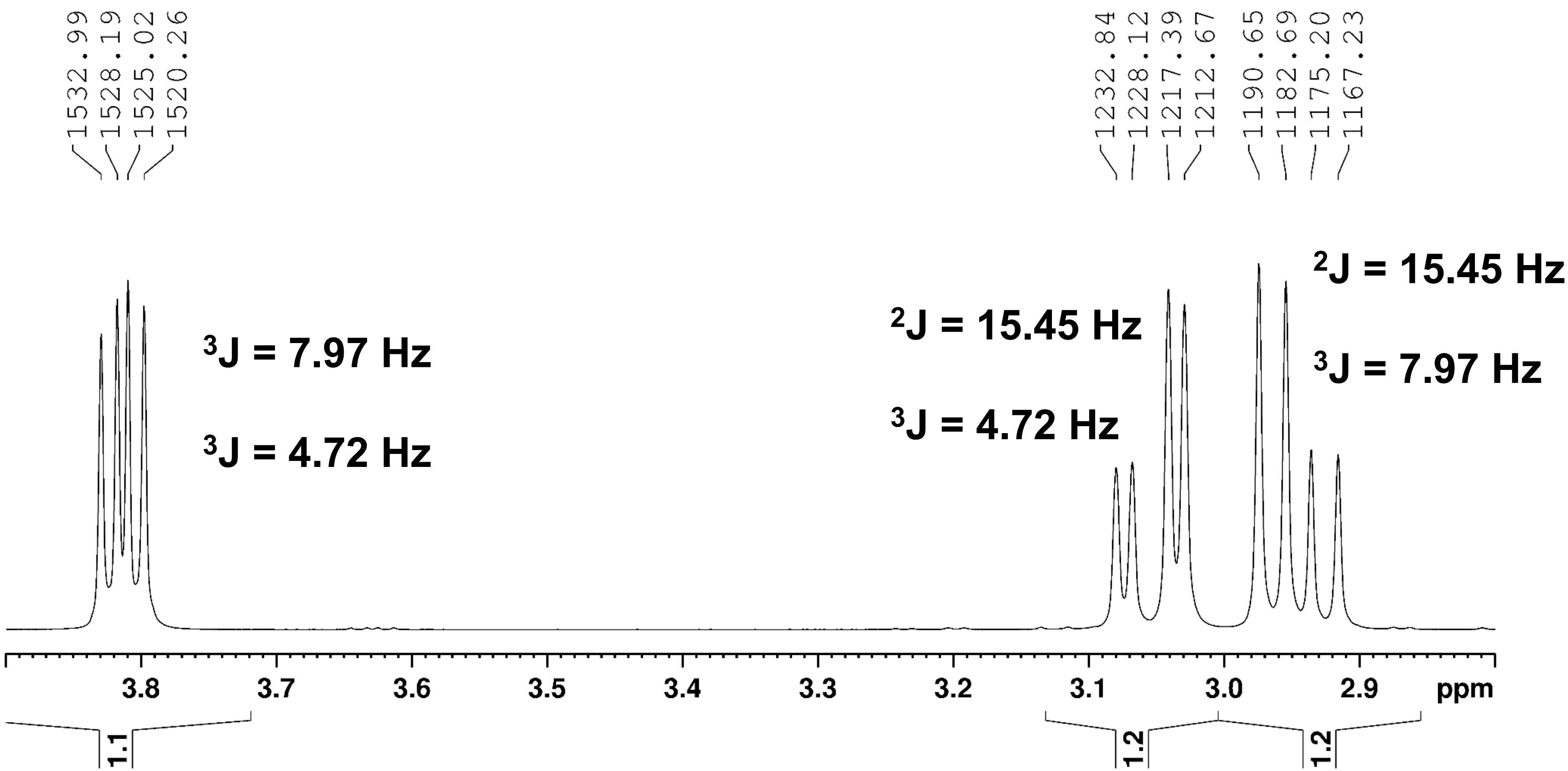
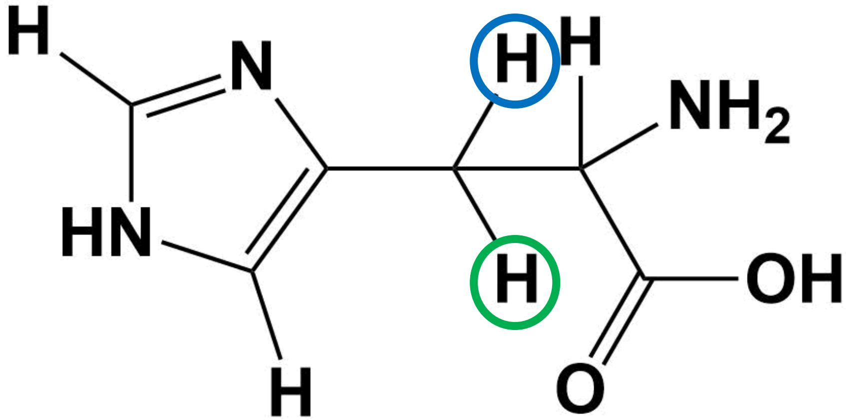
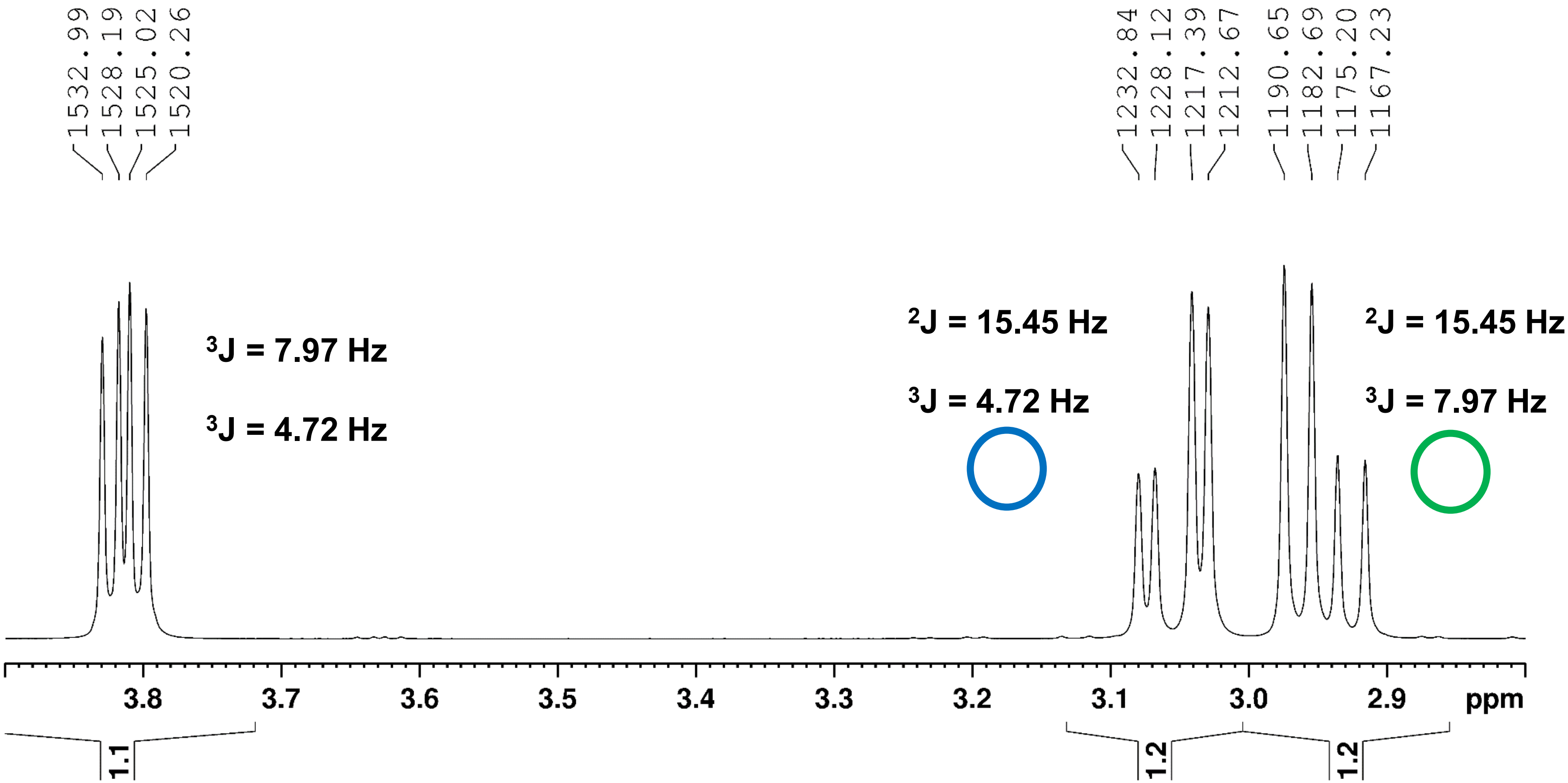


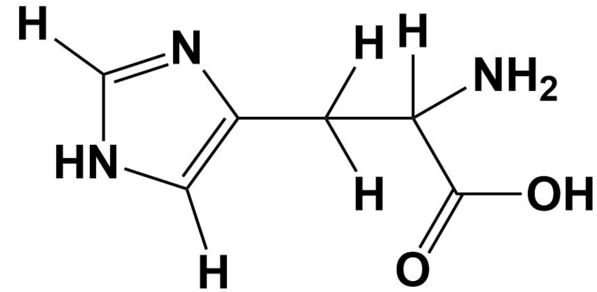


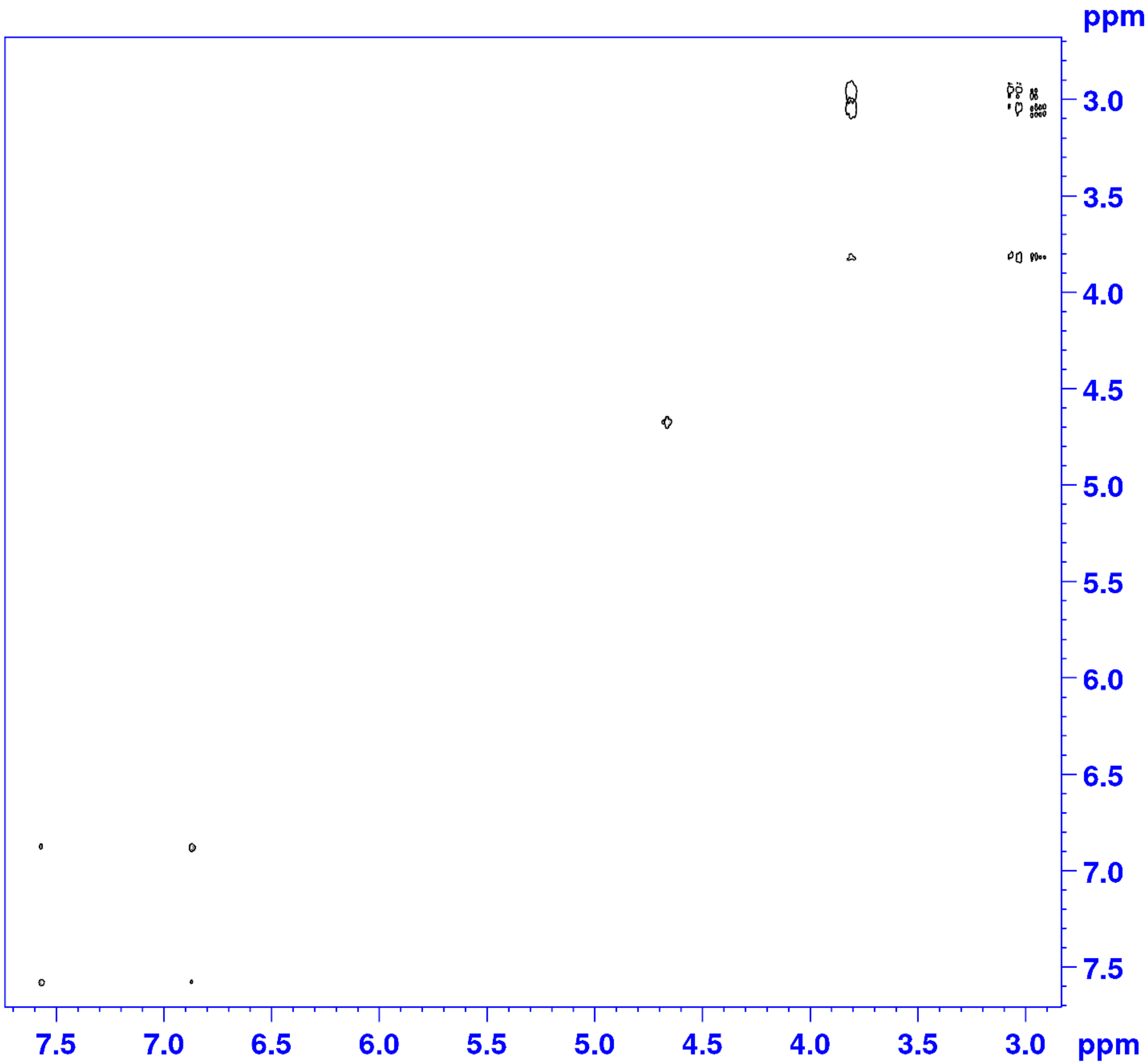
L-Histidin,
^{1}H NMR in D_2O





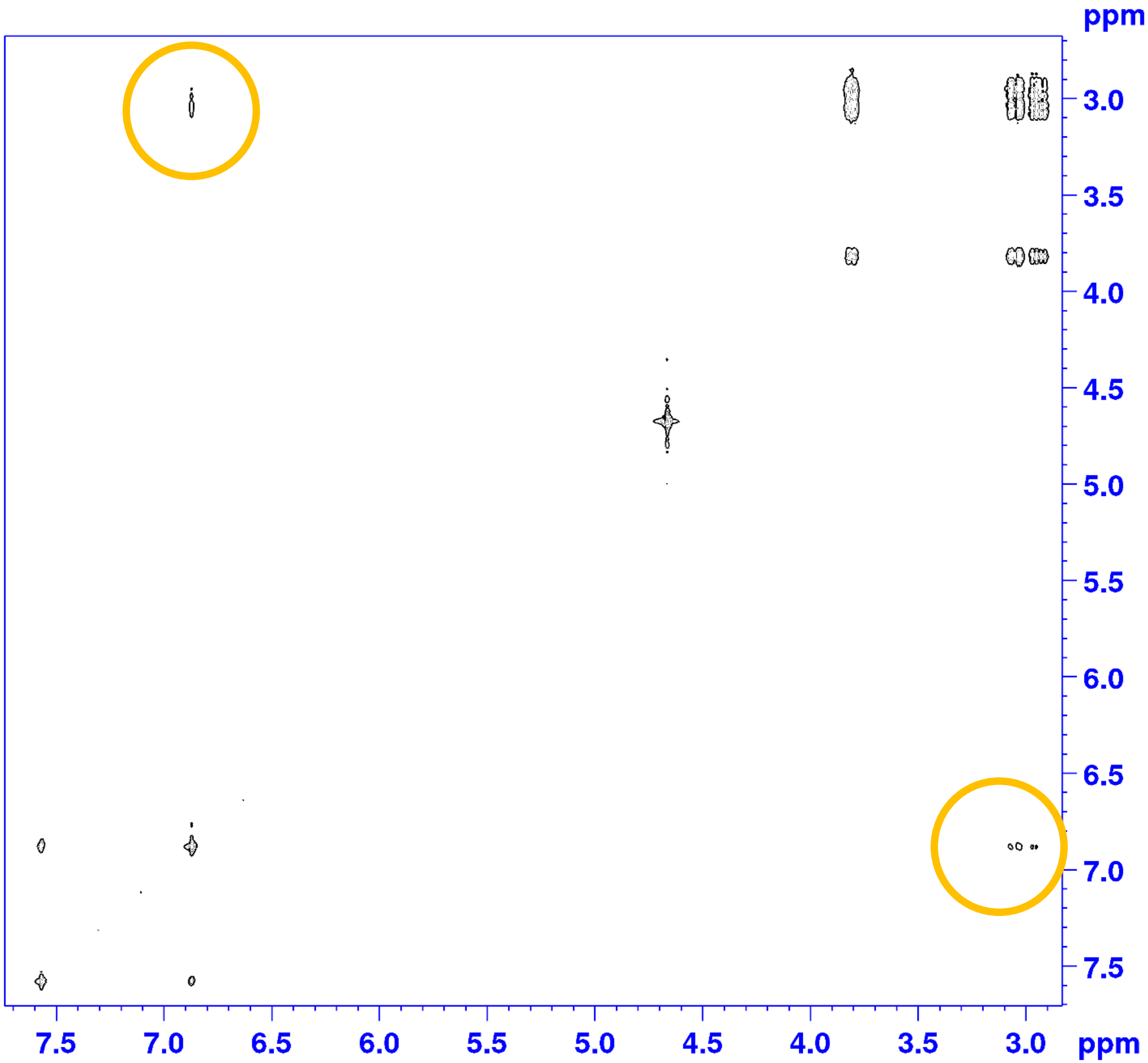
L-Histidin,
COSY NMR in D_2O

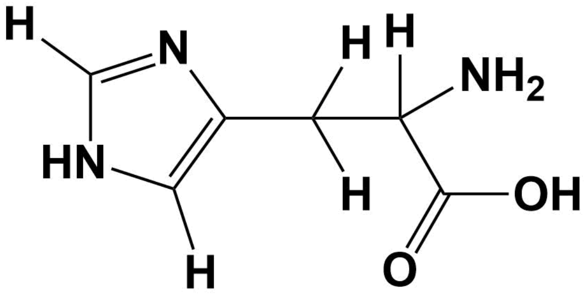




The intensity is proportional to sin πJt.

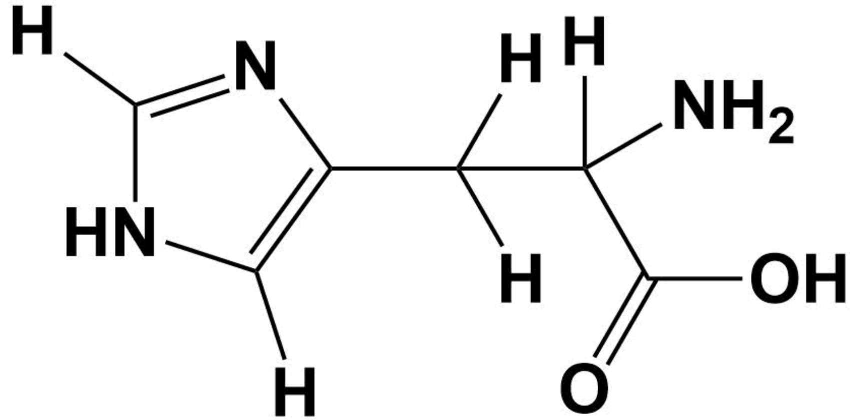
L-Histidin, COSY NMR in D_2O

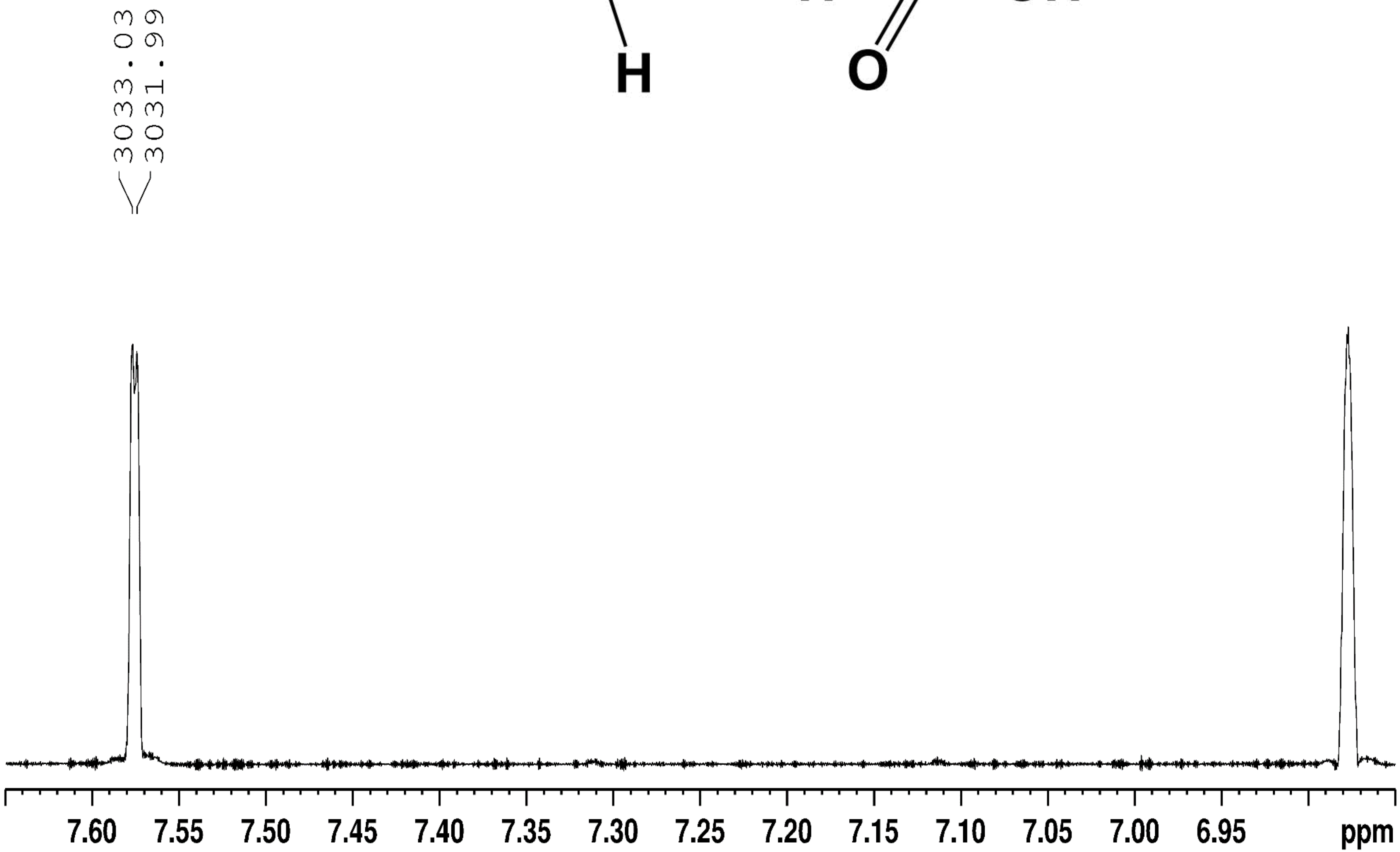




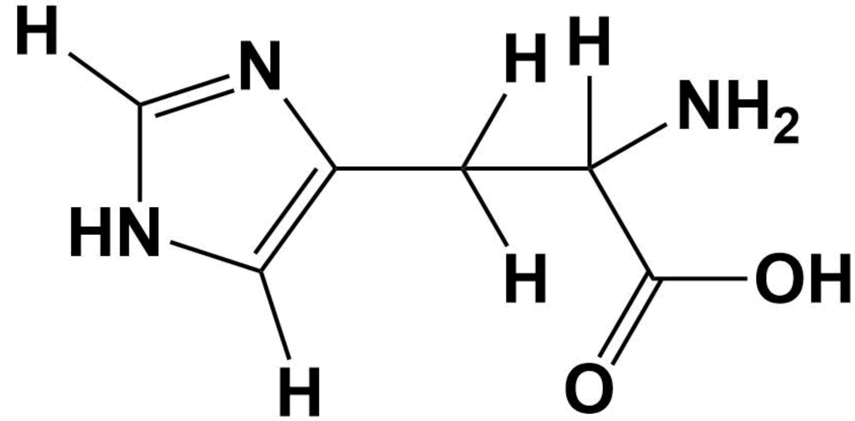
The intensity is proportional to sin πJt.

