NMR for Battery

SHORT DISCUSSION

KAIST 화학과 NMR실

Battery type

Liquid electrolytes

Solid polymer electrolytes

Polymer gel electrolytes

Nanocomposite polymer and gel electrolytes

Liquid electrolytes

Anion
- Conc. 0.5 ~ 1.0 M
- Mobility : BF_4^- > ClO_4^- > PF_6^- > Tf^- > $TFSI^-$
  - Size

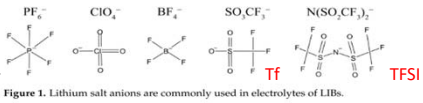


Figure 1. Lithium salt anions are commonly used in electrolytes of LIBs.

Aprotic solvent
- Ethylene carbonate, propylene carbonate, γ-butyrolactone, so on
  - High dielectric constant
  - High viscosity, low m.p.

Thinner :
- dimethyl carbonate(DMC), ethyl methyl carbonate(EMC), diethyl carbonate(DEC), 1,2-dimethyl ether(DME)

Nuclei

1H : chemical shift, DOSY
- Absolute referencing

6Li, 7Li : chemical shift, DOSY, T1/T2, Heteronuclear NOE

19F : chemical shift, DOSY, qNMR, Heteronuclear NOE

13C : chemical shift

31P : chemical shift, qNMR

17O : chemical shift

11B : chemical shift

35Cl/37Cl : chemical shift

NMR for battery

Solvation number
- Chemical shift : Lewis basicity of solvent
  - Solvation number (Gutmann Donor number)
- DOSY : Diffusion coefficient
- Relaxation
  - T1 relaxation
  - T2 relaxation

Quantitative NMR
- T1, decoupling

1. Chemical shift

Background

Shielding
- $\sigma = \sigma_d + \sigma_p + \sigma_o$
  - σ_d : Diamagnetic shielding
    - local spherical electron density (usually small)
  - σ_p : Paramagnetic shielding
    - p or d electron. Opposite in sign to σ_d (large)
  - σ_o : remote group effect
    - ring current, dipolar effect, solvent effect …

$$\sigma_d = \frac{e^2}{3mc^2} \cdot \frac{Z_{eff}}{\alpha_0 n^2} = 17.8 \times 10^{-6} \frac{Z_{eff}}{n^2}$$

$$\sigma_p = -\frac{e^2 h^2 L(L+1)}{3m^2 c^2 \Delta E} \left\langle \frac{1}{r^3} \right\rangle_{n,l}$$
$$= -7.67 \times 10^{-16} \frac{(Z_0 Z)^{3/2} L(L+1)}{n^3 l(l+1)(l+\frac{1}{2})\Delta E}$$

Nuclei
- Proton : $\sigma_d >> \sigma_p$
  - High energy 1s -2p gap (paramagnetic shielding is negligible)
- Most metal : $\sigma_p >> \sigma_d$
  - Low energy gap when n≥3 (diamagnetic shielding is negligible)

1. Chemical shift

Gutmann number

Gutmann acceptor number
- Lewis acidity
- ^{31}P chemical shift

Gutmann donor number
- Lewis basicity : hydrogen bond
  - 1:1 adduct formation between solvent and SBCl5 (Lewis acid)
  - Negative enthalpy
  - DN =0 when solvent is 1,2-dichloroethane(non-coordinating solvent)
- Stability & reactivity of metal species in solution

1. Chemical shift

Na^+ Solvation cage

Cation : sodium (Na+)

Anion
- Concentration dependency
  - Dependent : I^-, SCN^-
  - Independent : BPh_4^- , ClO_4^-

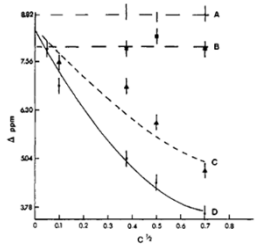
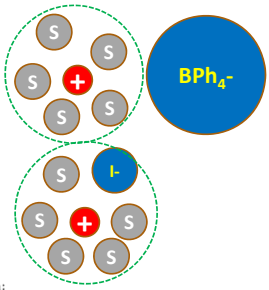
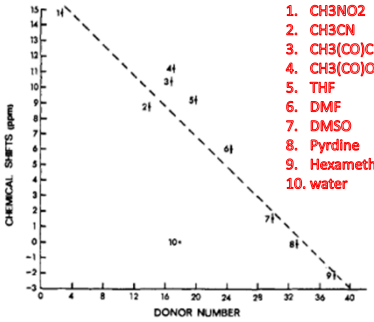


Figure 1. Variation in the ^{23}Na chemical shifts with concentration: (A) $NaBPh_4$ in acetone, (B) $NaBPh_4$ in acetonitrile, (C) NaI in acetonitrile, (D) NaI in acetone.



1. Chemical shift

Na^+ - Solvent



1. CH_3NO_2
2. CH_3CN
3. $CH_3(CO)CH_3$
4. $CH_3(CO)OCH_2CH_3$
5. THF
6. DMF
7. DMSO
8. Pyrdine
9. Hexamethylphosphoramide
10. water

Figure 4. Plot of the ^{23}Na chemical shift for $NaClO_4$ *vs.* Gutmann's donor numbers: (1) nitromethane, (2) acetonitrile, (3) acetone, (4) ethyl acetate, (5) THF, (6) DMF, (7) DMSO, (8) pyridine, (9) hexamethylphosphoramide, (10) water.

