Observation of adsorbed ions or molecules in carbon materials (ternary GICs) using solid state NMR

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^{23}Na NMR study of Na in carbon

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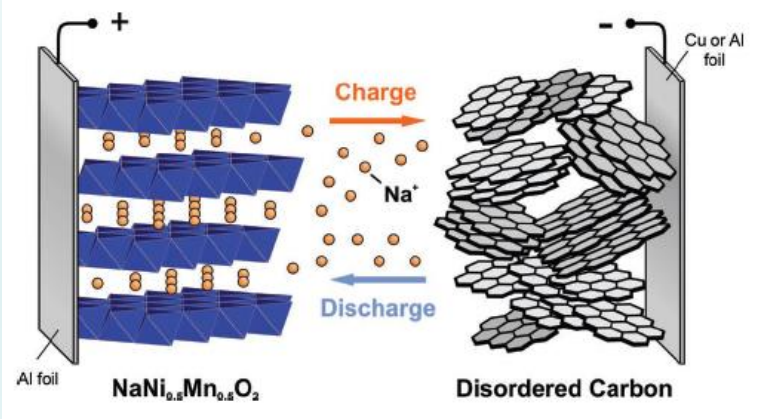
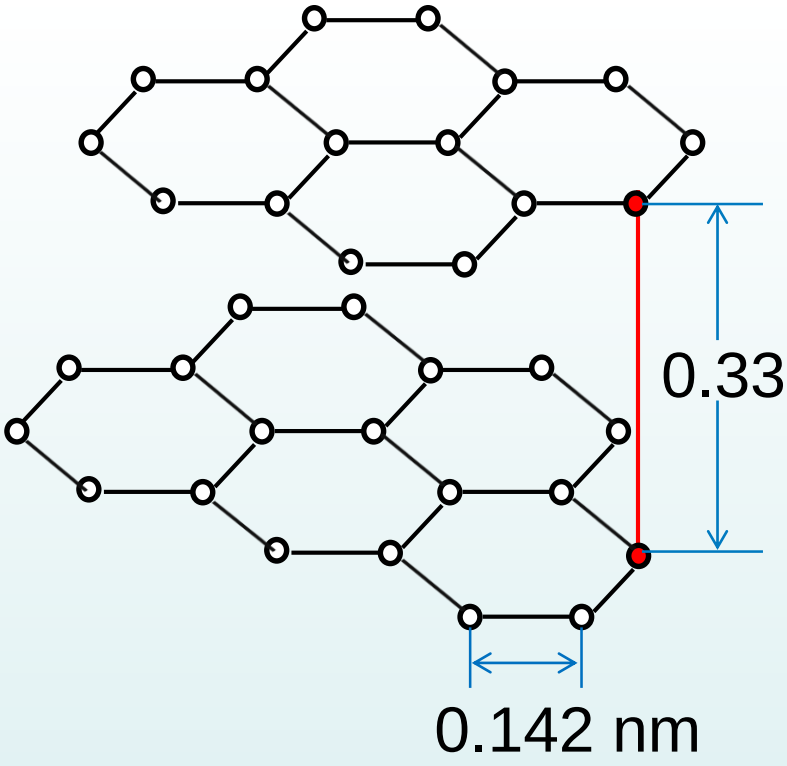
intercalation	Lithium	Sodium
into graphite		
secondary GIC	✓	✗
ternary GIC	✓	✓
into hard carbon	✓	✓