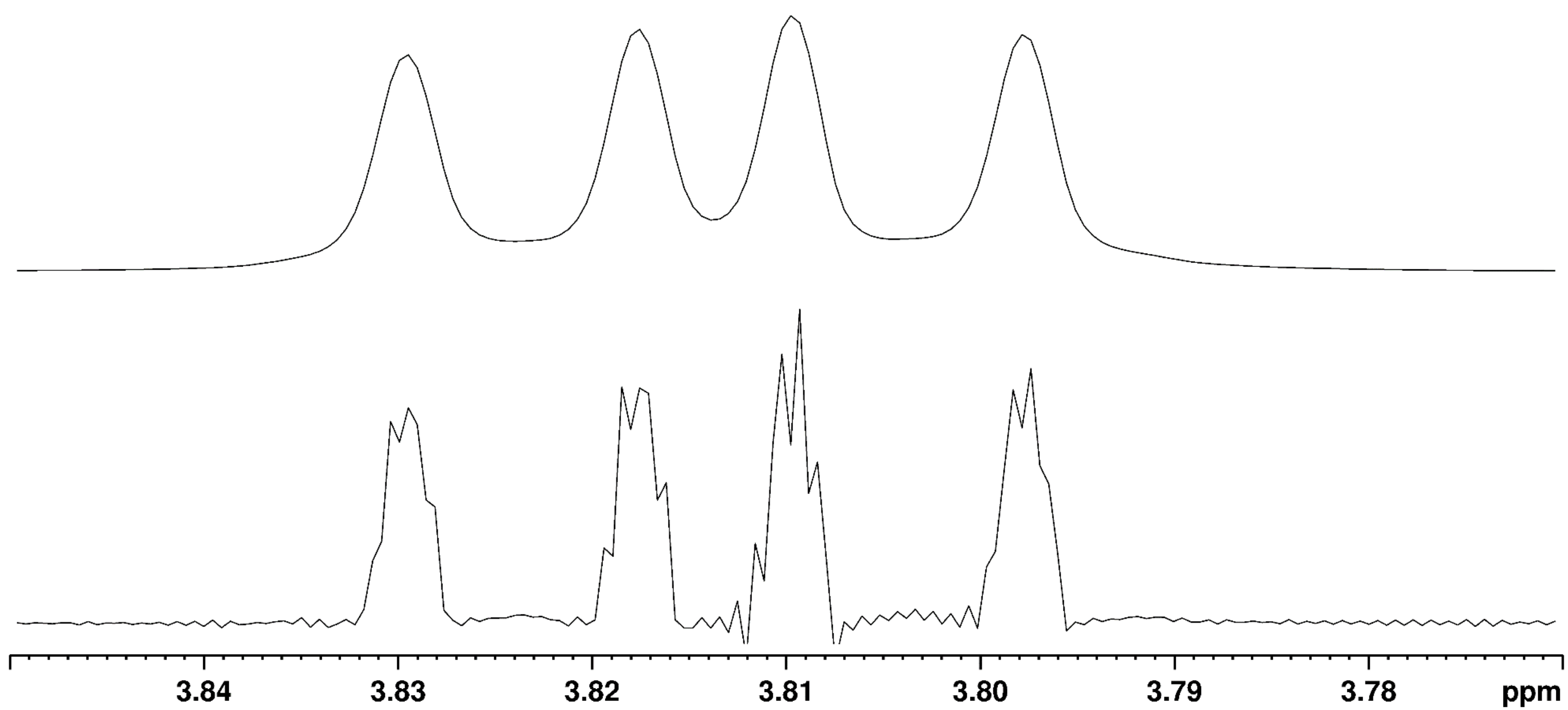
L-Histidin,
^{1}H NMR in D_2O



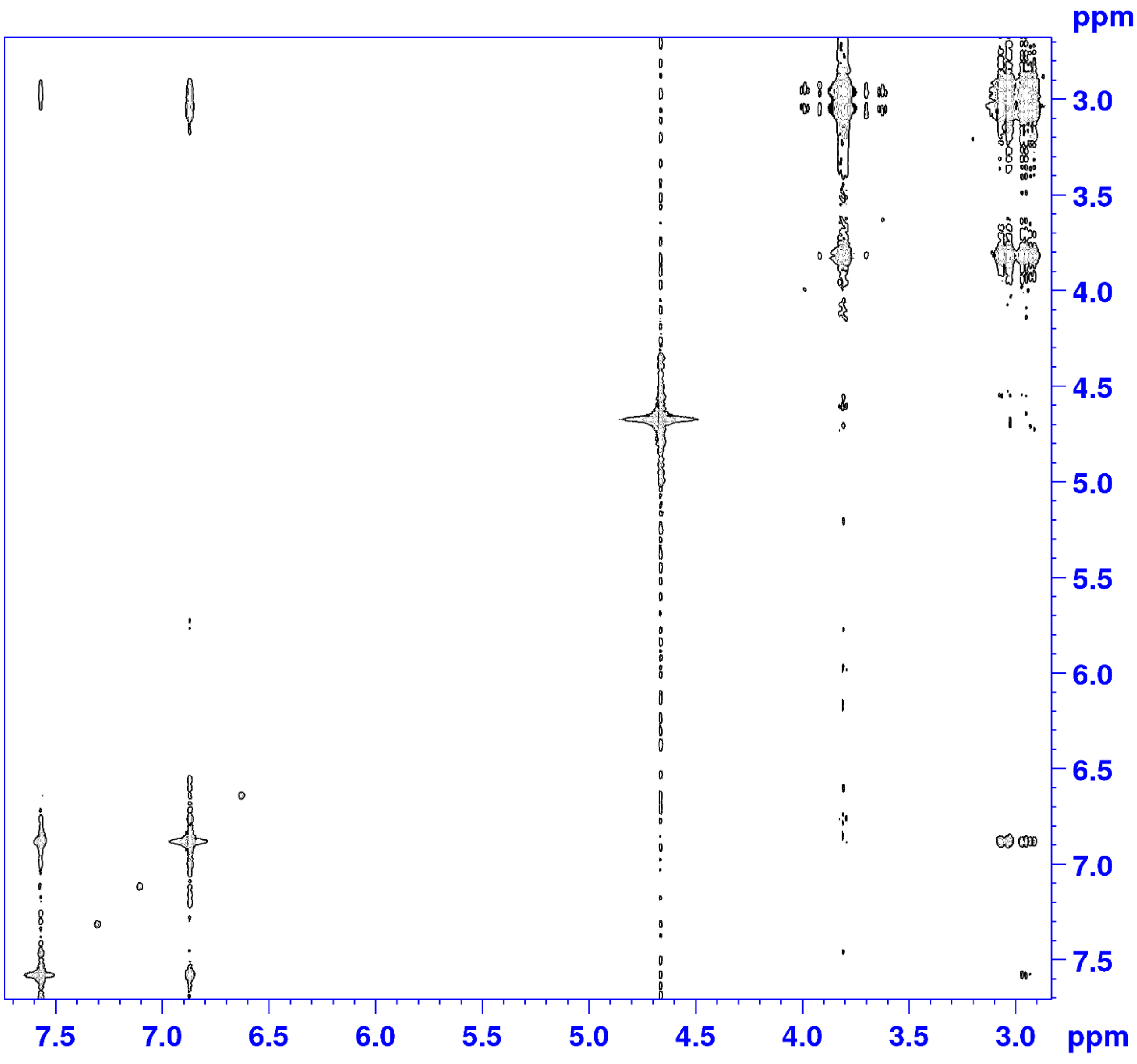


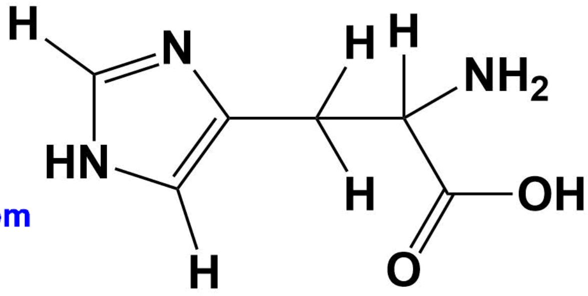
L-Histidin,
^{1}H NMR in D_2O



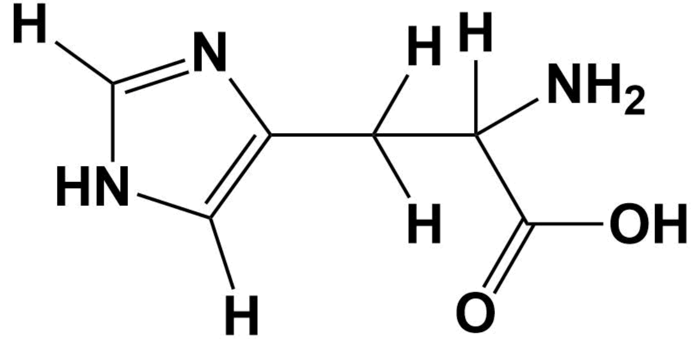


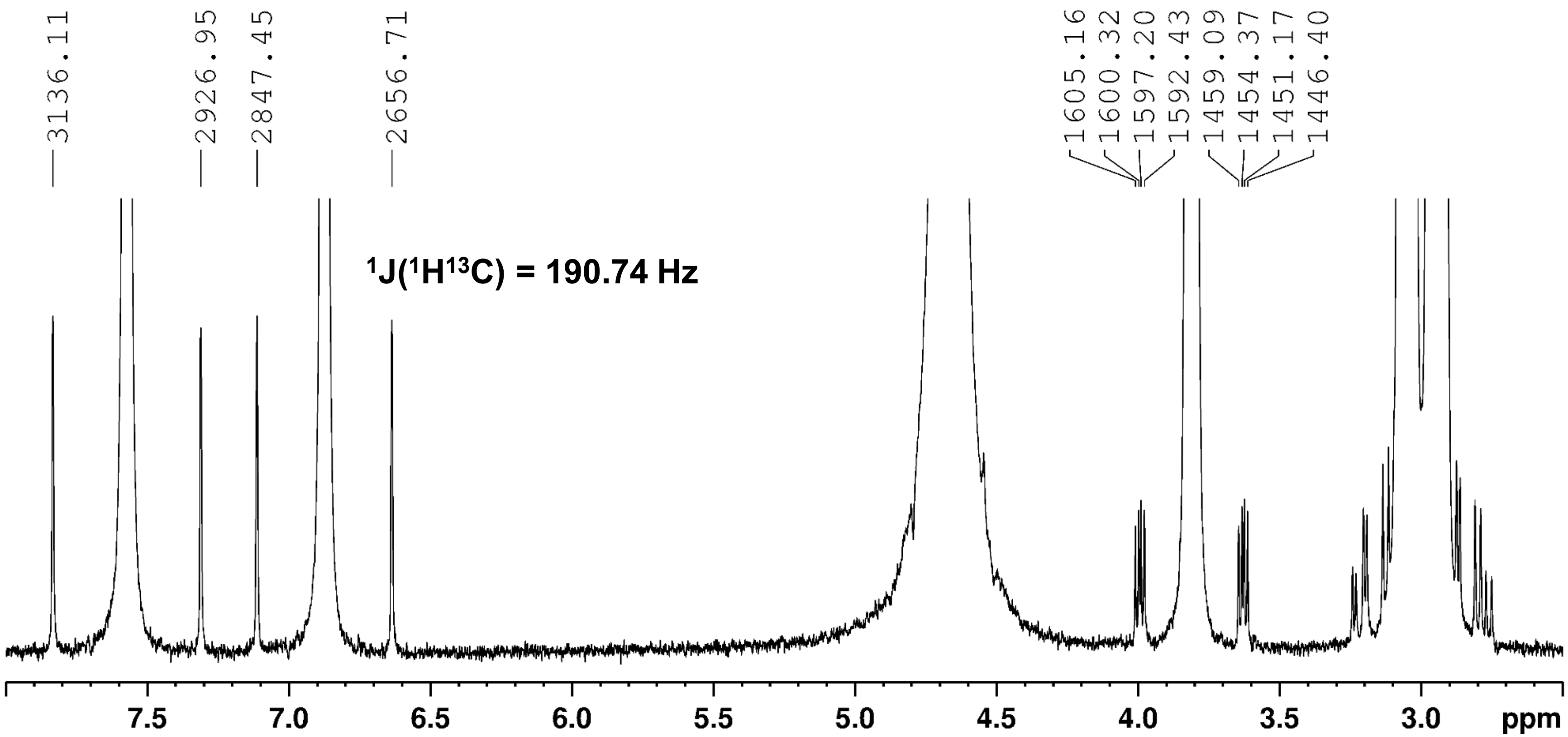
L-Histidin,
COSY NMR in D_2O





L-Histidin,
^{1}H NMR in D_2O

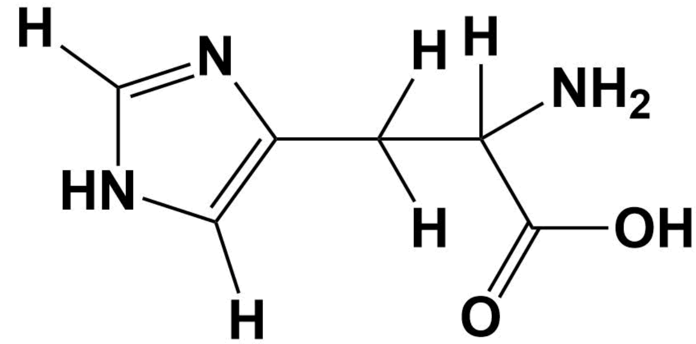


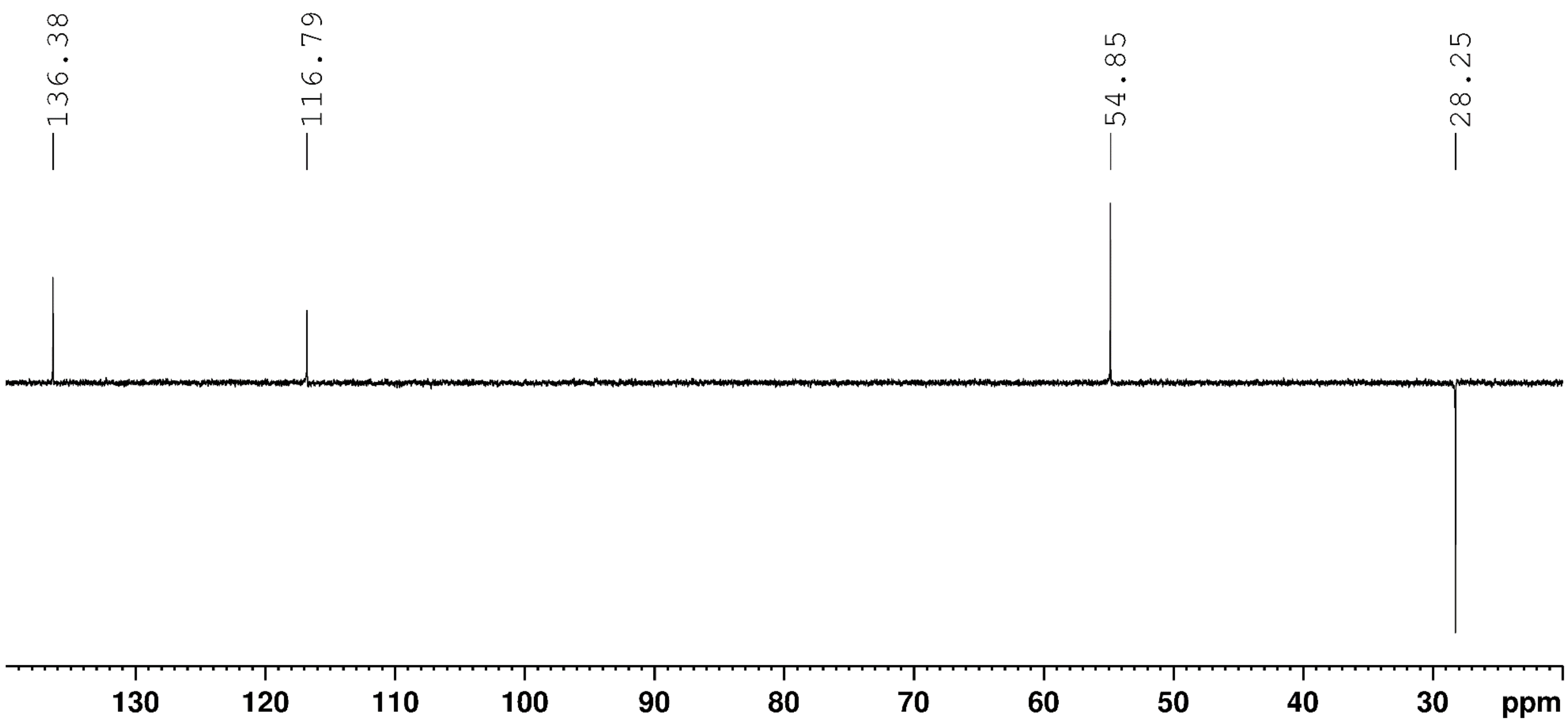


$^{1}J(^{1}H^{13}C) = 209.16$ Hz

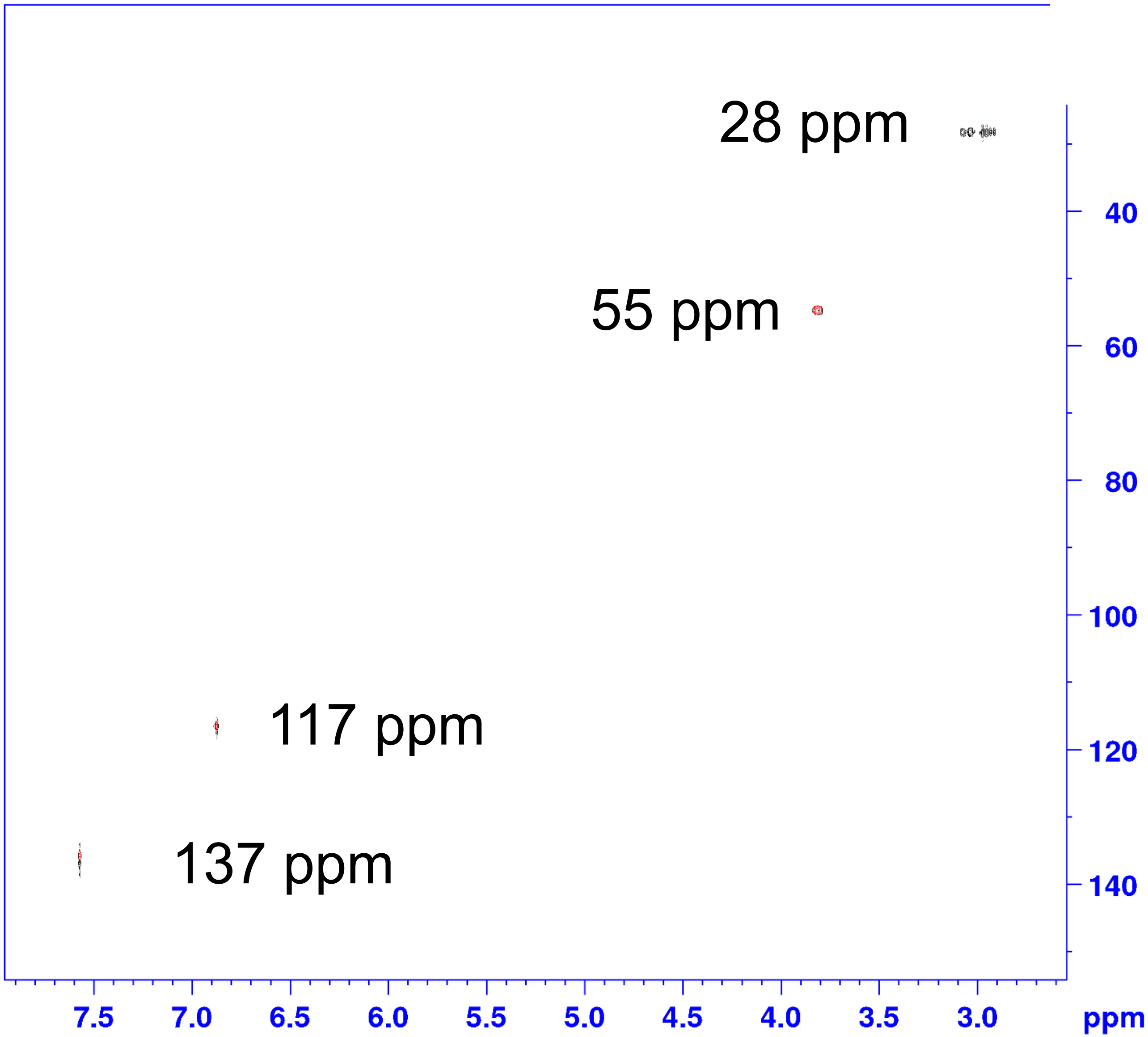
$^{1}J(^{1}H^{13}C) = 146.07$ Hz

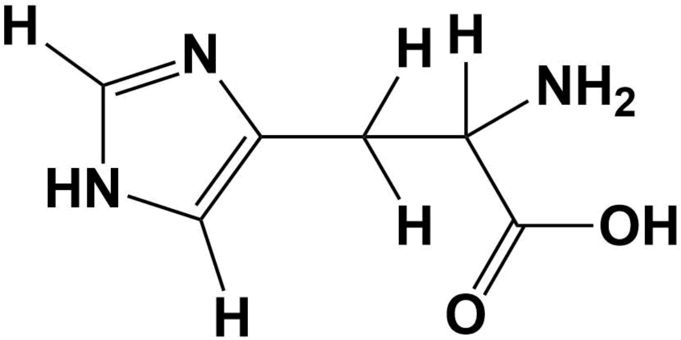
L-Histidin,
DEPT-135 NMR in D_2O





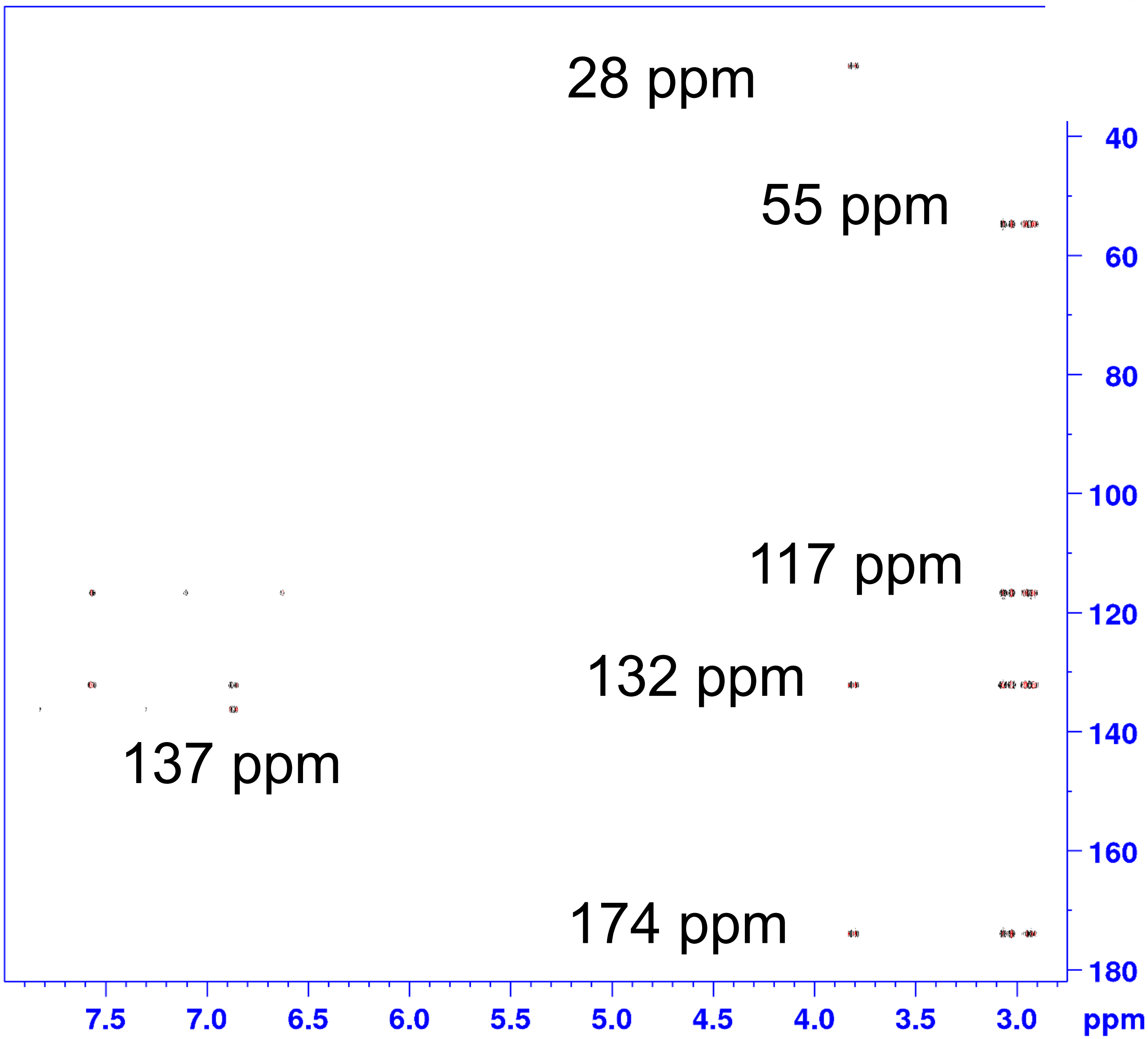
L-Histidin,
HSQC-DEPT NMR in D_2O

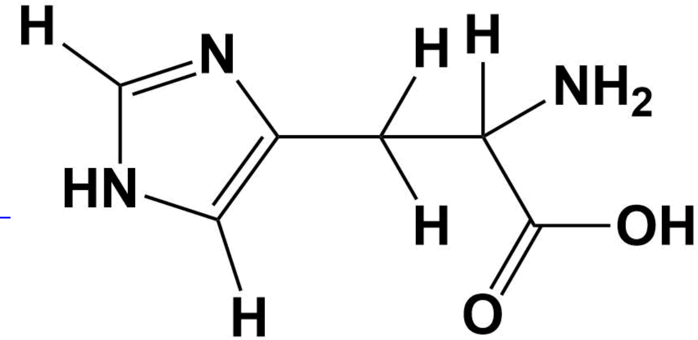




^{1}H, ppm	^{13}C, ppm
2.93 & 3.05	28
3.81	55
6.88	117
7.58	137

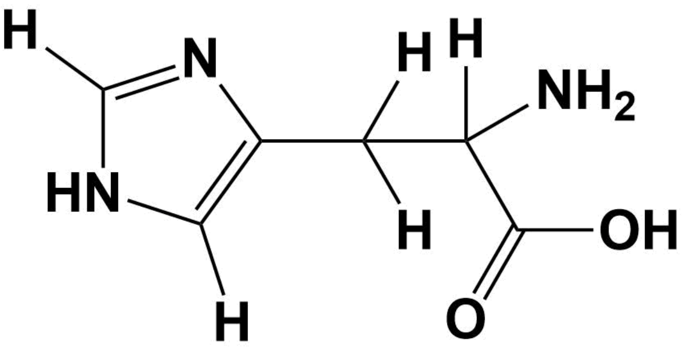
L-Histidin, HMBC NMR in D_2O

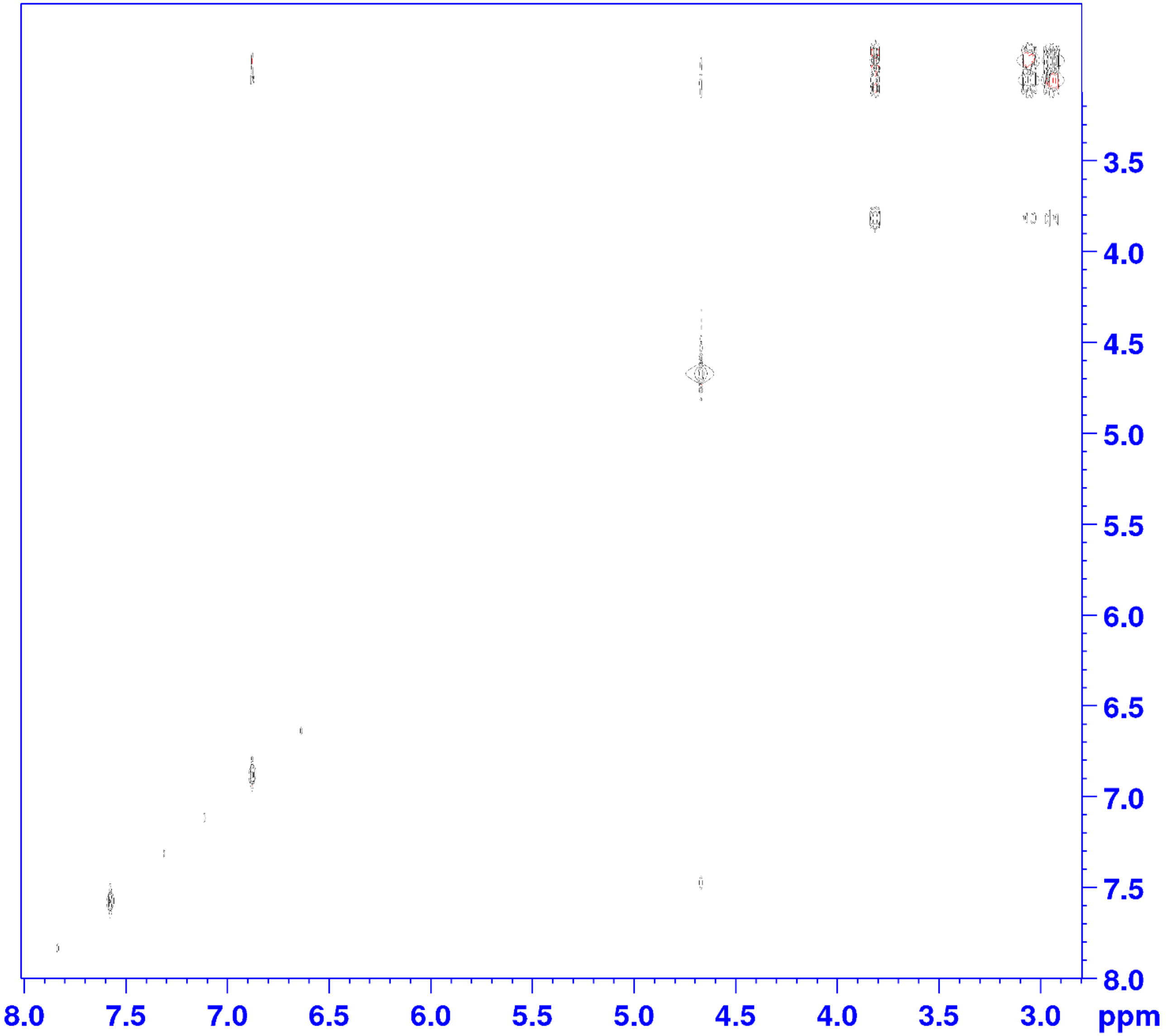




^{1}H, ppm	^{13}C, ppm
2.93 & 3.05	28
3.81	55
6.88	117
7.58	137

L-Histidin, NOESY NMR in D_2O





INSTITUT FÜR
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UNIVERSITÄT REGENSBURG

THREE CUPS OF "MODERN NMR SPECTROSCOPY" ESPRESSO

Ilya G. Shenderovich

http://homepages.uni-regensburg.de/~shi56087/

Physical background of NMR	NMR in practice	A research lecture
1. Classical and quantum-mechanical descriptions 2. T_1 and T_2 Relaxations 3. Chemical shift 4. Spin-spin scalar coupling 5. Spin systems of the first and the second orders 6. Chemical exchange 7. Two-dimensional NMR	1. NMR in solution 1.1 From spectrum to structure 1.2. Typical protocol for structure elucidation 2. NMR in the solid state 2.1 Orientation-dependent interactions 2.1 Measurements of internuclear distances 2.3 NMR of surfaces and amorphous solids	NMR Study of Hydrogen Bonding in Solution Down to 100 K

NMR Chemical Shifts of Common Laboratory Solvents as Trace Impurities

Organometallics **2010**, 29, 2176-2179 (**DOI:** 10.1021/om100106e)

Table 1. ^{1}H NMR Data[a]

	proton	mult	THF-d_8	CD_2Cl_2	$CDCl_3$	toluene-d_8	C_6D_6	C_6D_5Cl	$(CD_3)_2CO$	$(CD_3)_2SO$	CD_3CN	TFE-d_3	CD_3OD	D_2O
solvent residual signals			1.72 3.58	5.32	7.26	2.08 6.97 7.01 7.09	7.16	6.96 6.99 7.14	2.05	2.50	1.94	5.02 3.88	3.31	4.79
water	OH	s	2.46	1.52	1.56	0.43	0.40	1.03	2.84[b]	3.33[b]	2.13	3.66	4.87	
acetic acid	CH_3	s	1.89	2.06	2.10	1.57	1.52	1.76	1.96	1.91	1.96	2.06	1.99	2.08
acetone	CH_3	s	2.05	2.12	2.17	1.57	1.55	1.77	2.09	2.09	2.08	2.19	2.15	2.22
acetonitrile	CH_3	s	1.95	1.97	2.10	0.69	0.58	1.21	2.05	2.07	1.96	1.95	2.03	2.06
benzene	CH	s	7.31	7.35	7.36	7.12	7.15	7.20	7.36	7.37	7.37	7.36	7.33	
tert-butyl alcohol	CH_3	s	1.15	1.24	1.28	1.03	1.05	1.12	1.18	1.11	1.16	1.28	1.40	1.24
	OH	s[c]	3.16			0.58	0.63	1.30		4.19	2.18	2.20		
chloroform	CH	s	7.89	7.32	7.26	6.10	6.15	6.74	8.02	8.32	7.58	7.33	7.90	

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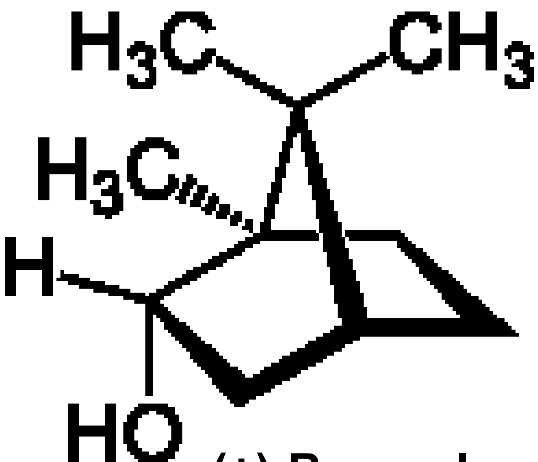
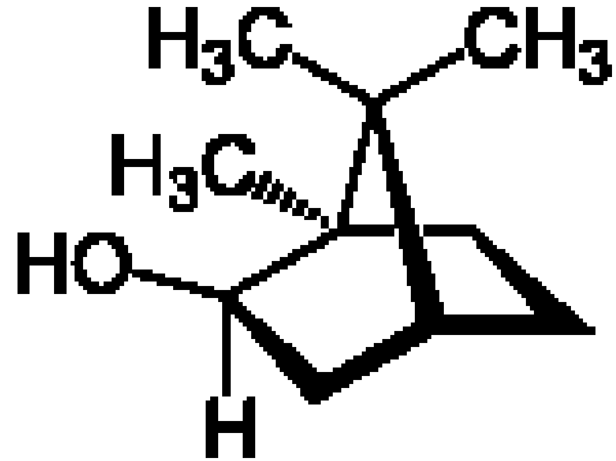
Physical background of NMR	NMR in practice	A research lecture
1. Classical and quantum-mechanical descriptions	1. NMR in solution	NMR Study of Hydrogen Bonding in Solution Down to 100 K
2. T_1 and T_2 Relaxations	1.1 From spectrum to structure	
3. Chemical shift	1.2. Typical protocol for structure elucidation	
4. Spin-spin scalar coupling	2. NMR in the solid state	
5. Spin systems of the first and the second orders	2.1 Orientation-dependent interactions	
6. Chemical exchange	2.1 Measurements of internuclear distances	
7. Two-dimensional NMR	2.3 NMR of surfaces and amorphous solids	



(+)-Borneol



(+)-Isoborneol

$C_{10}H_{18}O$

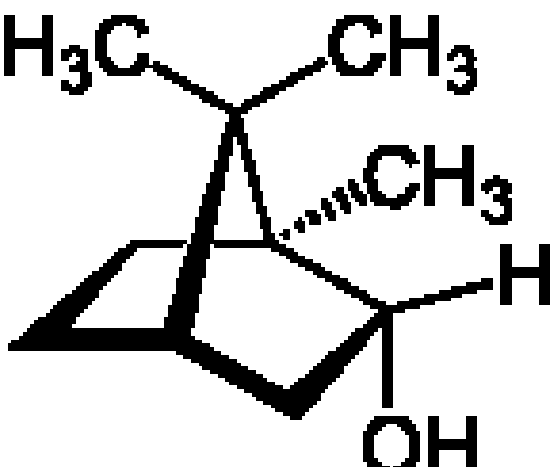
Spectrometer (6:44 min)

^{1}H NMR (1:25 min)
DEPT-135 (3:37 min)
COSY (10:33 min)

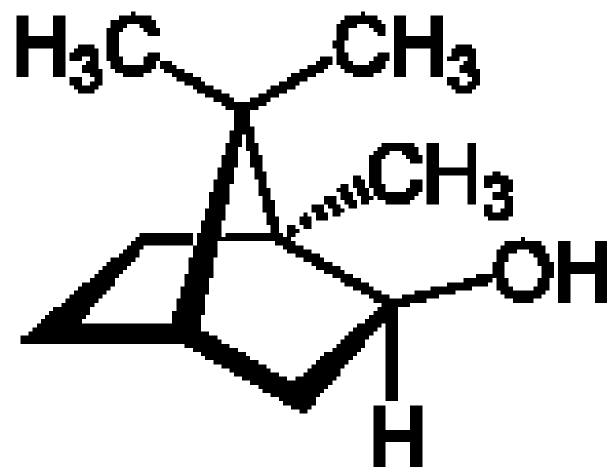
HSQC-DEPT (20:11 min)
HMBC (20:44 min)

NOESY (28:58 min)

^{13}C NMR (55:05 min)

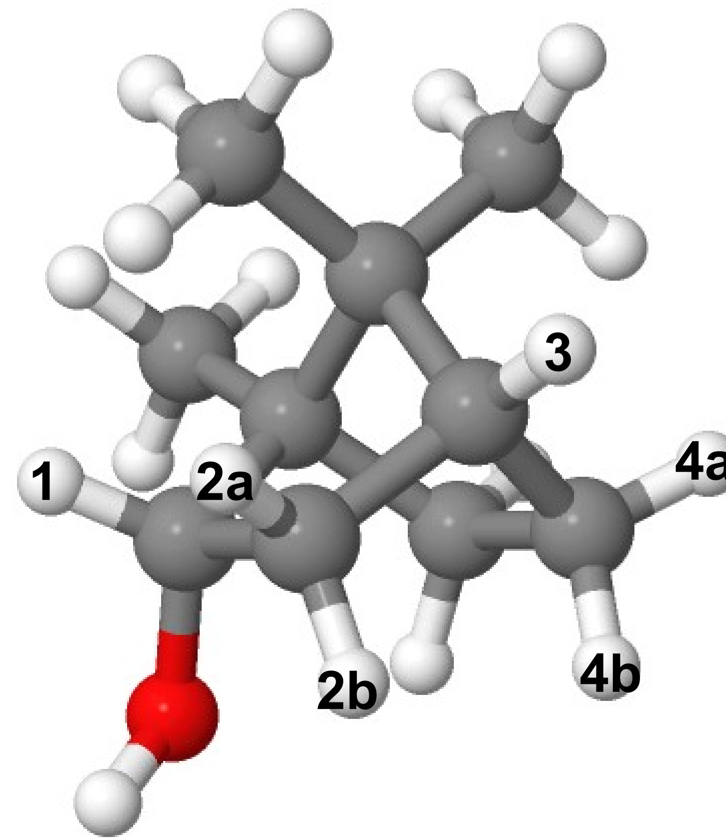


(-)-Borneol



(-)-Isoborneol

Borneol



Karplus equation:

$$J_{HH}(\varphi) \approx 12\cos^2\varphi - \cos\varphi + 2$$

$\phi(1\text{-}2a) \approx 5^0 \rightarrow J(1\text{-}2a) \approx 11$ Hz
$\phi(1\text{-}2b) \approx 125^0 \rightarrow J(1\text{-}2b) \approx 5$ Hz

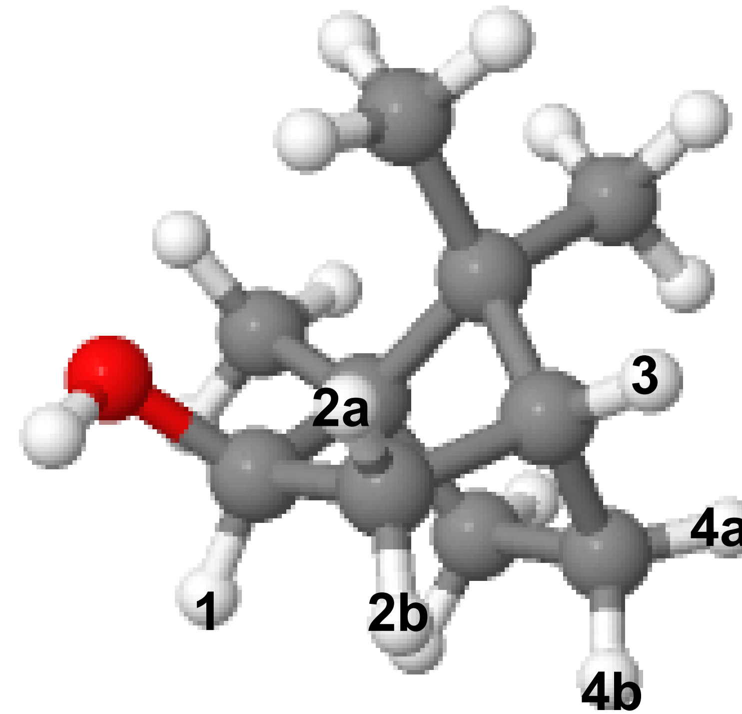
$\phi(3\text{-}2a) \approx 40^0 \rightarrow J(3\text{-}2a) \approx 7$ Hz
$\phi(3\text{-}2b) \approx 80^0 \rightarrow J(3\text{-}2b) \approx 1$ Hz

$\phi(3\text{-}4a) \approx 40^0 \rightarrow J(3\text{-}4a) \approx 7$ Hz
$\phi(3\text{-}4b) \approx 80^0 \rightarrow J(3\text{-}4b) \approx 1$ Hz

Karplus equation:

$$J_{HH}(\varphi) \approx 12\cos^2\varphi - \cos\varphi + 2$$

Iso-Borneol

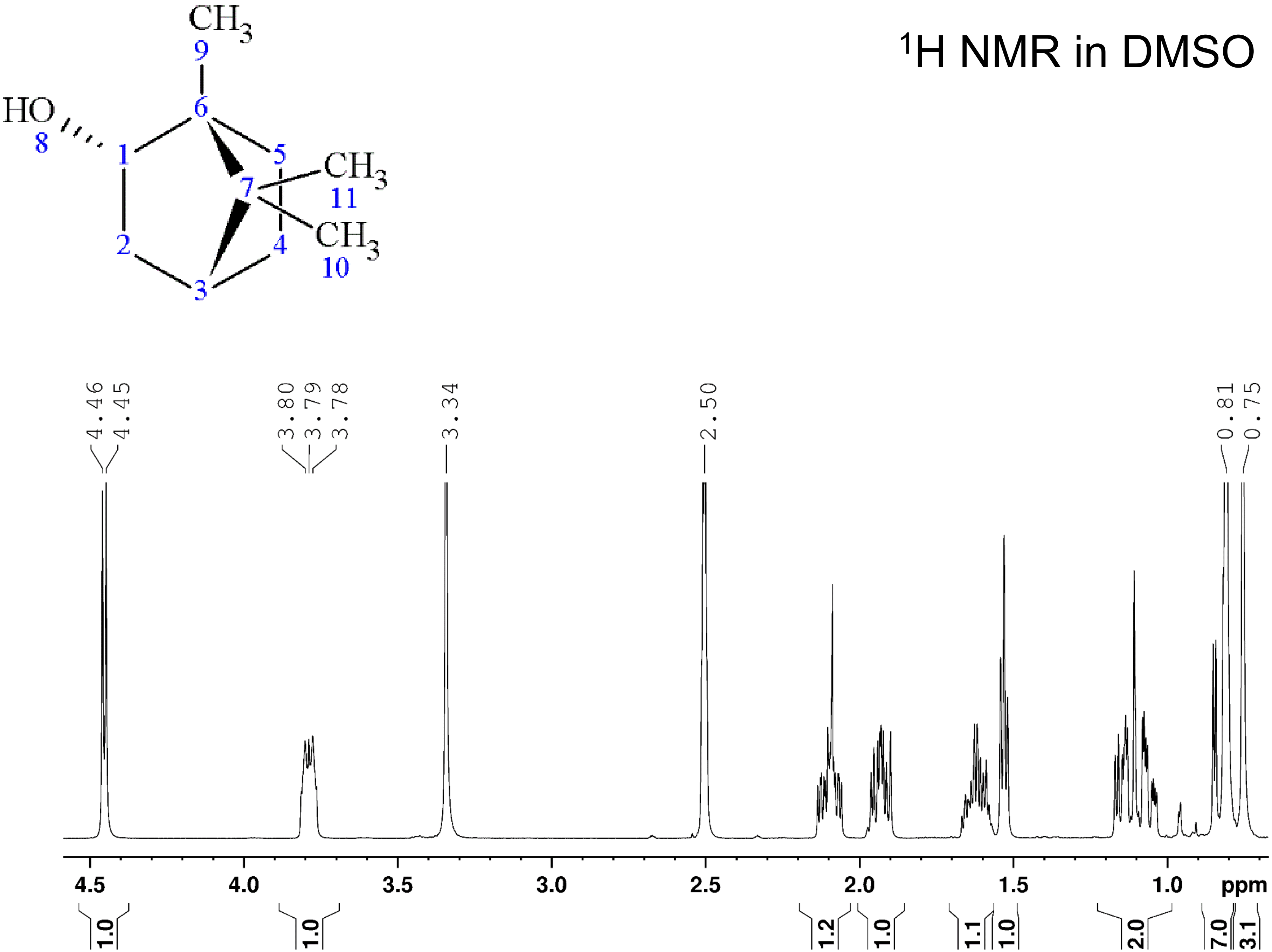


$\phi(1\text{-}2b) \approx 6^0 \rightarrow J(1\text{-}2b) \approx 11$ Hz
$\phi(1\text{-}2a) \approx 126^0 \rightarrow J(1\text{-}2a) \approx 5$ Hz

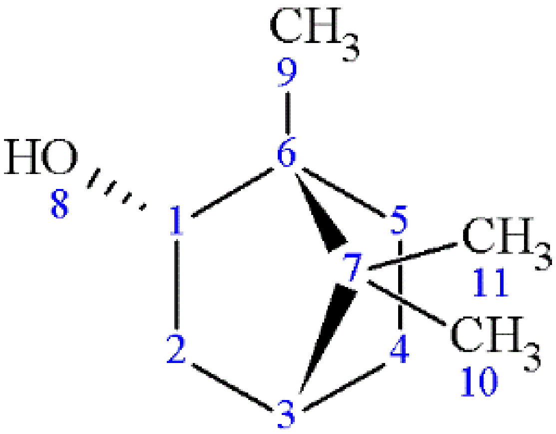
$\phi(3\text{-}2a) \approx 45^0 \rightarrow J(3\text{-}2a) \approx 7$ Hz
$\phi(3\text{-}2b) \approx 75^0 \rightarrow J(3\text{-}2b) \approx 1$ Hz

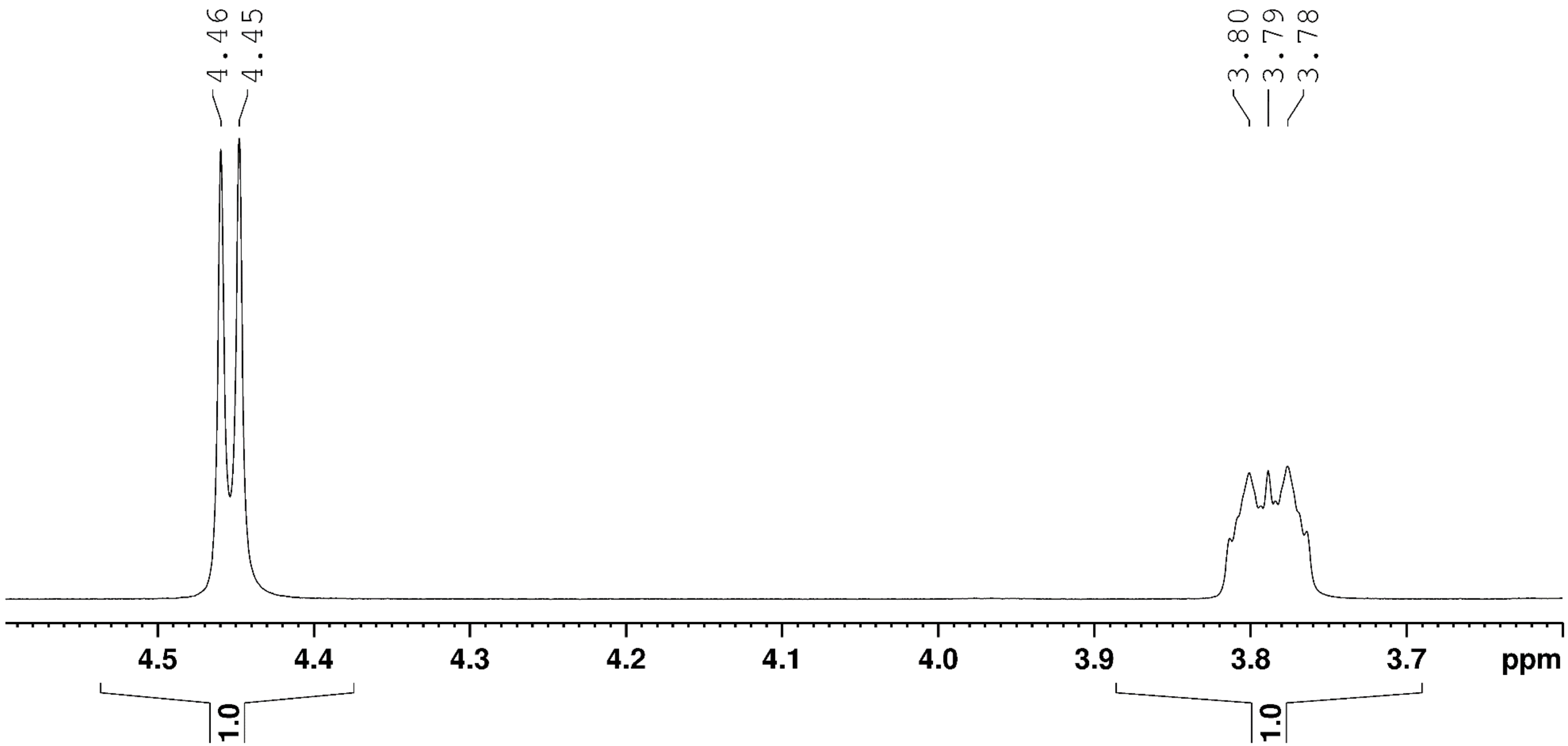
$\phi(3\text{-}4a) \approx 45^0 \rightarrow J(3\text{-}4a) \approx 7$ Hz
$\phi(3\text{-}4b) \approx 75^0 \rightarrow J(3\text{-}4b) \approx 1$ Hz