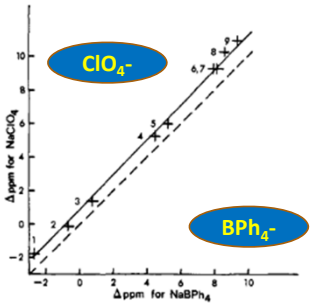


Figure 5. Plot of the ^{23}Na chemical shift for $NaClO_4$ *vs.* that for $NaBPh_4$ in various solvents: (1) hexamethylphosphoramide, (2) pyridine, (3) DMSO, (4) methanol, (5) DMF, (6) acetonitrile, (7) THF, (8) acetone, (9) ethyl acetate.

Donor number : Chemical shifts ➔ Linear

1. Chemical shift

Na^+ - Solvent

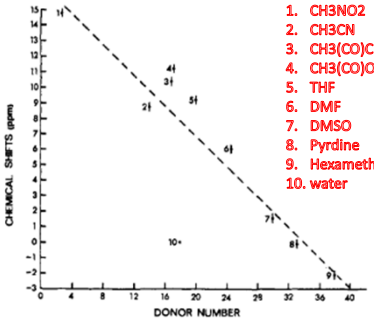


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Figure 4. Plot of the ^{23}Na chemical shift for $NaClO_4$ *vs.* Gutmann's donor numbers: (1) nitromethane, (2) acetonitrile, (3) acetone, (4) ethyl acetate, (5) THF, (6) DMF, (7) DMSO, (8) pyridine, (9) hexamethylphosphoramide, (10) water.

Donor number : Chemical shifts ➔ Linear

Solvent	Donor Number	^{23}Na shift [ppm]
Nitromethane	2.7	-12.7184
Acetanhydride	10.5	-11.3866
Benzonitrile	11.9	-6.7318
Acetonitrile	14.1	-6.9038
Acetone	17	-7.2938
γ-butyrolactone	18	-8.2835
THF	20	-7.5993
n-Pentanol	25	-2.6268
DMF	26.6	-4.2517
DMSO	29.8	-0.0245
H_2O	33	0
Pyridin	33.1	-0.11
Isopropanol	36	-0.6233
t-Butanol	38	-0.0733
HMPA	38.8	2[a]
Ethylendiamine	55[b]	12.4618

[a]Popov [b]Gutmann

1. Chemical shift

Lithium

Chemical shift range : ~ 6 ppm

- Effect of different solvent
  - $\sigma_{sol} = \sigma_b + \sigma_a + \sigma_w + \sigma_E$
    - σ_b : bulk magnetization
    - σ_a : anisotropy in magnetic susceptibility of solvent molecules
    - **σ_w : Van der Waals interaction between solute and solvent**
    - **σ_E : polar effect on the electronic structure of the solute caused by the electric field due to the charge distribution in neighboring solvent molecules**
  - Shielding
    - σ_d , σ_p : average radii of atomic orbital
    - σ_p ← altered energy level of the solute
- Donor number vs Chemical shift
  - Na : $\sigma_p >> \sigma_d$ // n=3 → quantitative
  - Li : $\sigma_p \approx \sigma_d$ // n=2 → qualitative

$$\sigma_d = \frac{e^2}{3mc^2} \cdot \frac{Z_{eff}}{\alpha_0 n^2} = 17.8 \times 10^{-6} \frac{Z_{eff}}{n^2}$$

$$\sigma_p = -\frac{e^2\hbar^2 L(L+1)}{3m^2c^2\Delta E}\left\langle \frac{1}{r^3} \right\rangle_{n,l}$$

$$= -7.67 \times 10^{-16} \frac{(Z_0 Z)^{3/2} L(L+1)}{n^3 l(l+1)(l+\frac{1}{2})\Delta E}$$

DN = (2.106 * $^{23}\delta$)+ 32.74

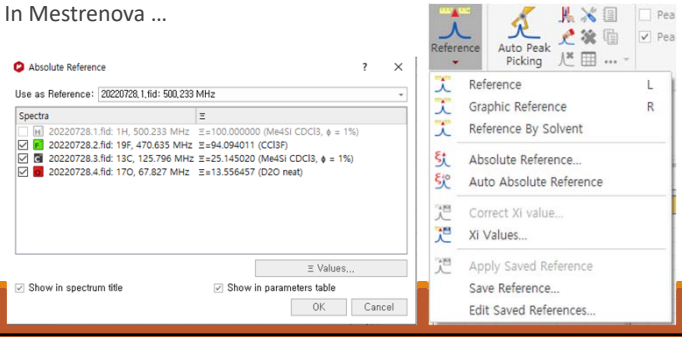
(proxy comparison only)

1. Chemical shift

Referencing

Absolute reference

- Unified chemical shift scale
- IUPAC Recommendation 2001 (revised 2008)
  - 1H : reference to TMS
    - If TMS is not available, residual solvent peak can be used instead.
  - Other nuclei : referenced against 1H spectra
- In Mestrenova …