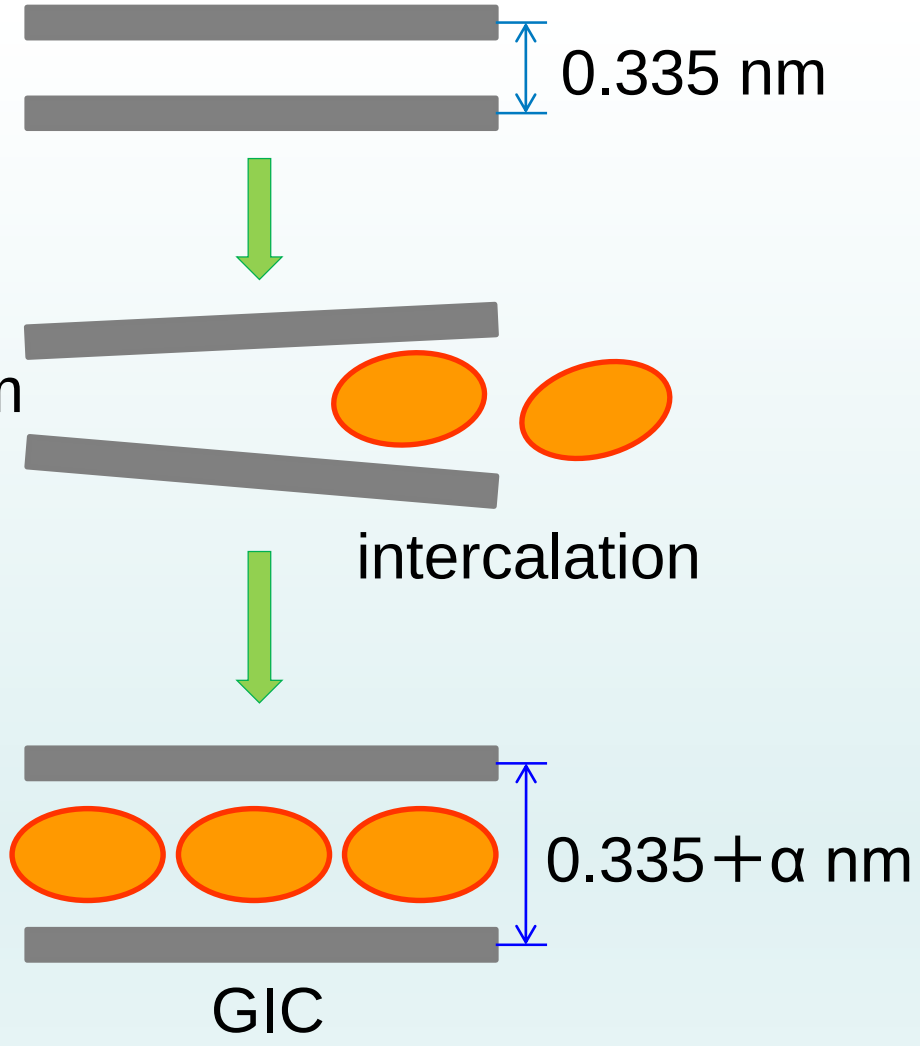
- **Li can be intercalated both into graphite and hard carbon.**
- **Na^+ doesn't intercalate and form secondary GIC (NaC_x).**
- **Hard carbon anode or ternary GICs must be used for Na^+ ion battery.**



- **Solid state NMR study of Na Ion stored in Hard Carbon was presented in Carbon 2015 (ES32).**

Graphite intercalation compound (GIC)





Alkali metal - organic molecule Ternary GICs

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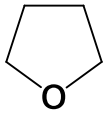
Several donor-type ternary GICs have been reported.
Structures have been predicted only from layer distances estimated from powder XRD. Dynamics (& orientation) of molecules was hardly discussed.

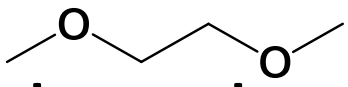
M^+: Li^+, Na^+, K^+

co-intercalated molecules:

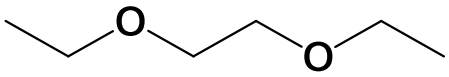
- **NH_3** **Benzene**
- **tetrahydrofuran(THF)**



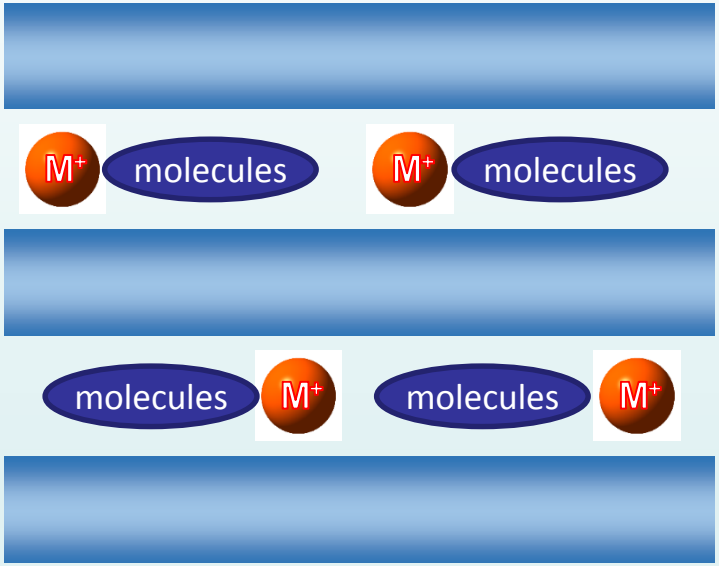
- **1,2-dimethoxy-ethane(DME)**



- **1,2-diethoxy-ethane(DEE)**



- **Ethylenediamine**
- ***n*-alkylamine**



Not Intercalated :
EC, DMC, ...