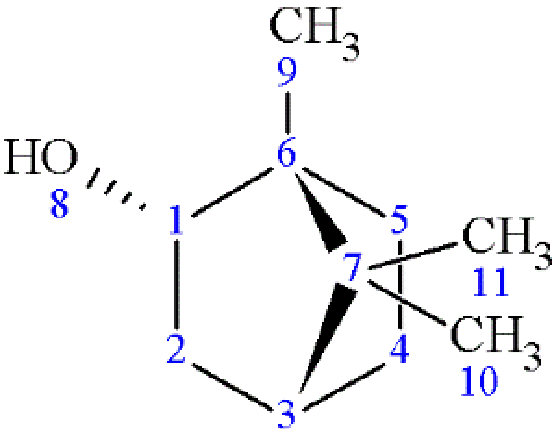
^{1}H NMR in DMSO



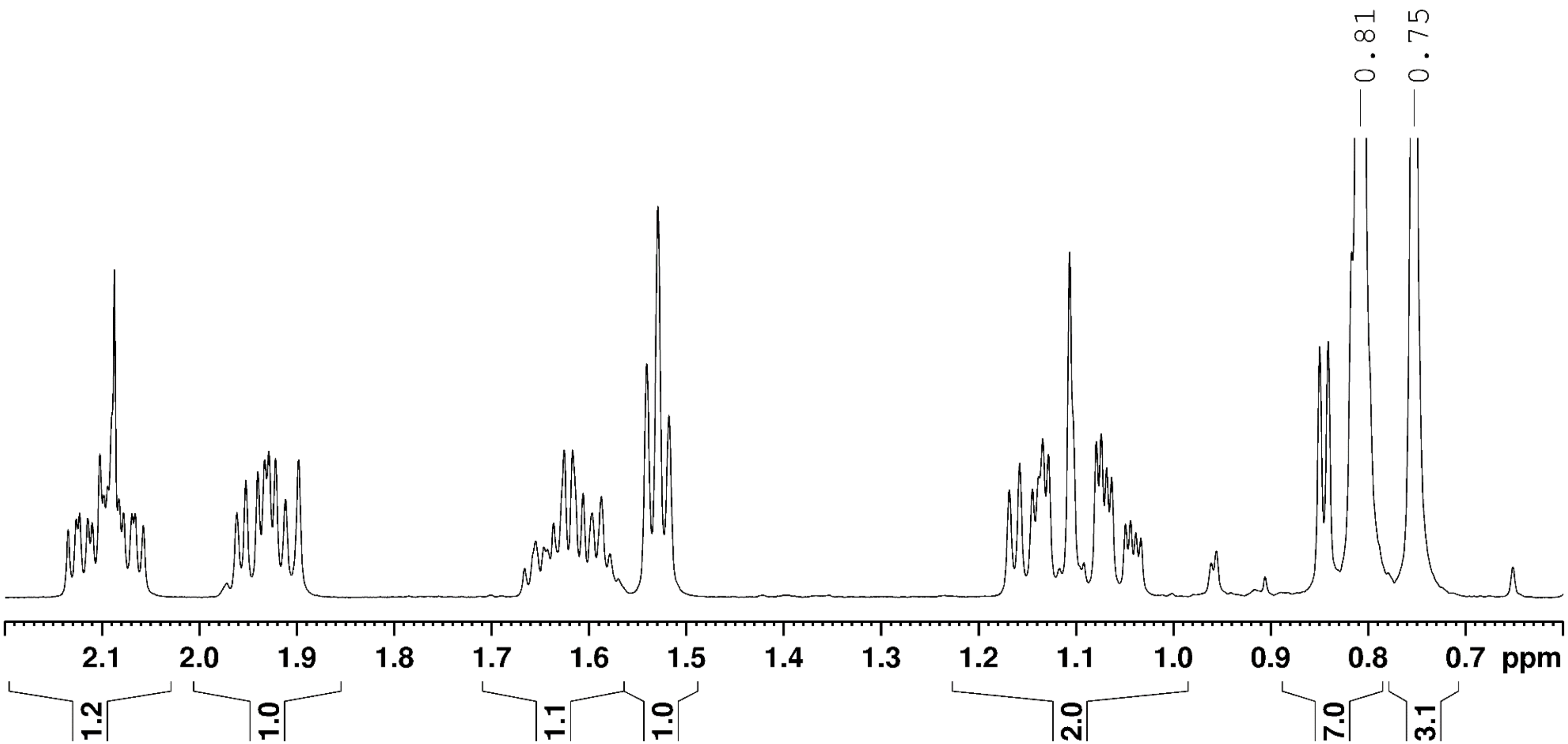
^{1}H NMR in DMSO

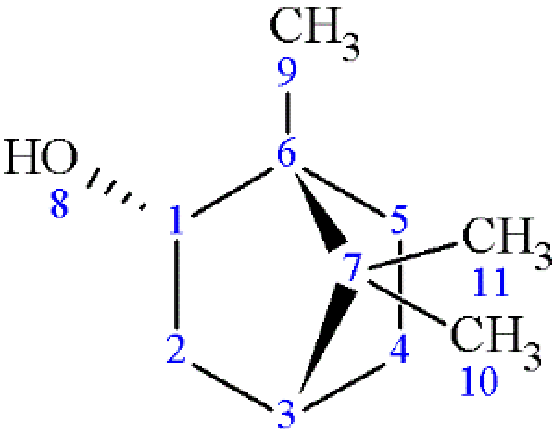




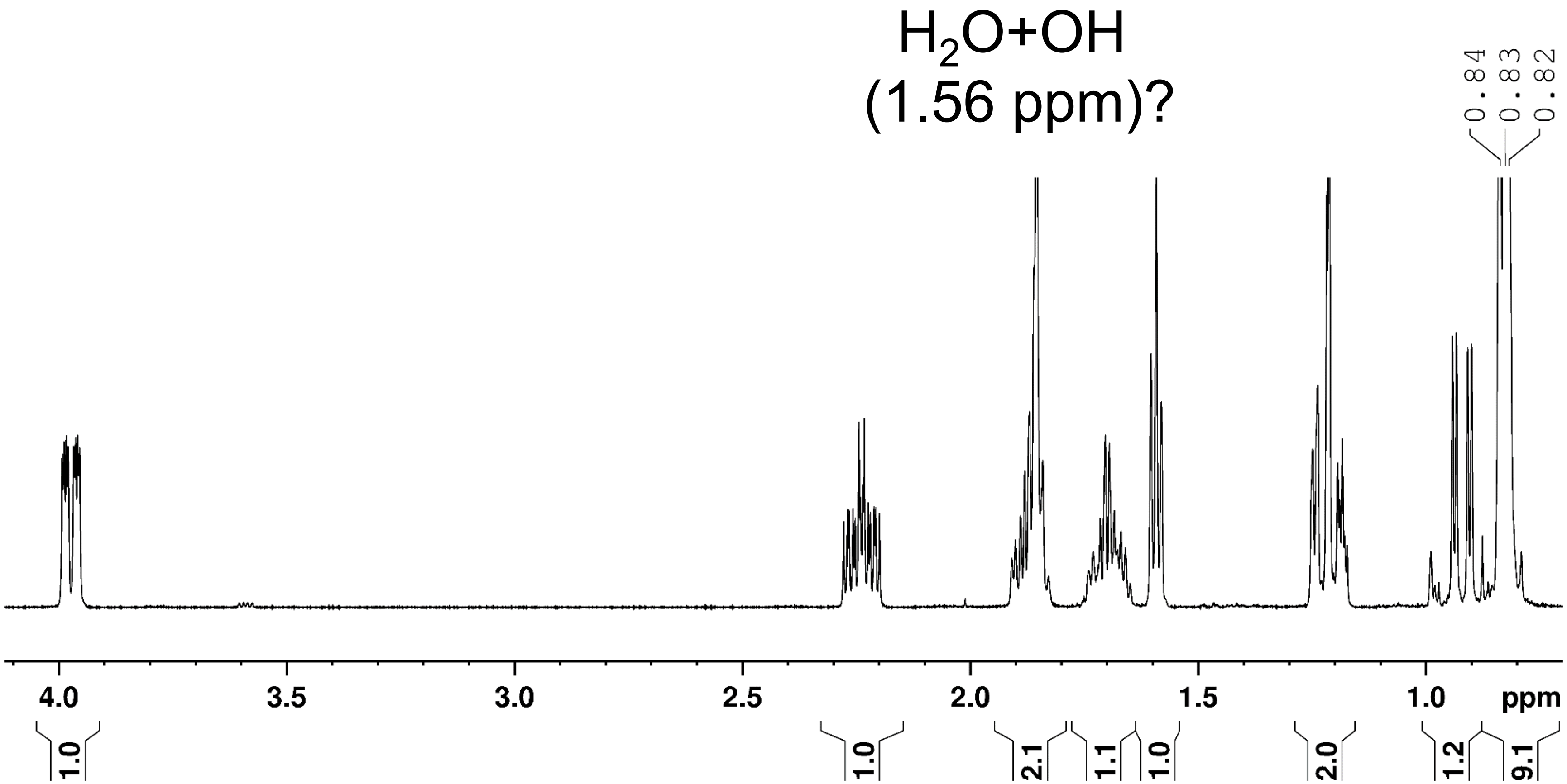


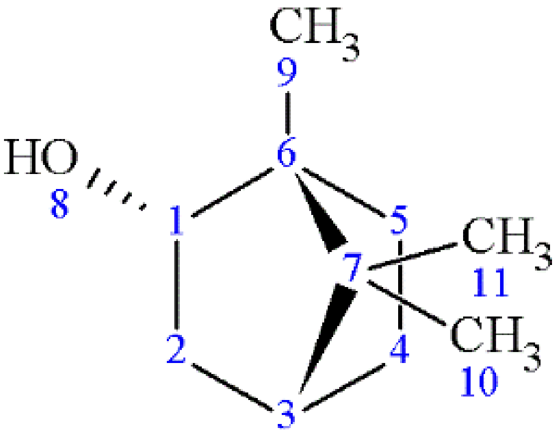
^1H NMR in DMSO





^{1}H NMR in $CDCl_3$



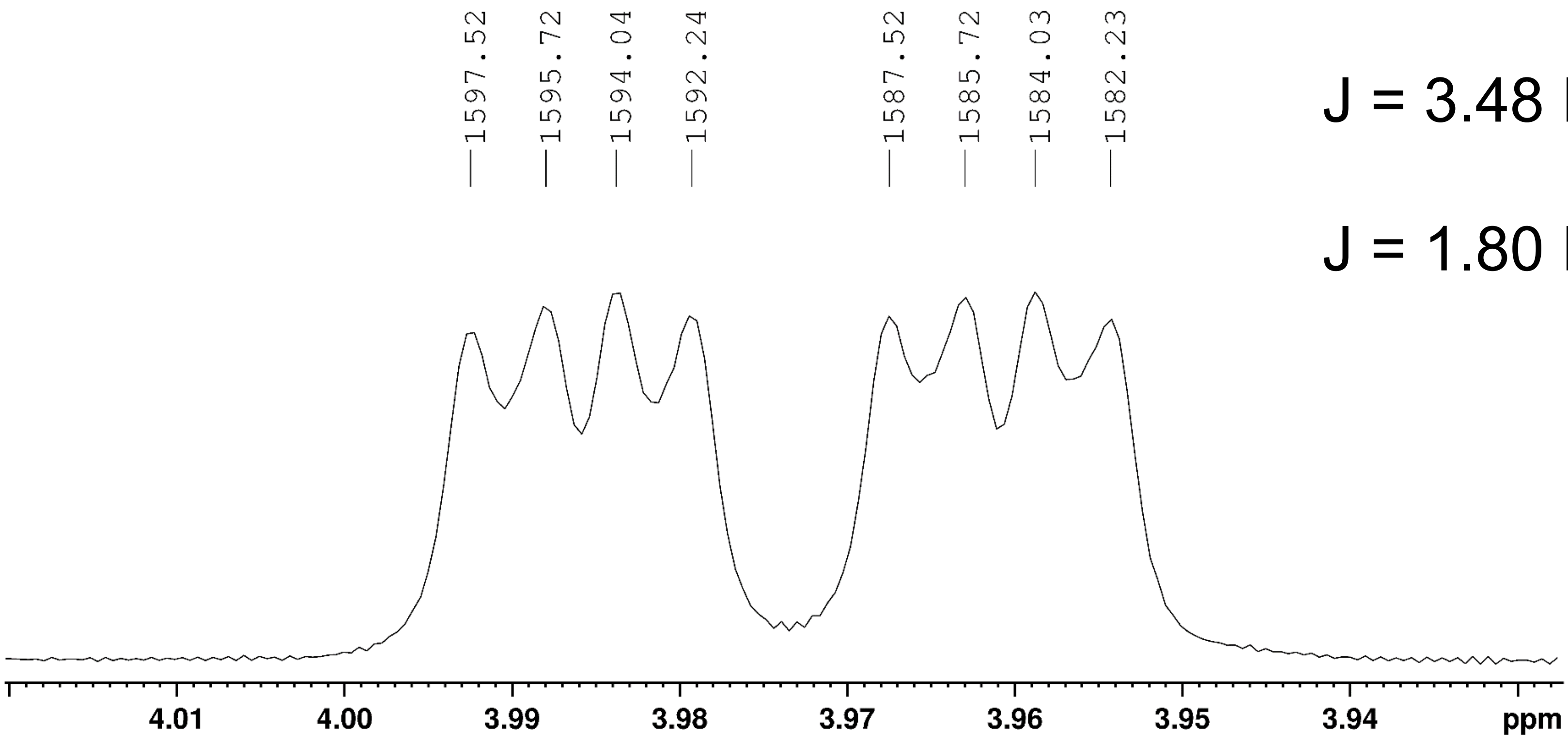


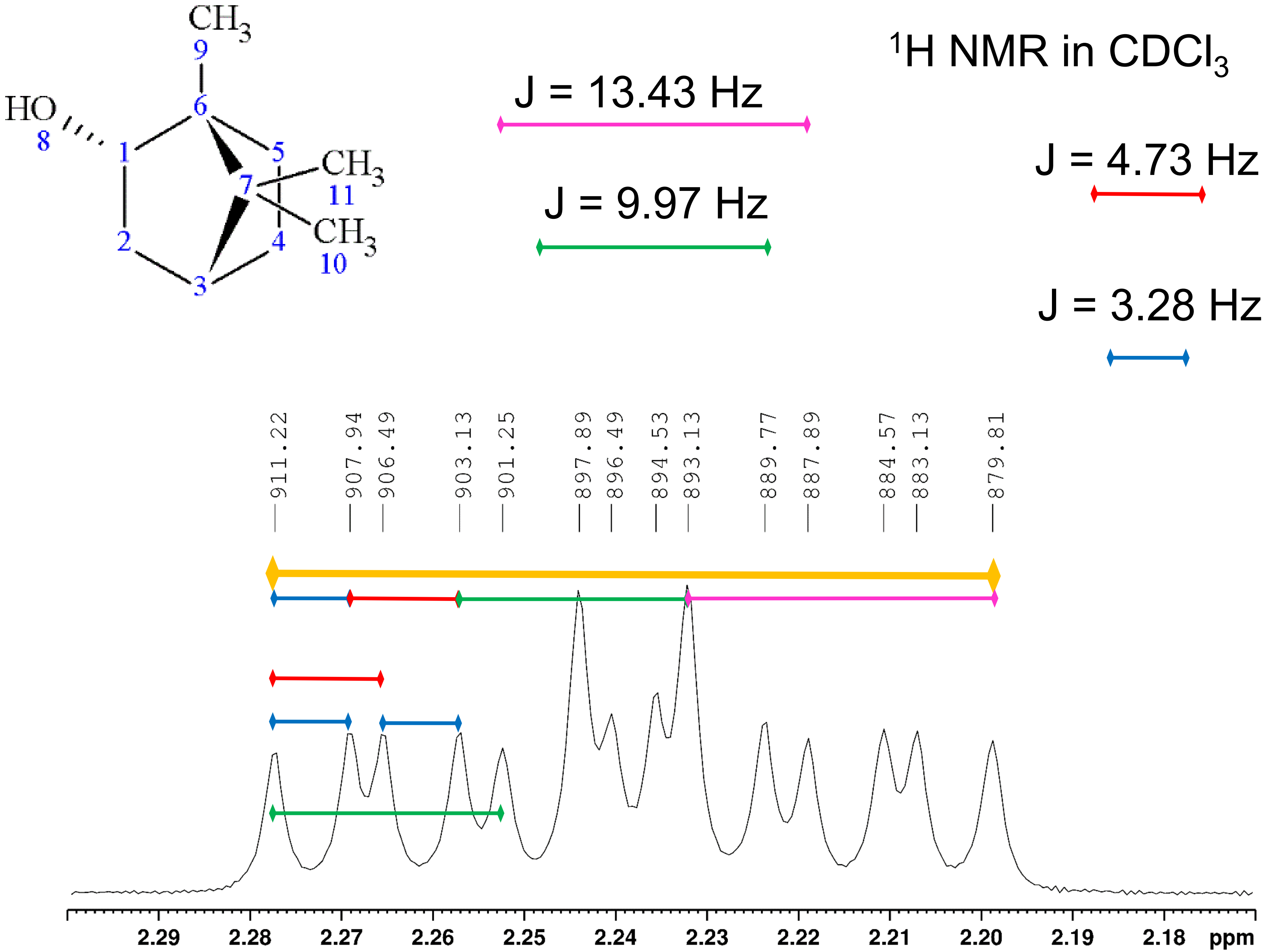
^{1}H NMR in $CDCl_3$

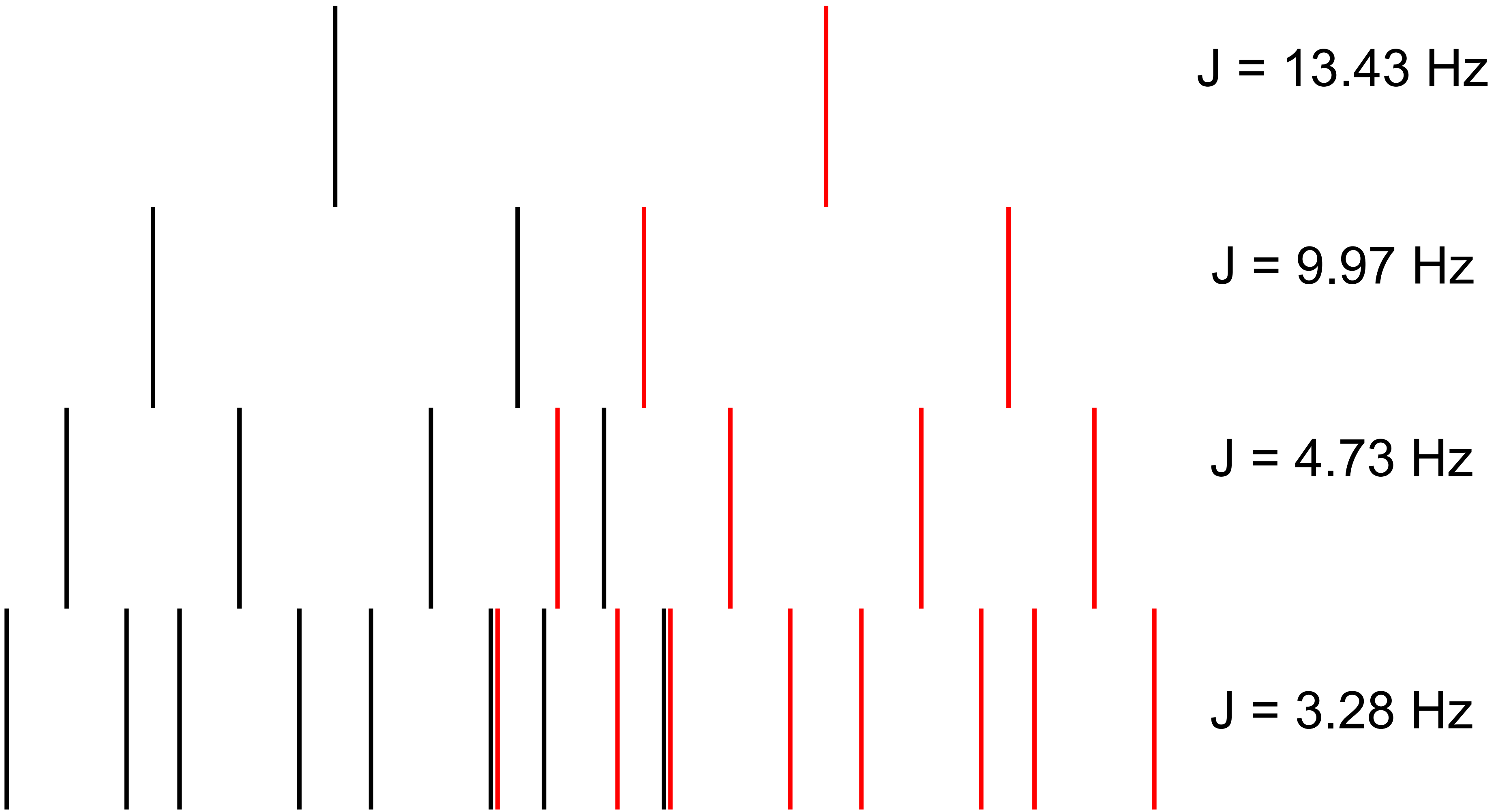
J = 10.00 Hz

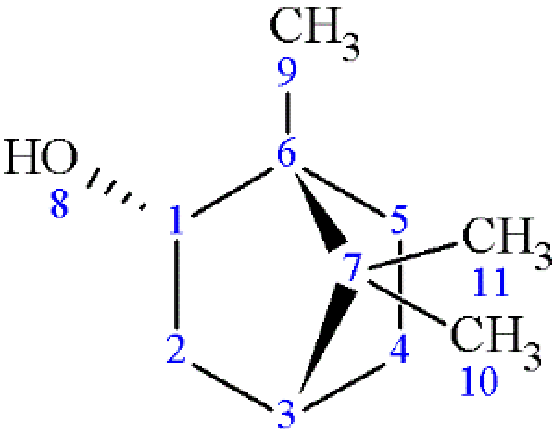
J = 3.48 Hz

J = 1.80 Hz

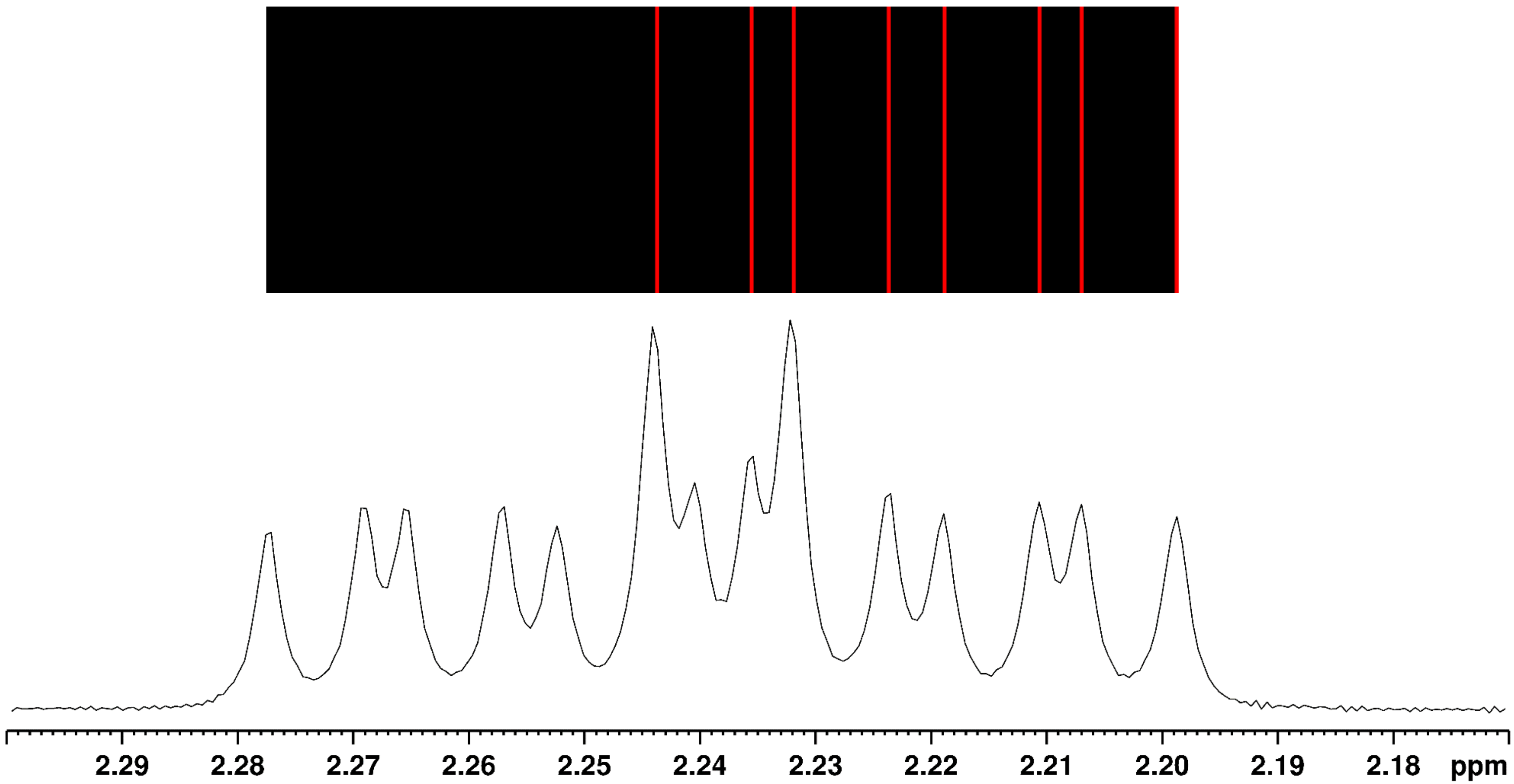


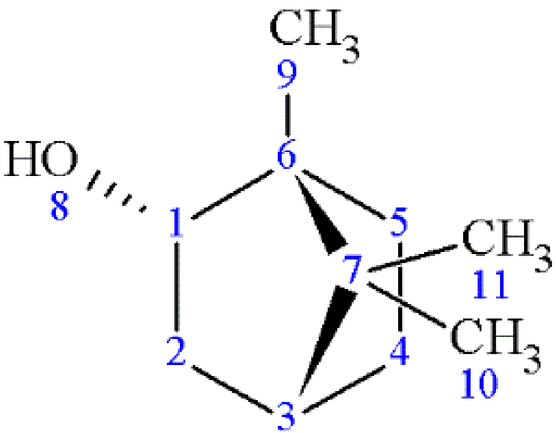

CH3
9
HO
8
6
1
5
CH3
7
11
2
4
CH3
3
10
J = 13.43 Hz
J = 9.97 Hz
1H NMR in CDCl3
J = 4.73 Hz
J = 3.28 Hz
911.22
907.94
906.49
903.13
901.25
897.89
896.49
894.53
893.13
889.77
887.89
884.57
883.13
879.81
2.29
2.28
2.27
2.26
2.25
2.24
2.23
2.22
2.21
2.20
2.19
2.18
ppm


J = 13.43 Hz
J = 9.97 Hz
J = 4.73 Hz
J = 3.28 Hz

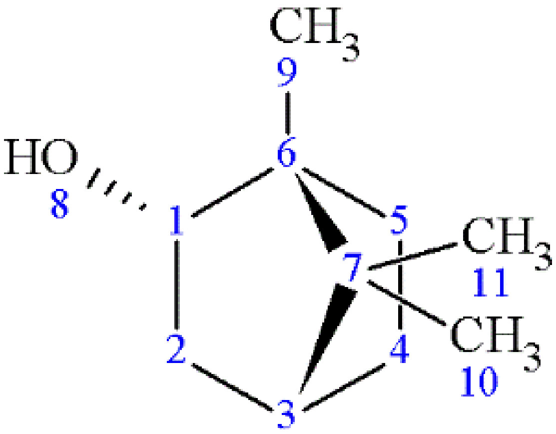


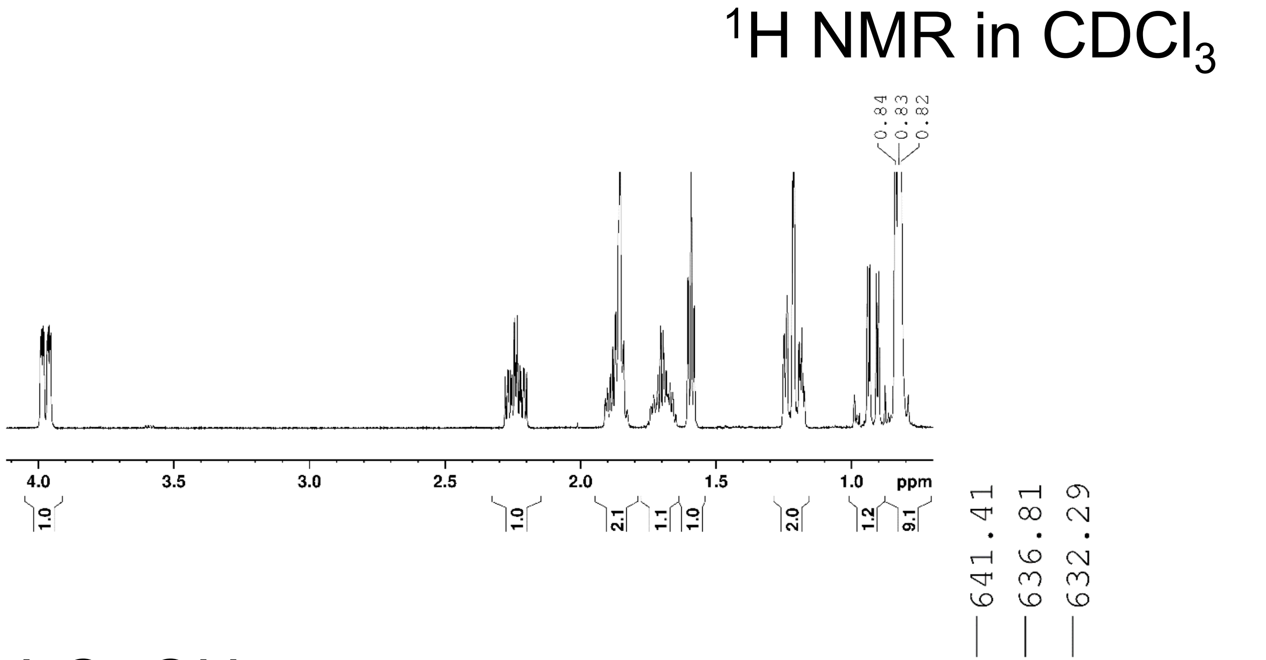
^1H NMR in $CDCl_3$

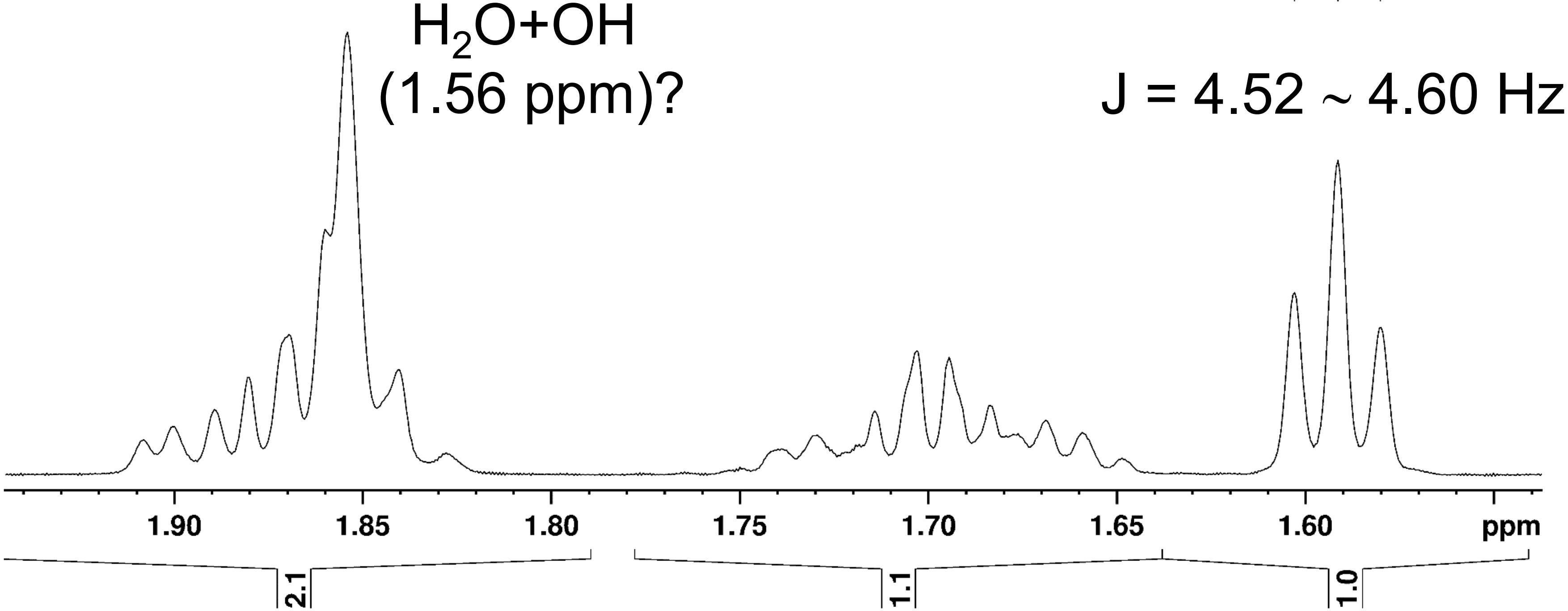


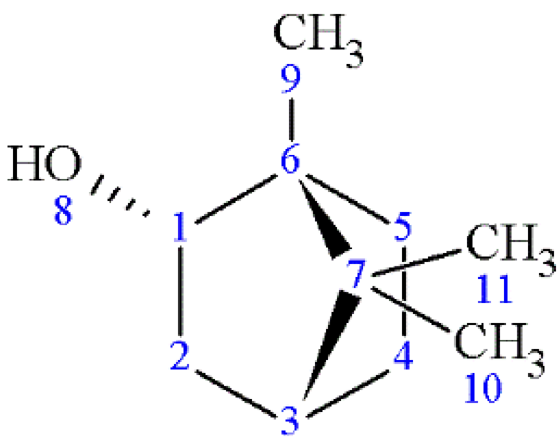


ID ^{1}H	δ, ppm		Int ^{1}H	CH_x x =	Multiplet		Commectivity	
	^{1}H	^{13}C			Type	J,Hz	HMBC	COSY
1	3.97		1		ddd	10.00 3.48 1.80		
2	2.24		1		dddd	13.43 9.97 4.73 3.28		

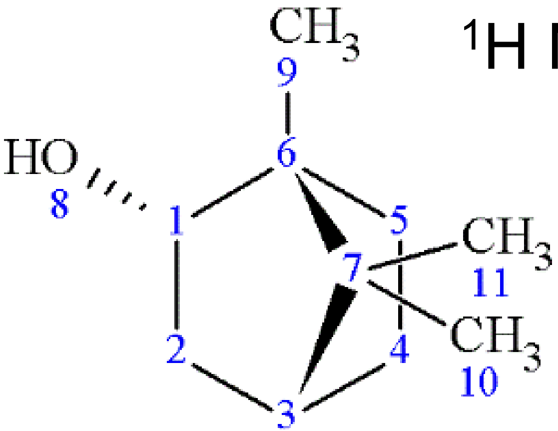

CH3
9
HO
8
6
1
5
CH3
7
11
2
CH3
4
3
10


1H NMR in CDCl3
0.84
0.83
0.82
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.0
1.0
2.1
1.1
1.0
2.0
1.2
9.1
641.41
636.81
632.29

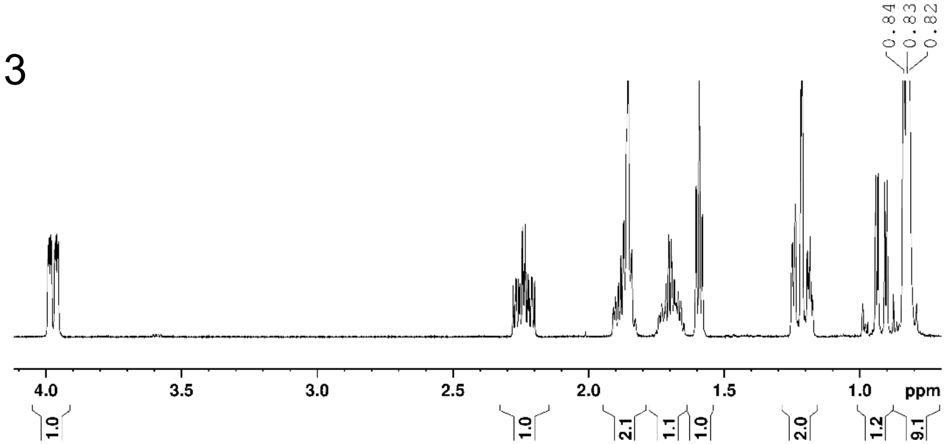

H2O+OH
(1.56 ppm)?
J = 4.52 ~ 4.60 Hz
1.90
1.85
1.80
1.75
1.70
1.65
1.60
ppm
2.1
1.1
1.0

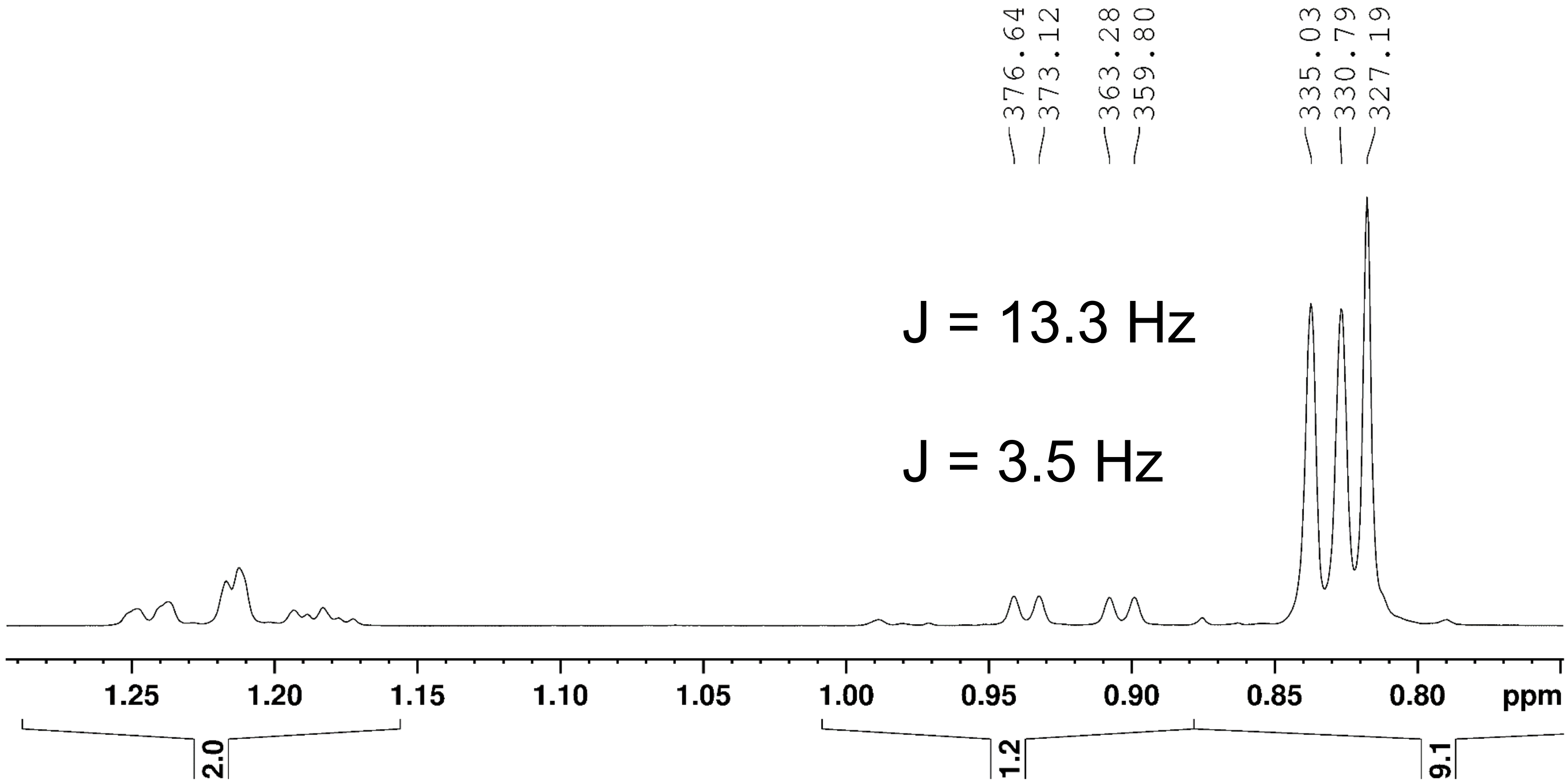


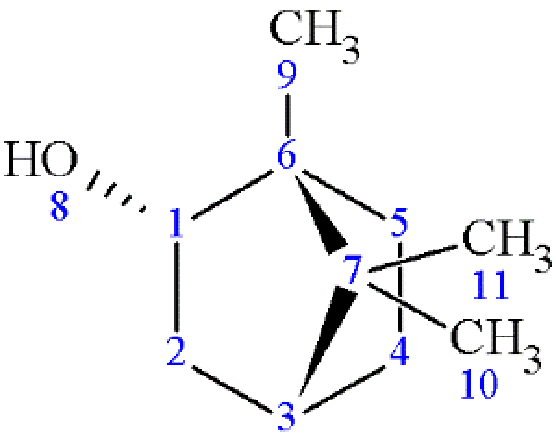
ID ^1H	δ, ppm		Int ^1H	CH_x x =	Multiplet		Commectivity	
	^1H	^{13}C			Type	J,Hz	HMBC	COSY
1	3.97		1		ddd	10.00 3.48 1.80		
2	2.24		1		dddd	13.43 9.97 4.73 3.28		
3	1.86		2		M			
4	1.70		1		M			
5	1.59		1		dd	4.5- 4.6		



^{1}H NMR in $CDCl_3$

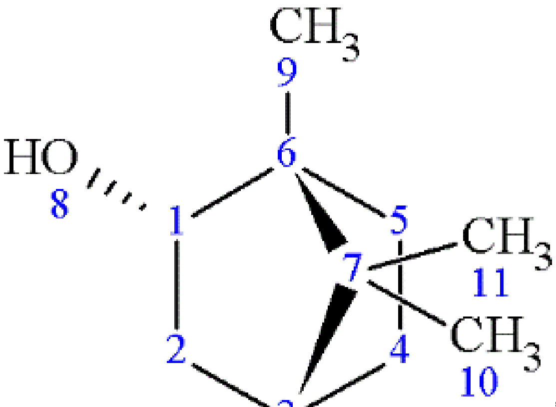


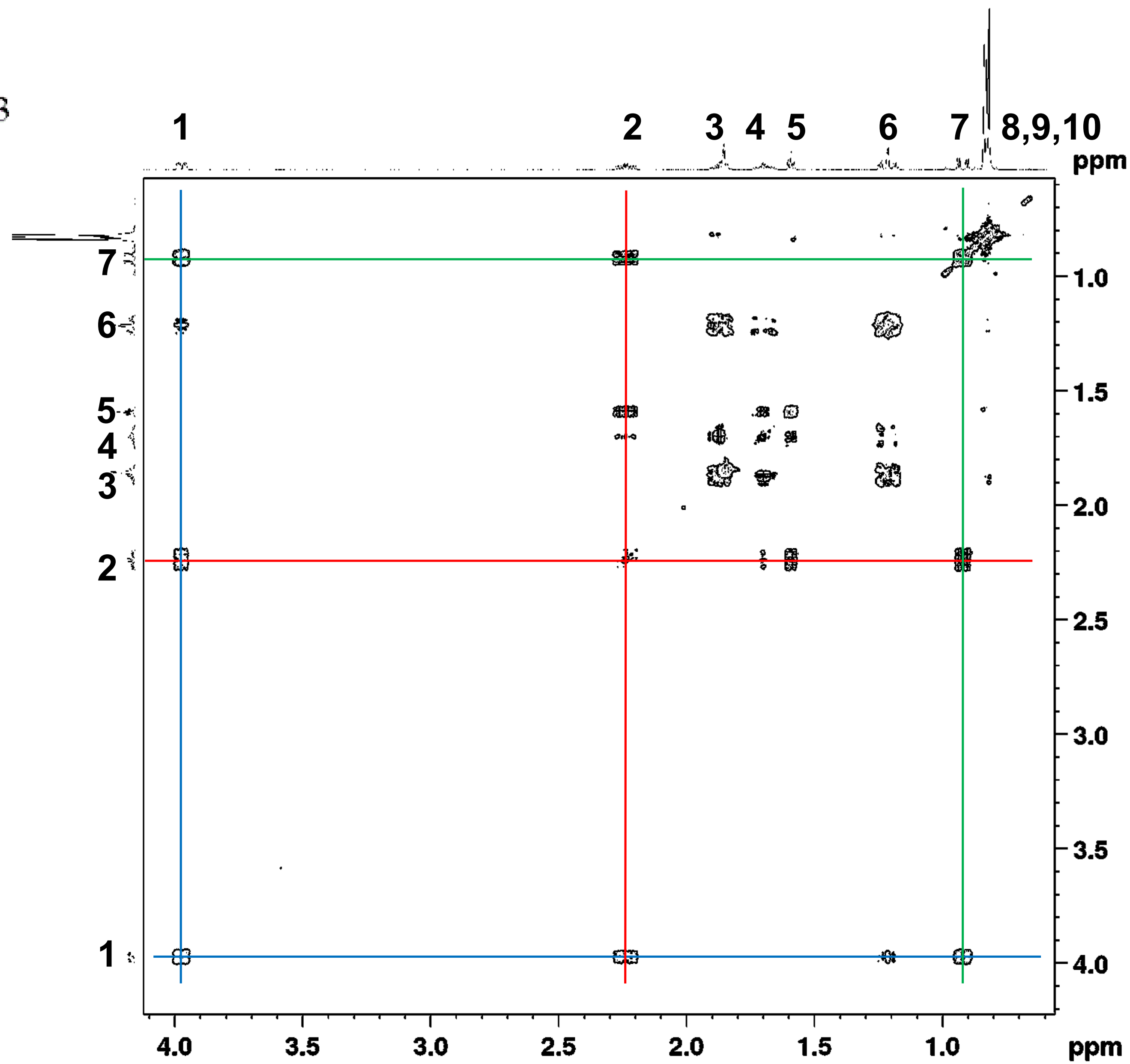


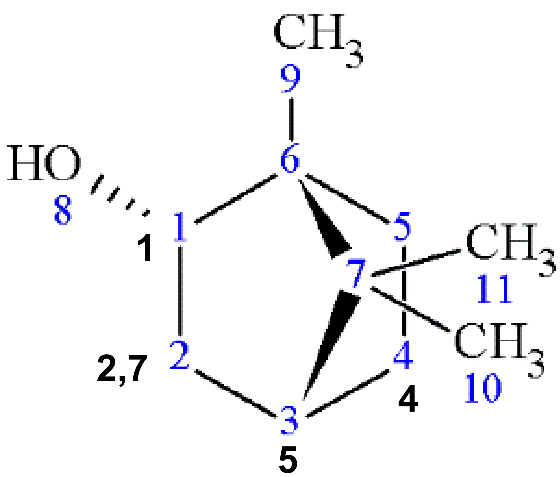


ID ^1H	δ, ppm		Int ^1H	CH_x x =	Multiplet		Commectivity	
	^1H	^{13}C			Type	J,Hz	HMBC	COSY
1	3.97		1		ddd	10.00 3.48 1.80		
2	2.24		1		dddd	13.43 9.97 4.73 3.28		
3	1.86		2		M			
4	1.70		1		M			
5	1.59		1		dd	4.5- 4.6		
6	1.21		2		M			
7	0.92		1		dd	13.3 3.5		
8	0.838		3		s			
9	0.827		3		s			
10	0.818		3		s			

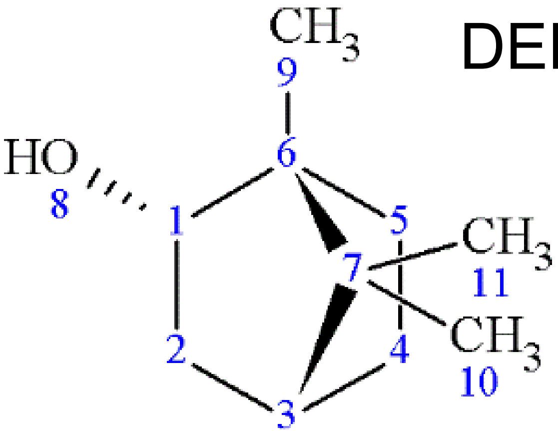
SY NMR in $CDCl_3$



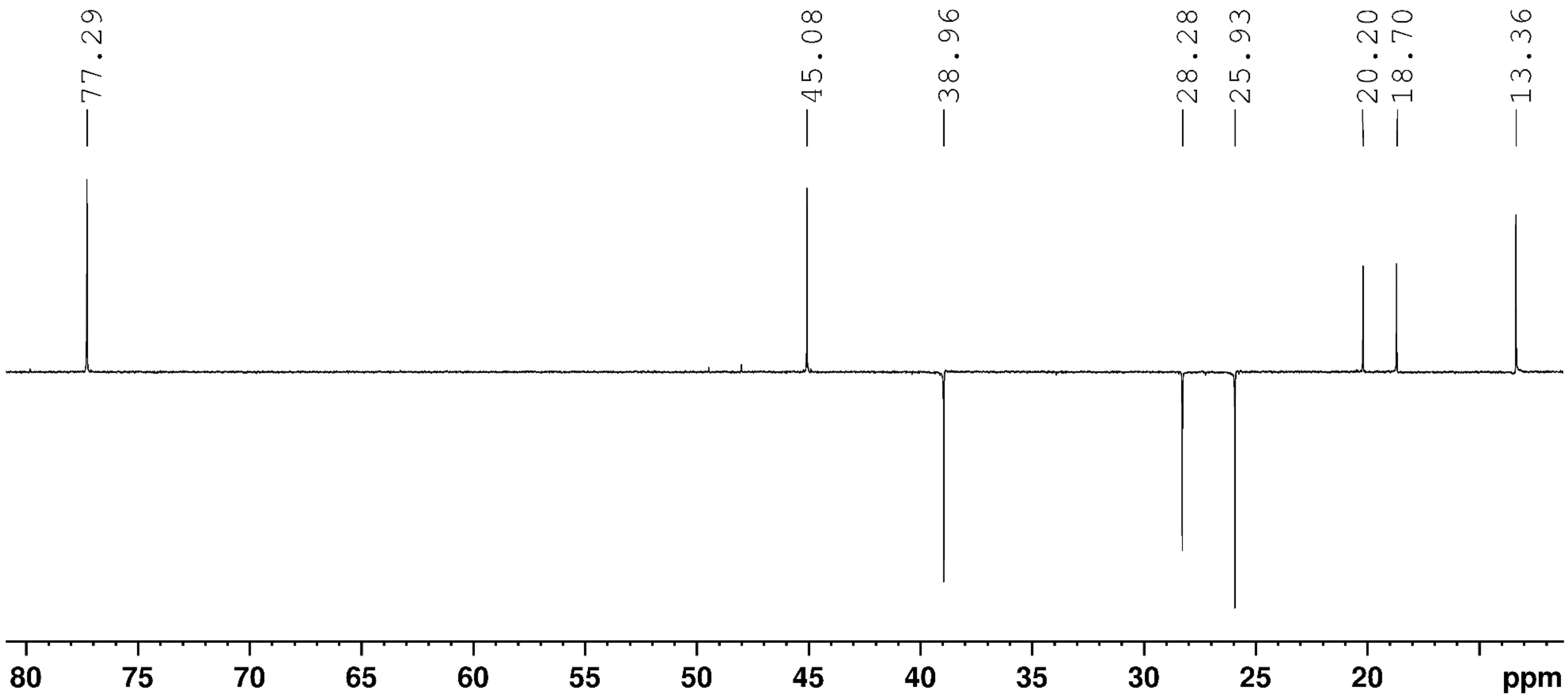




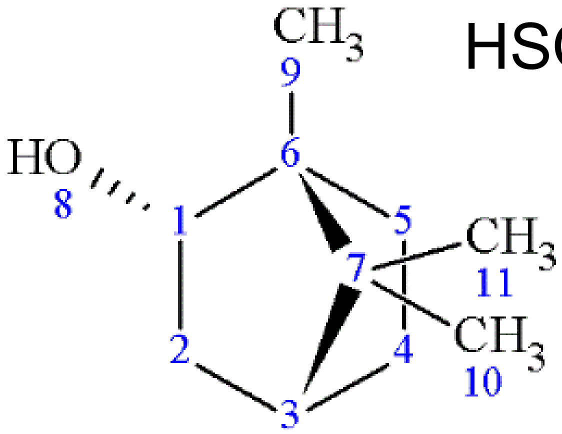
ID ^{1}H	δ, ppm		Int ^{1}H	CH_x x =	Multiplet		Commectivity	
	^{1}H	^{13}C			Type	J,Hz	HMBC	COSY
1	3.97		1		ddd	10.00 3.48 1.80		2 7 6
2	2.24		1		dddd	13.43 9.97 4.73 3.28		7 1 5 4
3	1.86		2		M			4,6,10
4	1.70		1		M			3,5,6,2
5	1.59		1		dd	4.5- 4.6		2,4,8
6	1.21		2		M			3,4,9
7	0.92		1		dd	13.3 3.5		2 1
8	0.838		3		s			5
9	0.827		3		s			6
10	0.818		3		s			3

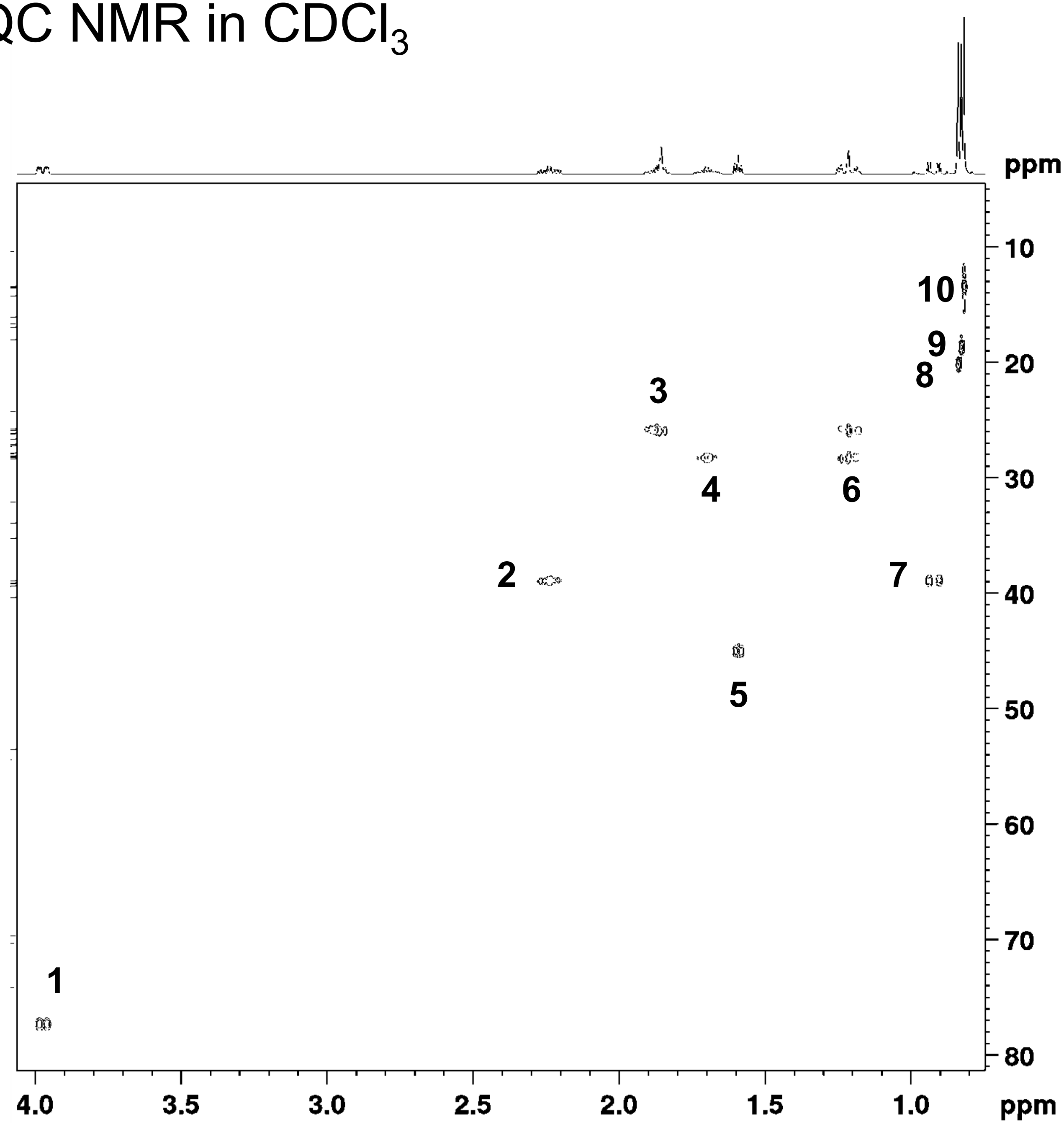


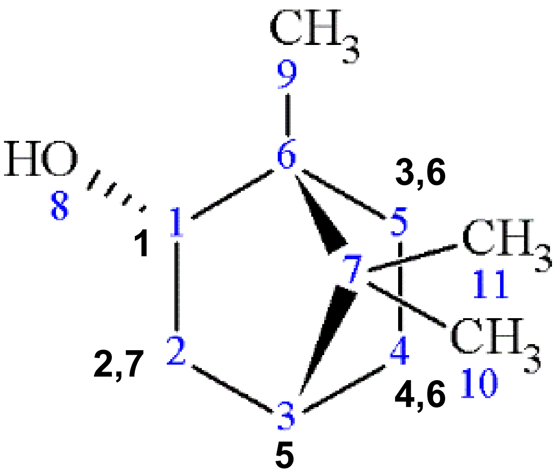
DEPT-135 NMR in $CDCl_3$



HSQC NMR in $CDCl_3$

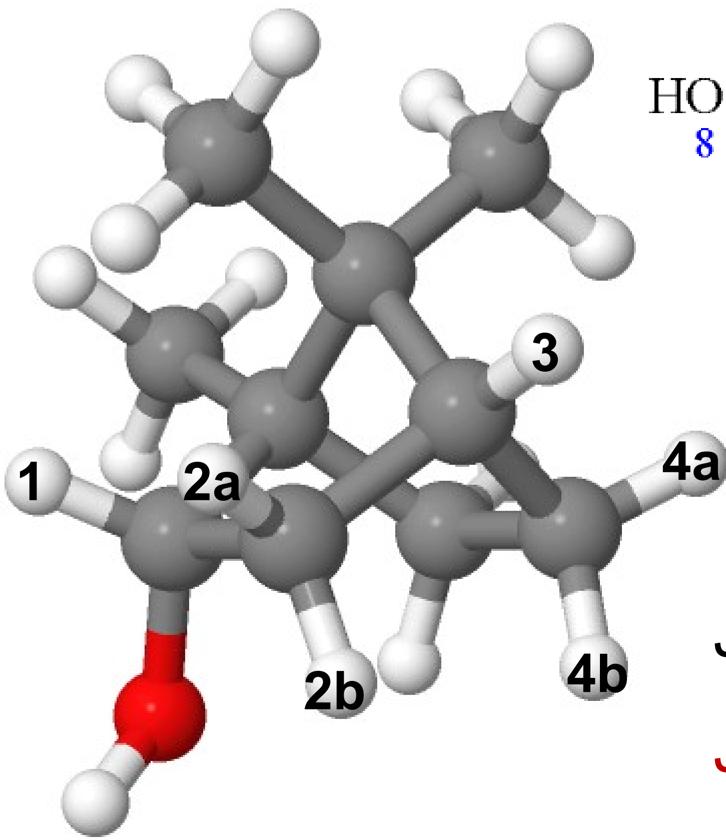


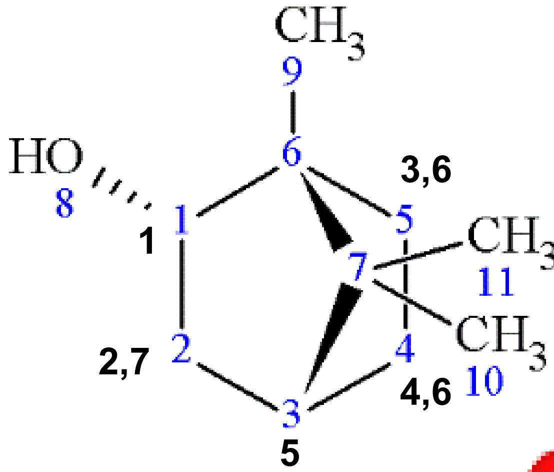




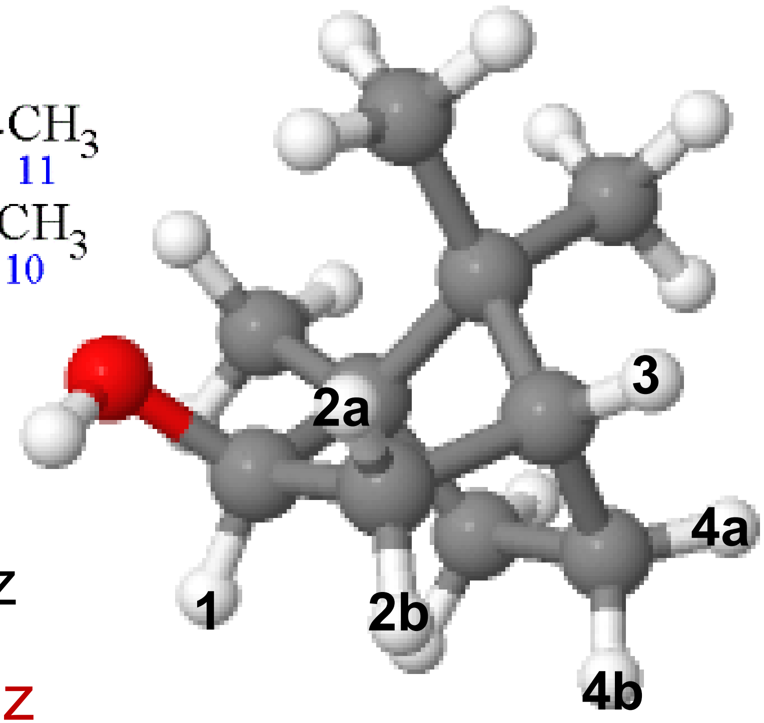
ID ^1H	δ, ppm		Int ^1H	CH_x x =	Multiplet		Commectivity	
	^1H	^{13}C			Type	J,Hz	HMBC	COSY
1	3.97	77.3	1	1	ddd	10.00 3.48 1.80		2 7 6
2	2.24	39.0	1	2	dddd	13.43 9.97 4.73 3.28		7 1 5 4
3	1.86	25.9	1		M			4,6,10
4	1.70	28.3	1	2	M			3,5,6,2
5	1.59	45.1	1	1	dd	4.5- 4.6		2,4,8
6	1.21	28.3 25.9	2	2	M			3,4,9
7	0.92	39.0	1	2	dd	13.3 3.5		2 1
8	0.838	20.2	3	3	s			5
9	0.827	18.7	3	3	s			6
10	0.818	13.4	3	3	s			3