2. DOSY

Introduction

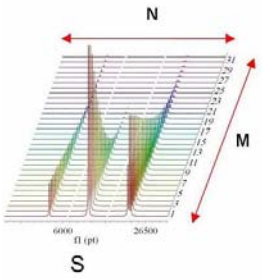
NMR chromatography

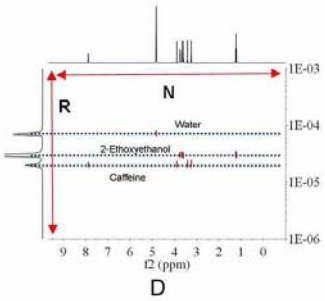
Diffusion coefficient

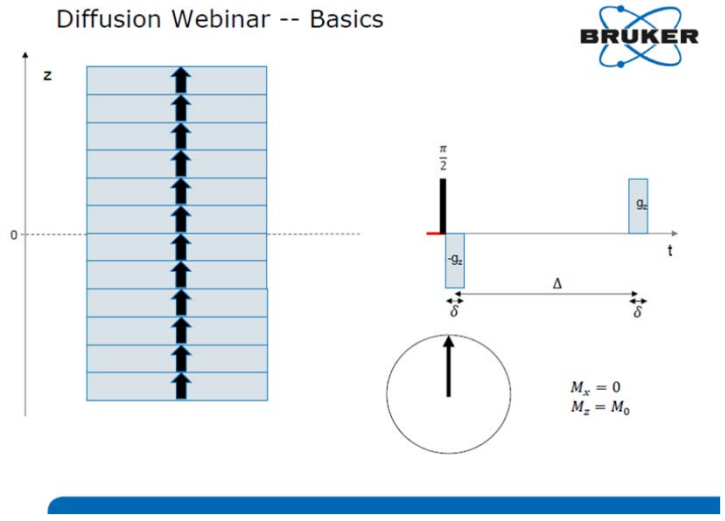
- Cluster
- Complex
- Single molecule
- Ion liquid