^{2}H NMR analysis of Na, K- ternary GICs

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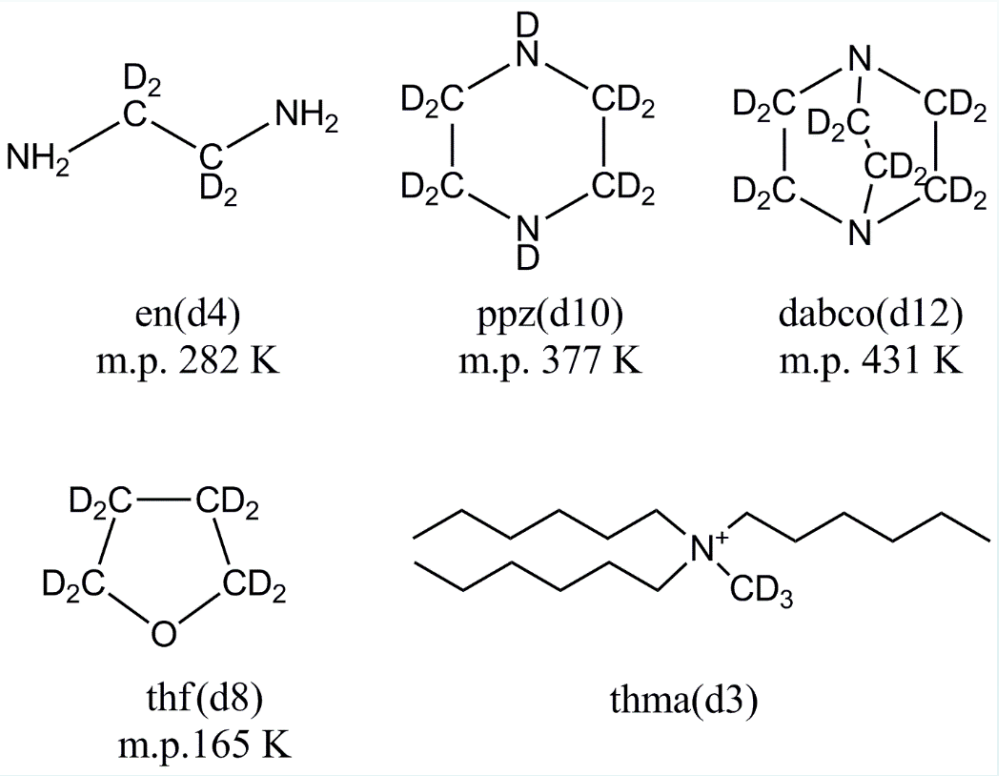
Dynamics and structure of (deuterated) diamine, ammonium are investigated using wide line solid state ^{2}H NMR

(^{1}H NMR research ・・・・・prevented by background signals)



Prepared samples

- **Na-en(d4)-GIC**
- **Na-thf(d8)-GIC**
- **K-ppz(d10)-GIC**
- **K-dabco(d12)-GIC**
- **thma-(d3)-GIC**

- **GO-en(d4)**

K.Gotoh et al., *J. Phys. Chem. C*, 2015.

Syntheses of GICs and GO compounds

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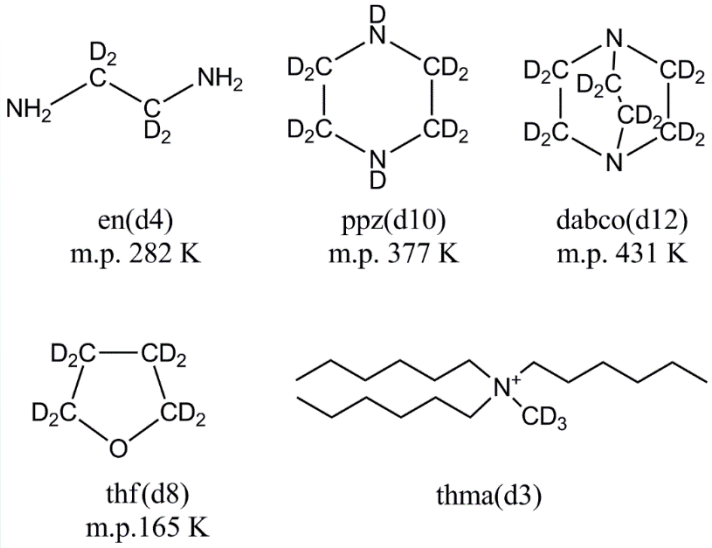
- **Na-en(d4)-GIC, Na-thf(d8)-GIC**

Graphite 50 mg + Na 30 mg (+naphthalene 5 mg) into en(d4) or THF(d8) 0.5 mL

⇒ stirred in N_2 atmosphere for 3 days

$[Na(en)_{1.0}]C_{15}$, $[Na(thf)_{3.5}]C_{32}$



- **K-ppz(d10)-GIC, K-dabco(d12)-GIC**

Sealed secondary GIC (KC_8) 50 mg and ppz(d10) 23 mg or dabco(d12) 20 mg in a glass tube

⇒ heated at 140 ˚C or 170 ˚C for 12 h

$[K(ppz(d10))_{0.5\sim0.7}]C_8$

$[K(dabco(d12))_{1.4\sim2.0}]C_8$

- **thma-(d3)-GIC**

Exchange reaction of Na-en-GIC 80 mg with $(C_6H_{13})_3(CD_3)NI$ 0.02mmol in DMSO 2 mL.