Borneol





Iso-Borneol



ϕ(1-2a) ≈ 5^0 → J(1-2a) ≈ 11 Hz
ϕ(1-2b) ≈ 125^0 → J(1-2b) ≈ 5 Hz

ϕ(3-2a) ≈ 40^0 → J(3-2a) ≈ 7 Hz
ϕ(3-2b) ≈ 80^0 → J(3-2b) ≈ 1 Hz

ϕ(3-4a) ≈ 40^0 → J(3-4a) ≈ 7 Hz
ϕ(3-4b) ≈ 80^0 → J(3-4b) ≈ 1 Hz

J(1,2) = 10 Hz

J(1,7) = 3.5 Hz

J(2,5) = 4.7 Hz

J(7,5) = 0 Hz

J(5,4) = 4.5 Hz

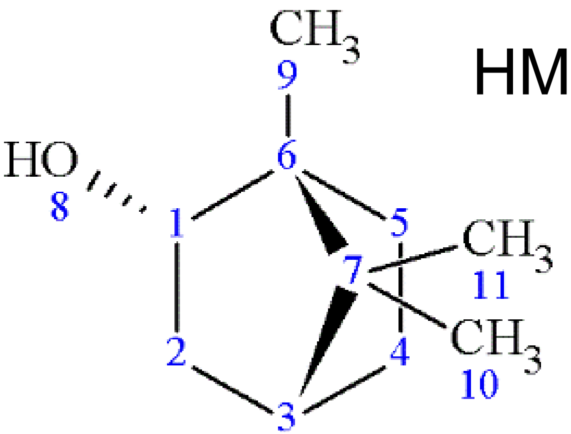
J(5,6) = 0 Hz

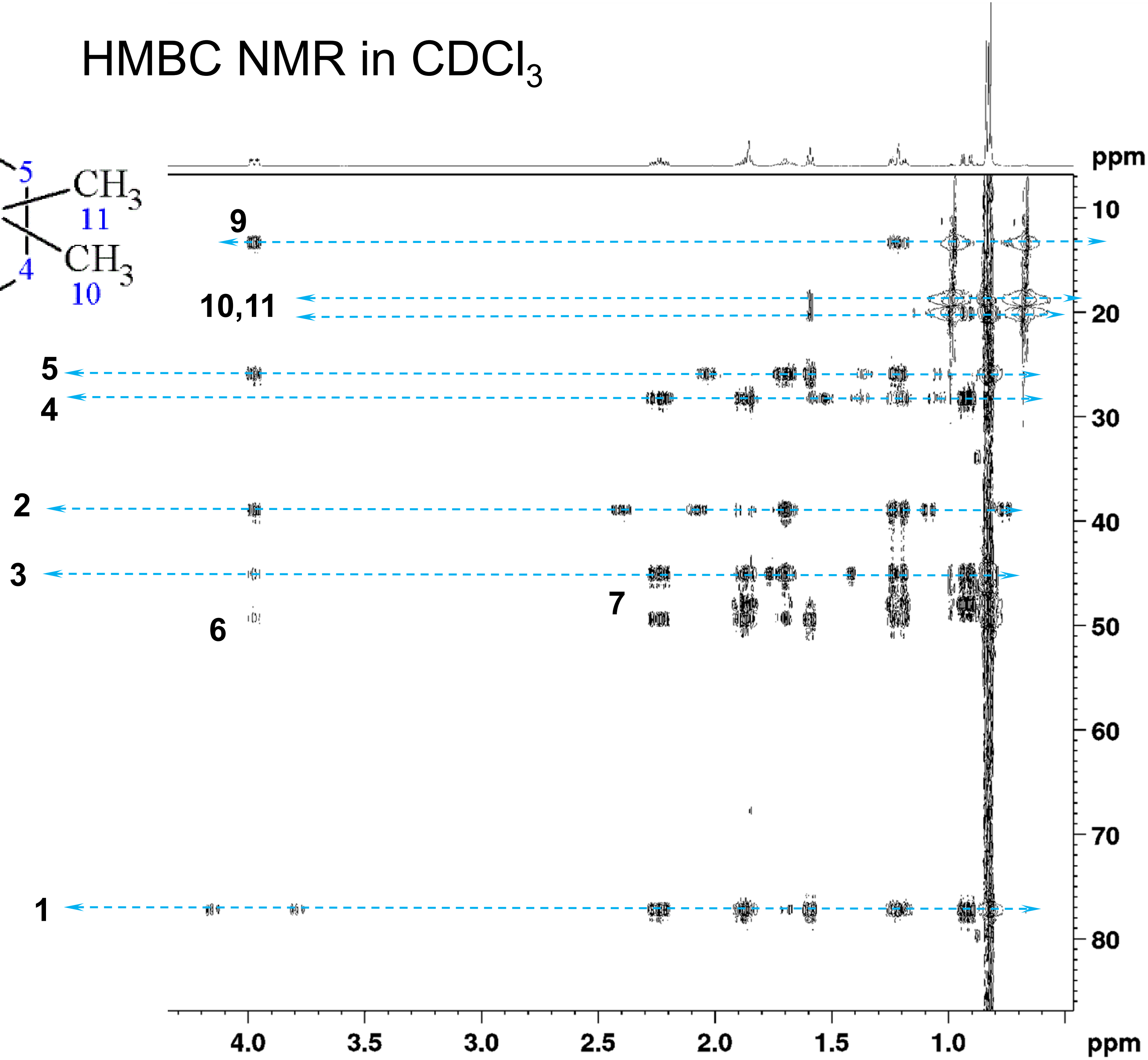
ϕ(1-2b) ≈ 6^0 → J(1-2b) ≈ 11 Hz
ϕ(1-2a) ≈ 126^0 → J(1-2a) ≈ 5 Hz

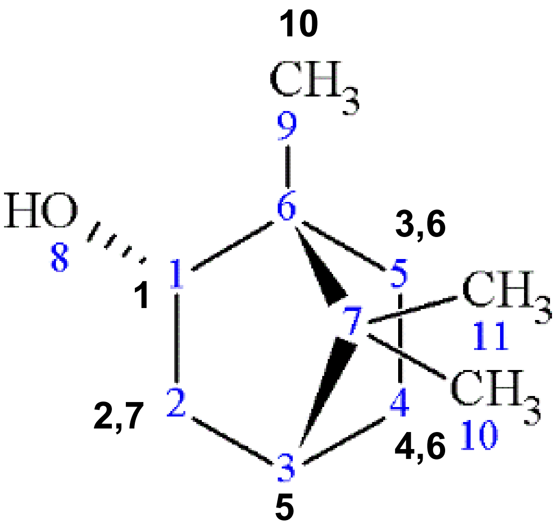
ϕ(3-2a) ≈ 45^0 → J(3-2a) ≈ 7 Hz
ϕ(3-2b) ≈ 75^0 → J(3-2b) ≈ 1 Hz

ϕ(3-4a) ≈ 45^0 → J(3-4a) ≈ 7 Hz
ϕ(3-4b) ≈ 75^0 → J(3-4b) ≈ 1 Hz

HMBC NMR in $CDCl_3$

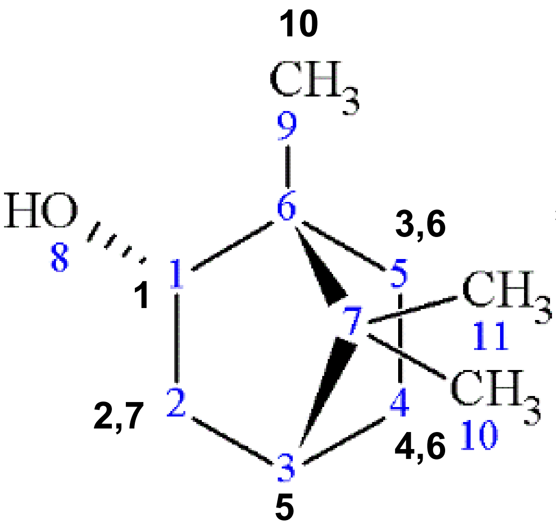


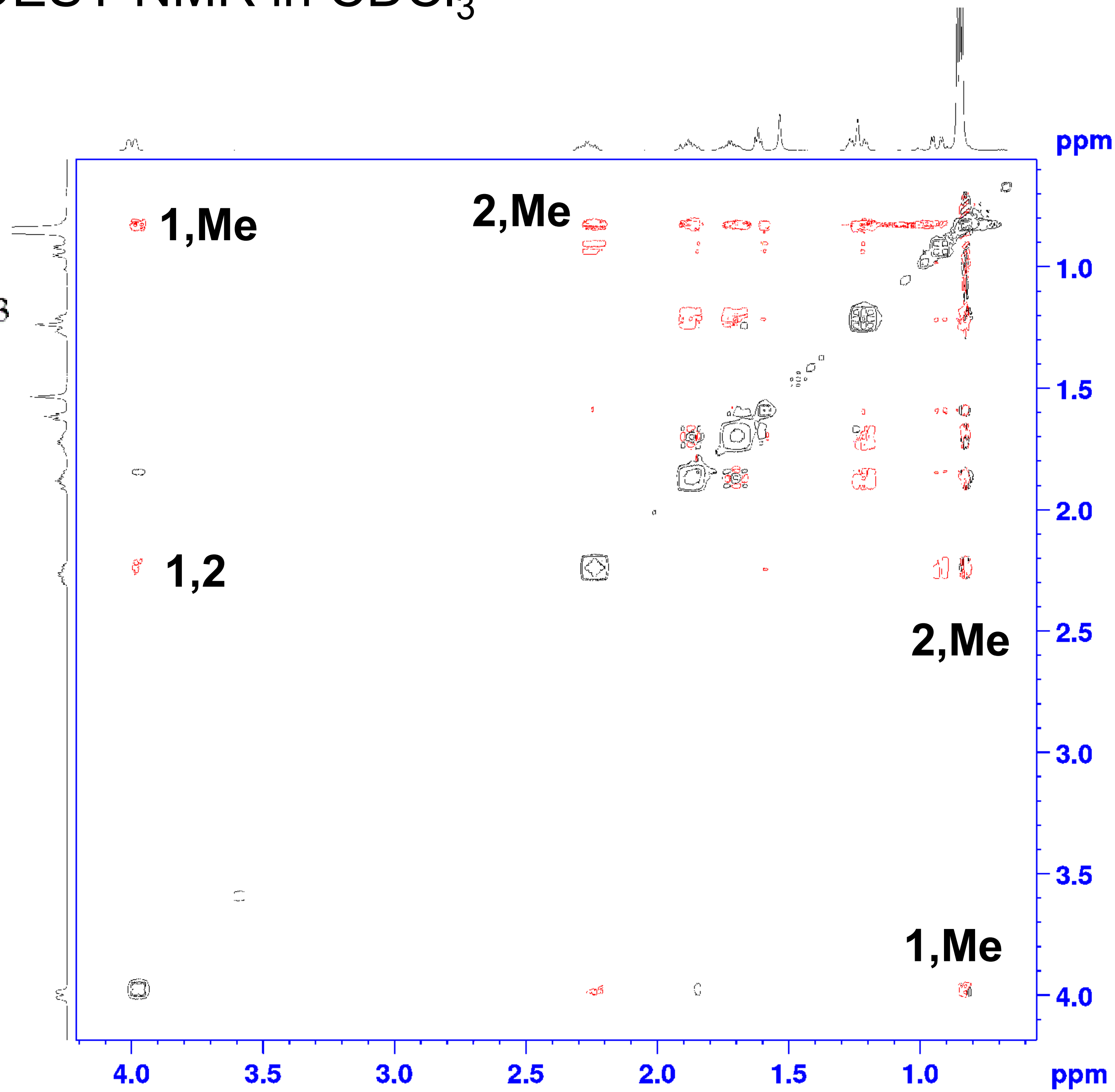




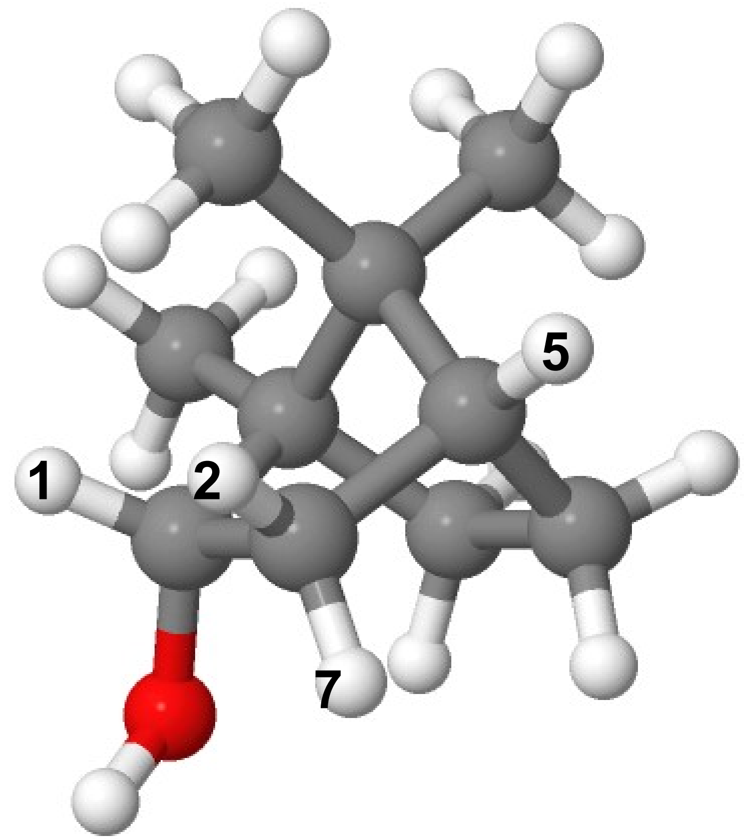
ID ^{1}H	δ, ppm		Int ^{1}H	CH_x x =	Multiplet		Commectivity	
	^{1}H	^{13}C			Type	J,Hz	HMBC	COSY
1	3.97	77.3	1	1	ddd	10.00 3.48 1.80	2C,3C, 5C, 6C, 9C	2 7 6
2	2.24	39.0	1	2	dddd	13.43 9.97 4.73 3.28	1C, 3C, 4C, 6C	7 1 5 4
3	1.86	25.9	1		M		1C, 3C, 4C, 6C, 7C	4,6,10
4	1.70	28.3	1	2	M		1C, 2C, 3C, 5C, 6C	3,5,6,2
5	1.59	45.1	1	1	dd	4.5- 4.6	1C, 5C, 6C, 10C, 11C	2,4,8
6	1.21	28.3 25.9	2	2	M		1C, 2C, 3C, 4C, 5C, 6C, 7C, 9C	3,4,9
7	0.92	39.0	1	2	dd	13.3 3.5	1C, 3C, 4C, 7C	2 1
8	0.838	20.2	3	3	s		3C, 7C	5
9	0.827	18.7	3	3	s		3C, 7C	6
10	0.818	13.4	3	3	s		1C, 5C, 6C, 7C, 11C	3

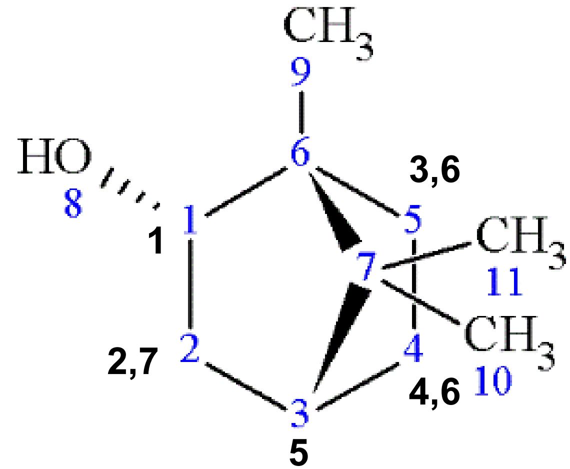
NOESY NMR in $CDCl_3$



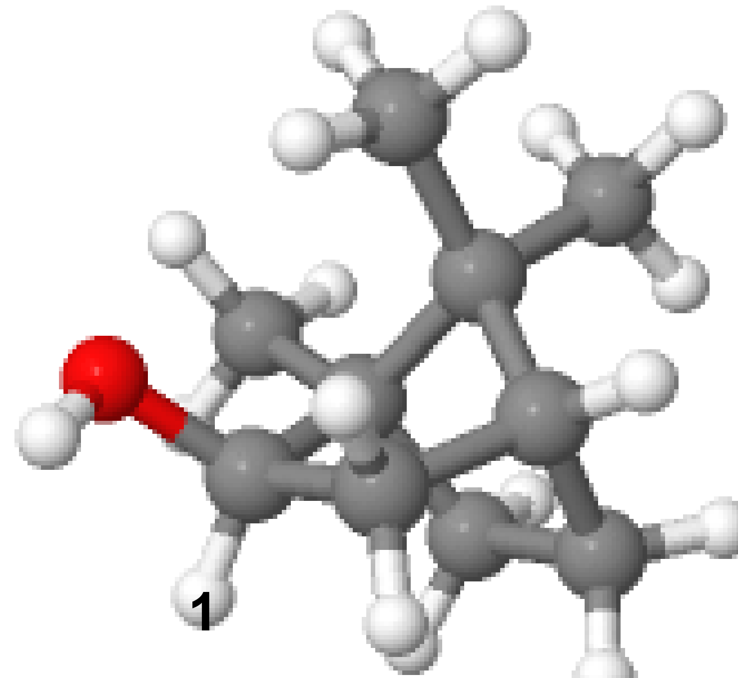


Borneol



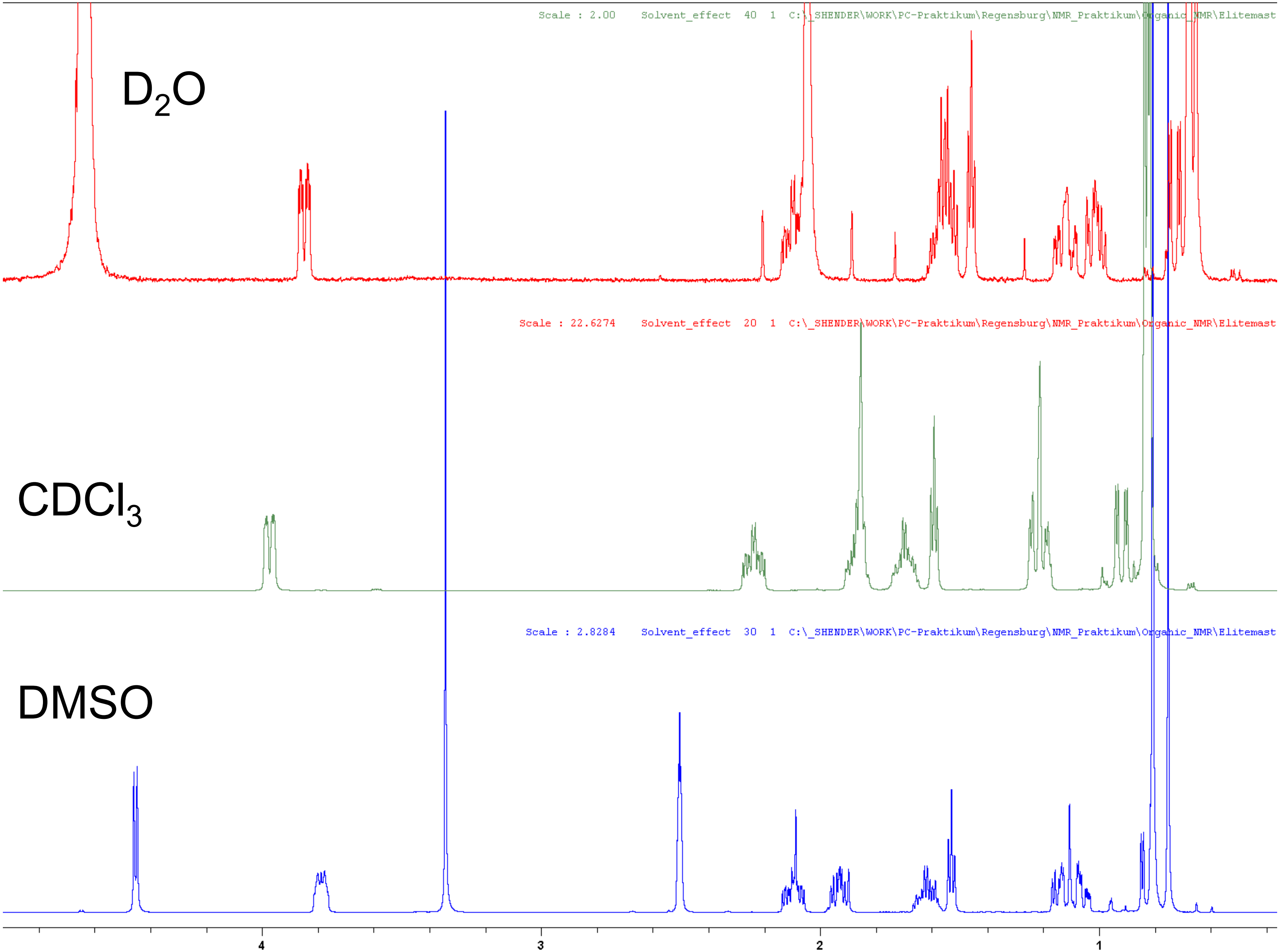


Iso-Borneol

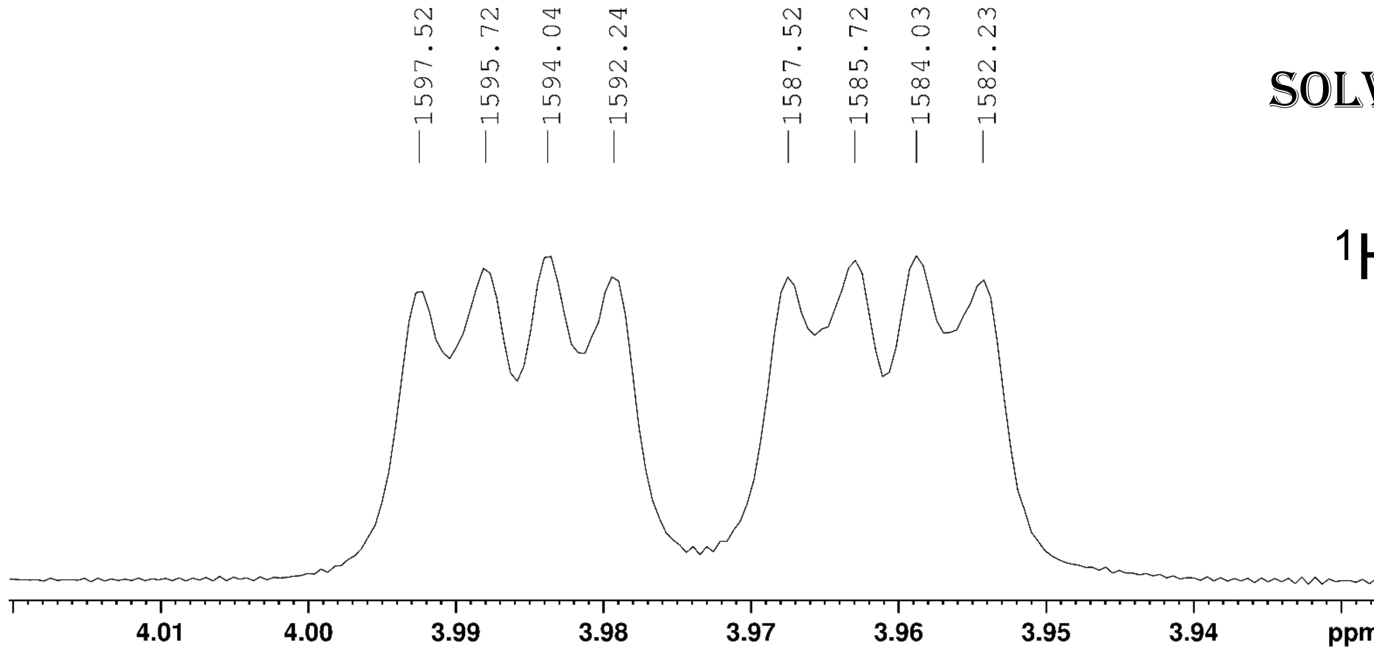


NOE: 1-2, 1-Me, 2-Me

SOLVENT EFFECT

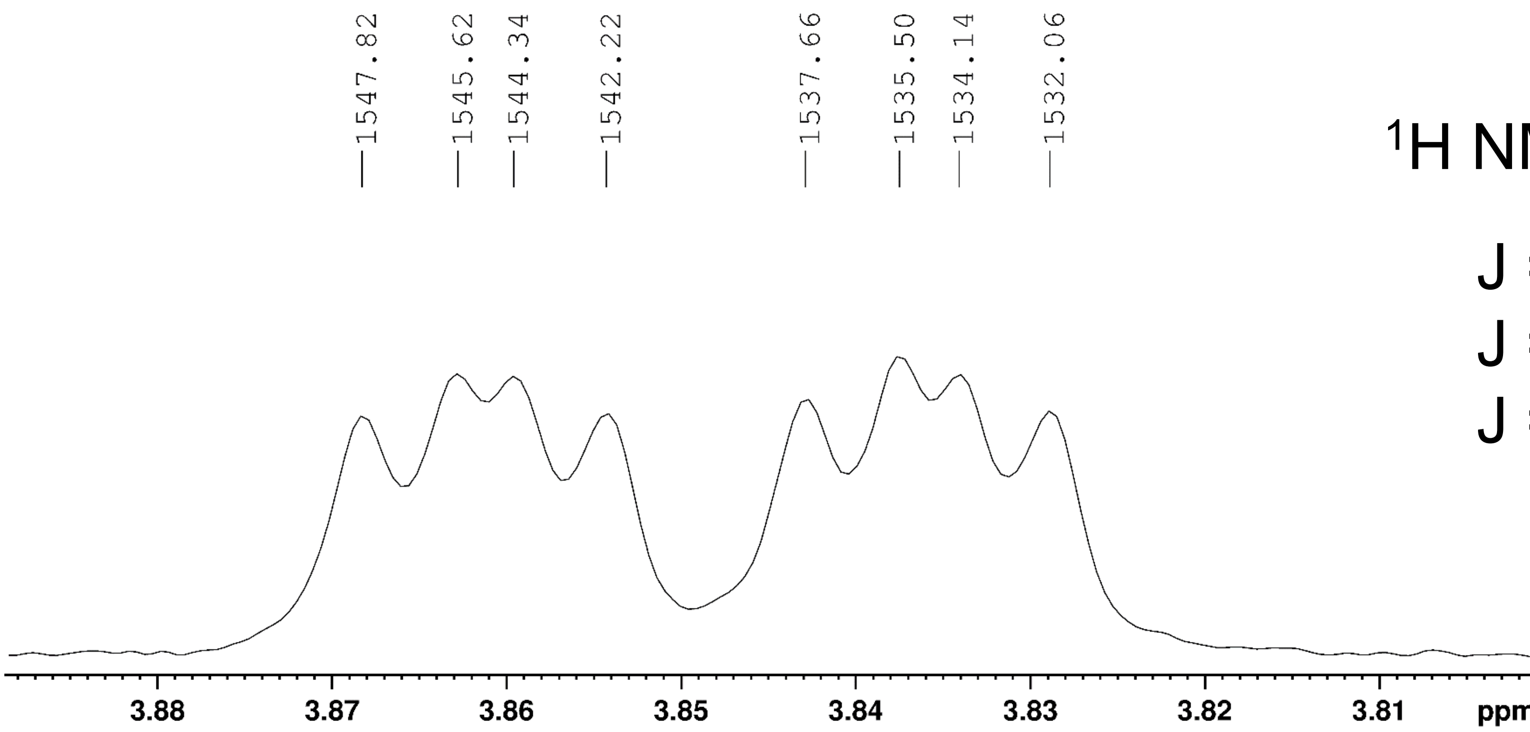


SOLVENT EFFECT



^{1}H NMR in $CDCl_3$

J = 10.00 Hz
J = 3.48 Hz
J = 1.8 Hz



^{1}H NMR in D_2O

J = 10.16 Hz
J = 3.48 Hz
J = 2.2 Hz

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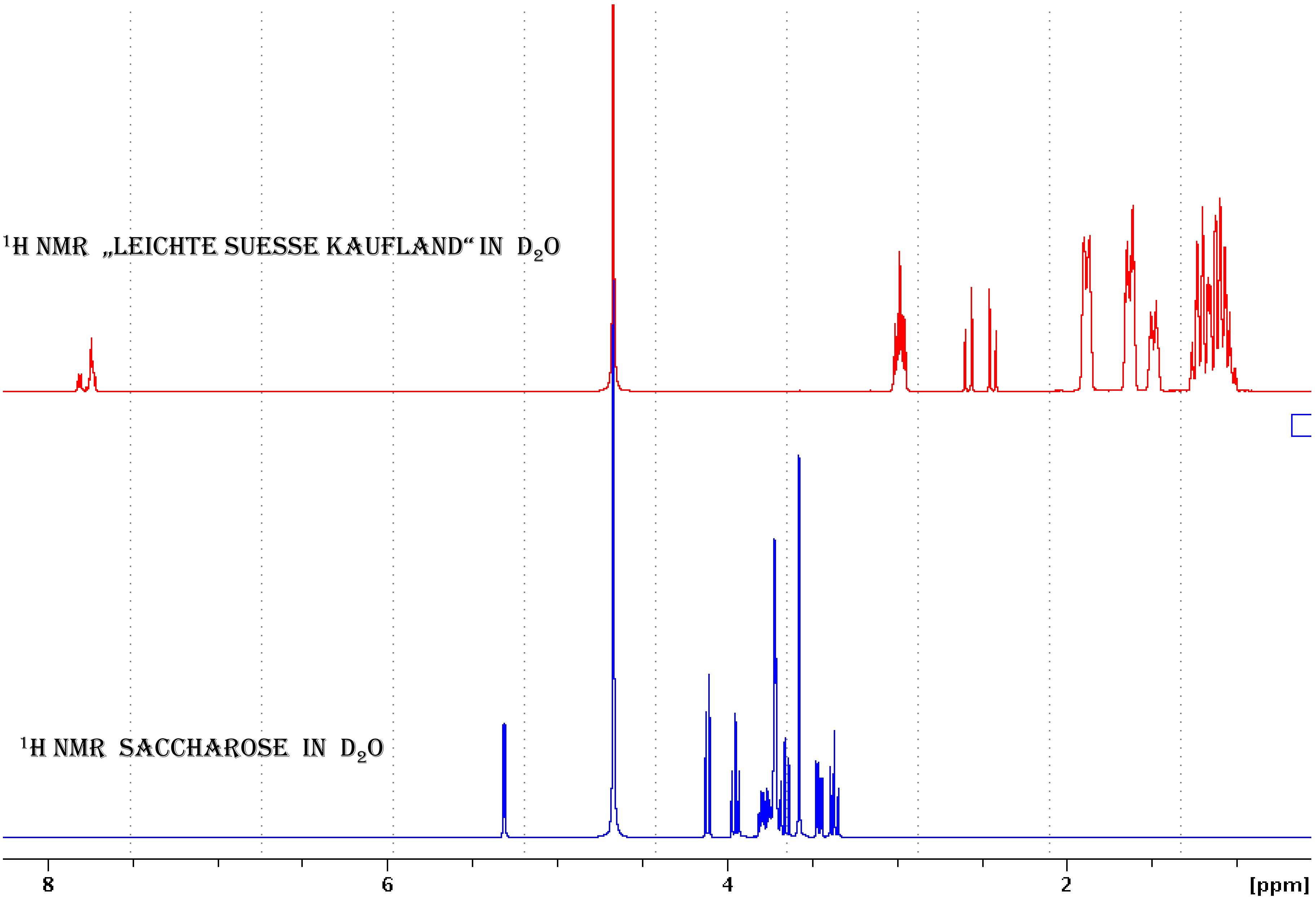
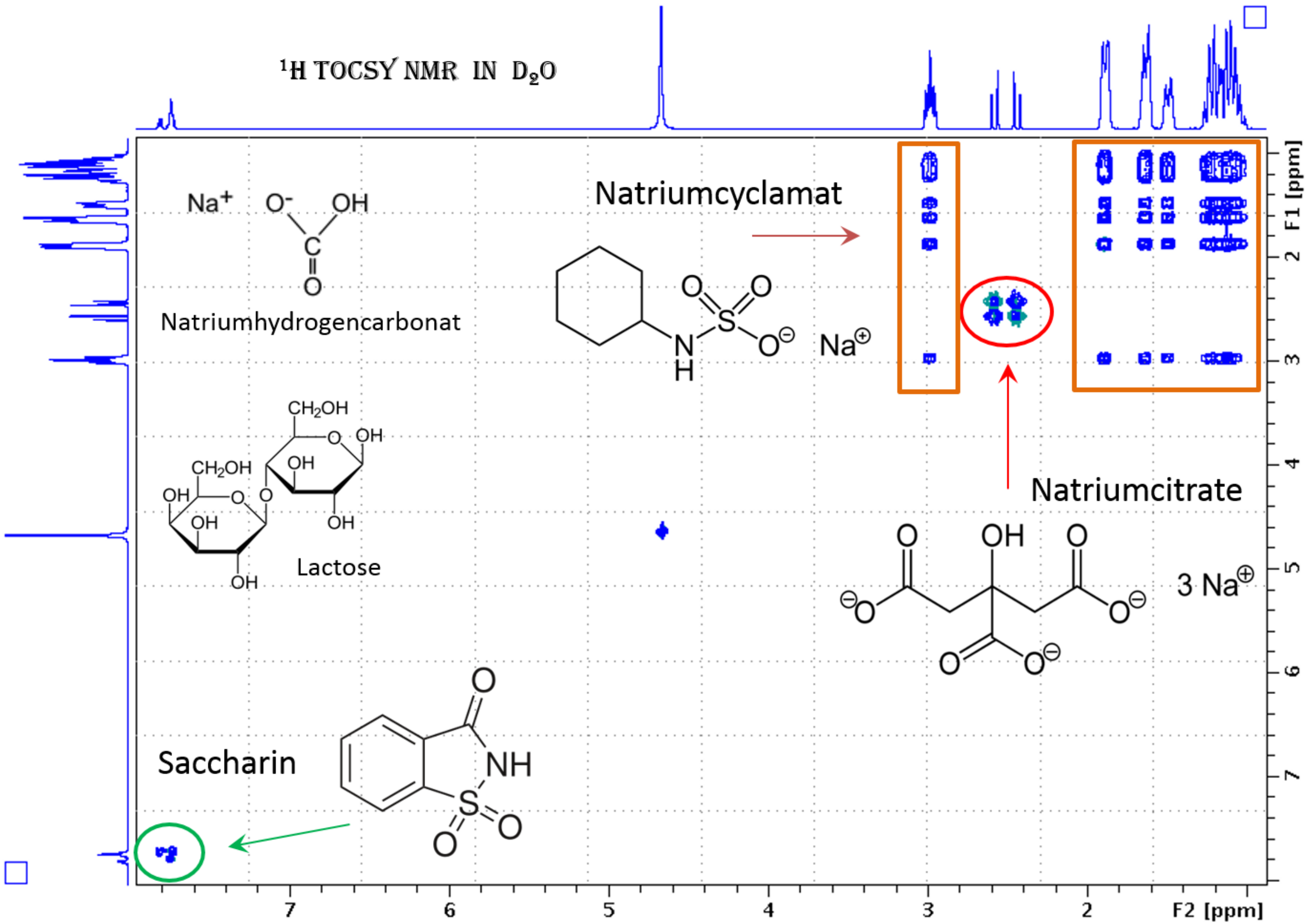
ARTIFICIAL SWEETENER „LEICHTE SUESSE KAUFLAND“:

NATRIUMCYCLAMAT, SACCHARIN, NATRIUMHYDROGENCARBONAT, LACTOSE, NATRIUMCITRATE



„LEICHTE SUESSE KAUFLAND":

NATRIUMCYCLAMAT, SACCHARIN, NATRIUMHYDROGENCARBONAT, LACTOSE, NATRIUMCITRATE



„LEICHTE SUESSE KAUFLAND":

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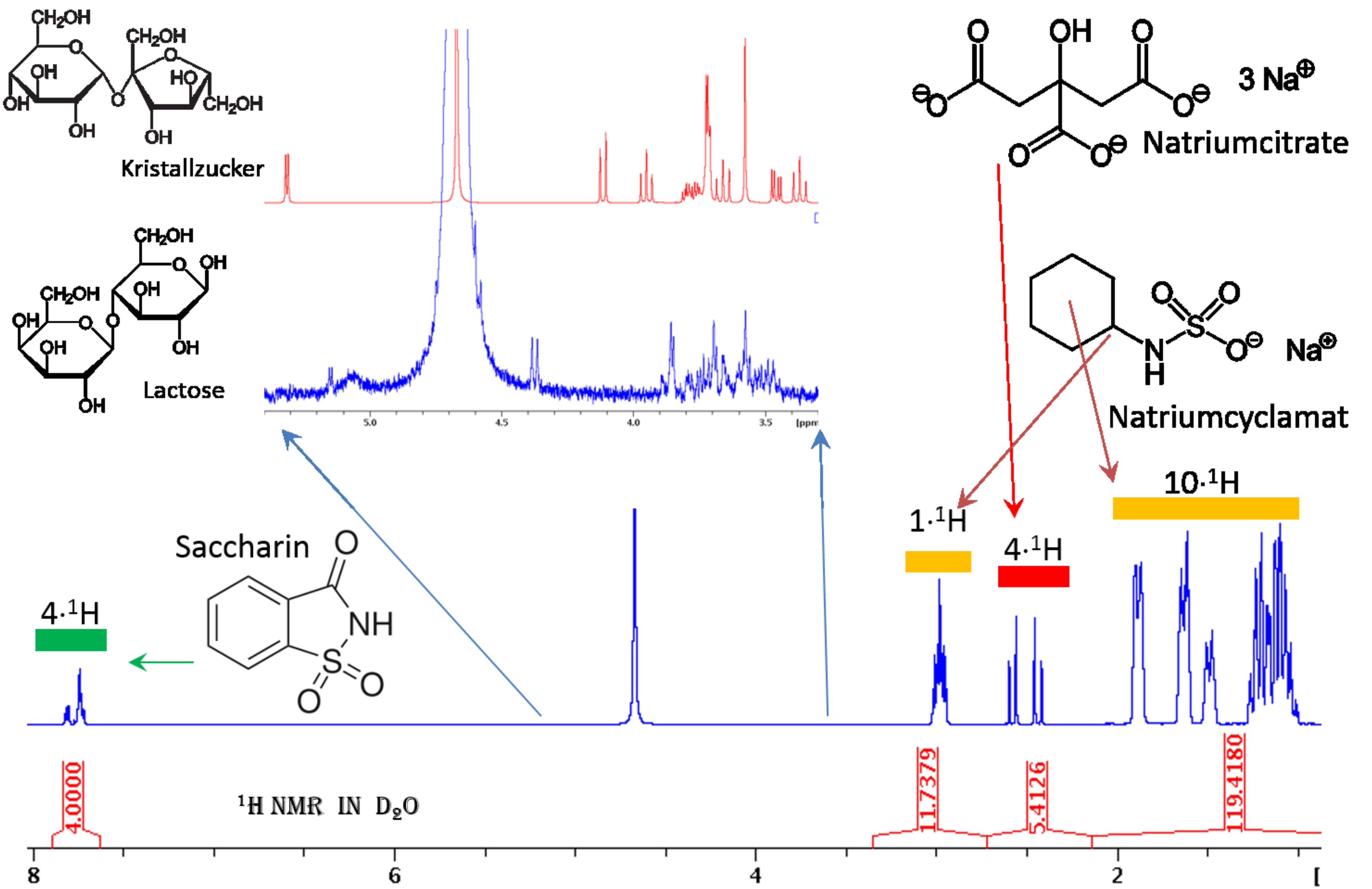
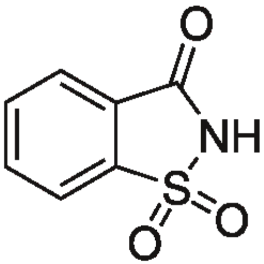
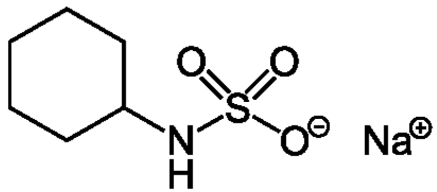


Artificial Sweetener „Leichte Suesse Kaufland“:



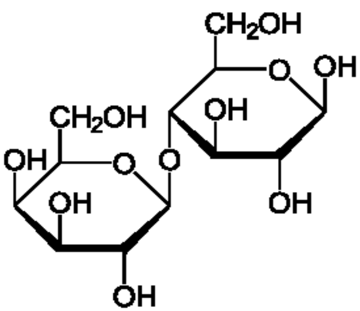
1 Part Saccharin (4 mg/Tablet):

i. 300-400 times sweeter than Sucrose.
ii. 5 mg/kg body-weight (ca. 60 Tabletten, 275 g Sucrose).
iii. Do not provoke tooth decay.
iv. Has a bitter taste.