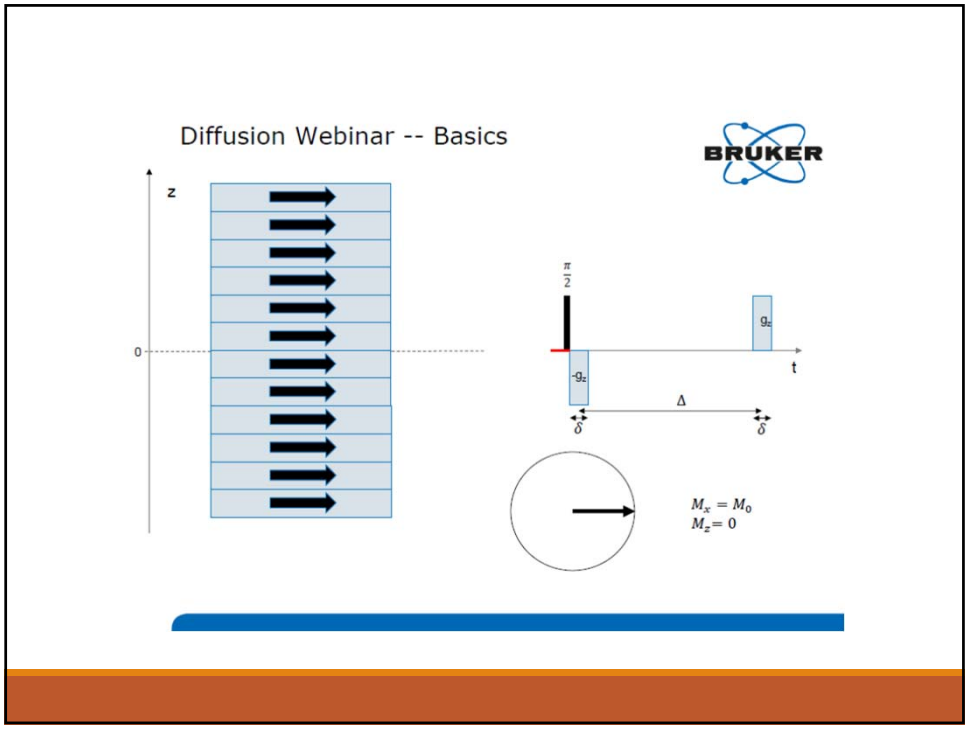
Nuclei

- 1H
- 19F : anion
- 7Li : cation





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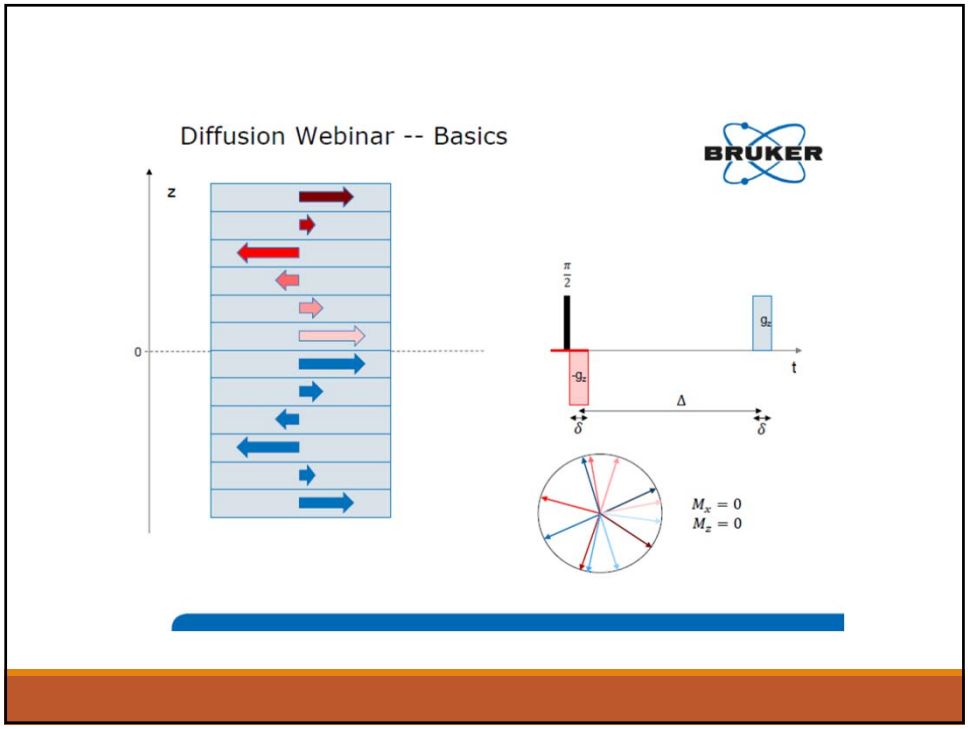
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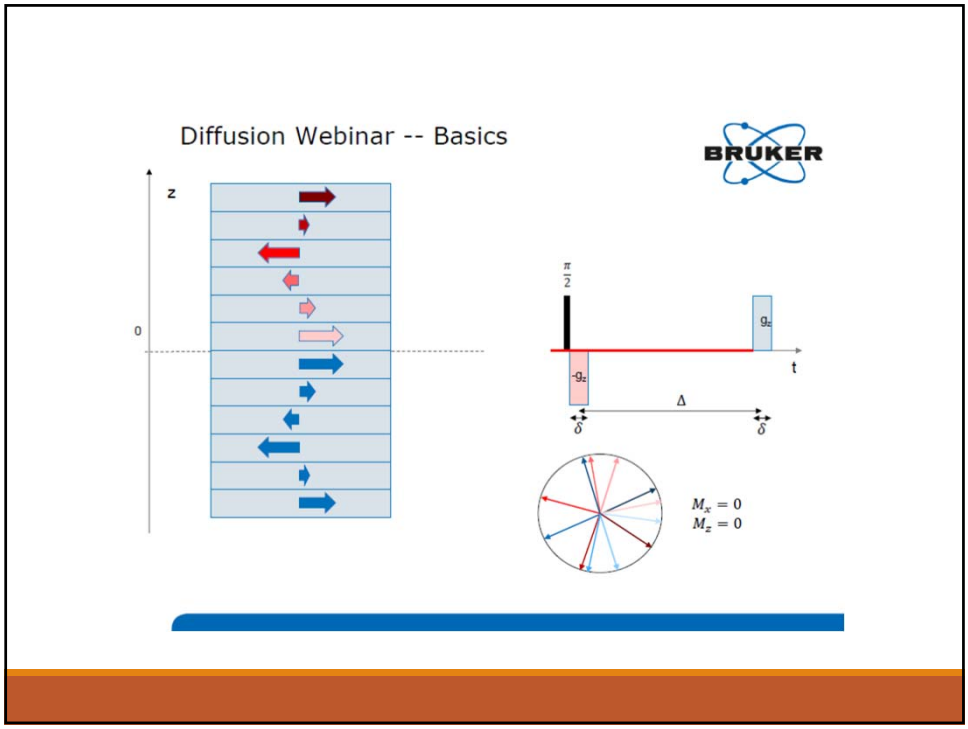
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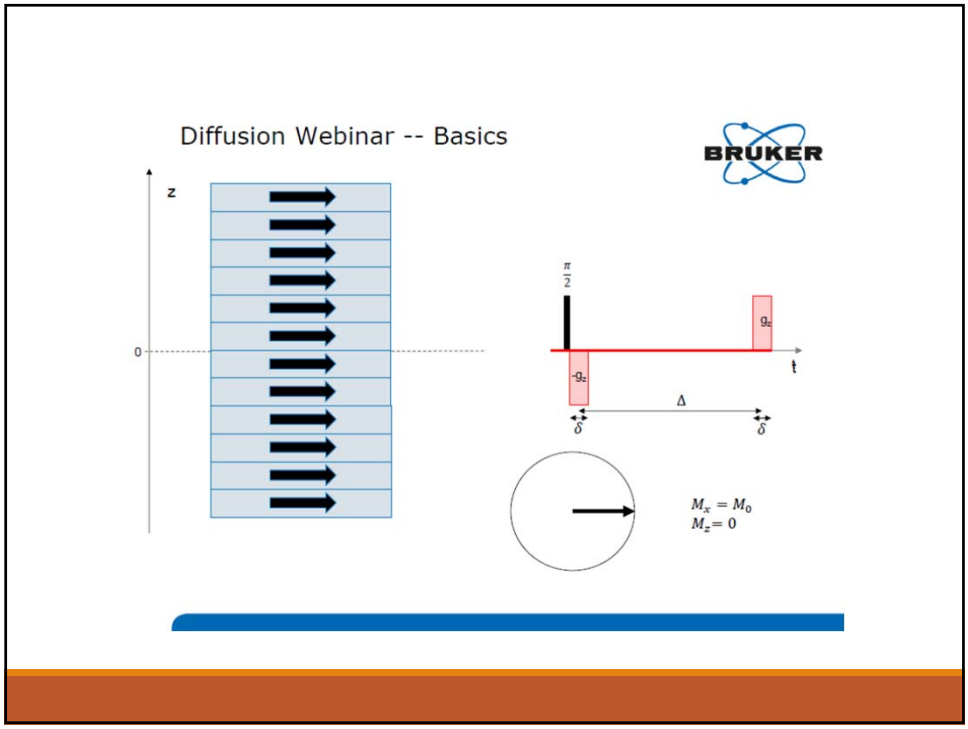
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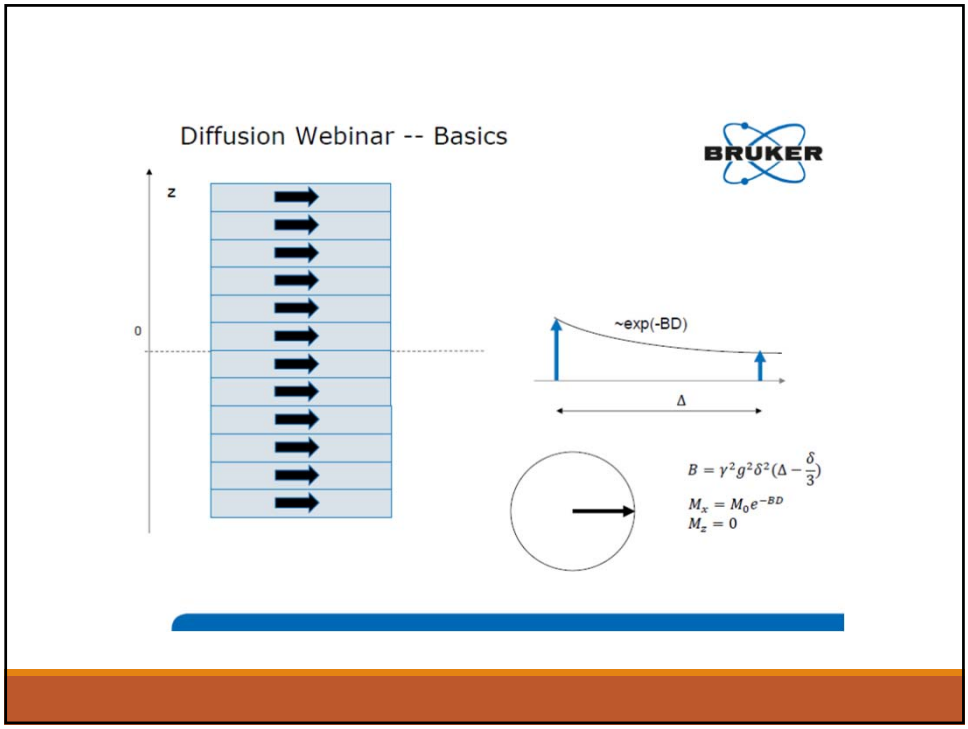