⇒ $[(C_6H_{13})_3(CD_3)N]C_{85}$

- **GO-en(d4)**

Graphite oxide (prepared by Brodie's method) 50 mg + en(d4) 0.05 mL

⇒ stirred for 2 h

GO-en(d4)

PXRD patterns of GICs and GO compound products

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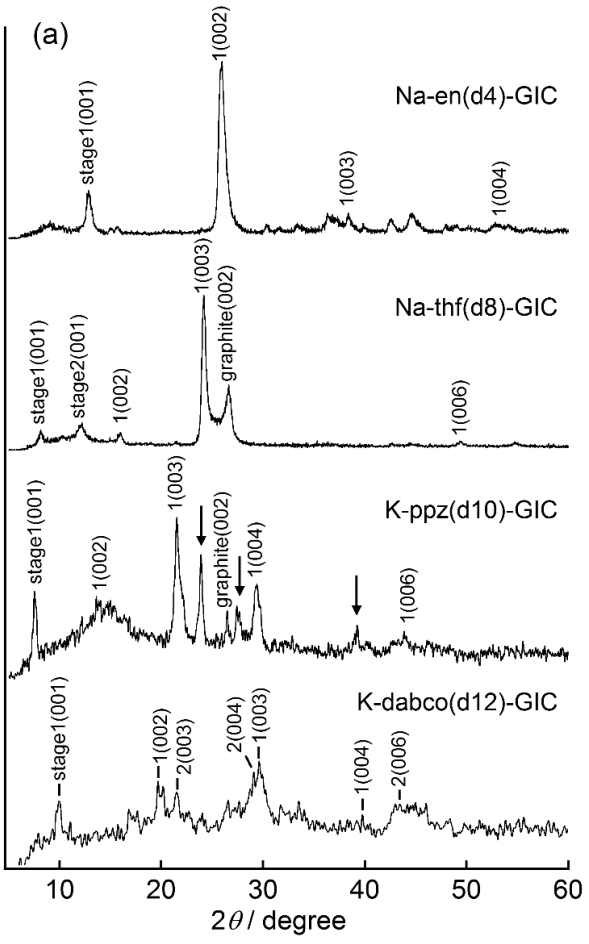

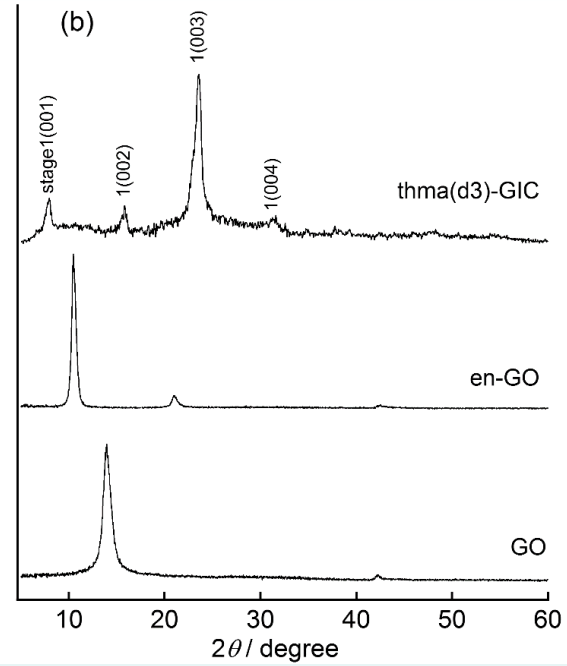

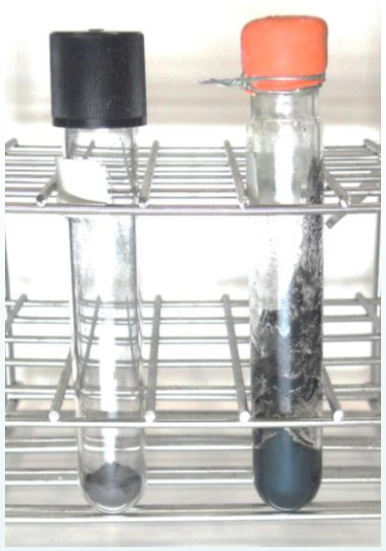

Graphite GIC

	d / nm	height / nm
Na-en(d4)-GIC	0.693	0.358
Na-thf(d8)-GIC	1.100	0.765
K-ppz(d10)-GIC	1.210	0.875
K-dabco(d12)-GIC	0.899	0.564
thma(d3)-GIC	1.130	0.795
GO	0.635	0.300
en(d4)-GO	0.842	0.507