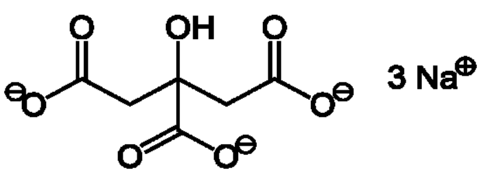
12 Parts Natriumcyclamate (40 mg/Tablet):

i. 30 times sweeter than Sucrose.
ii. 7 mg/kg body-weight (ca. 9 Tablet, 39 g Sucrose).
iii. Provoke cancer?



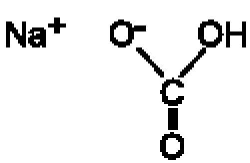
0.015 Parts Lactose (a table top sweetene?):

i. Milk sugar, 6 times less sweet than Sucrose.



1.4 Parts Natriumcitrate (shelf-life extension?):

i. Acidity regulator.
ii. Contributing a tart flavor.



4 Parts Sodium bicarbonate (shelf-life extension?):

i. Baking soda. (dissolution assistance?)

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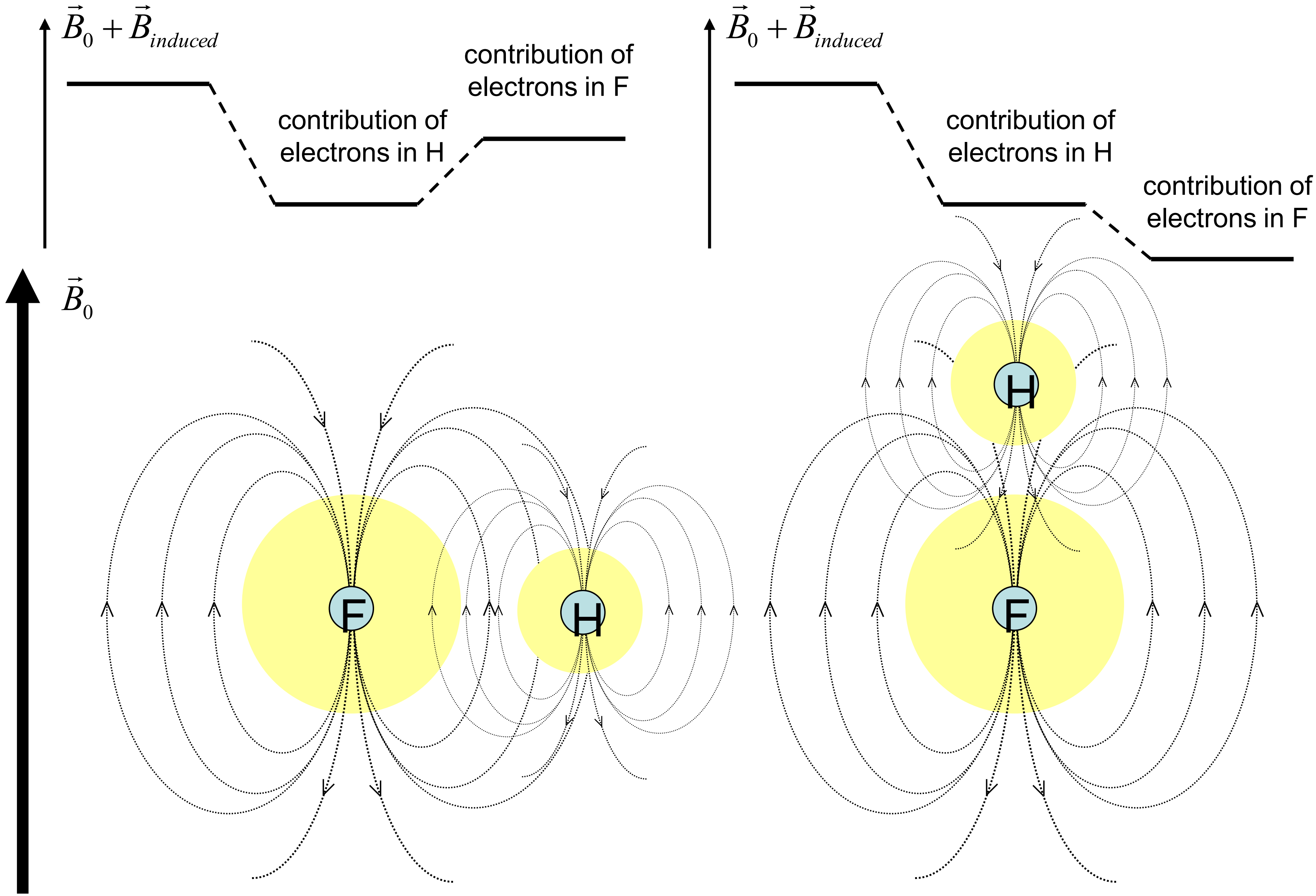
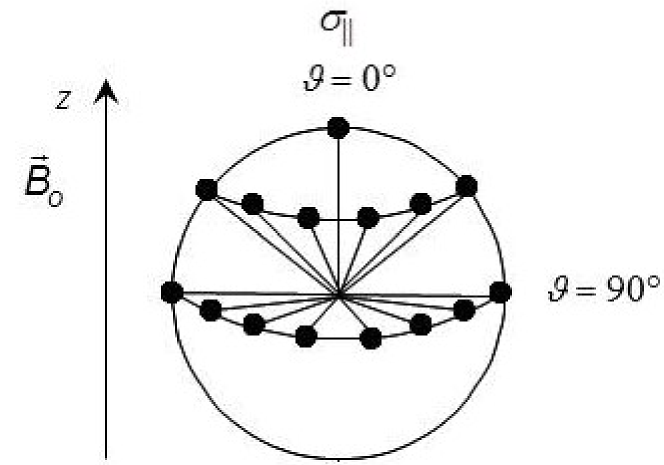
Chemical shift anisotropy

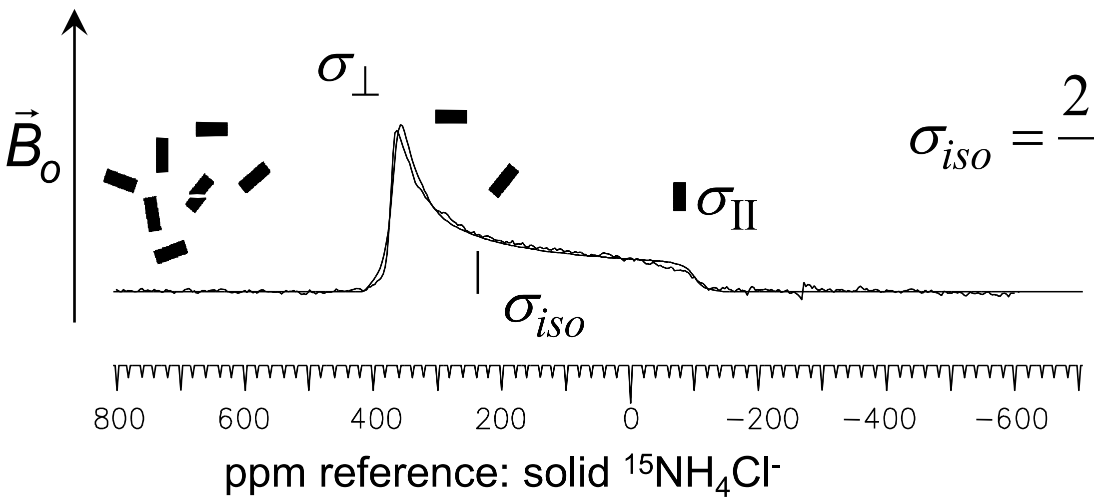


Chemical shift anisotropy

$[(CO)_5Cr{-}C{\equiv}N\cdots H\cdots N{\equiv}C{-}Cr(CO)_5]^-$

$AsPh_4^+$

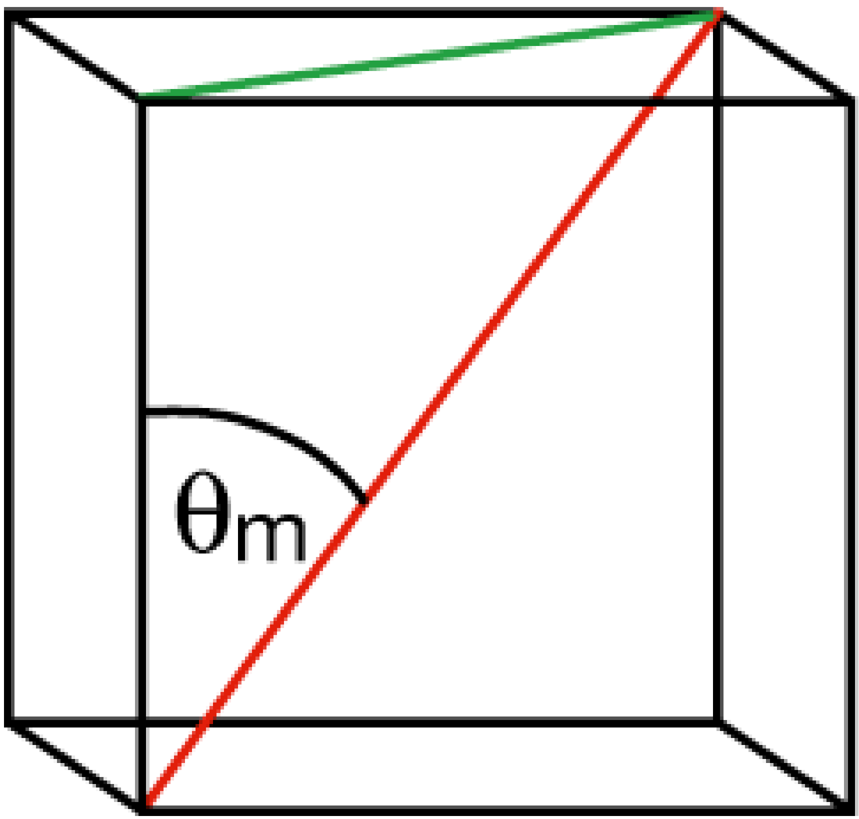




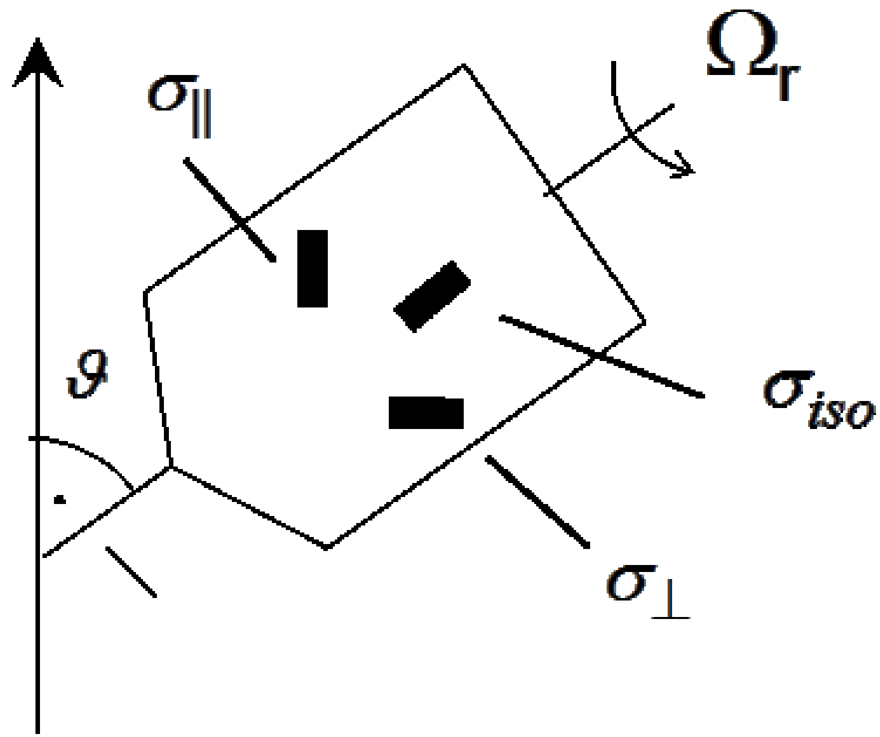
$$\sigma_{iso} = \frac{2\sigma_{II} + \sigma_{\perp}}{3}$$

H.Benedict, H.H.Limbach, M. Wehlan, W. P. Fehlhammer, N. S. Golubev, R. Janoschek, *J. Am. Chem. Soc.* **1998**, *120*, 2939

Magic-angle-spinning



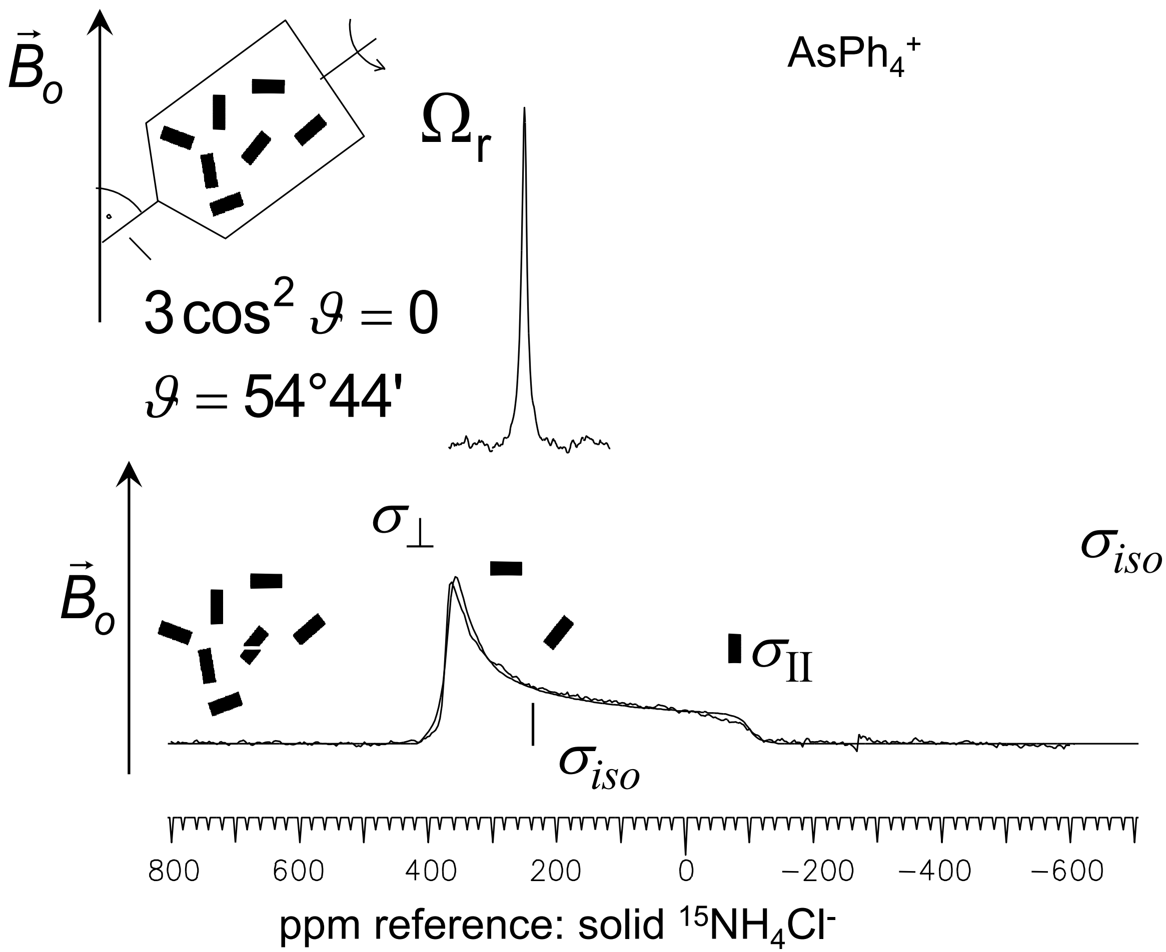
$$3\cos^2\theta - 1 = 0,\ \theta = 54°44'$$



Magic-angle-spinning

$[(CO)_5Cr–C≡N\cdots H\cdots N≡C–Cr(CO)_5]^-$

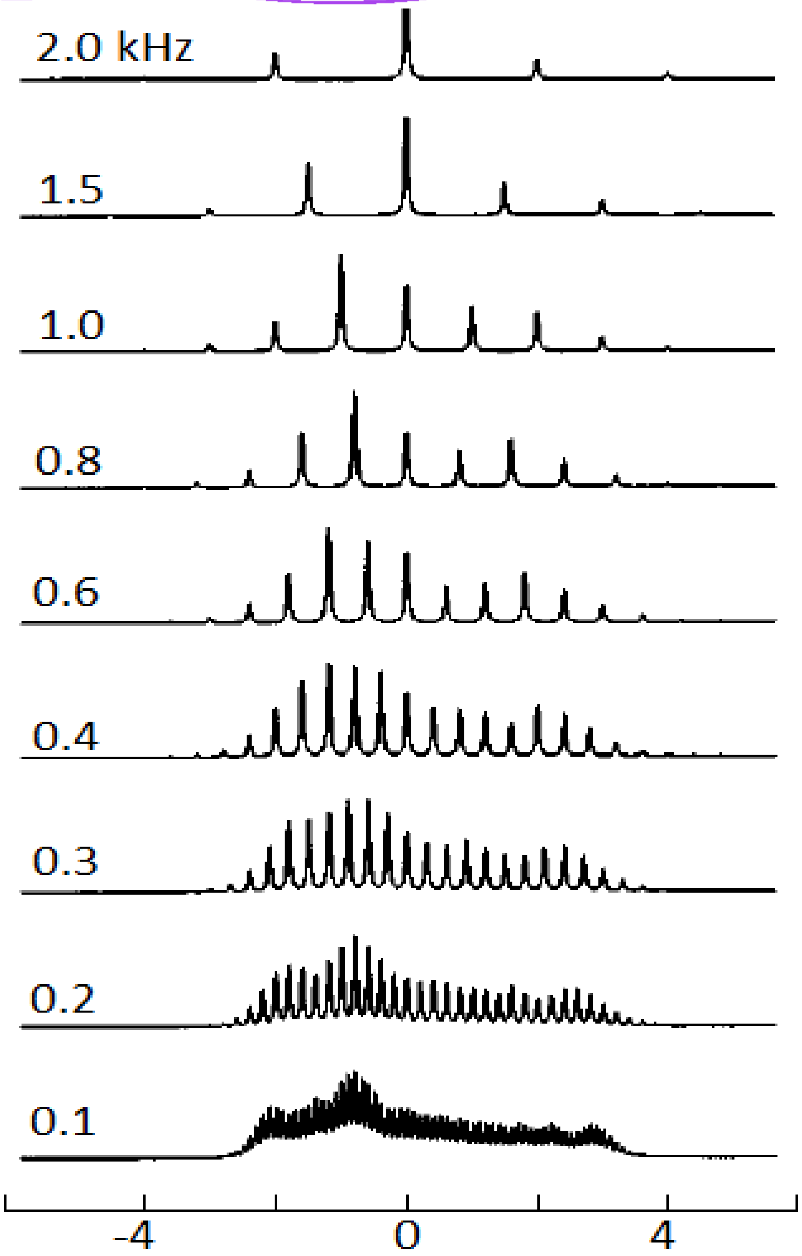
$AsPh_4^+$



$$\sigma_{iso} = \frac{2\sigma_{II} + \sigma_\perp}{3}$$

H.Benedict, H.H.Limbach, M. Wehlan, W. P. Fehlhammer, N. S. Golubev, R. Janoschek, *J. Am. Chem. Soc.* **1998**, *120*, 2939

MAS sidebands



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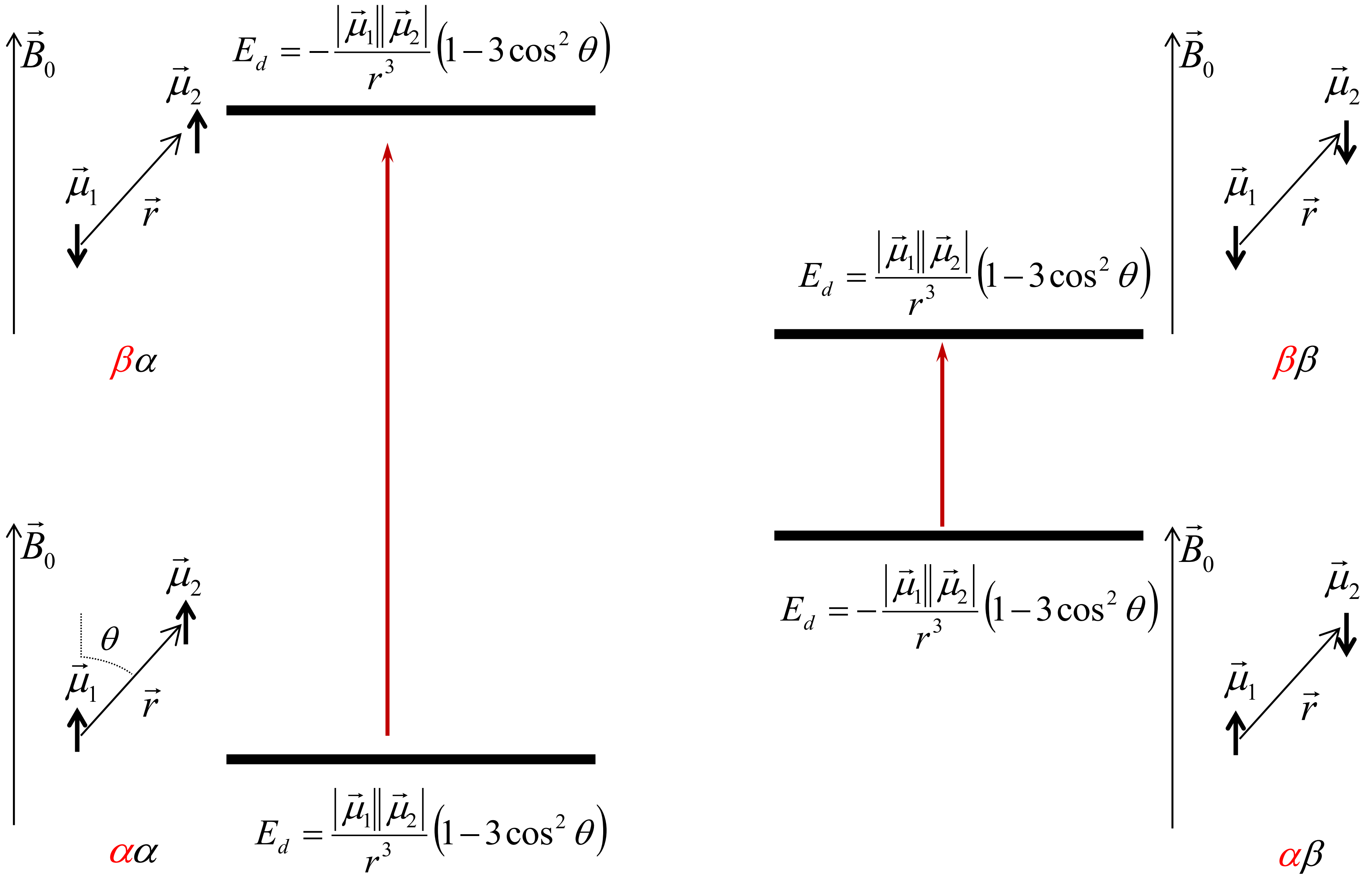
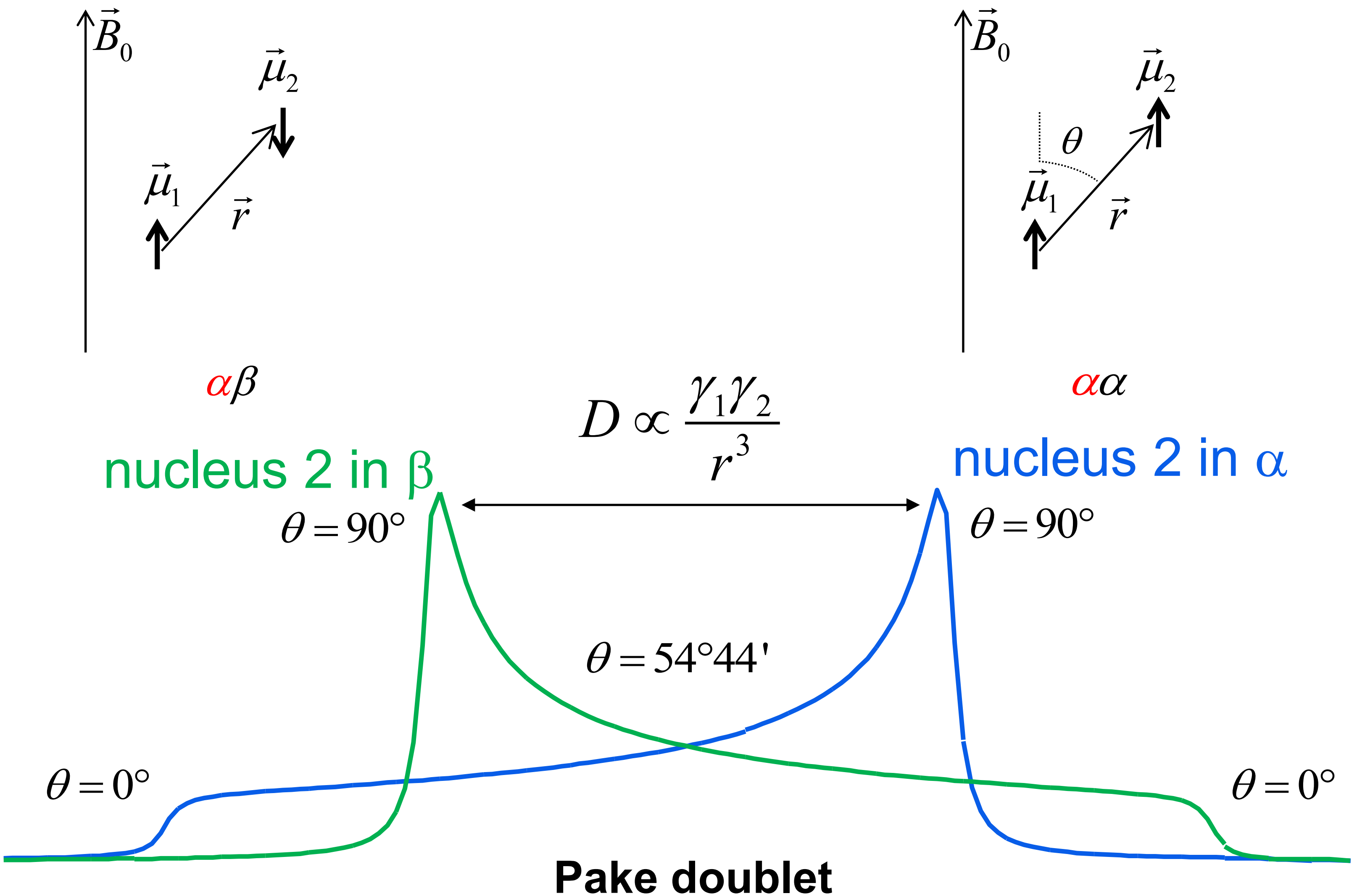
7. Two-dimensional NMR	2.3 NMR of surfaces and amorphous solids	

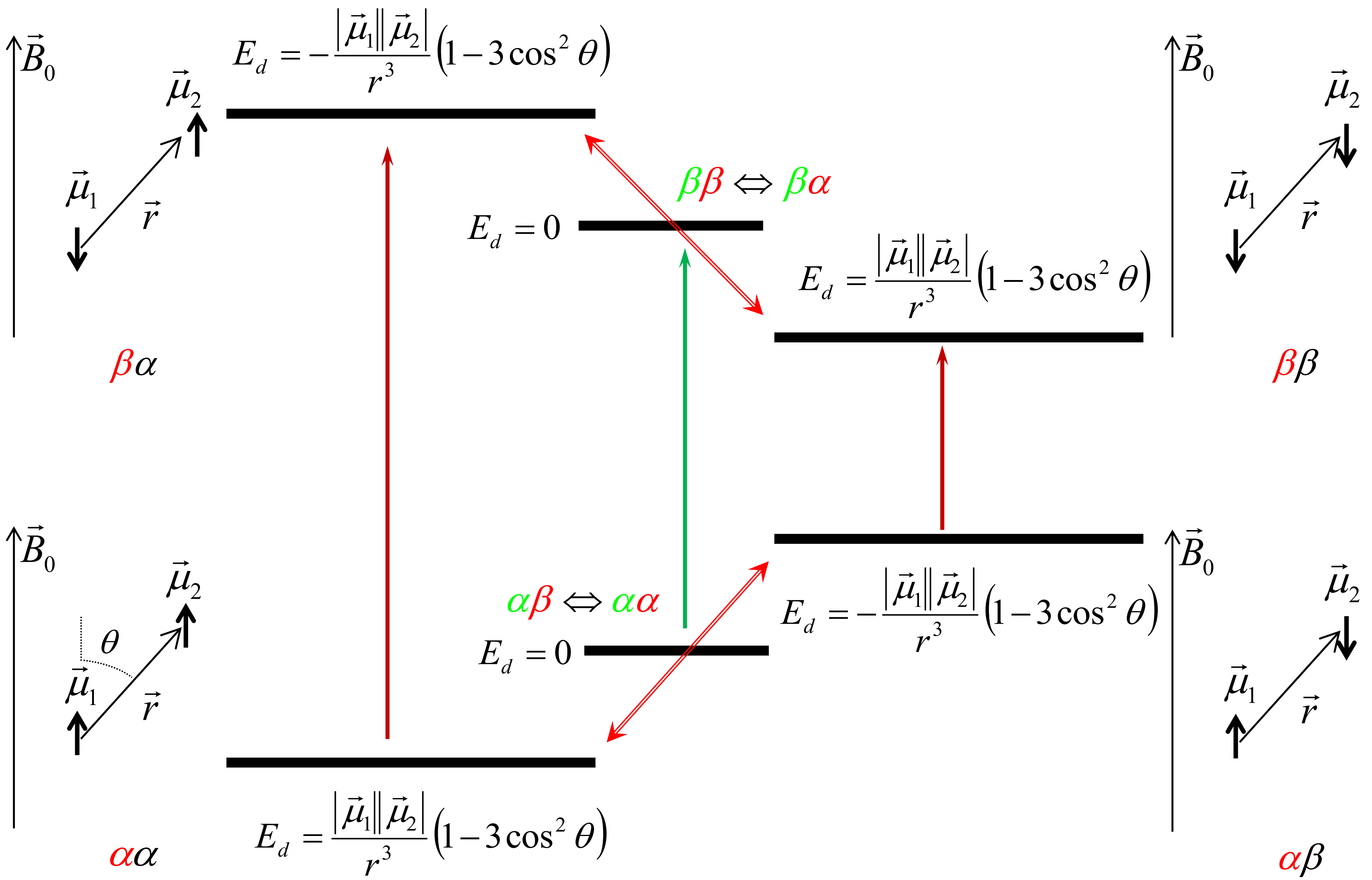
Internal Spin Interactions: Dipolar Coupling



Internal Spin Interactions: Dipolar Coupling

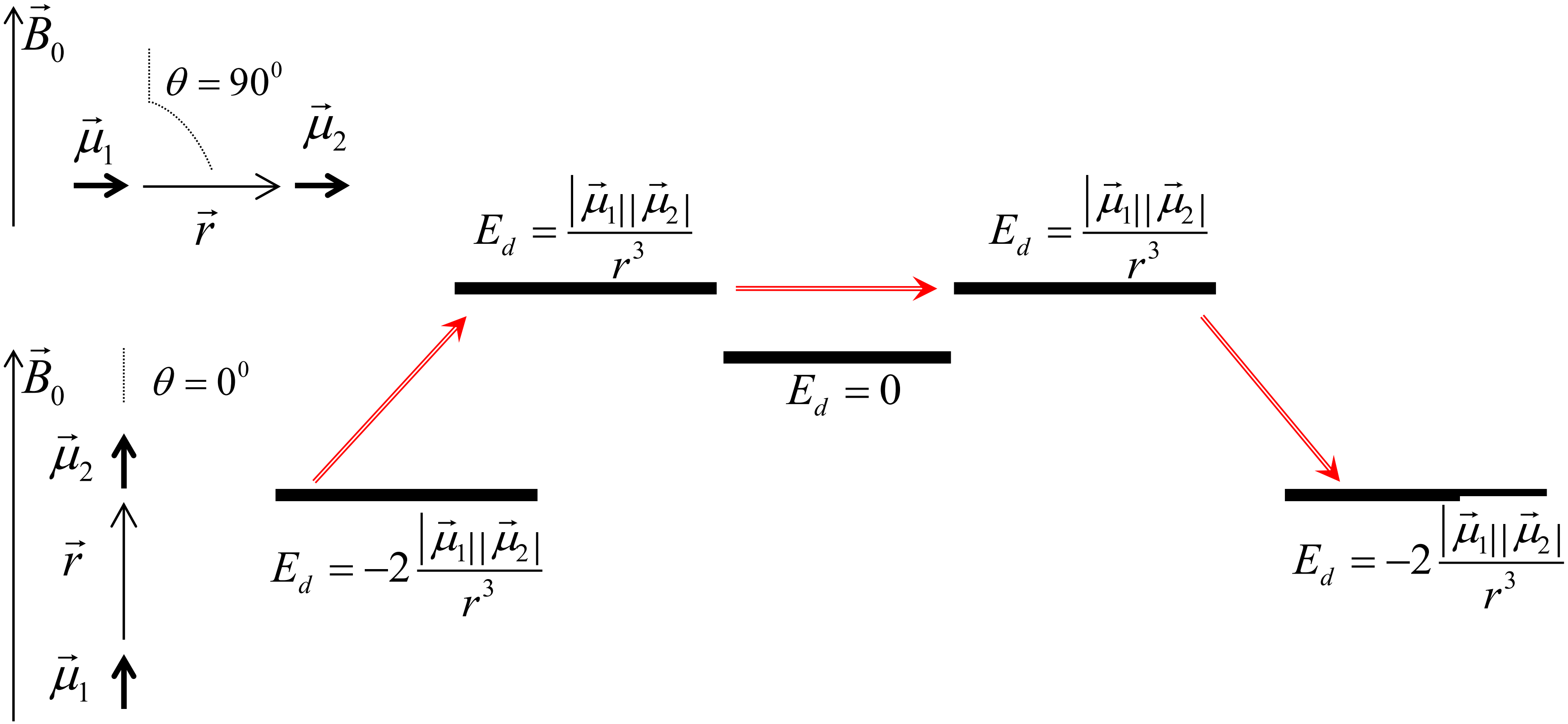


Internal Spin Interactions: Dipolar Coupling



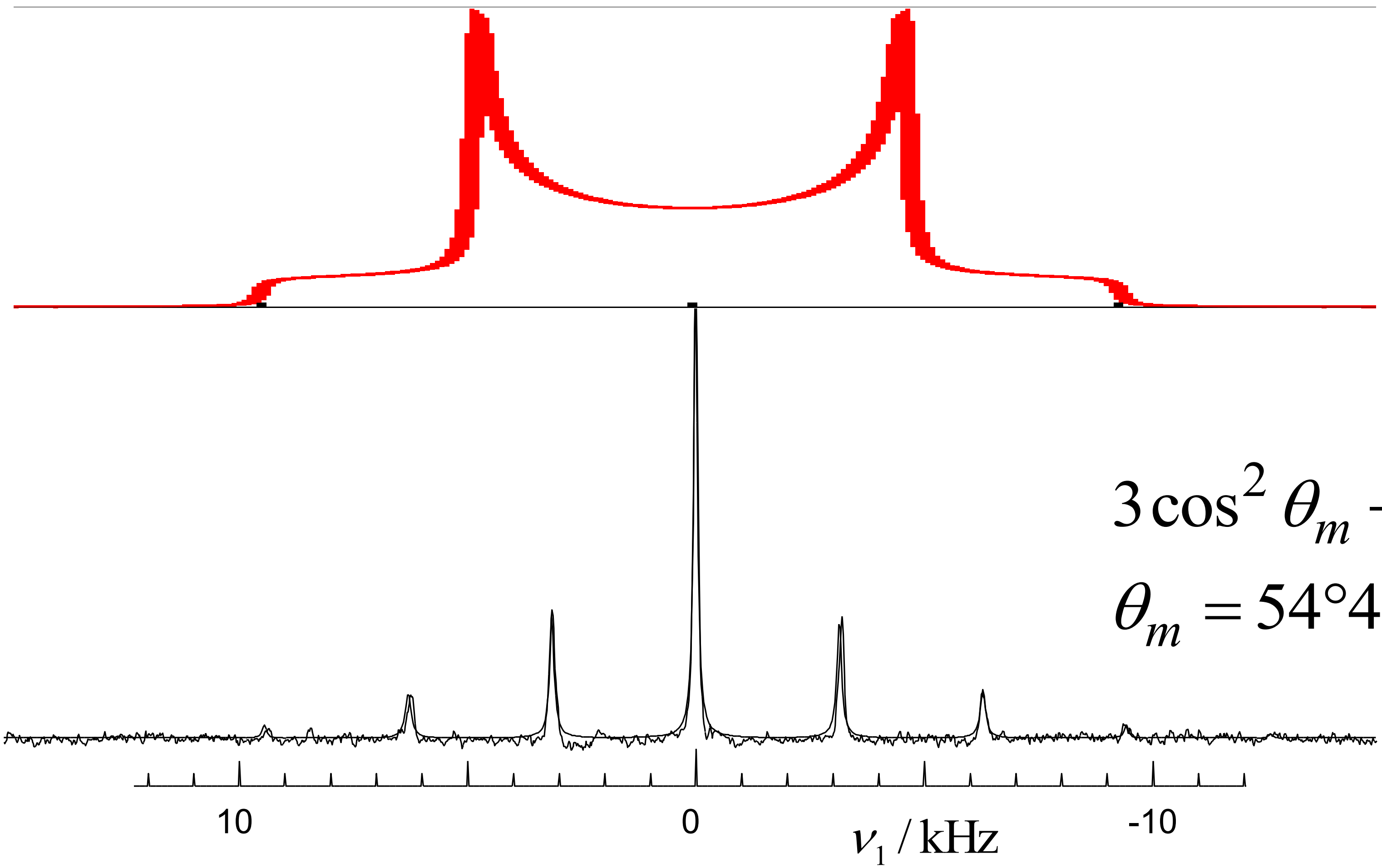
Internal Spin Interactions: Dipolar Coupling

$$E_d = \frac{\vec{\mu}_1 \vec{\mu}_2}{r^3}\left(1 - 3\cos^2\theta\right)$$



Internal Spin Interactions: Dipolar Coupling

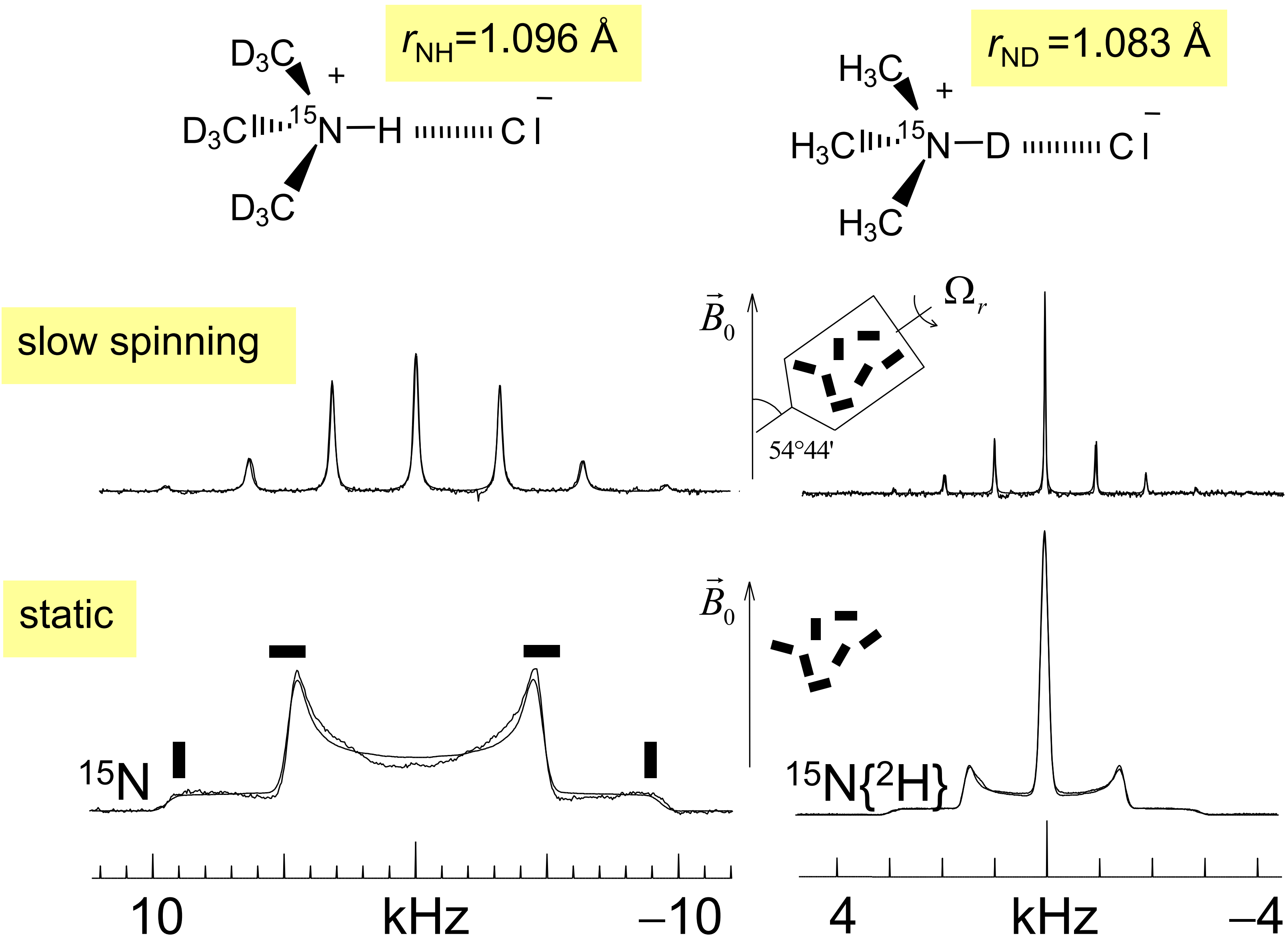
$$D \propto \frac{\gamma_1 \gamma_2}{r^3}$$



$$3\cos^2\theta_m - 1 = 0$$

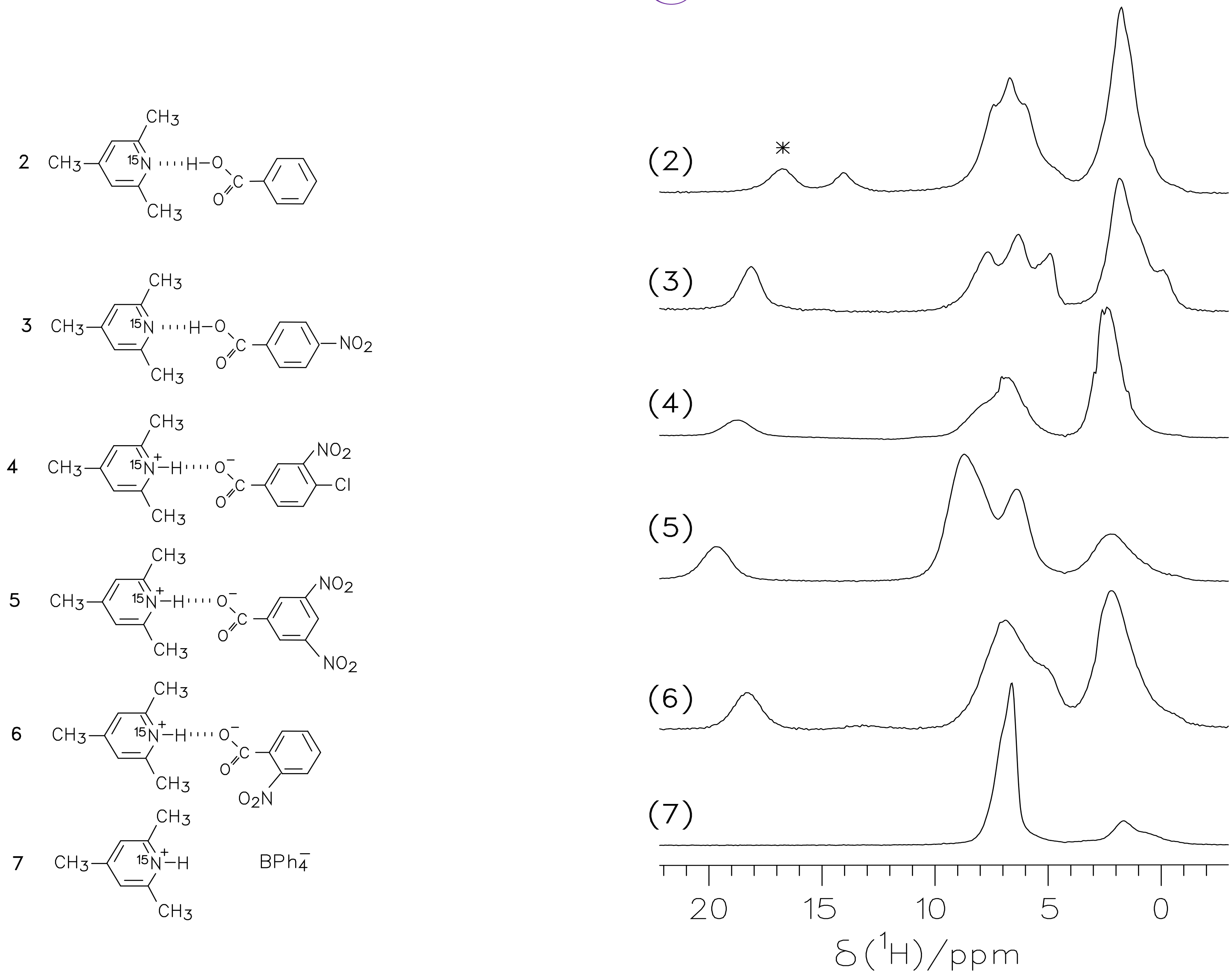
$$\theta_m = 54°44'$$

^{1}H-^{15}N and ^{2}H-^{15}N dipolar interaction without CSA



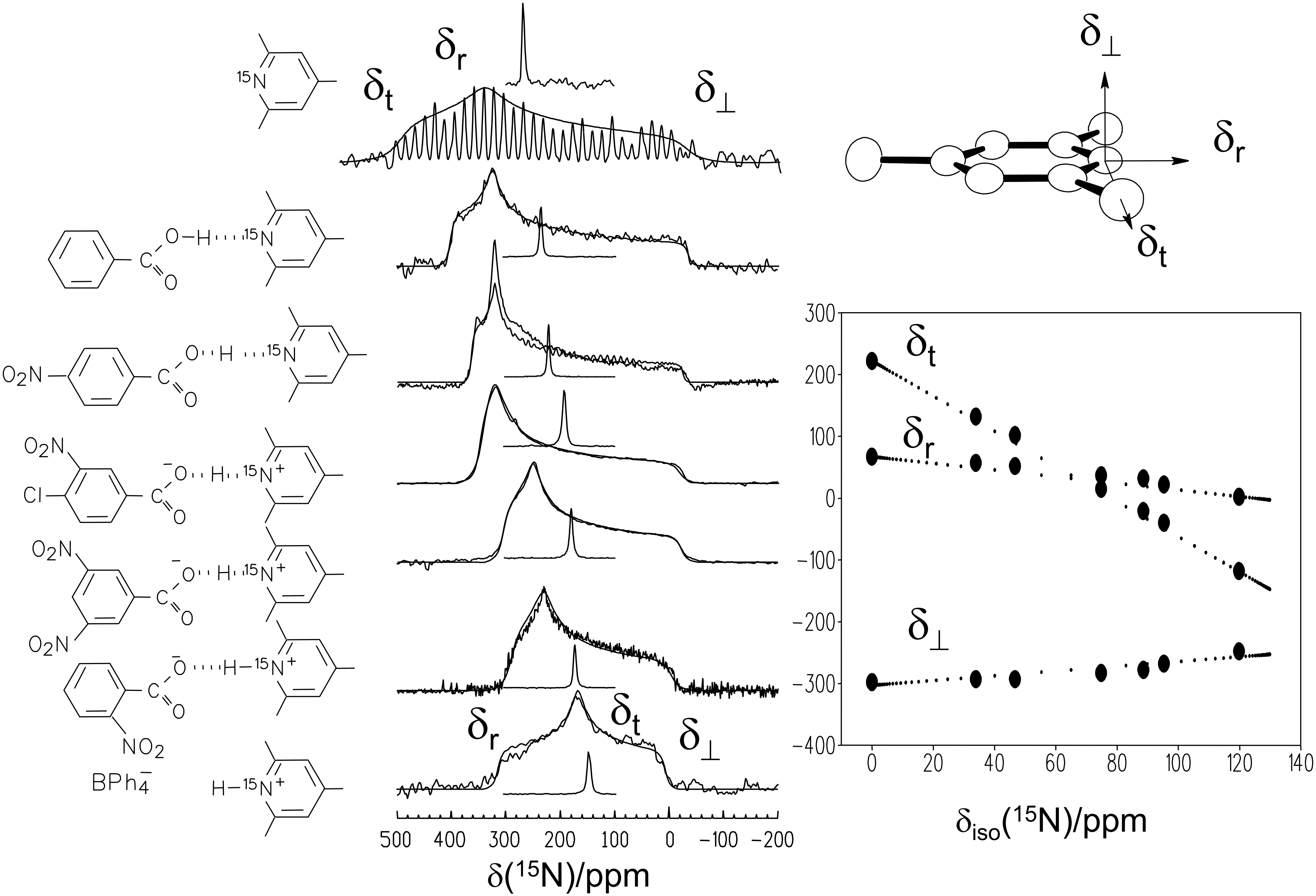
Ch. Hoelger, H.H.Limbach, *J. Phys.Chem.*, 1994, *98*, 11803.