2. DOSY

Introduction

Einstein-Smoluchowski relation

$$I = I_0 \, e^{-D\gamma^2 g^2 \delta^2 (\Delta - \delta/3)}$$

where I is the observed intensity, I_0 the reference intensity (unattenuated signal intensity), D the diffusion coefficient, γ the gyromagnetic ratio of the observed nucleus, g the gradient strength, δ the length of the gradient, and Δ the diffusion time. To simplify this equation some parameters are often combined

Fraction of transverse magnetization refocused after a spin echo with gradient refocusing[a]

Δ/ms	small molecule[b]	medium sized molecule[c]	macro molecule[d]
2	0.99	1.00	1.00
100	0.55	0.88	0.97

[a] Calculated for the pulse sequence shown above for two gradients of strength 10 G cm^{-1} and duration, τ, 2 ms; relaxation is ignored. [b] Diffusion constant, D, taken as that for water, which is 2.1×10^{-9} m^2 s^{-1} at ambient temperatures. [c] Diffusion constant taken as 0.46×10^{-9} m^2 s^{-1}. [d] Diffusion constant taken as 0.12×10^{-9} m^2 s^{-1}.

2. DOSY

Introduction

Einstein-Stoke equation

$$D = \frac{kT}{6\pi\,\eta\,r_s}$$

where k is the Boltzmann constant, T the temperature, η the viscosity of the liquid and r_s the (hydrodynamic) radius of the molecule.