Properties of spin 1 and 3/2 nuclei

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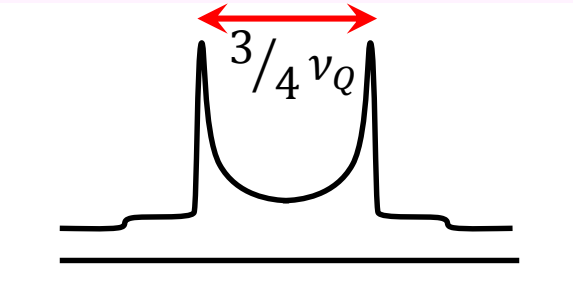
NMR active nuclei

Isotope	Spin (I)	Natural Abundance	Quadrupole moment	Sensitivity (relative)	NMR frequency
^{1}H	1/2	99.98 (%)	— (10^{-28} m^2)	1.00	100 (MHz)
^{2}H	**1**	**0.015**	**-2.73×10^{-3}**	**9.65×10^{-3}**	**15.351**
^{7}Li	3/2	92.58	-4.5×10^{-2}	0.29	38.863
^{23}Na	3/2	100	0.12	9.25×10^{-2}	26.451

^{2}H, ^{7}Li, ^{23}Na have nuclear quadrupole moment (eQ), which interacts with electric field gradient (eq) in samples.



Powder pattern of I=1 nuclei

(removed)

Powder pattern of I=3/2 nuclei

Quadrupolar coupling constant (qcc; $\nu_Q = \frac{e^2qQ}{2h}$) can be estimated from the distance between splitting horns.

Na-en(d4)-GIC

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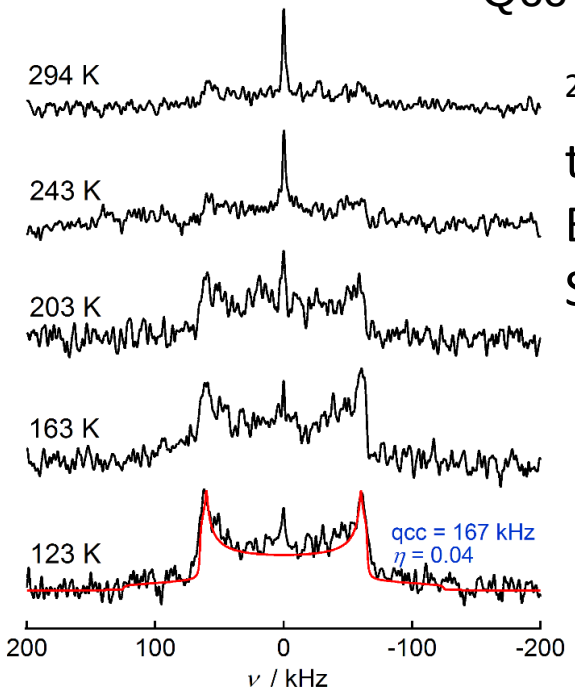
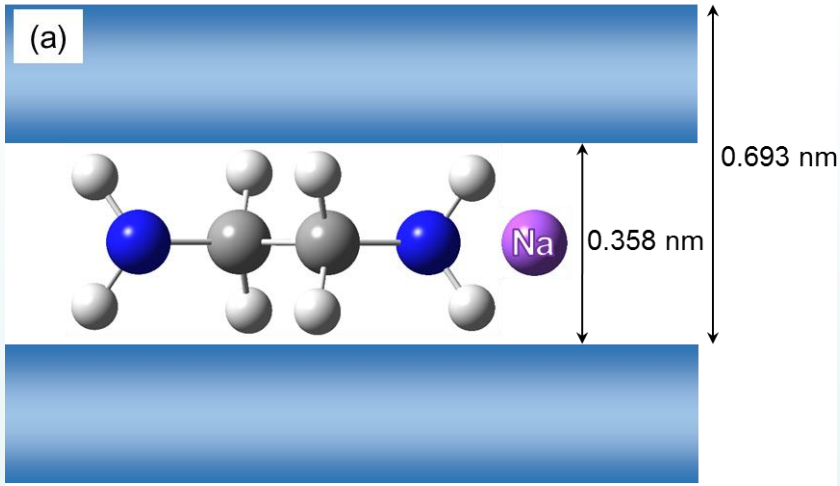
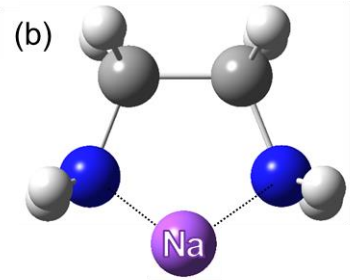
Qcc of rigid deuterated methylene groups (-CD_2-): 167 kHz