^{1}H MAS NMR @ 10 kHz



Ph. Lorente, I.G.Shenderovich, G.Buntkowsky, N.S.Golubev, G.S.Denisov, H.H. Limbach, *Magn. Reson. Chem.* 2001, *39*, S18

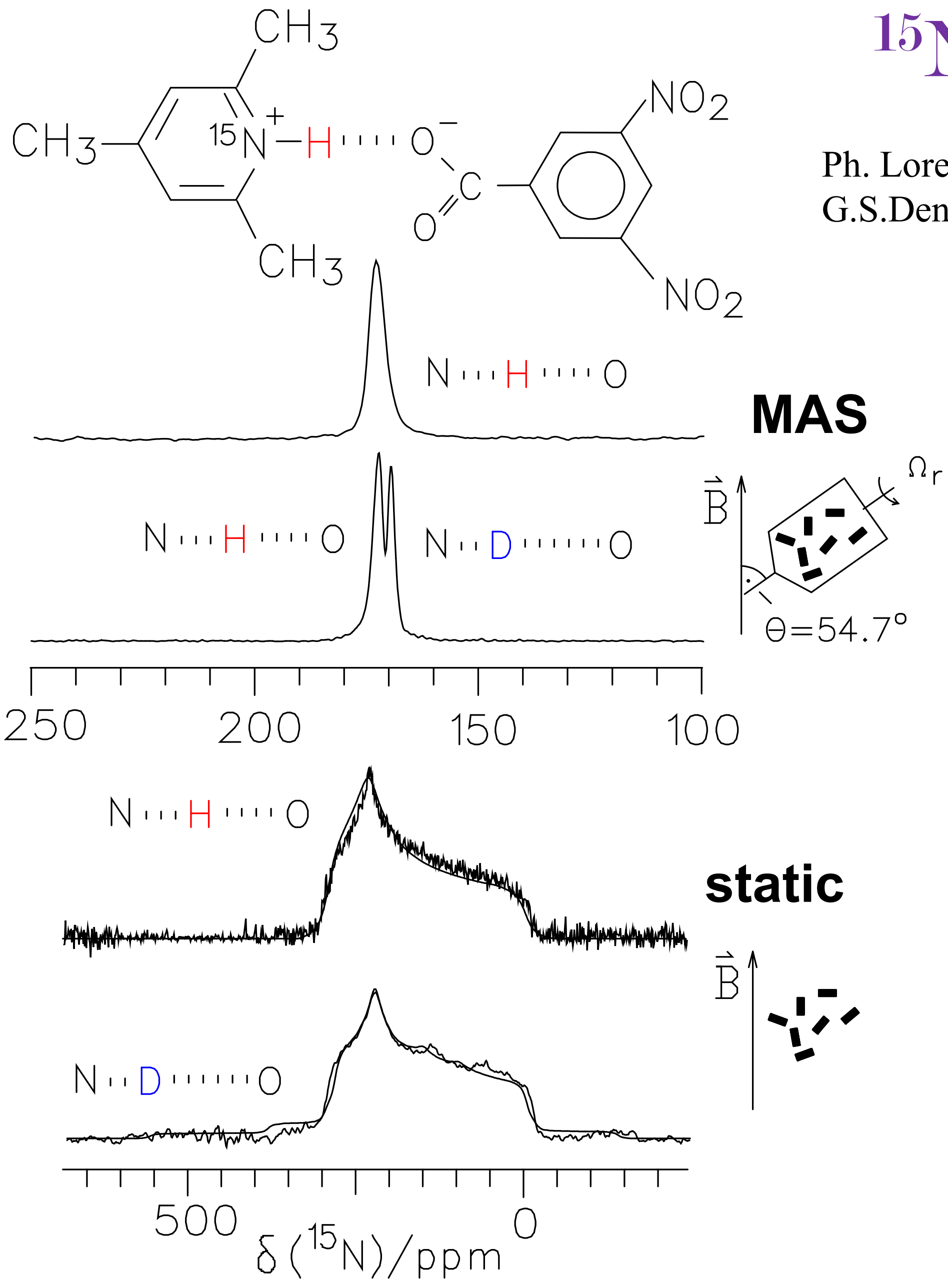
^{15}N CSA of solid 1:1 complexes of collidine-^{15}N with acids



Ph. Lorente, I.G.Shenderovich, G.Buntkowsky, N.S.Golubev, G.S.Denisov, H.H. Limbach, *Magn. Reson. Chem.* 2001, *39*, S18

^{15}N-^{2}H Dipolar Coupling

Ph. Lorente, I.G.Shenderovich, G.Buntkowsky, N.S.Golubev, G.S.Denisov, H.H. Limbach, *Magn. Reson. Chem.* 2001, *39*, S18



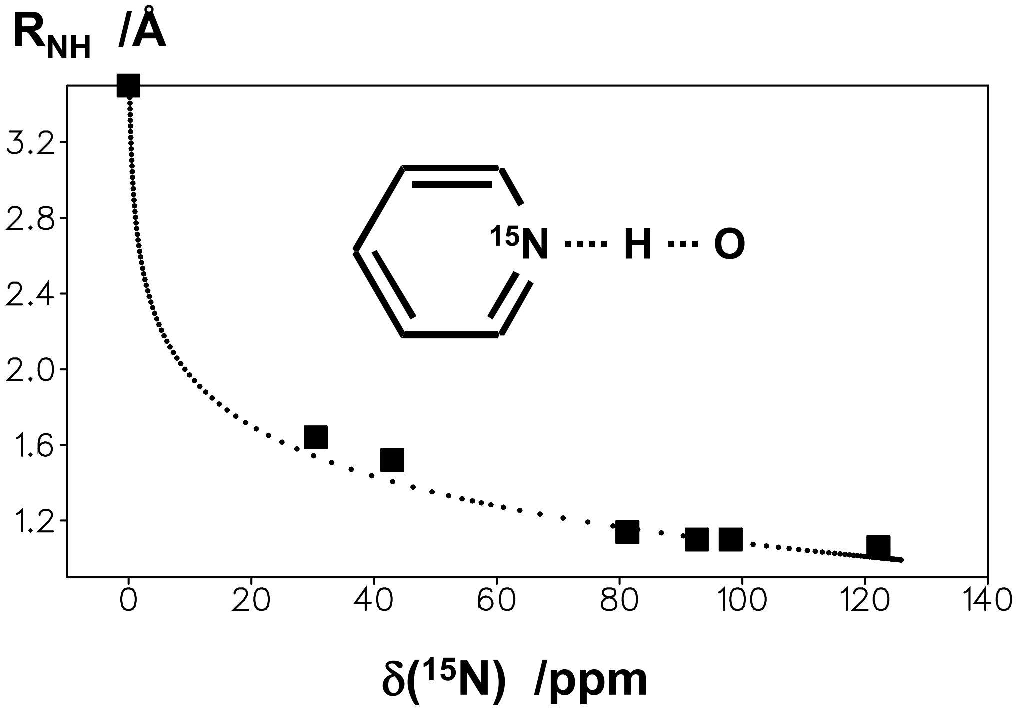
H/D isotop effect on chemical shift

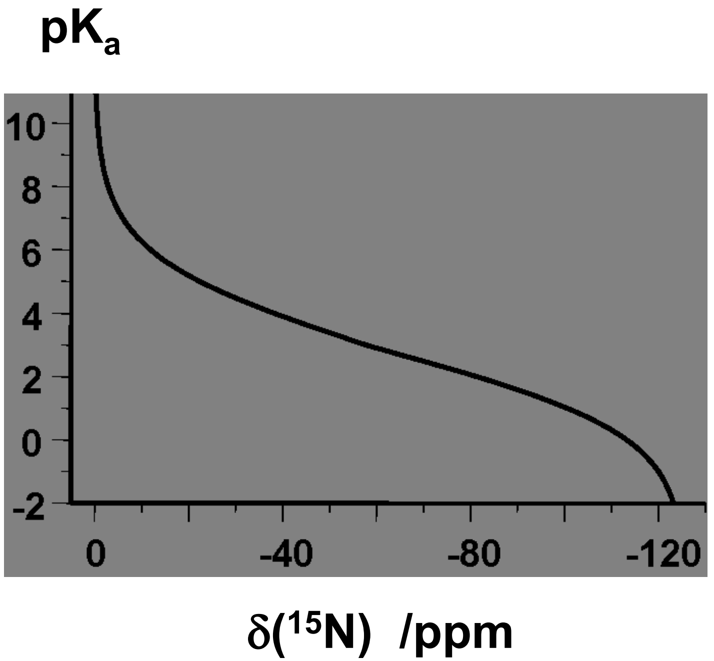
chemical shift tensor

^{15}N-^{2}H dipolar coupling

$D^{ND} \sim R^{-3}_{ND}$

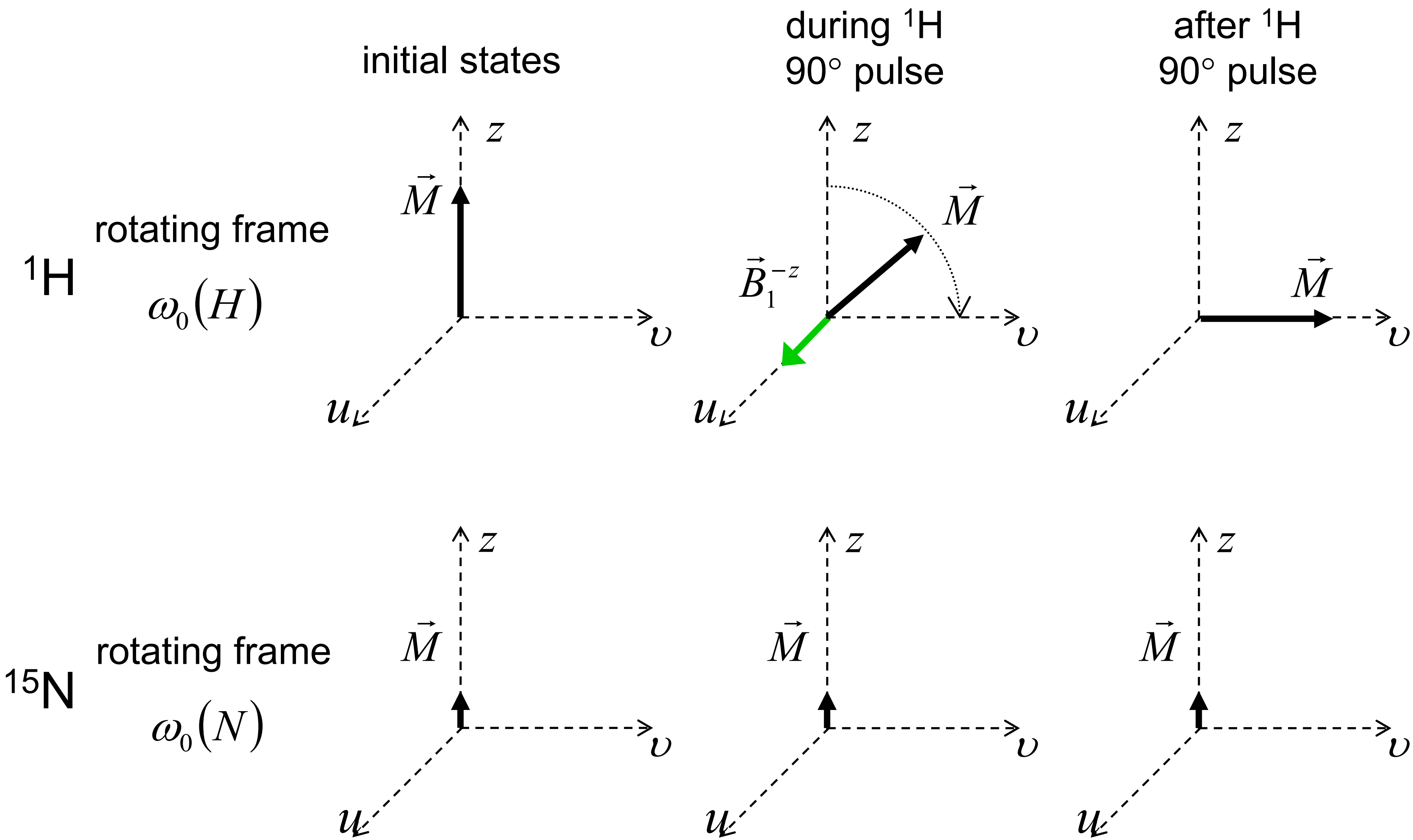
^{15}N NMR Chemical Shift as a Measure of "Acidity"





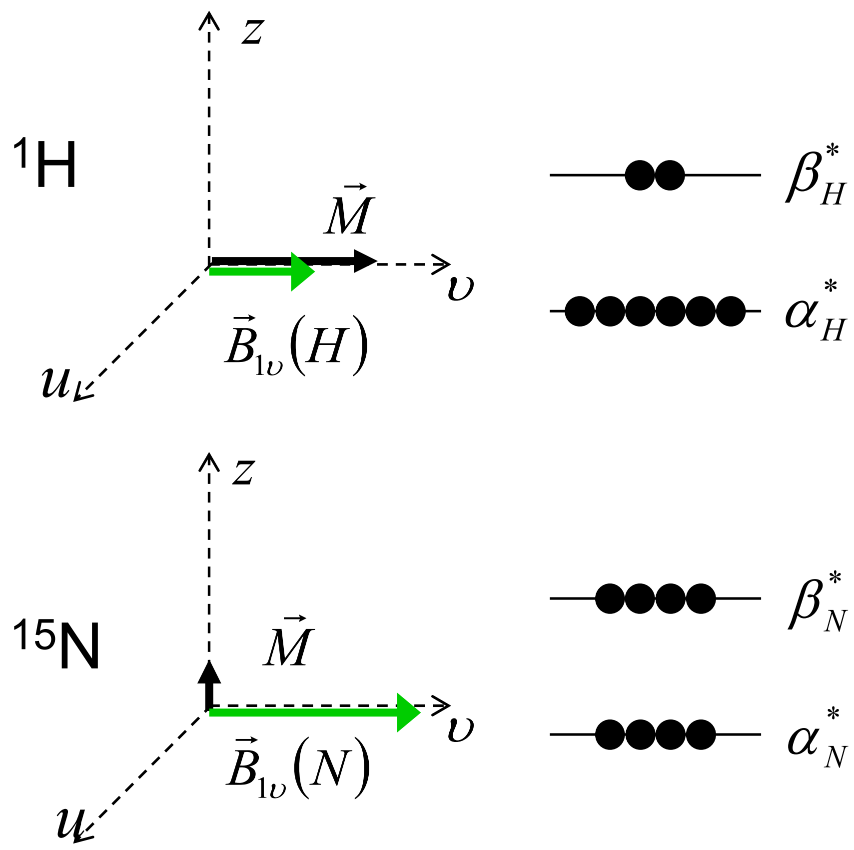
Ph. Lorente, I.G.Shenderovich, G.Buntkowsky, N.S.Golubev, G.S.Denisov, H.H. Limbach, *Magn. Reson. Chem.* 2001, *39*, S18

Cross polarisation (CP) – before contact pulse

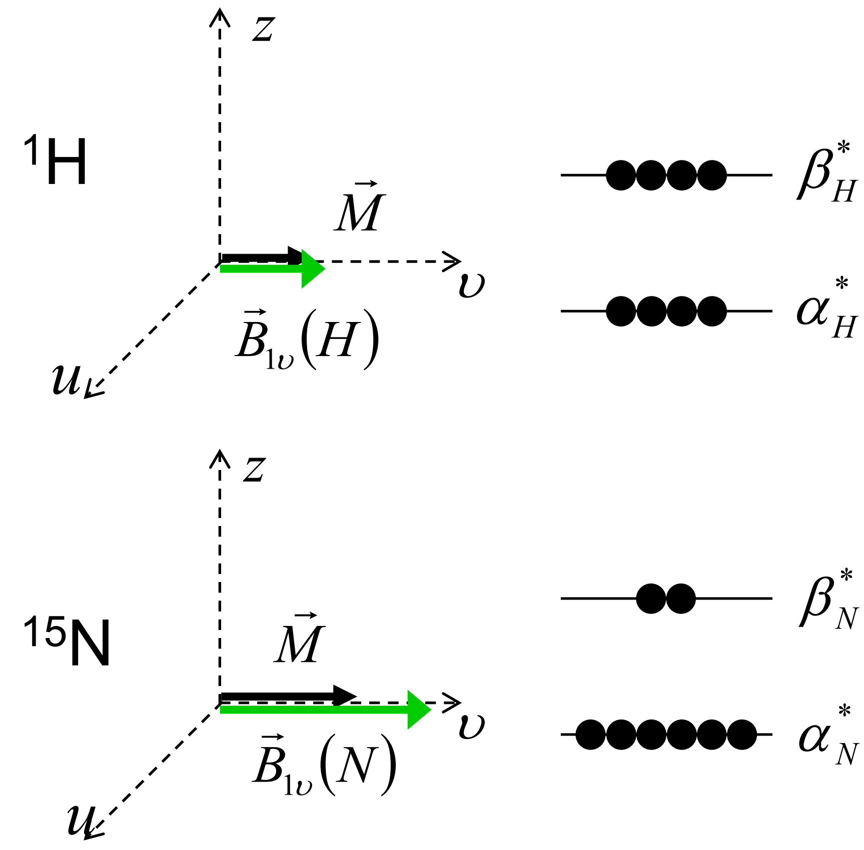


Cross polarisation (CP) –contact pulse

in the beginning of
^{1}H and ^{15}N contact pulses



at the end of
^{1}H and ^{15}N contact pulses

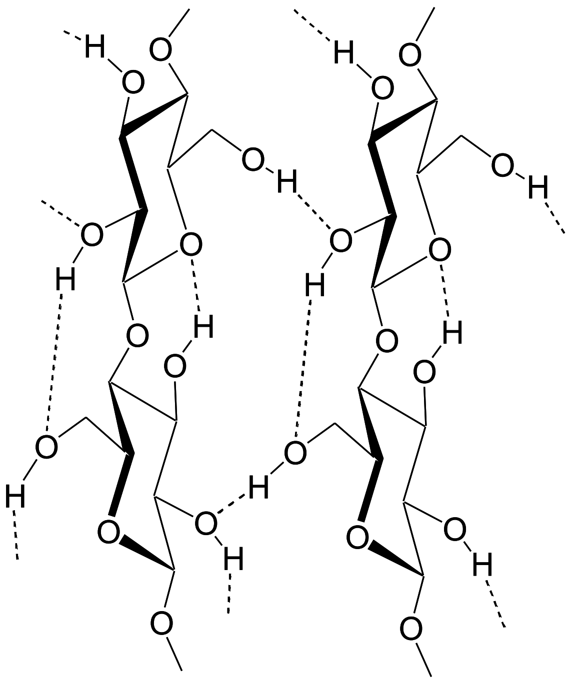


$$\omega_1(N) = \gamma_N B_{1\upsilon}(N) = \gamma_H B_{1\upsilon}(H) = \omega_1(H)$$

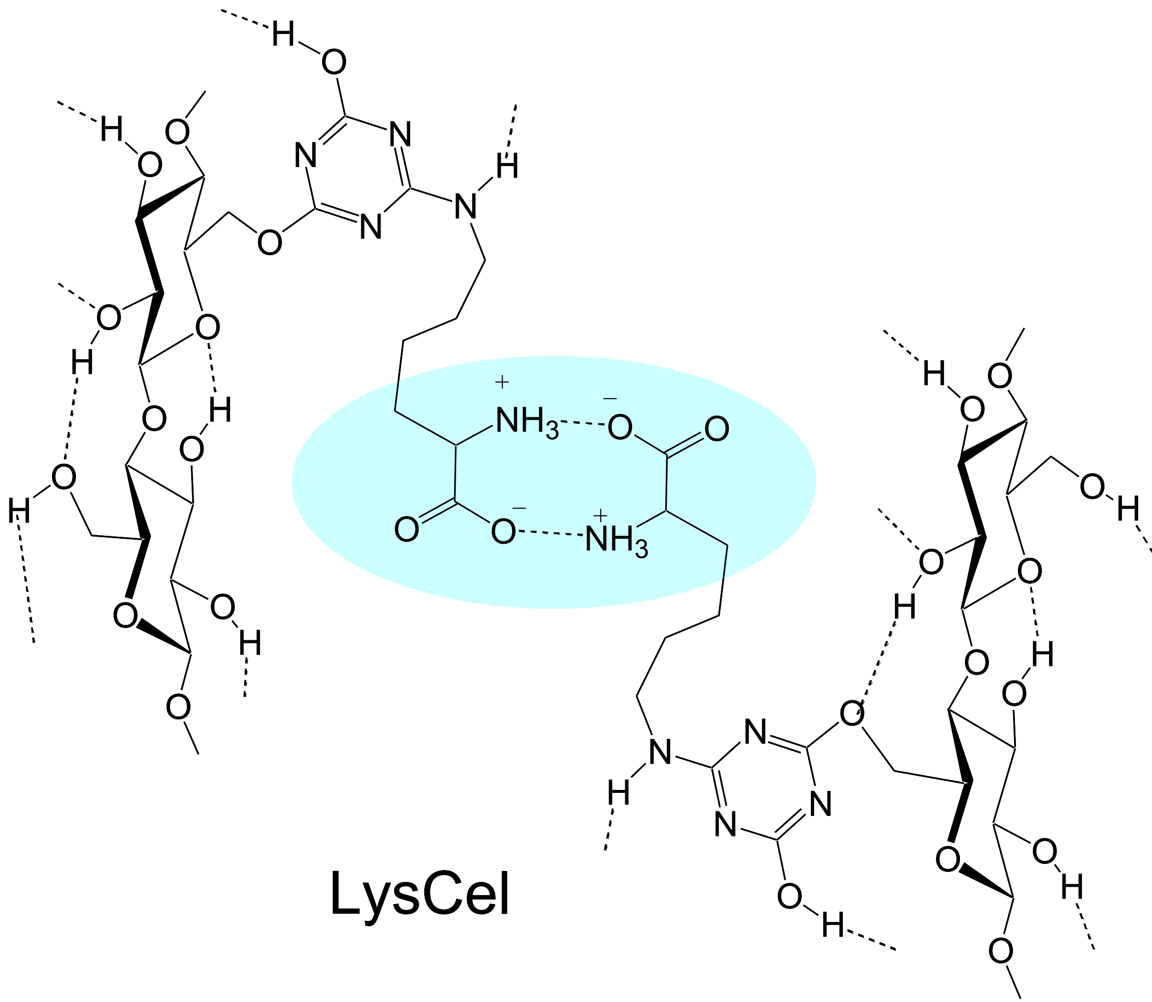
Hartmann-Hahn condition

Cellulose Grafted with Aminocarboxyl Groups

Wet paper tears easily



cellulose

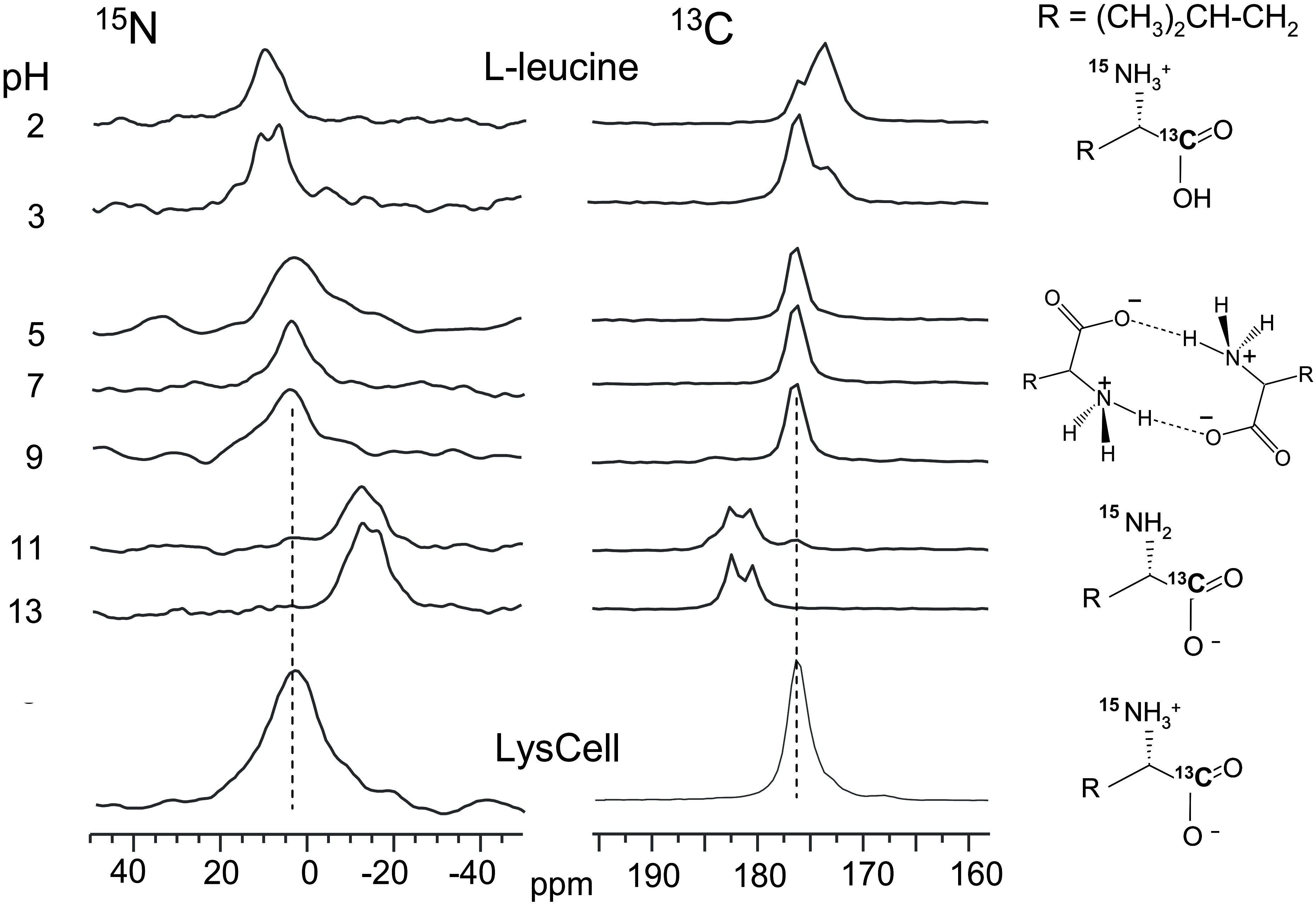


LysCel

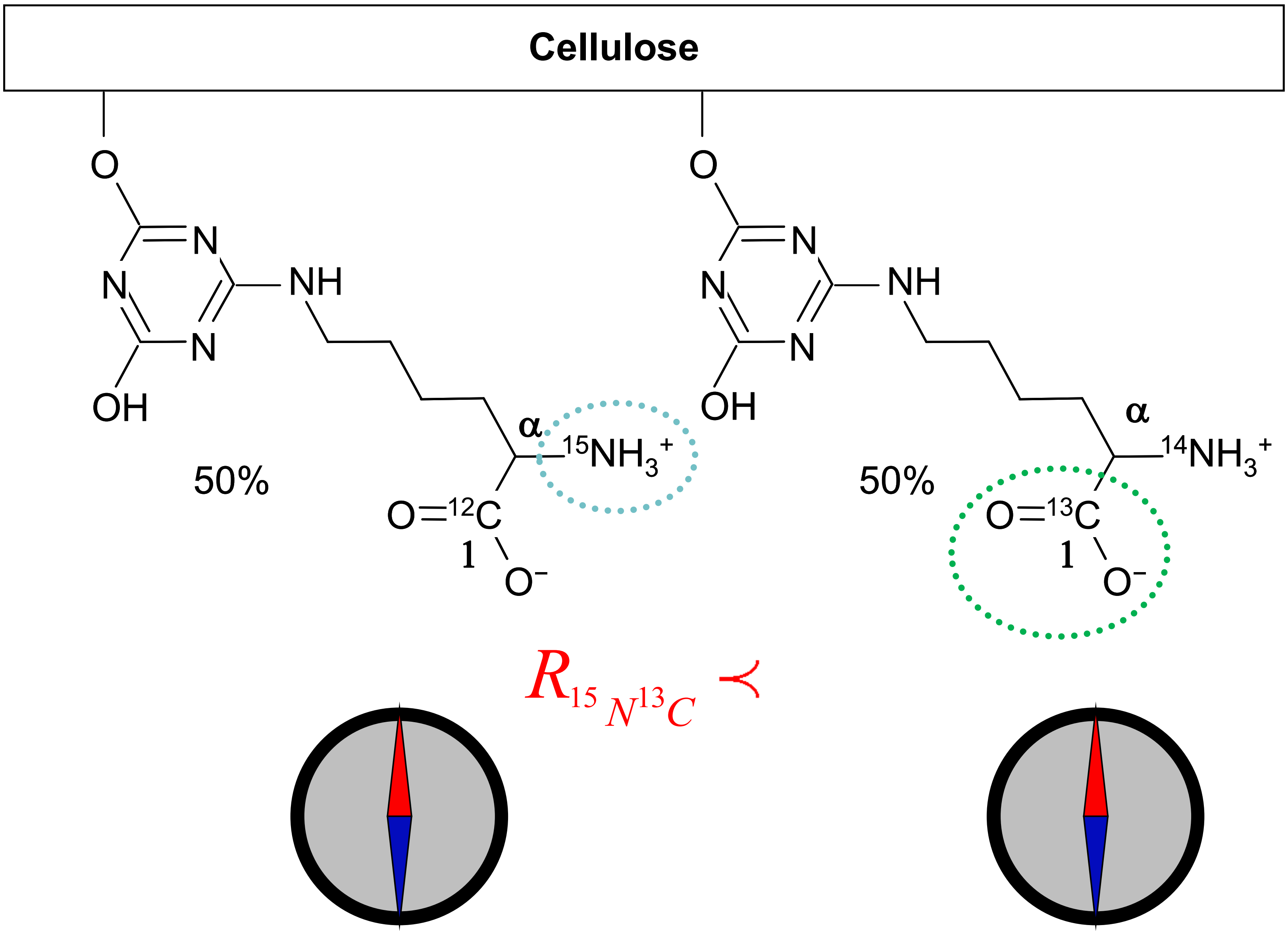
R. Manriquez, F.A. Lopez-Dellamary, J. Frydel, T. Emmler, H. Breitzke, G. Buntkowsky, H.-H. Limbach, I.G. Shenderovich *J. Phys. Chem. B* **2009**, *113*, 934.

30% wet-tensile-strength improvement

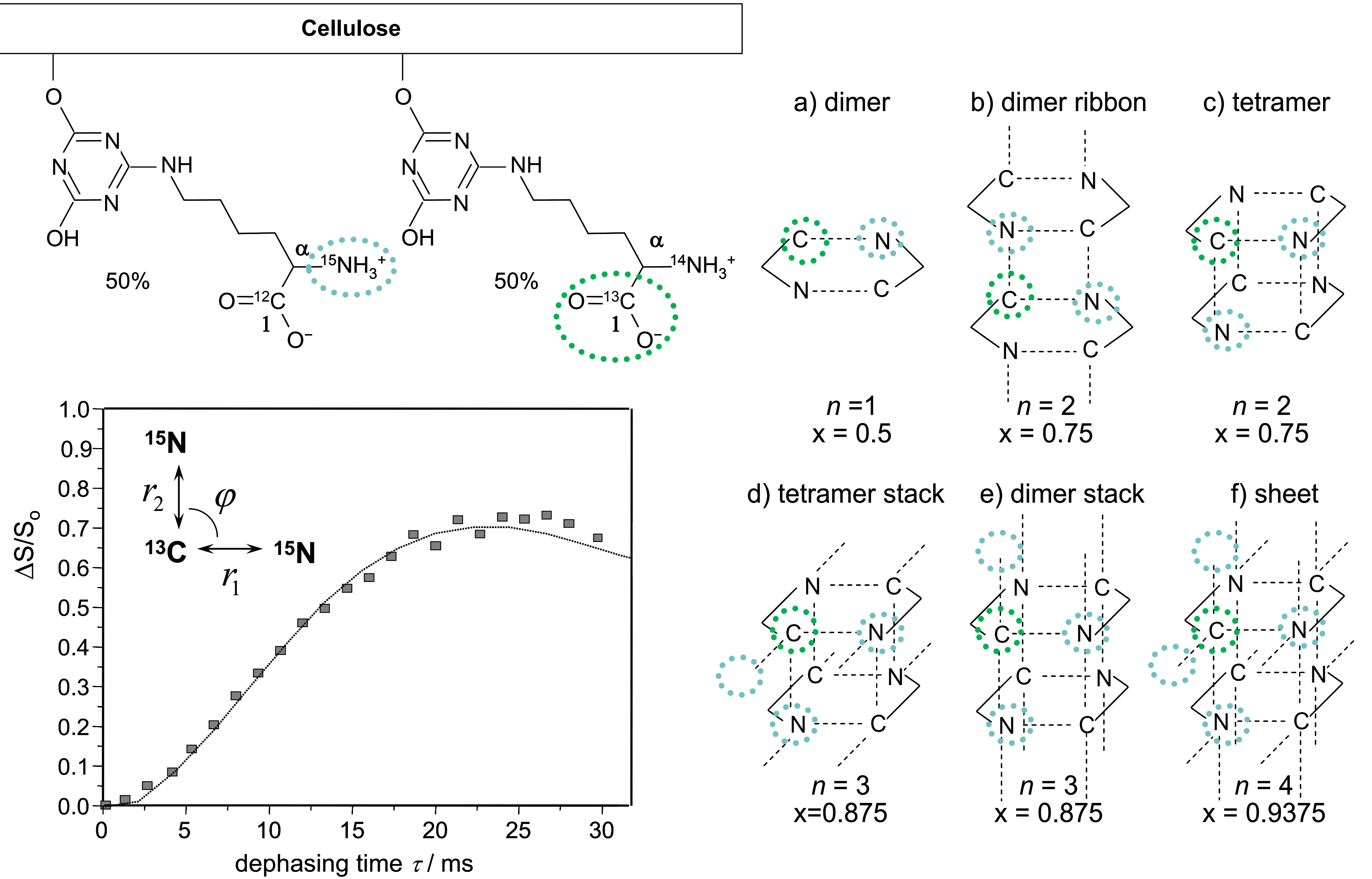
L-Leucine Lyophilized at Different pH



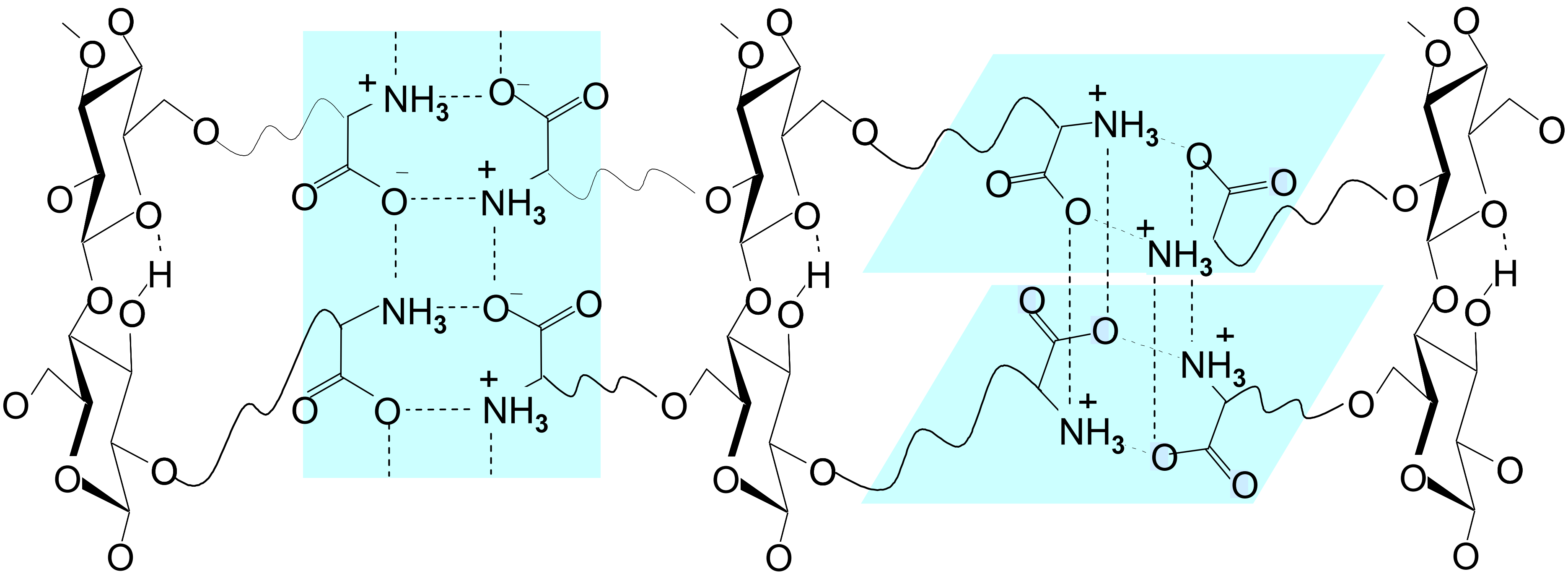
Isotopically Labeled Aminocarboxyl Groups



Number of ^{15}N in Close Proximity to ^{13}C



Cellulose Grafted with Aminocarboxyl Groups



30% wet-tensile-strength improvement is provided by zwitterionic dimers organized in ribbons or tetramers

R. Manriquez, F.A. Lopez-Dellamary, J. Frydel, T. Emmler, H. Breitzke, G. Buntkowsky, H.-H. Limbach, I.G. Shenderovich
J. Phys. Chem. B **2009**, *113*, 934.