- Problem
  - Viscosity
  - Temperature
  - Shape
    - Spherical : D∝ $\sqrt[3]{Mw}$, random coil/flat : D∝ $\sqrt[2]{Mw}$, rigid linear : D∝ $\sqrt[1]{Mw}$
- Internal referenced DOSY
  - Internal reference
    - Same viscosity, temperature
    - ex> toluene

Difficulties

- 1H : overlap, impurities
- 19F : wide range → stegp1s (no bipolar gradient version)
- 7Li : Not enough gradient → p30 value is limited

3. Relaxation

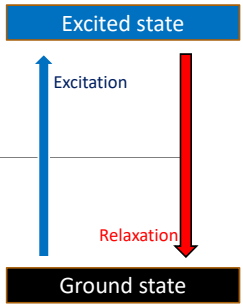
Introduction

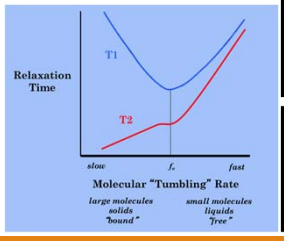
T1 relaxation

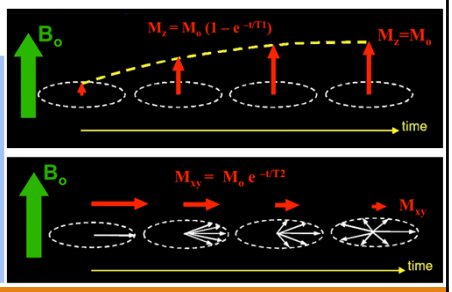
- Spin-lattice
- Longitudinal
- enthalpy

T2 relaxation

- Spin-spin
- Transverse
- entropy







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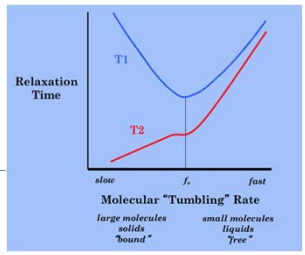
3. Relaxation

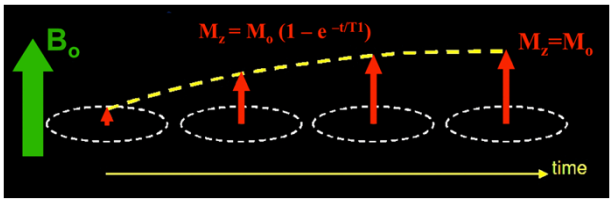
T1 Relaxation



Spin-lattice relaxation

- longitudinal relaxation
- Short when correlation time is similar to Larmor frequency
- Affected by temperature, viscosity, size of molecule …

Inversion-Recovery for T1 measurement



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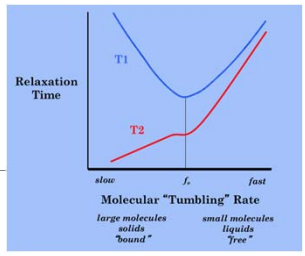
3. Relaxation

T2 Relaxation

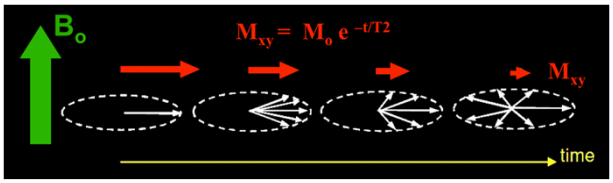


Spin-spin relaxation

- Transverse relaxation
- Larger cluster ➔ shorter T2
- Linewidth is related to inverse of T2
  - But Inhomogeneity of magnetic field

$$\frac{1}{T_2^*} = \frac{1}{T_2} + \frac{1}{T_2'}$$

CPMG for T2 measurement



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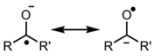
4. NMR tube

Air-tight NMR tube

Ketyl test

https://en.wikipedia.org/wiki/Ketyl



Purpose

- To keep solution from O_2 and water
  - H_2O : High donor number

J-young (Valved) NMR tube

Screwcap NMR tube

1) Just the cap.
2) Teflon tape on threads
3) Teflon tape outside
4) 1.5 turns parafilm
5) 5 turns parafilm
6) 3 turns electrical tape

Twitter @awhspeed 2021.10.21

Table 1 Normalized mean ketyl test time until colorless for different types of glassware

Glassware style	Time until colorless[a] (min)
25 mL Schlenk tube, greased ground glass stopper (**A**)	300 ± 10
50 mL Schlenk tube, greased ground glass stopper (**B**)	277 ± 46
50 mL round-bottom Schlenk flask, greased ground glass stopper (**C**)	129 ± 27
25 mL Schlenk tube, threaded PTFE stopper (**D**)	391 ± 57
NMR tube, standard cap (**E**)	413 ± 106
LPV NMR tube, threaded PTFE stopper (**F**)	5200 ± 400

[a] Times are reported with 95% confidence intervals. Times were normalized to 300 min for concurrently monitored standard 25 mL Schlenk tubes with ground glass stopcocks and stoppers. The number of trials was 65 for Schlenk tubes A, ten for NMR tubes E, and nine for all other glassware.

Dalton Trans., 2020, **49**, 15213-15218

4. NMR tube

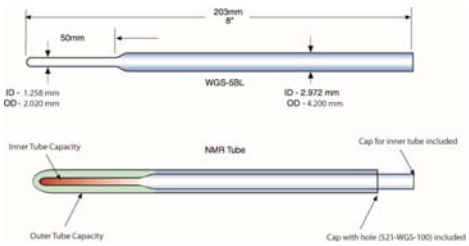
Coaxial NMR tube

Purpose

- For absolute referencing
- To avoid solvation effect of NMR solvent

Combination

- Outer tube + inner tube
  - Check O.D.
  - Not air-tight
- Outer tube + capillary
  - Check O.D.
  - Can be used for air-tight NMR tube