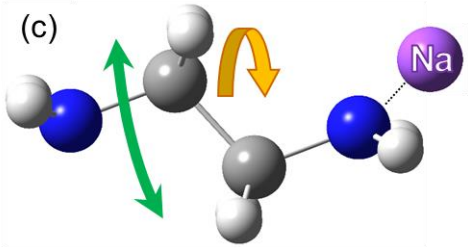


^{2}H NMR
two components
Broad: qcc= 167
Sharp: width= 2

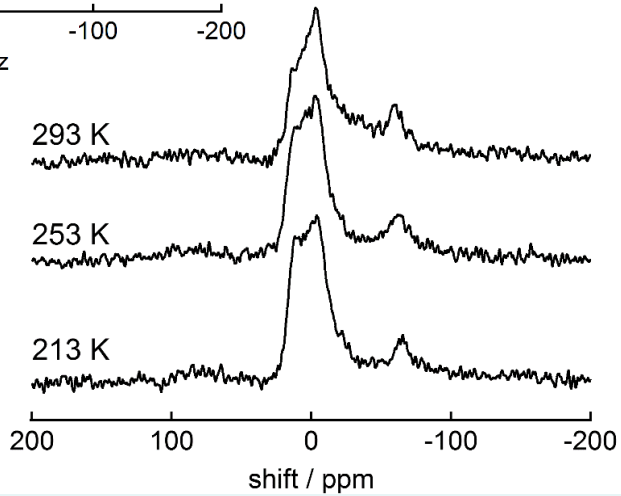




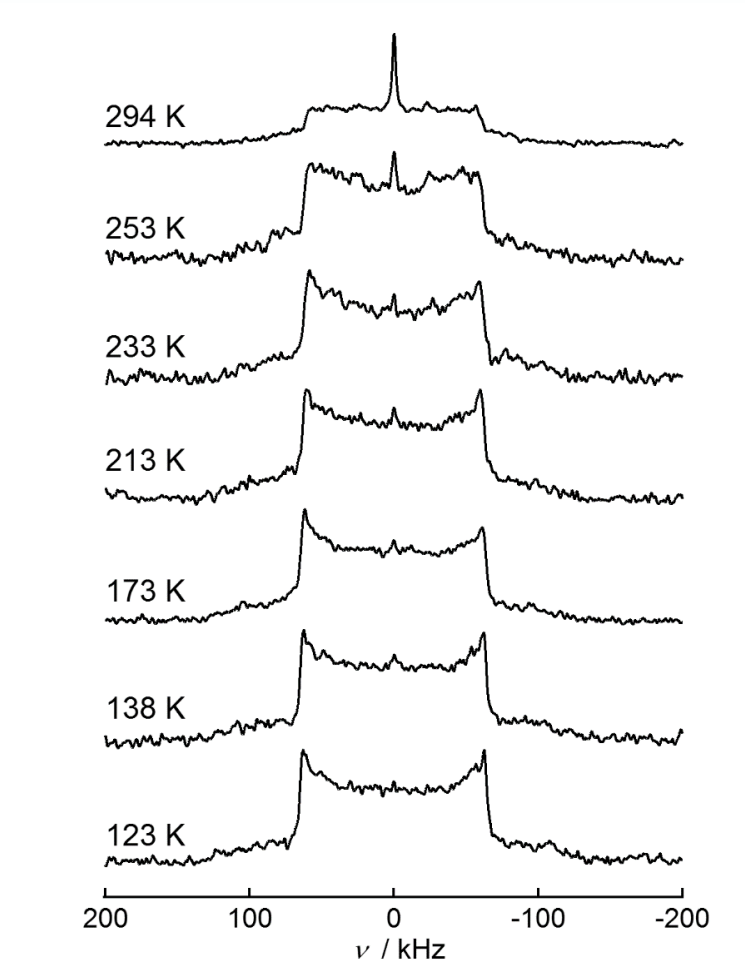
Nitrogens coordinate to Na ion.