INSTITUT FÜR
ORGANISCHE CHEMIE
UNIVERSITÄT REGENSBURG

THREE CUPS OF "MODERN NMR SPECTROSCOPY" ESPRESSO

Ilya G. Shenderovich

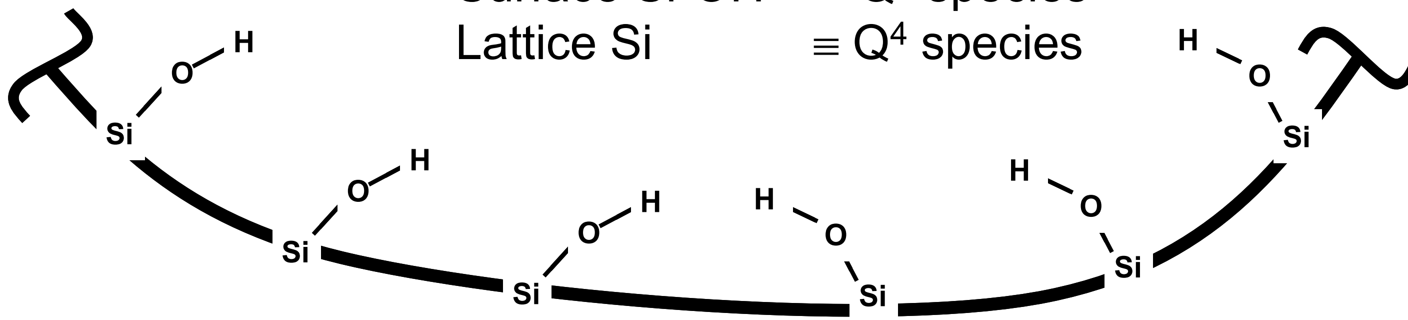
http://homepages.uni-regensburg.de/~shi56087/

Physical background of NMR	NMR in practice	A research lecture
1. Classical and quantum-mechanical descriptions 2. T_1 and T_2 Relaxations 3. Chemical shift 4. Spin-spin scalar coupling 5. Spin systems of the first and the second orders 6. Chemical exchange 7. Two-dimensional NMR	1. NMR in solution 1.1 From spectrum to structure 1.2. Typical protocol for structure elucidation 2. NMR in the solid state 2.1 Orientation-dependent interactions 2.1 Measurements of internuclear distances 2.3 NMR of surfaces and amorphous solids	NMR Study of Hydrogen Bonding in Solution Down to 100 K

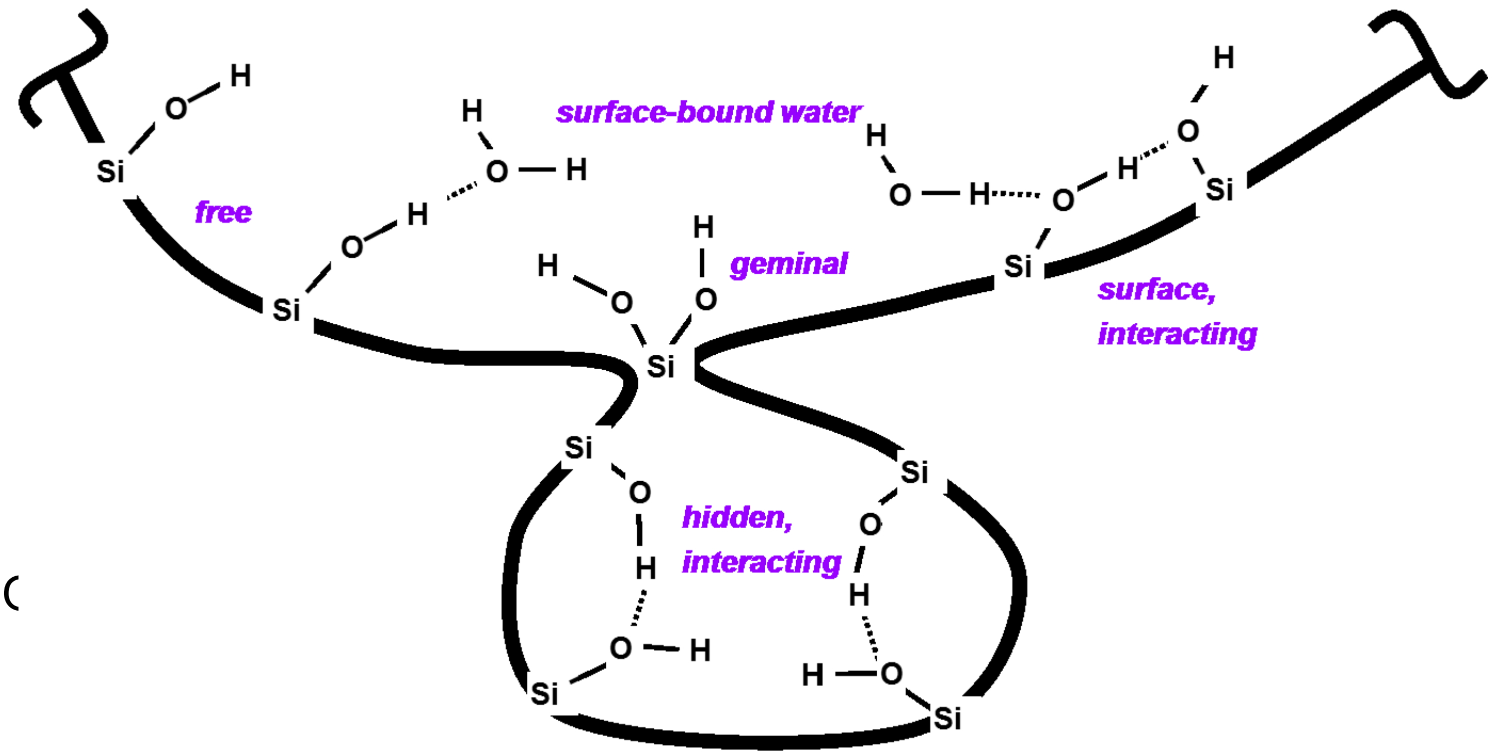
Pure siliceous materials

Idealized Surface

Surface Si-OH ≡ Q^3 species
Lattice Si ≡ Q^4 species



Rough Surface



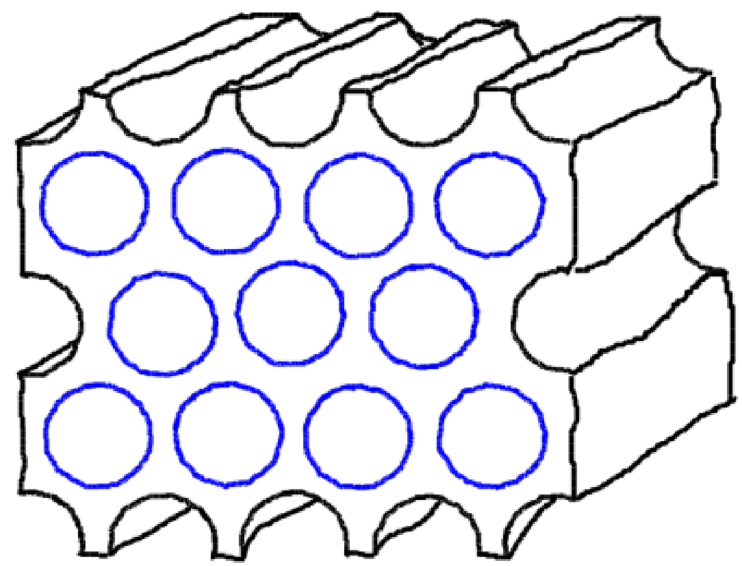
Geminal Si-((

NMR of Surfaces

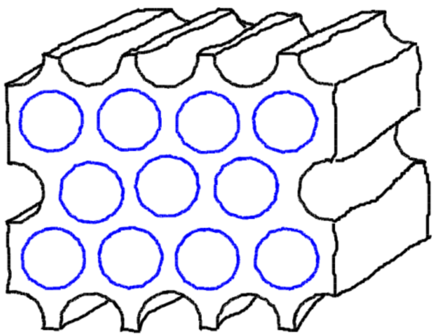
Mesoporous Silica Materials

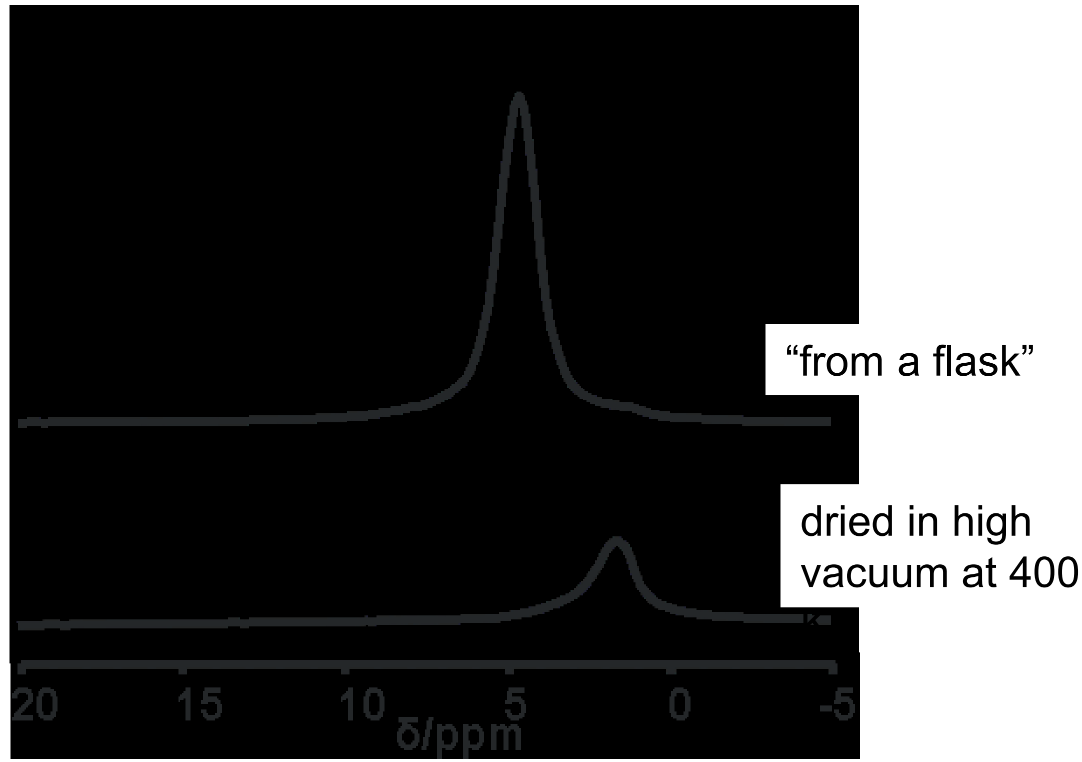
MCM-41, SBA-15 silica

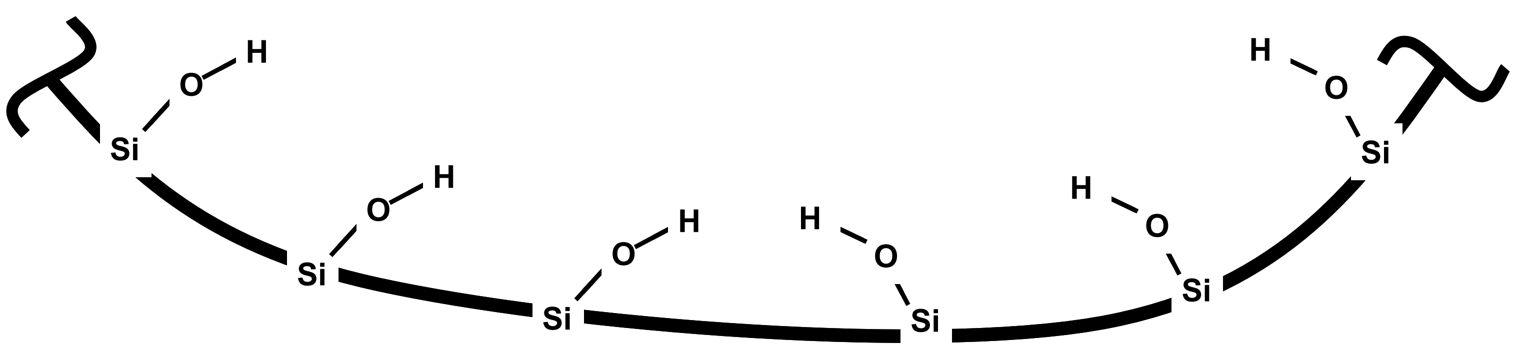
MCM-41, ∅ ~ 2 ÷ 4 nm
SBA-15 , ∅ ~ 7 ÷ 20 nm
Surface ~ 1000 m^2/g



^{1}H NMR at 300 K

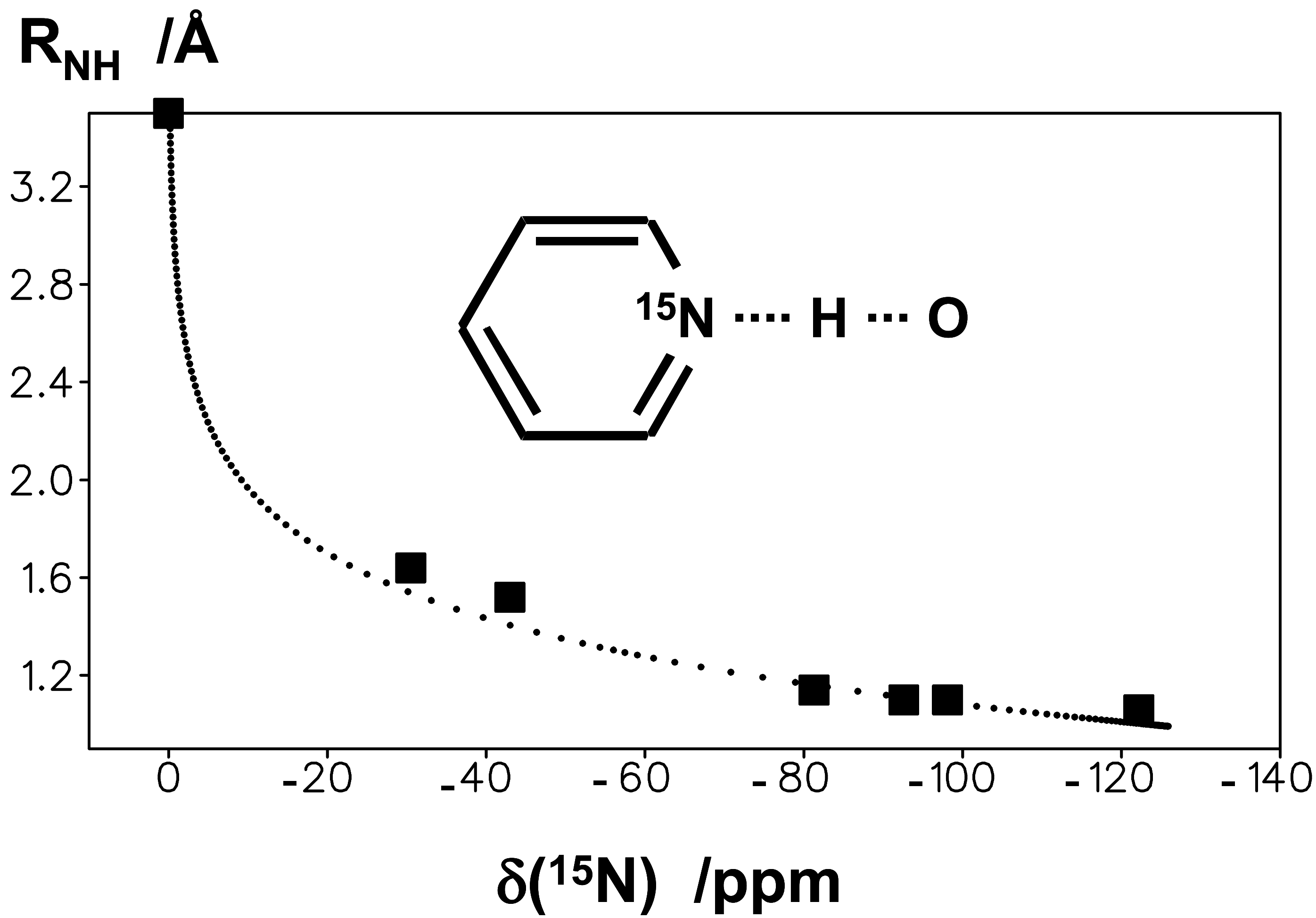






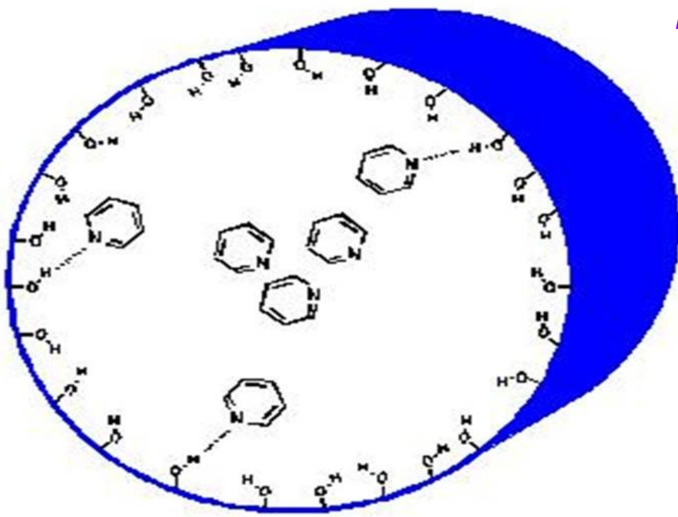
D. Mauder, D. Akcakayiran, S. B. Lesnichin, G. H. Findenegg, I. G. Shenderovich J. Phys. Chem. C 2009, 113: 19185.

^{15}N-pyridine as a sensor of "acidity"

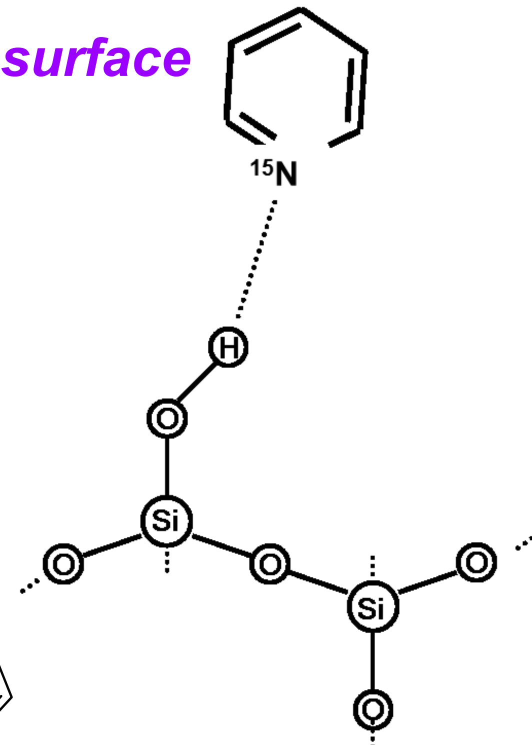


P. Lorente, I.G. Shenderovich, N.S. Golubev, G.S. Denisov, G. Buntkowsky G., H.-H. Limbach
Magn. Reson. Chem. 2001, 39: S18

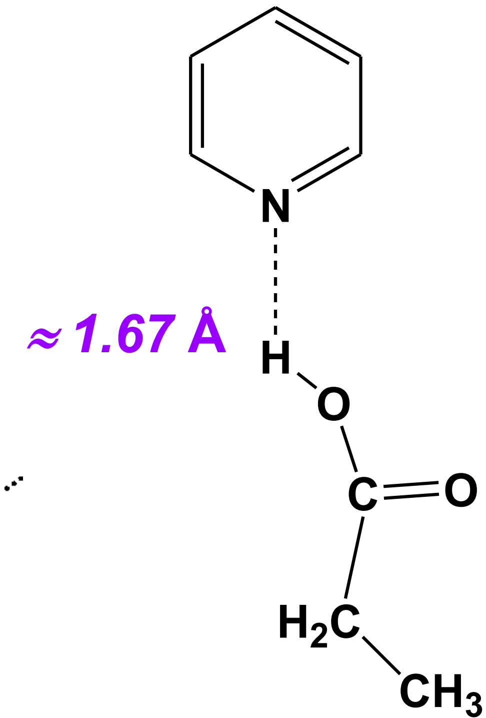
^{15}N NMR @ 130K



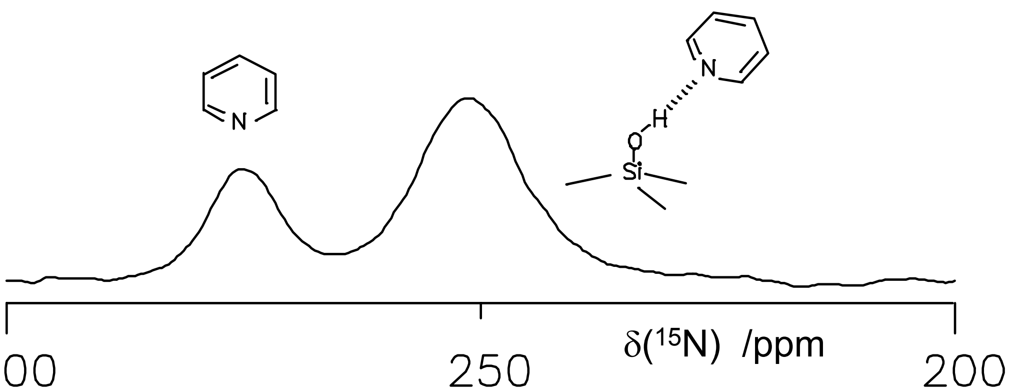
Dry surface



Crystal



Propionic acid

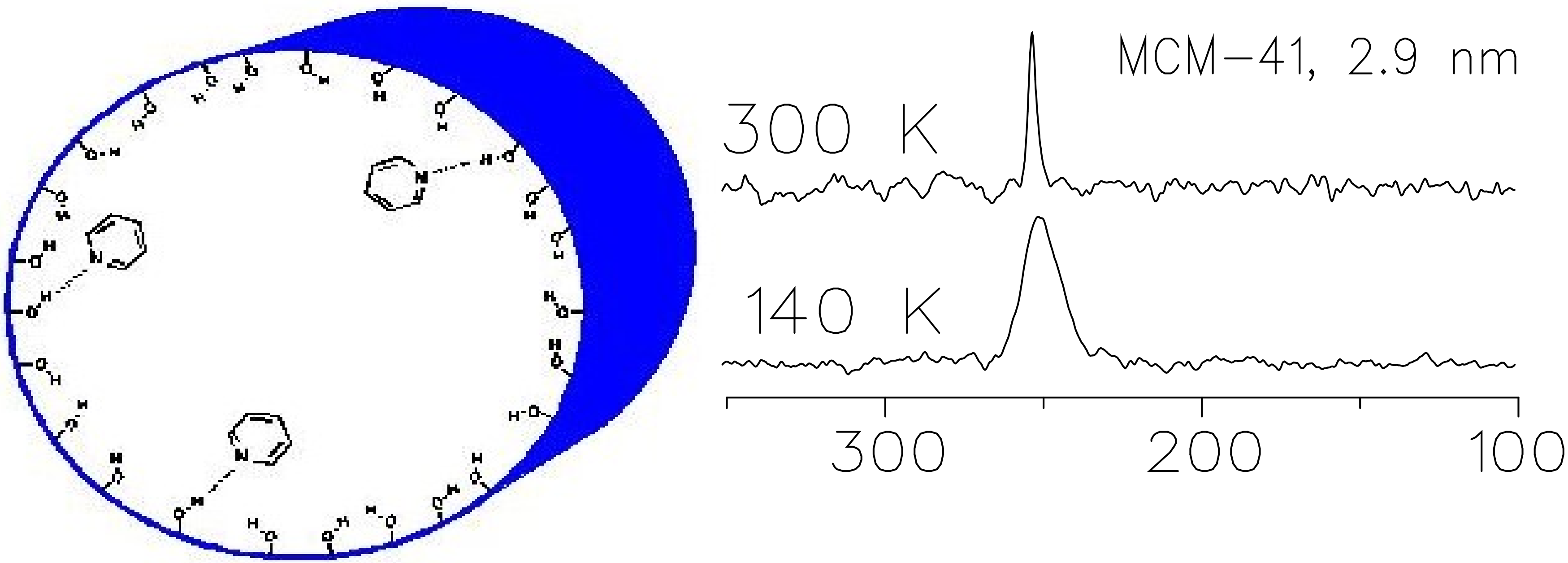


Density of OH-groups:

MCM-41 ≈ 2.9 nm^{-2}
SBA-15 ≈ 3.7 nm^{-2}

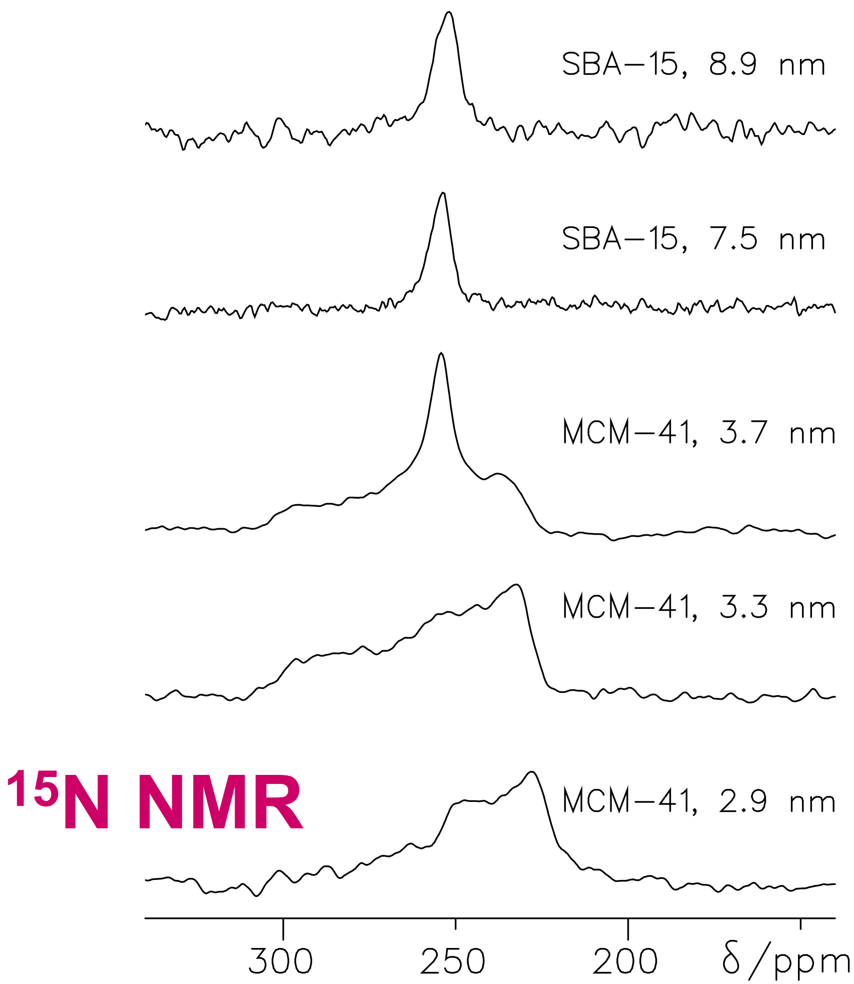
I.G. Shenderovich, G. Buntkowsky, A. Schreiber, E. Gedat, S. Sharif, J. Albrecht, N.S. Golubev, G.H. Findenegg, H.-H. Limbach
J. Phys. Chem. B 2003, 107: 11924-11939

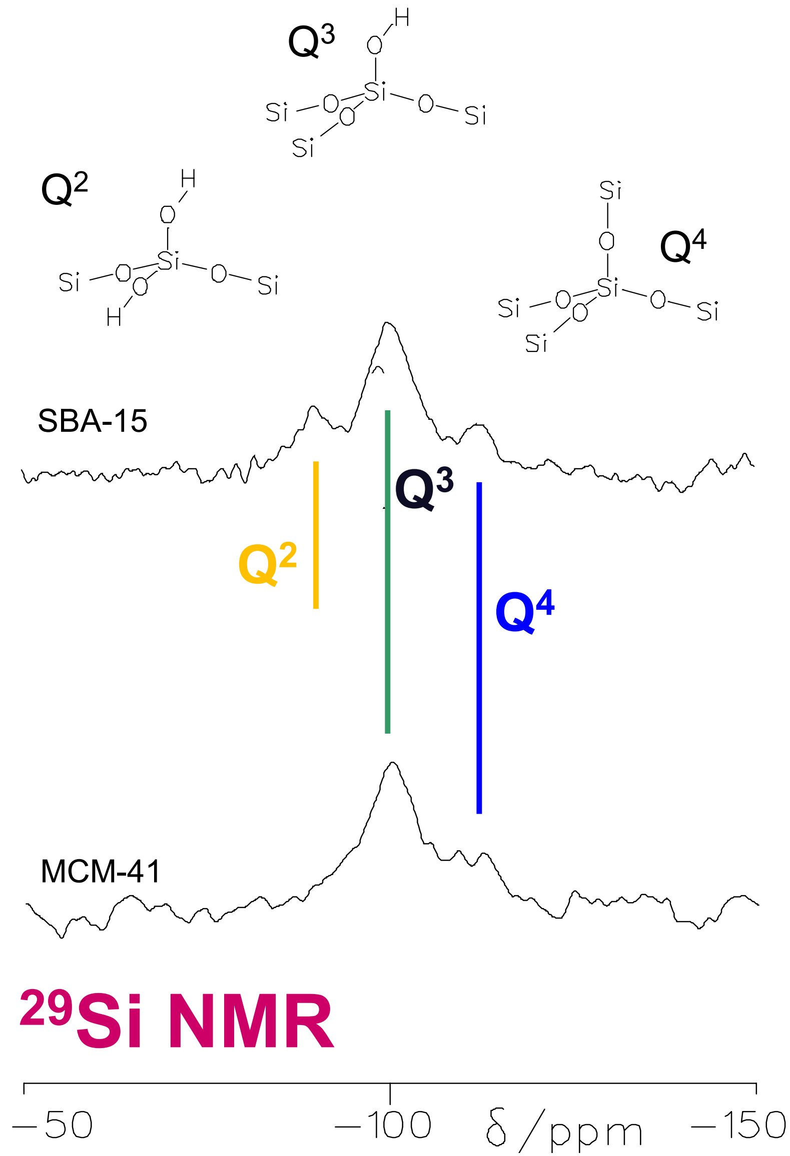
^{15}N NMR @ 300K



I.G. Shenderovich, G. Buntkowsky, A. Schreiber, E. Gedat, S. Sharif, J. Albrecht, N.S. Golubev, G.H. Findenegg, H.-H. Limbach J. Phys. Chem. B 2003, 107: 11924-11939

Pyridine dynamics inside MCM-41 and SBA-15 @ 300K

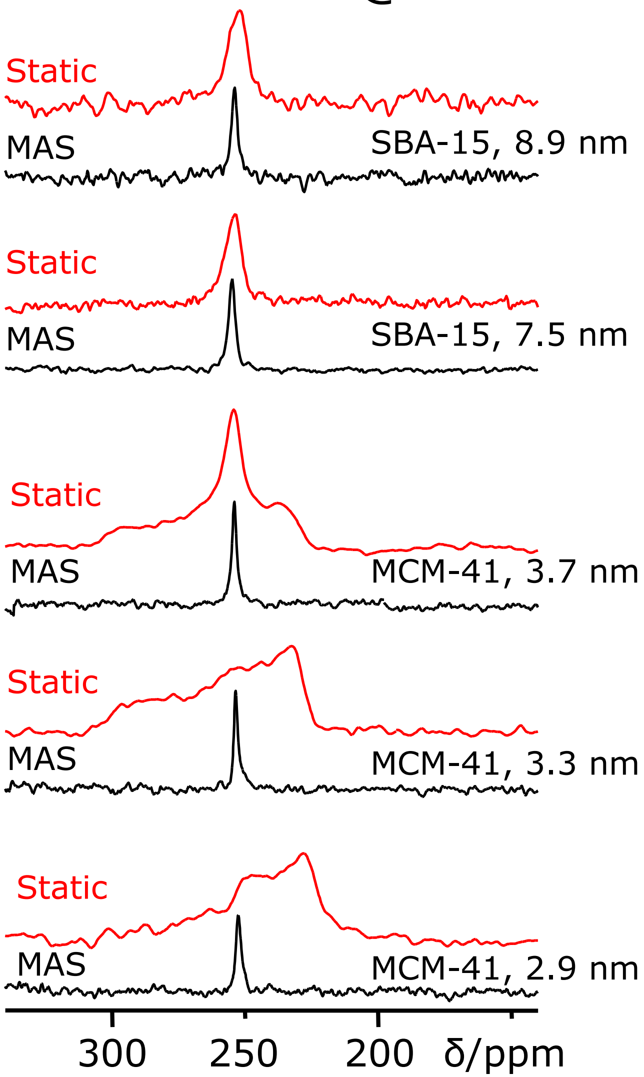


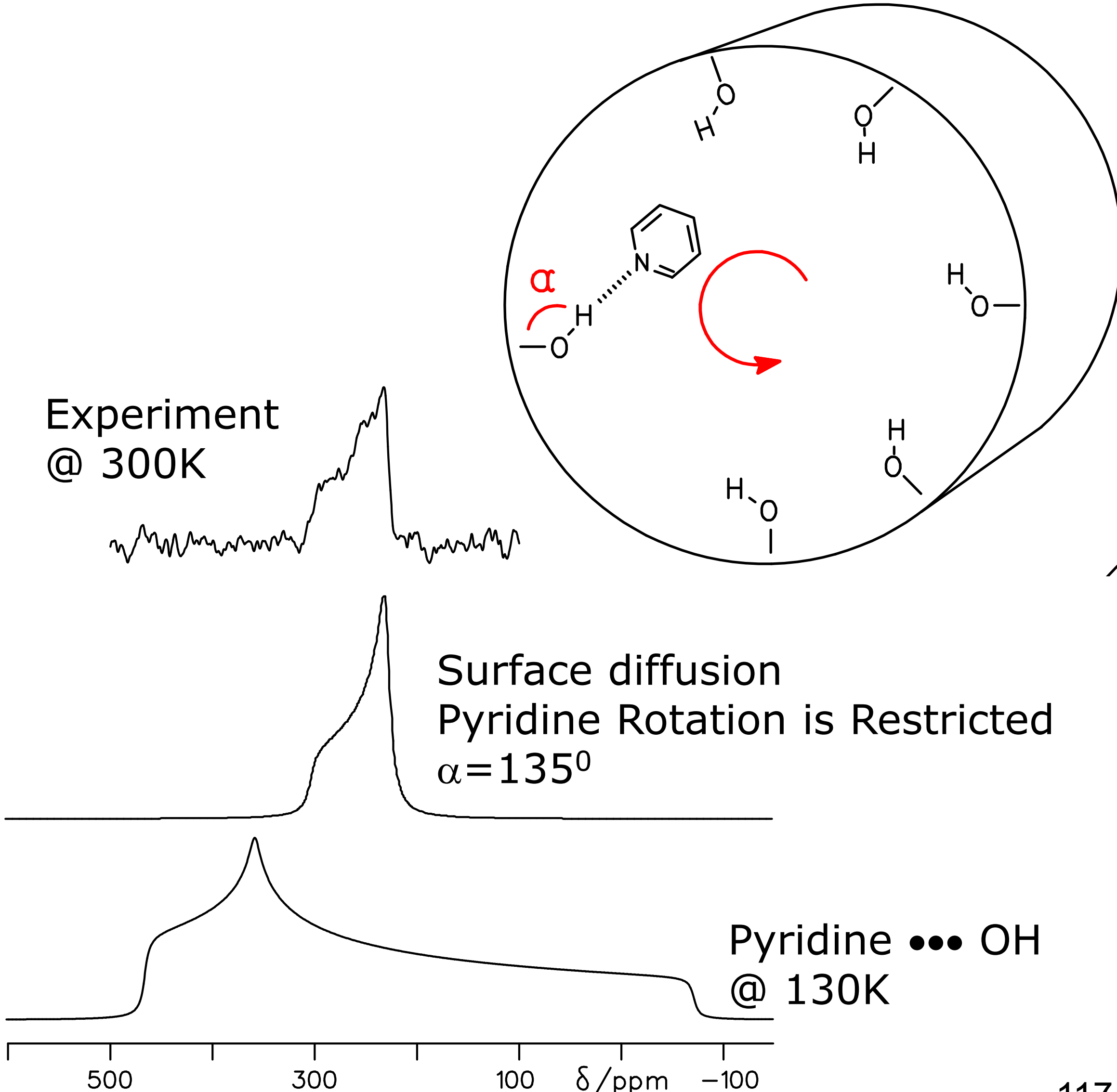


I.G. Shenderovich, G. Buntkowsky, A. Schreiber, E. Gedat, S. Sharif, J. Albrecht, N.S. Golubev, G.H. Findenegg, H.-H. Limbach J. Phys. Chem. B 2003, 107: 11924-11939

Morphology of Mesoporous Silica

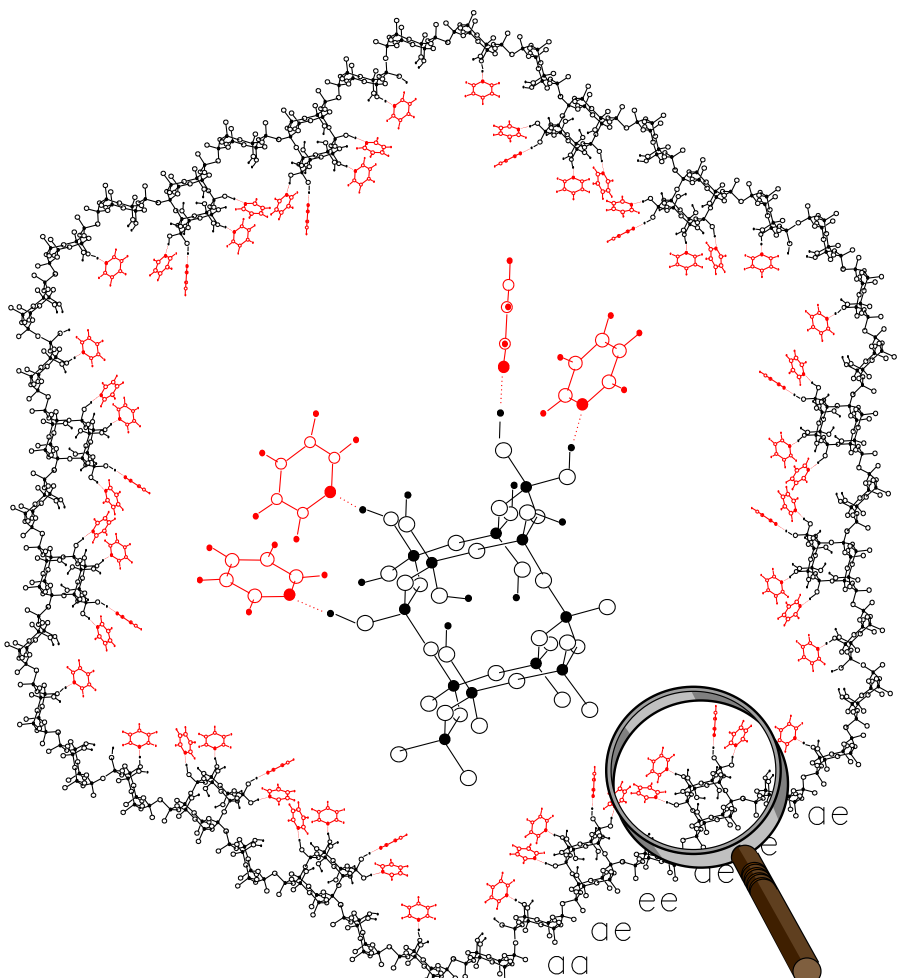
^{15}N MAS NMR @ 300K



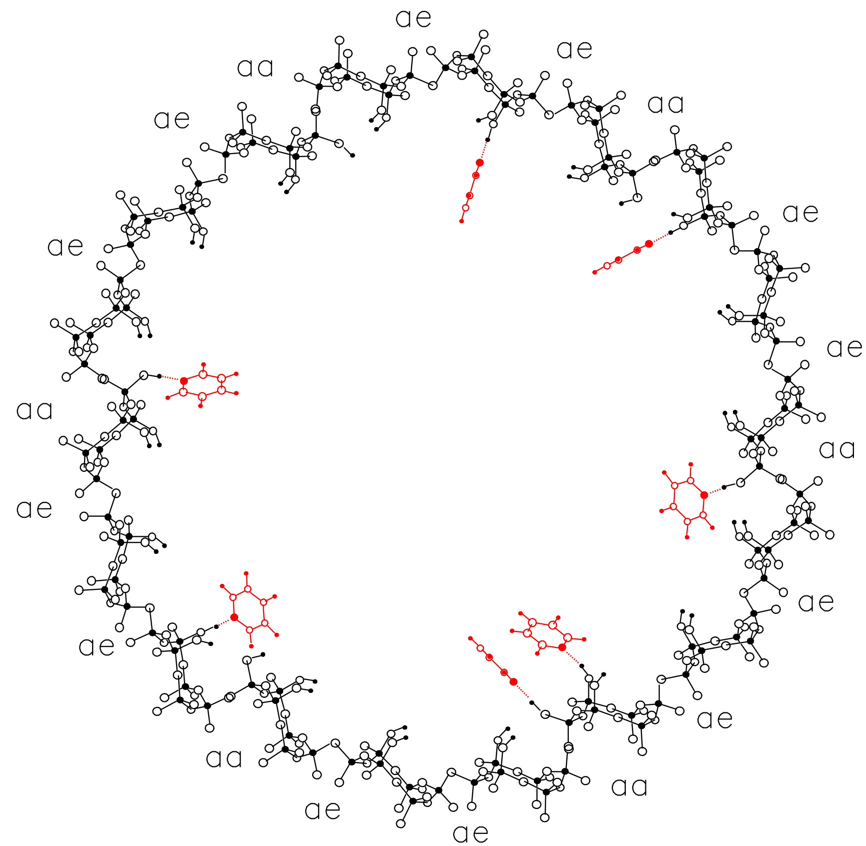


Inner surface of mesoporous silica

Rough surface
SBA-15

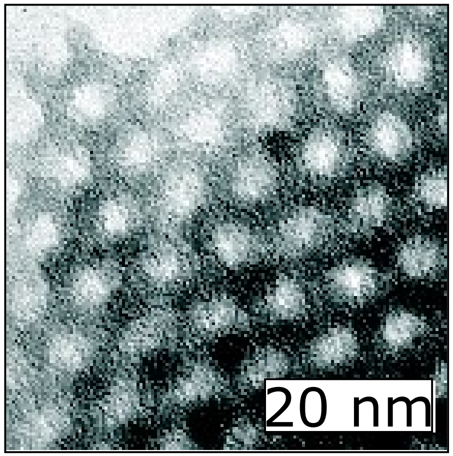


Idealized surface
MCM-41

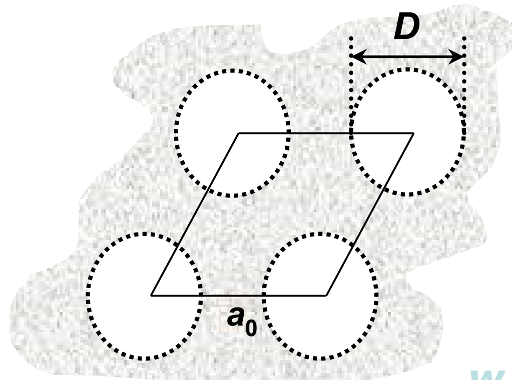


Structure of Amorphous Materials
Mesoporous Silica Materials

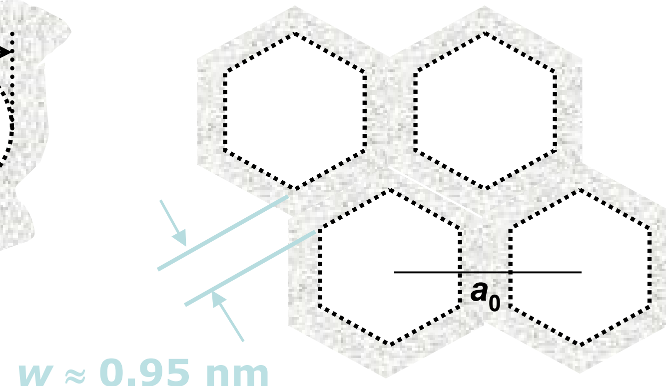
Input exp.: Silanol density (3 nm^{-2}); Pore diameter D; Lattice parameter a_0



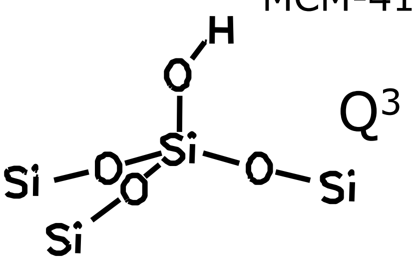
Transmission electron microscopy MCM-41

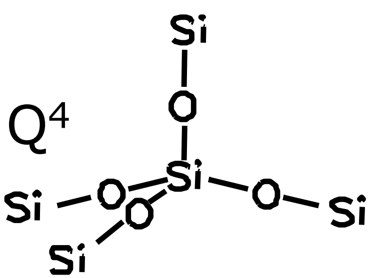


Circular Pores Model



Hexagonal Pores Model





MCM-41	$Q^3 : Q^4$		
	Exp.	**circular**	**hexagonal**
sample 1	0.32	0.27	0.35
sample 2	0.35	0.30	0.45