4. NMR tube

PTFE liner

Purpose
- To prevent HF from reaction to glass

FEB liner
- With thin wall NMR tube
- Should not be shrunk in NMR tube

PTFE NMR tube

5.qNMR

Introduction

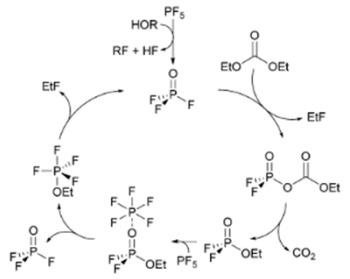


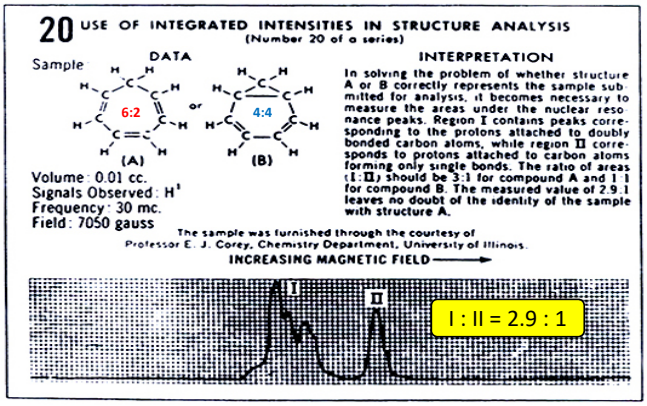
Fig. 1 Autocatalytic reaction mechanism for the degradation of $LiPF_6$ in carbonate solvents.[11,14]

Table S1: Bruker NMR measurement parameters.

Test series	Dilution series		Quantification	
Measurement	^{19}F {^1H}	^{13}C {^1H}	^{19}F	^{13}C {^1H}
Bruker pulse program	zgfhi gqn.2	zgpg30	zg	zgpg
Number of scans	64	256	32	64
d1 delay / s	8	2	2	2
Acquisition time / s	4	4.5	5	3.2

5.qNMR

Introduction



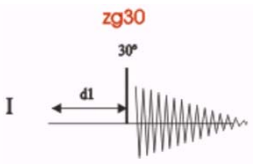
One of the earliest examples of the use of NMR in structure elucidation, as described in J. N. Shoolery's historical sketch. High-Resolution NMR : A Dream Come True. (Reproduced by permission of Varian Associates)

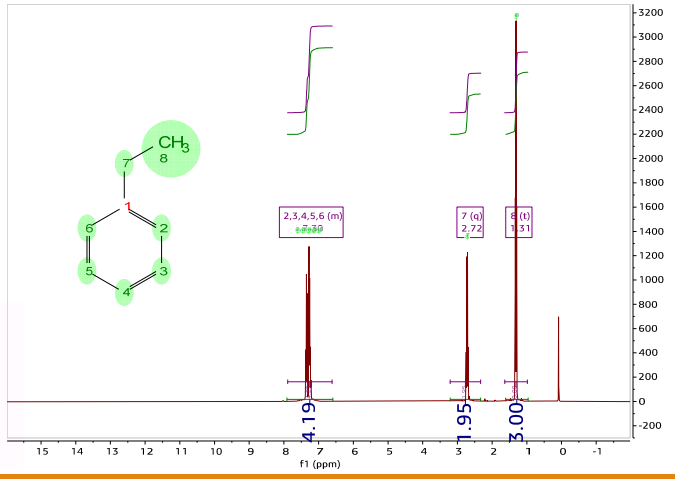
5.qNMR

Introduction

400Mhz, 298K
zg30
D1 : 1s
AQ : 4.56 s
NS : 26

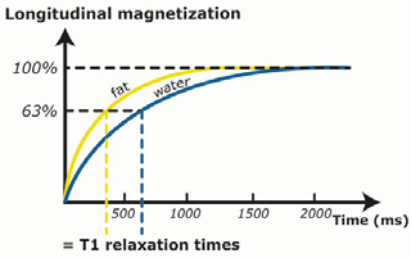
10%
Ethylbenzene
0.03% TMS
In CDCl3



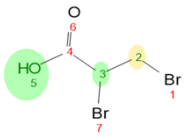


5.qNMR

Relaxation delay(D1)



- Sample : 2,3-DBPA in CDCl3 with 2% TMS
- 90 pulse, 400Mhz NMR, 298 K



Magnetisation recovery(%)

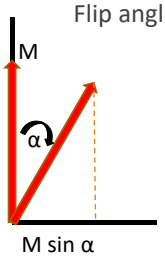
	90° pulse	30° pulse
1 * T1	>63.2	>81.6
5 * T1	>99.3	>99.7
7 * T1	>99.9	>99.9

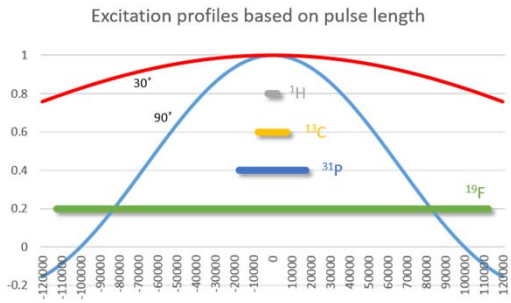
Intensity	5-OH	3-H	2a-H	2b-H	TMS	표준편차
T1(s)	5.37	8.22	1.49	1.36	11.18	
D1:2s	0.70	0.67	0.79	0.79	1.00	0.0536
D1:24s	0.70	0.67	0.71	0.71	1.00	0.0164
D1:60s	0.64	0.64	0.64	0.63	1.00	0.0043