^{23}Na MAS NMR
two components
qcc = 3.2 MHz



Na-thf(d8)-GIC



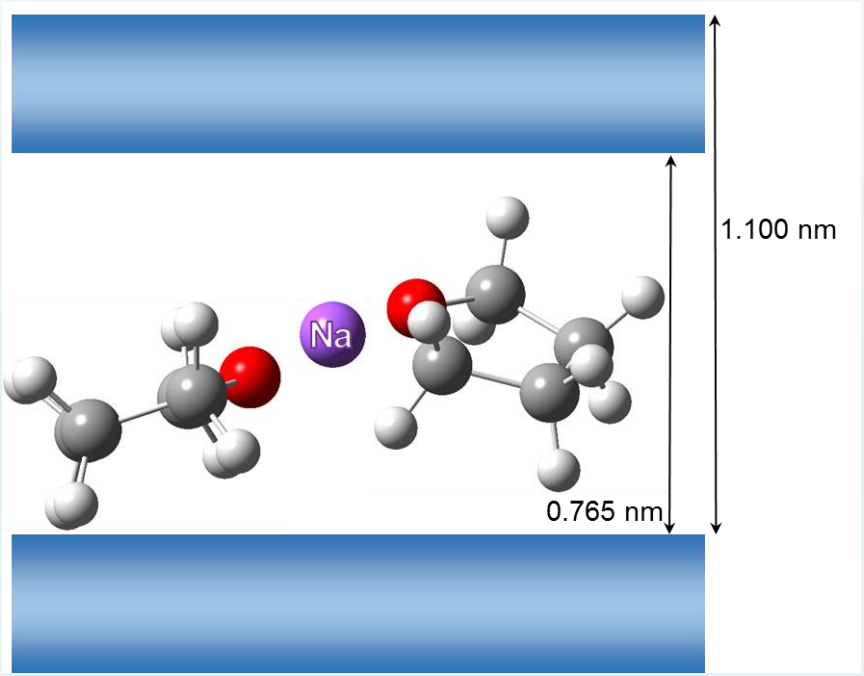
^{2}H NMR

> two components

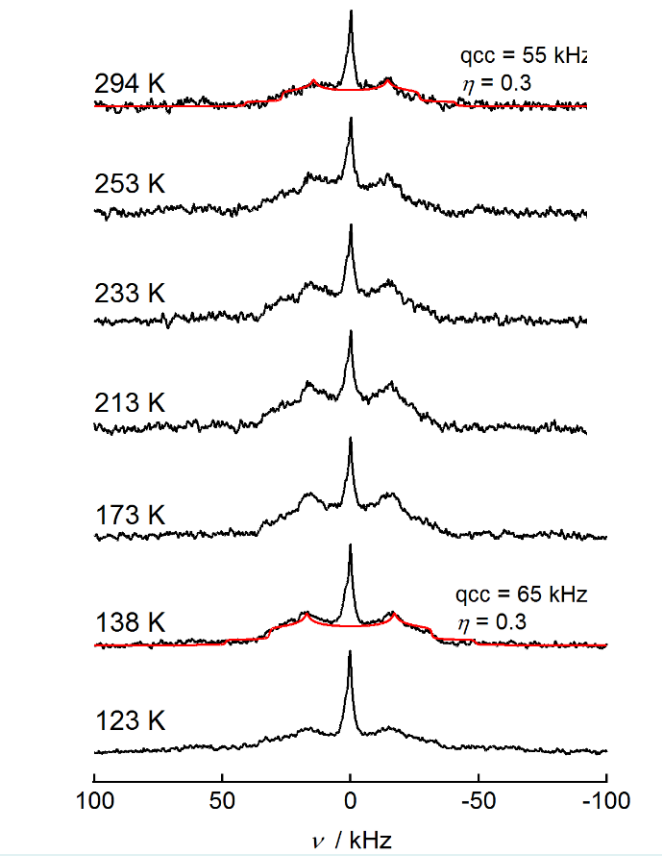
Broad: qcc= 167

Sharp: width= 2 (disappeared below 253 K)

(rigid and isotropic rotation)