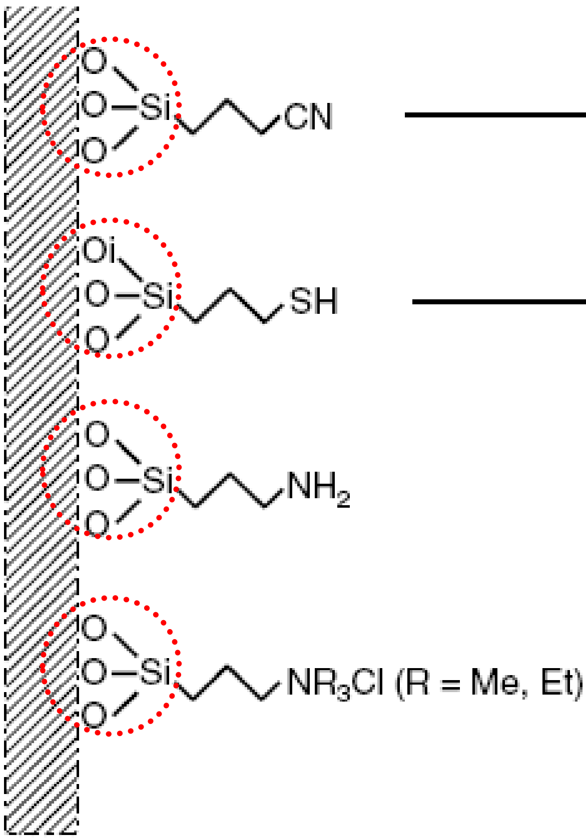
Distribution of the surface hydroxyl groups

Microporous and Mesoporous Materials 77 (2005) 1–45

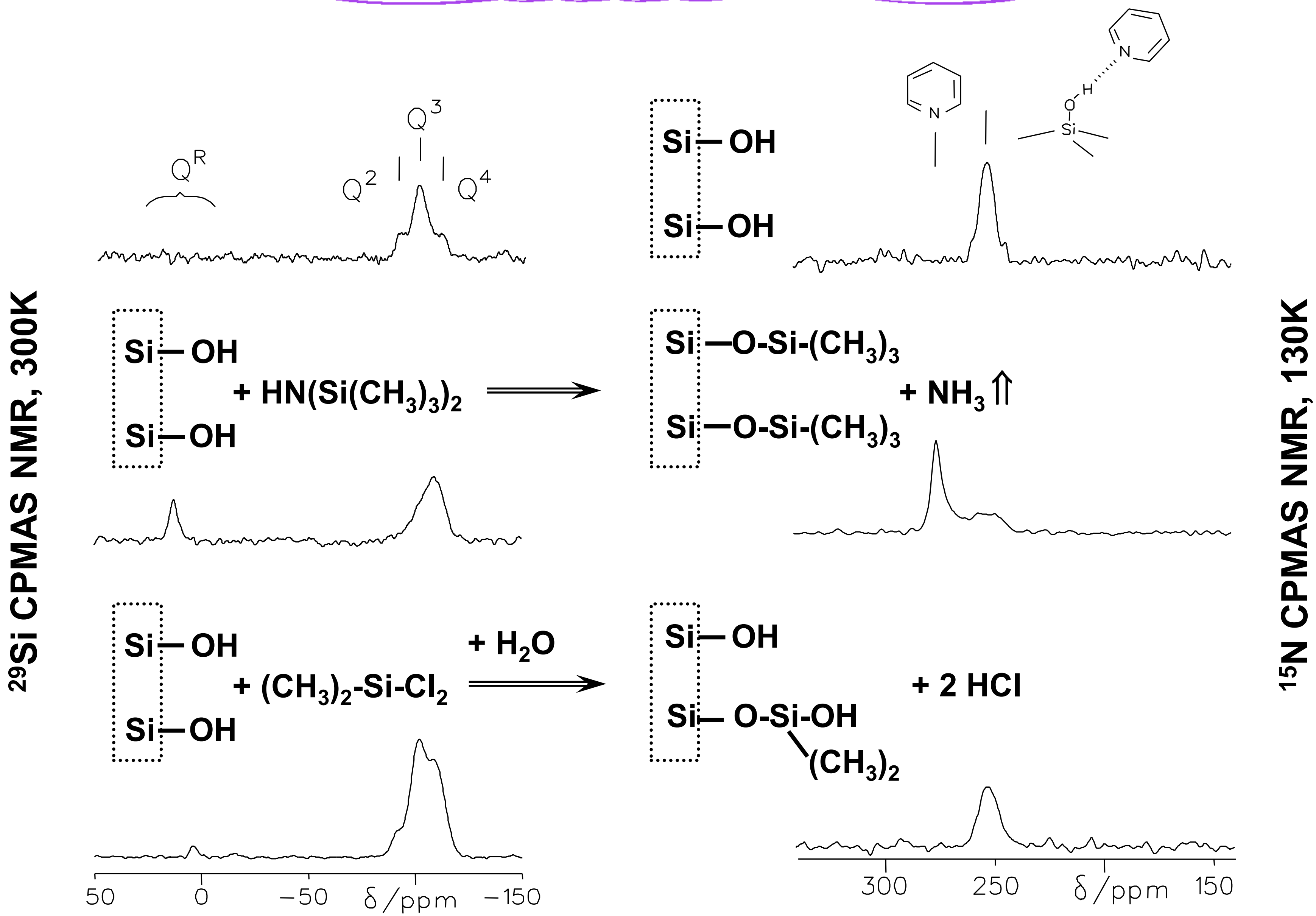
Review

Ordered mesoporous materials in catalysis

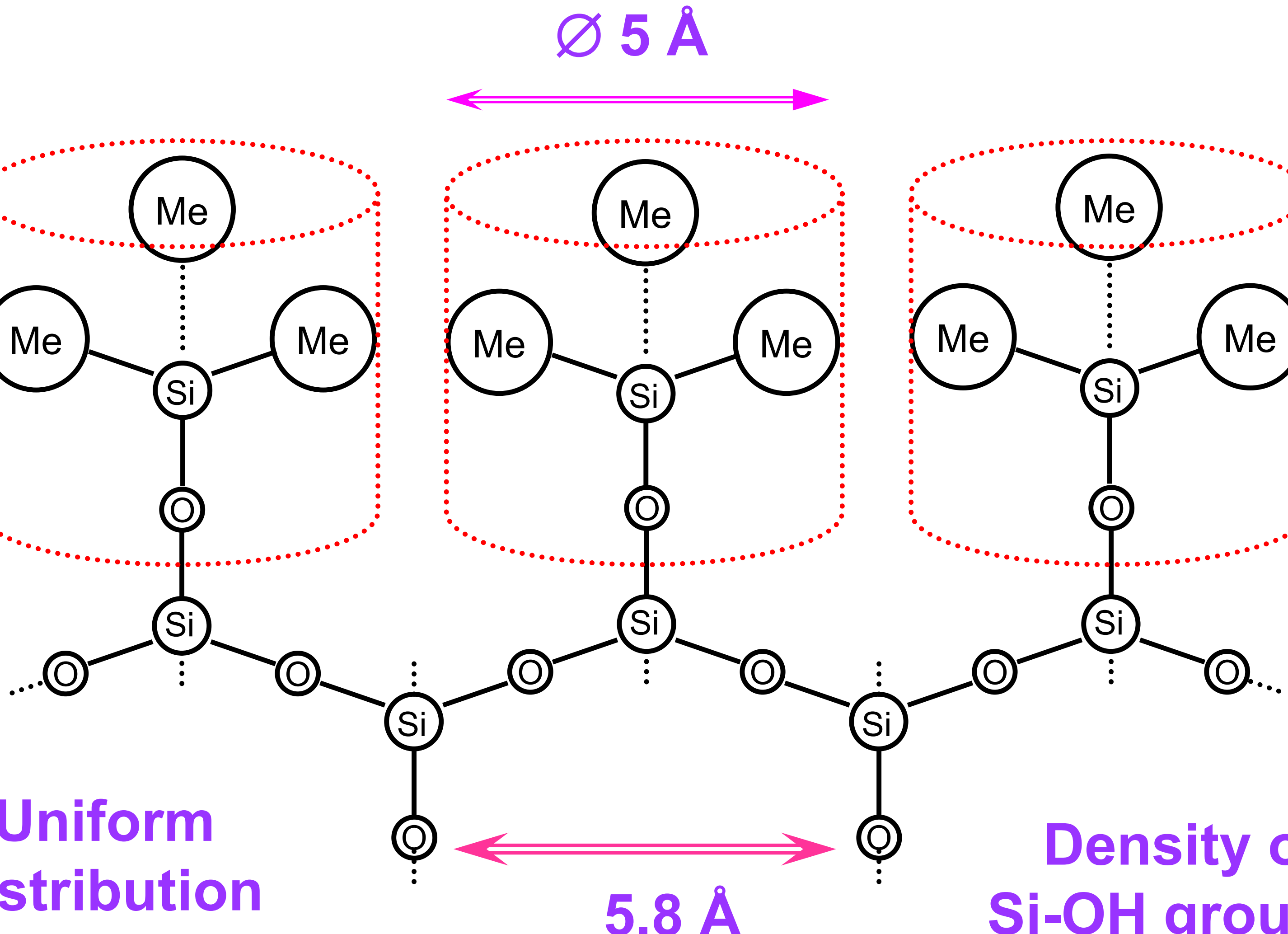
Akira Taguchi, Ferdi Schüth *



Distribution of the surface hydroxyl groups



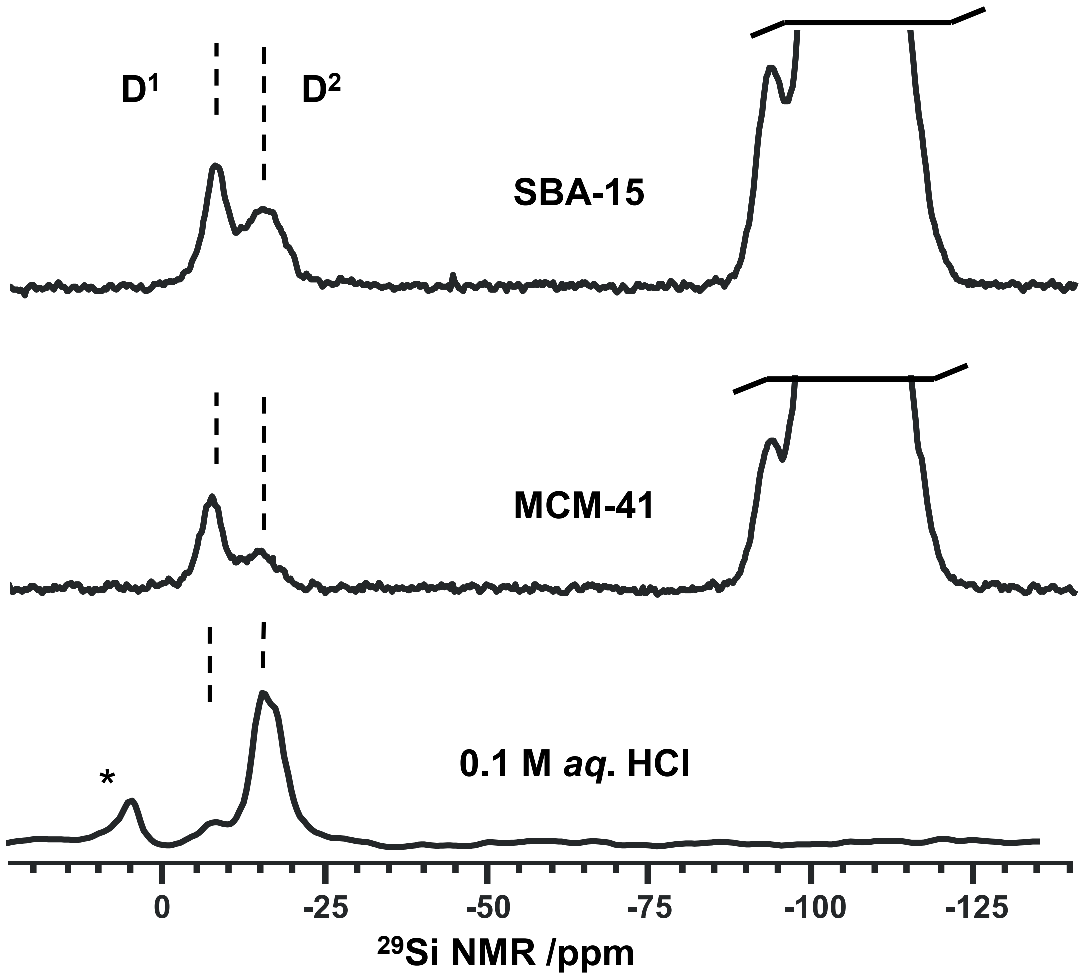
Distribution of the surface hydroxyl groups

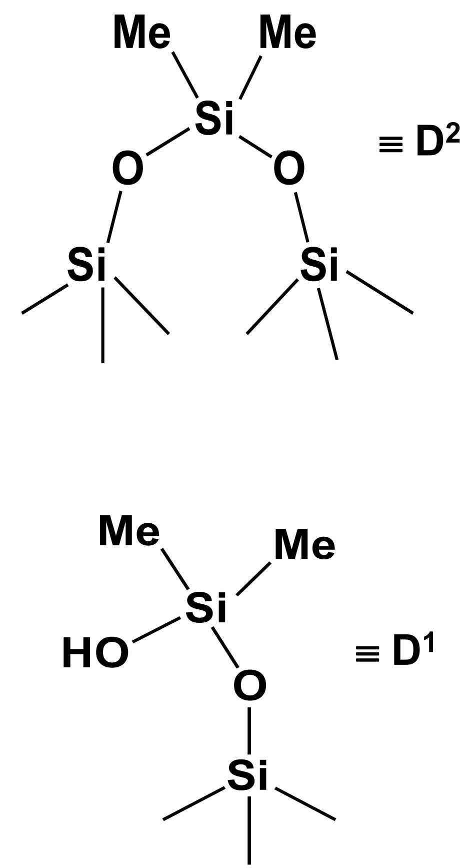


Uniform distribution assumption

Density of Si-OH groups: 2.9 nm^{-2} (MCM-41)

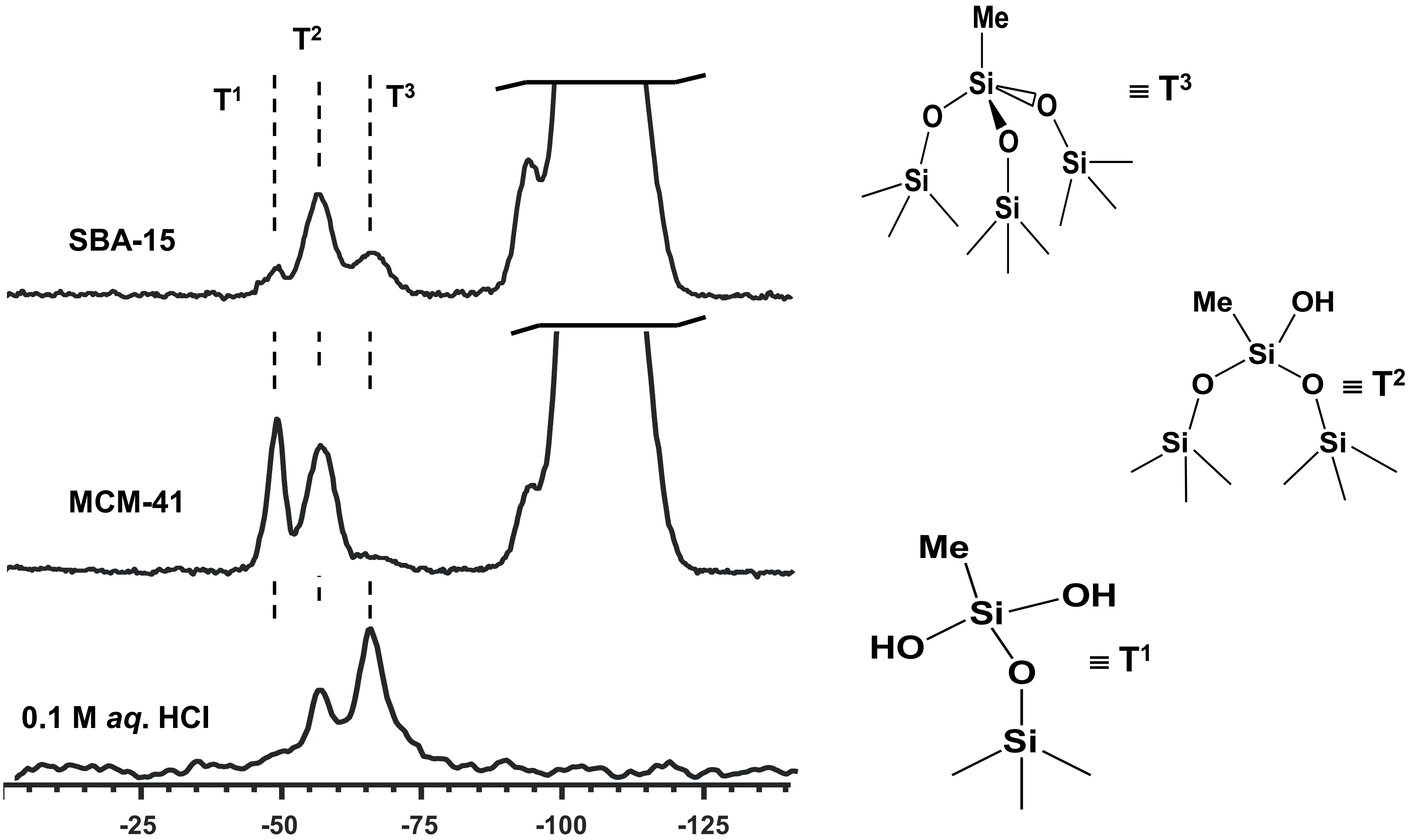
Surface functionalization





I.G. Shenderovich, D. Mauder, D. Akcakayiran, G. Buntkowsky, H.-H. Limbach, G.H. Findenegg
J. Phys. Chem. B 2007, 111: 12088-12096.

Surface functionalization



I.G. Shenderovich, D. Mauder, D. Akcakayiran, G. Buntkowsky, H.-H. Limbach, G.H. Findenegg
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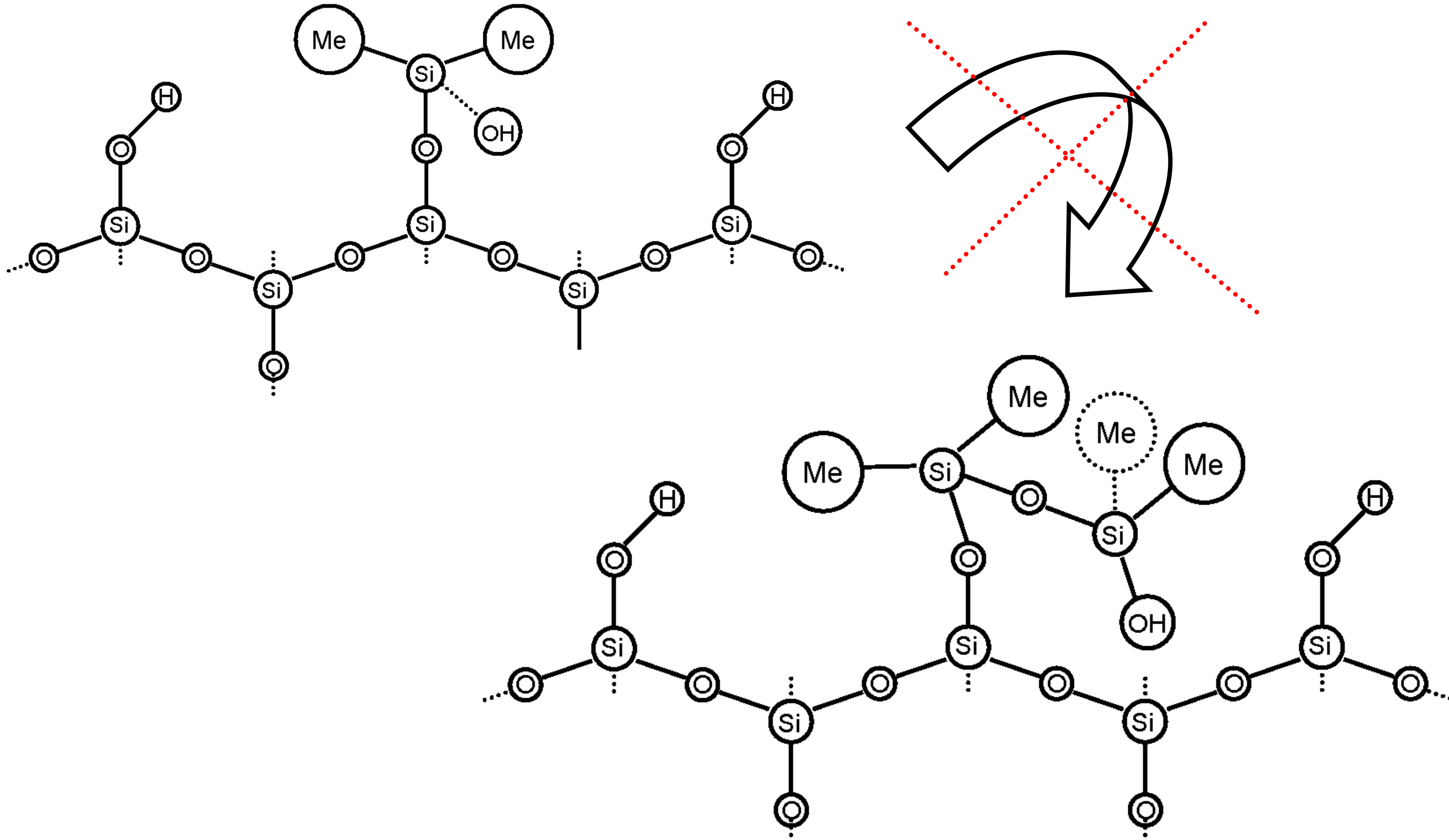
Surface functionalization



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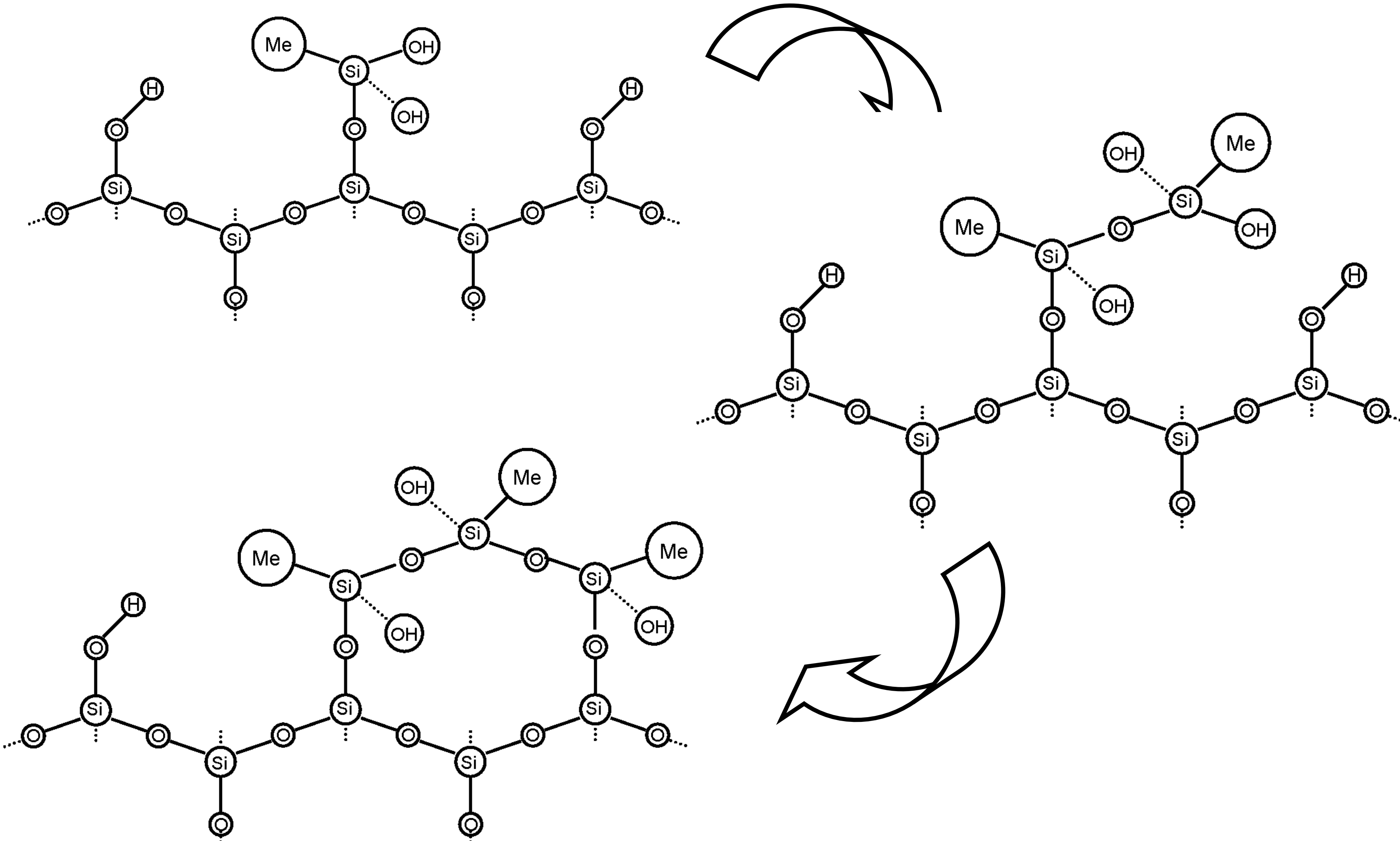
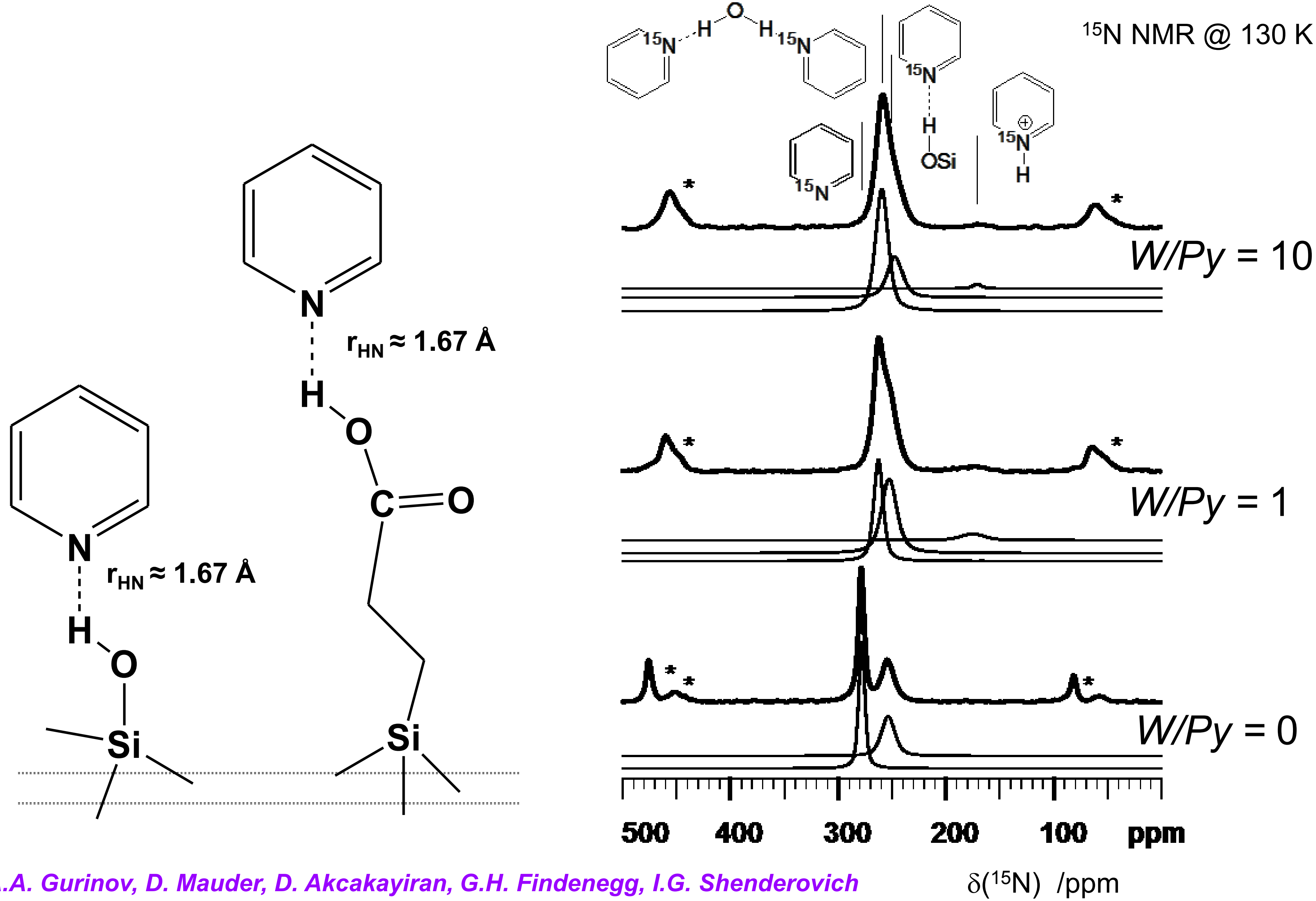
Surface functionalization



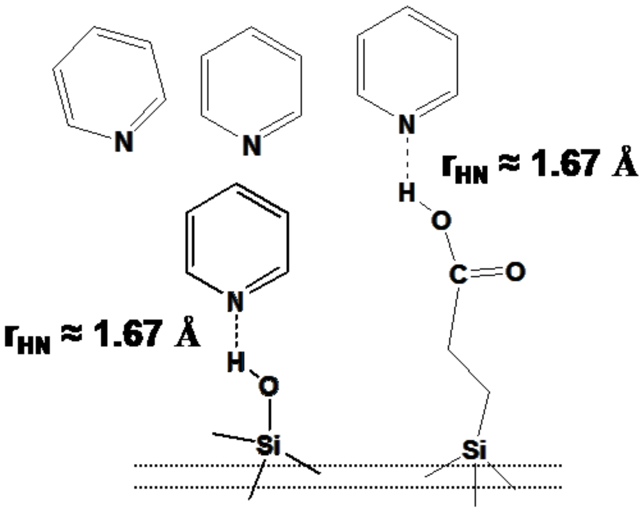
I.G. Shenderovich, D. Mauder, D. Akcakayiran, G. Buntkowsky, H.-H. Limbach, G.H. Findenegg
J. Phys. Chem. B 2007, 111: 12088-12096.

Propionic Acid Functionalized SBA-15

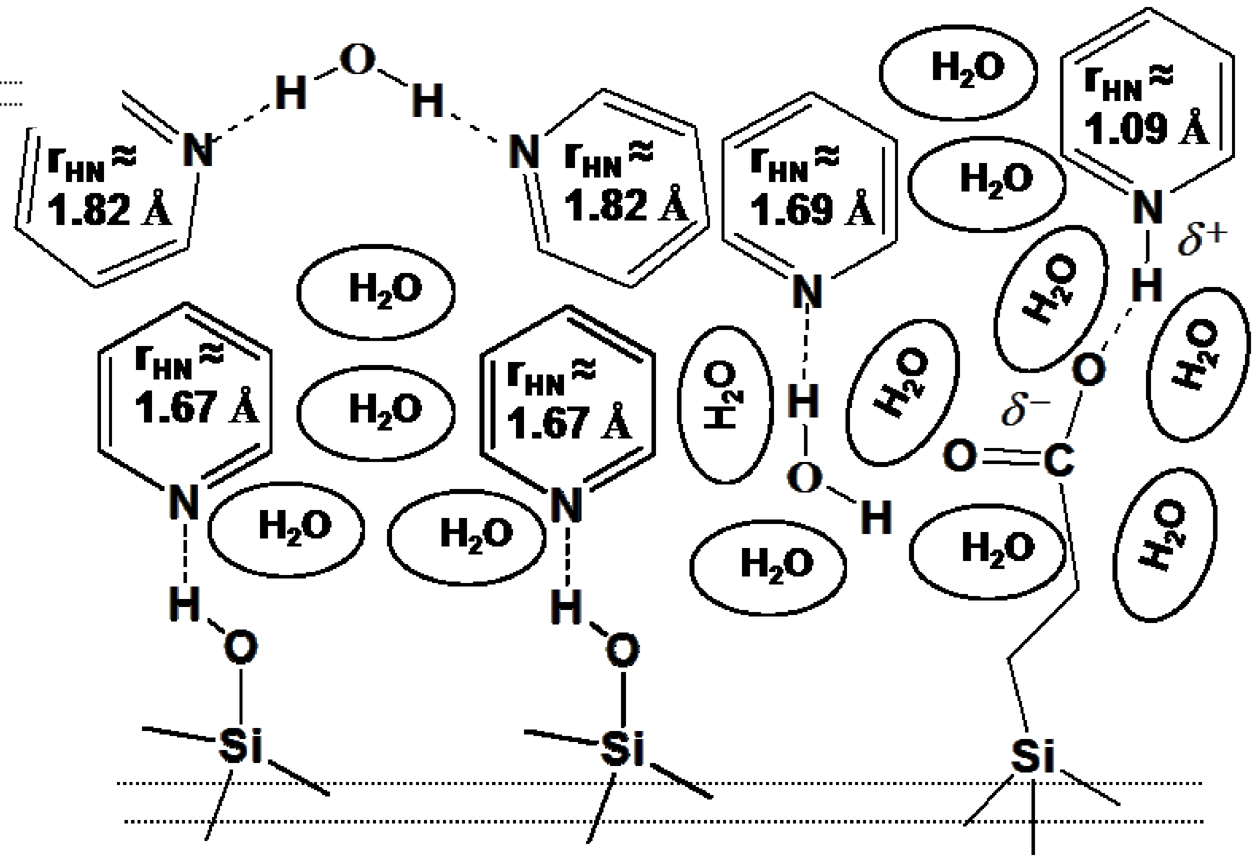


A.A. Gurinov, D. Mauder, D. Akcakayiran, G.H. Findenegg, I.G. Shenderovich
ChemPhysChem 2012, 2012, 13: 2282-2285.

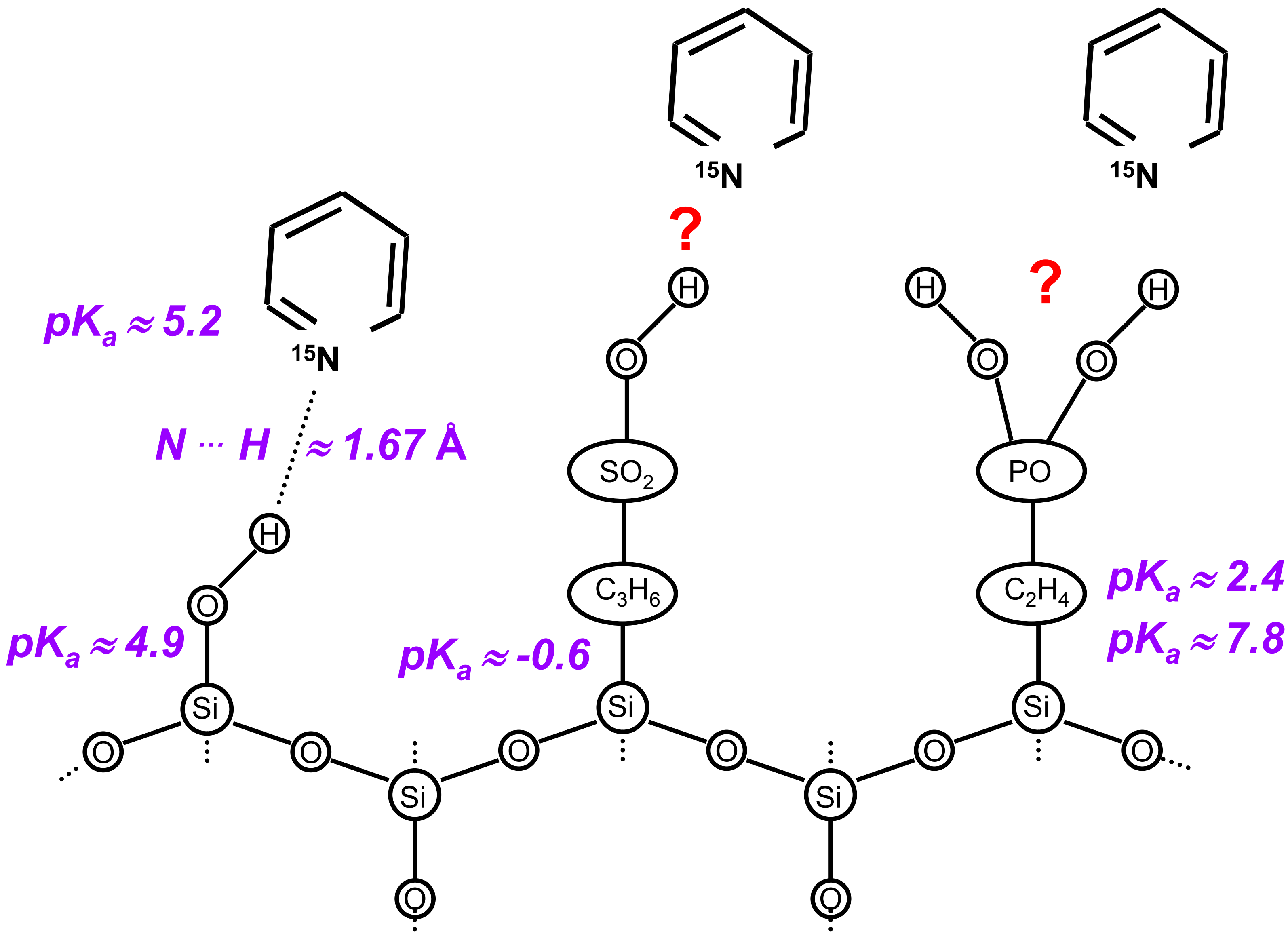
Propionic Acid Functionalized SBA-15



A.A. Gurinov, D. Mauder, D. Akcakayiran, G.H. Findenegg, I.G. Shenderovich
ChemPhysChem 2012, 13: 2282-2285.

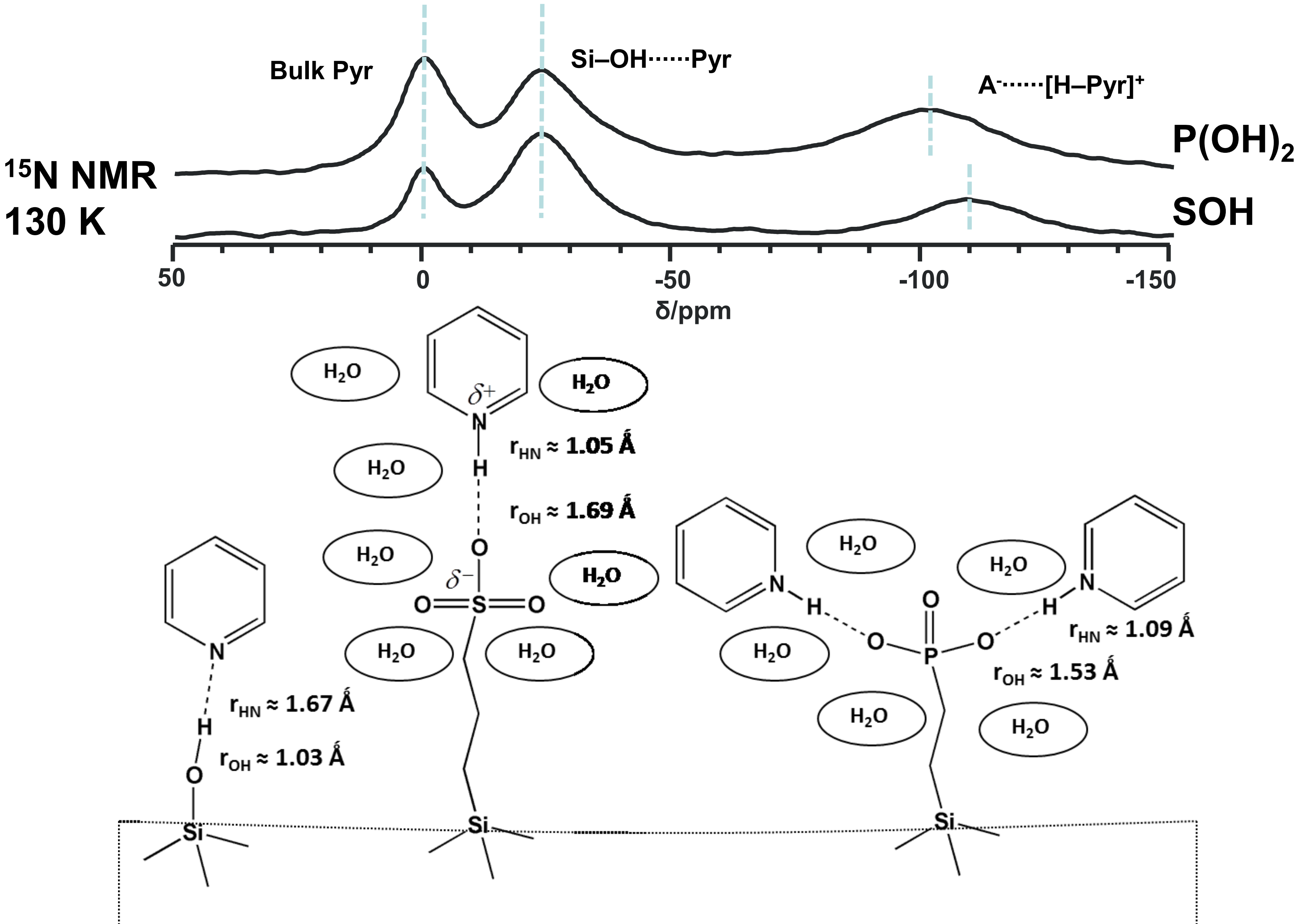


Strong Acids Functionalized SBA-15



D. Mauder, D. Akcakayiran, S. B. Lesnichin, G. H. Findenegg, I. G. Shenderovich J. Phys. Chem. C 2009, 113: 19185.

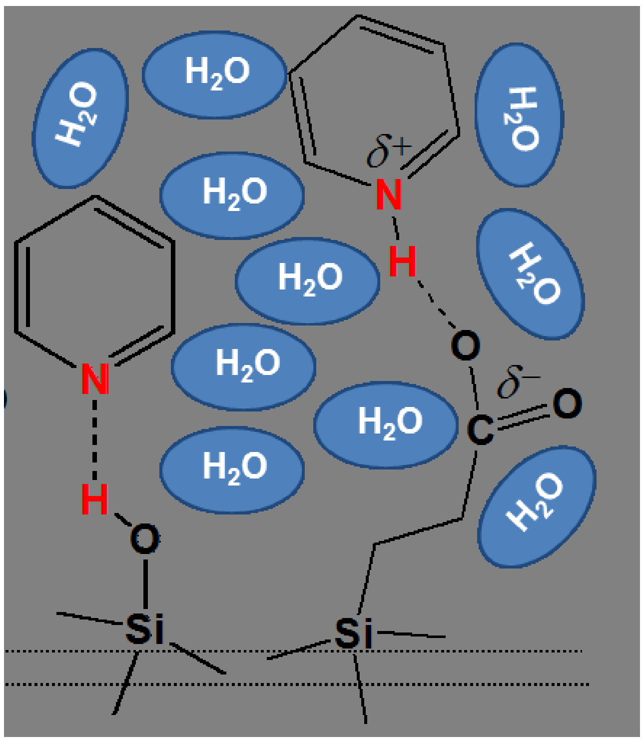
Strong Acids Functionalized SBA-15



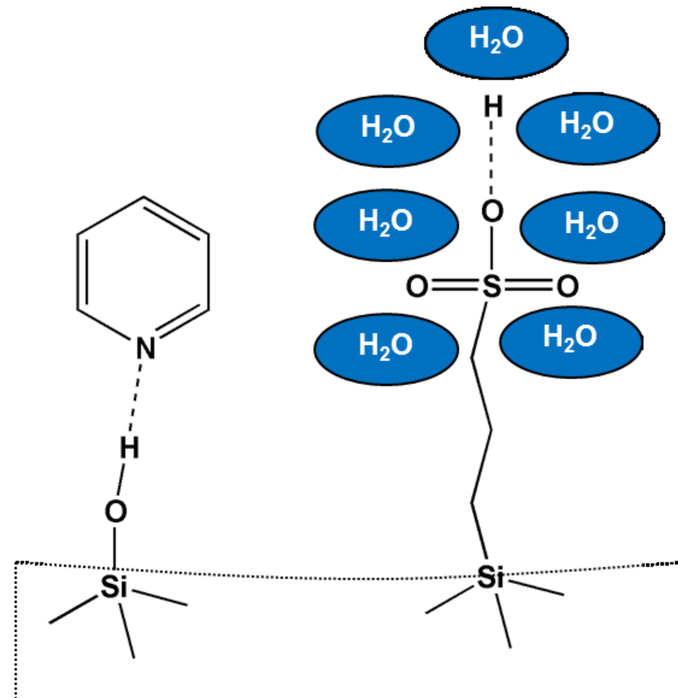
D. Mauder, D. Akcakayiran, S. B. Lesnichin, G. H. Findenegg, I. G. Shenderovich J. Phys. Chem. C 2009, 113: 19185.

Conclusion

Our ability to manipulate the chemical reactivity of a surface by a fluid filling is limited by:



steric hindrance caused by the structure of the surface



presence of chemisorbed species