5.qNMR

Flip angle

Flip angle : 30 (zg30) vs 90(zg)





Magnetisation recovery(%)

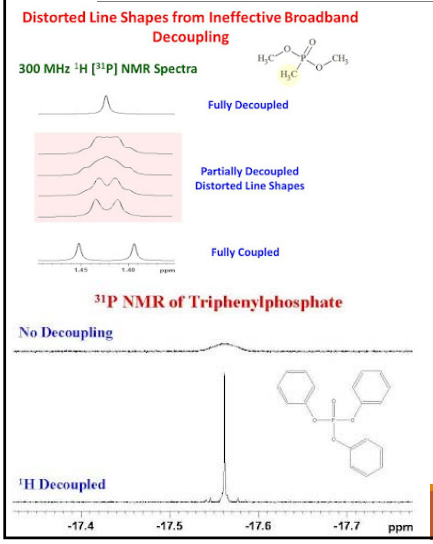
	90° pulse	30° pulse
1 * T1	>63.2	>81.6
5 * T1	>99.3	>99.7
7 * T1	>99.9	>99.9

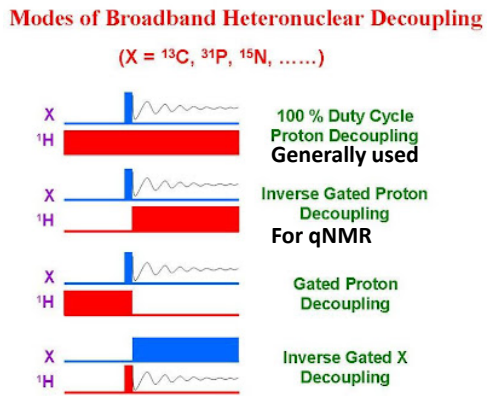
When pulsewidth = 10 us

- 19F : 22000 Hz in case of 30° pulse < 80% intensity
  - (58ppm for 400Mhz, 46ppm for 500Mhz)
- Bruker Avance
  - HDIII : zgfhqn.2(90°), NEO : zg(90°), zg30 (30°)

5.qNMR

Decoupling





5.qNMR

For qNMR...

Relaxation Delay : 3~7 * T1
- Total time : (D1 + AQ) * (NS + DS)
- Limit of Quantification (LOQ) : S/N

Flip angle
- 90° : For accuracy, Time saving // calibration is required (ex> pulsecal)
- 30° : For heternuclei (19F) // default p1 is acceptable (getprosol)

Decoupling
- No decoupling or inverse-gated decoupling

Processing
- Phase correction
- Baseline correction

5.qNMR

Nuclei – 1H, 13C, 31P

In case of 400, 500Mhz NMR

1H
- Pulprog : zg30 or zg
- D1 : 5 ~60 s
- AQ : 0.7 ~ 4 s
- SW : 12 ~ 20ppm
  - Automatic Processing
- TD : 16k ~64k
- NS : consider LOQ
  - Recommended : S/N > 1200: 1

13C, 31P
- Pulprog : zgig30 or zg30
- D1 : 10 ~ 60 s
- AQ : 0.3 ~ 4 s
- SW : < 300 ppm
  - decoupling
- TD : 16k ~ 128k
- NS : S/N > 150 : 1
- Decoupling : GARP4 or Waltz16

$$Expt \sim (D1+AQ) \times (NS+DS)$$

$$\frac{S}{N} \propto \sqrt{NS}$$

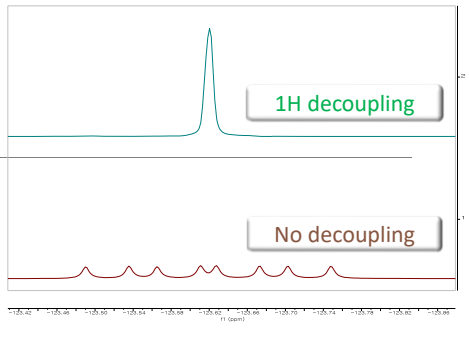
$$AQ = \frac{TD}{2 \times SWH}$$

SW

O1P

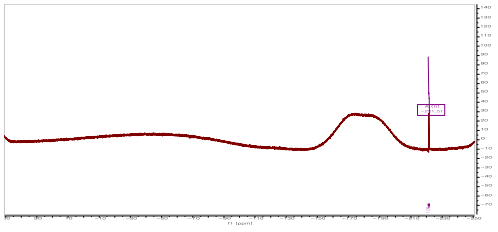
5.qNMR

Nuclei – 19F



pulprog
- Bruker Avance NEO
  - zg30 or zgig30
- Bruker Avance HDIII
  - zgfhqn or zgfhigqn.2

Other Parameters
- D1 : 5 ~60 s
- AQ : 0.3 ~ 4 s
  - Wiggle
- SW not too wide
- TD : 16k ~128k
- NS : consider LOQ
  - Recommended : S/N > 1200: 1
- Decoupling : GARP4 or Waltz16
  - Adiabatic decoupling



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