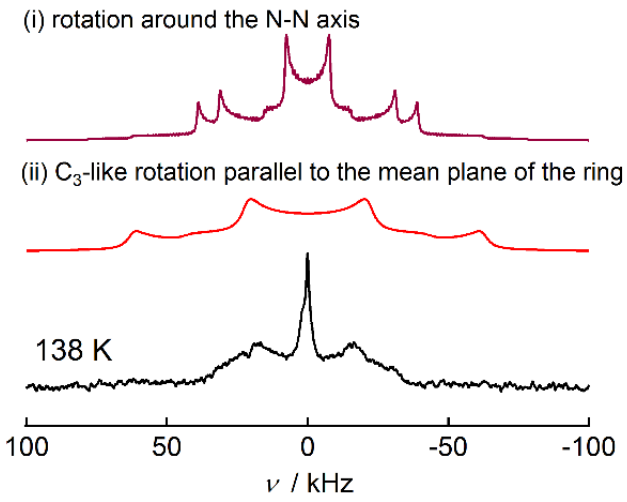


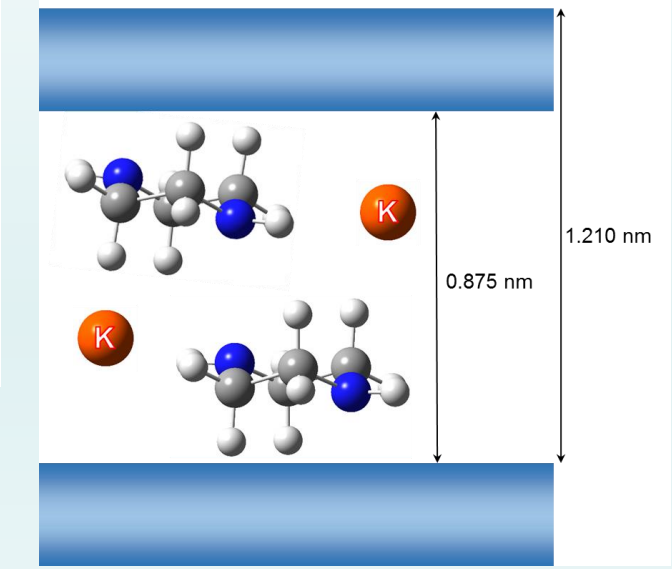
K-ppz(d10)-GIC

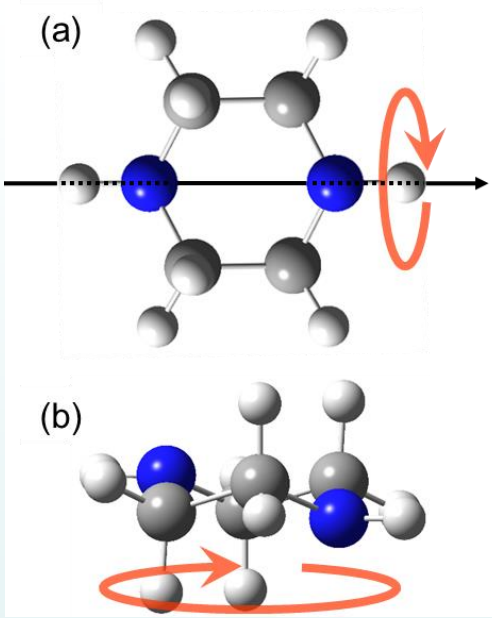


^{2}H NMR

> two components







Nitrogens don't coordinate to K ion.

K-dabco(d12)-GIC

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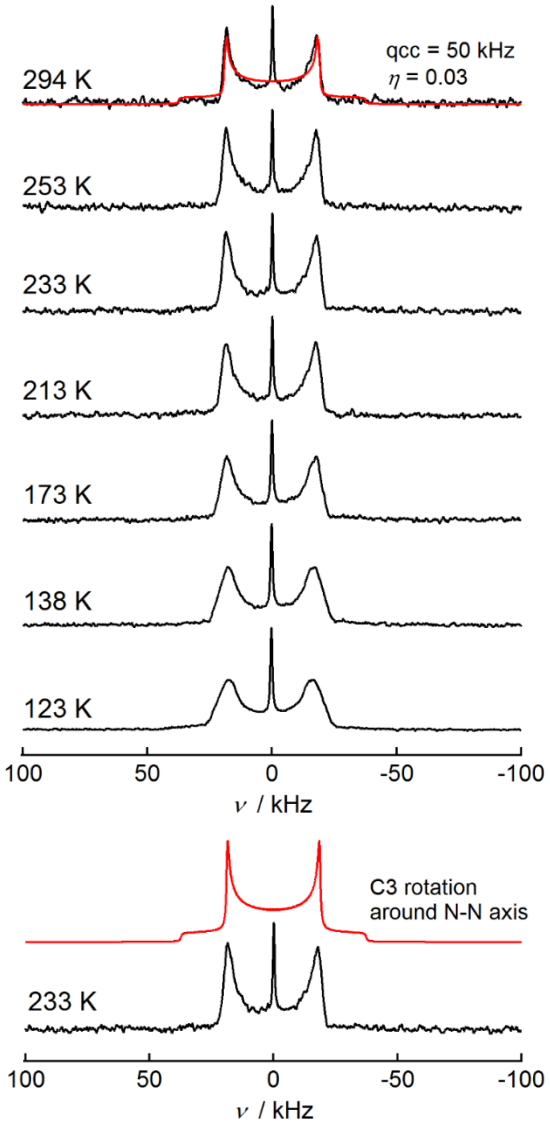


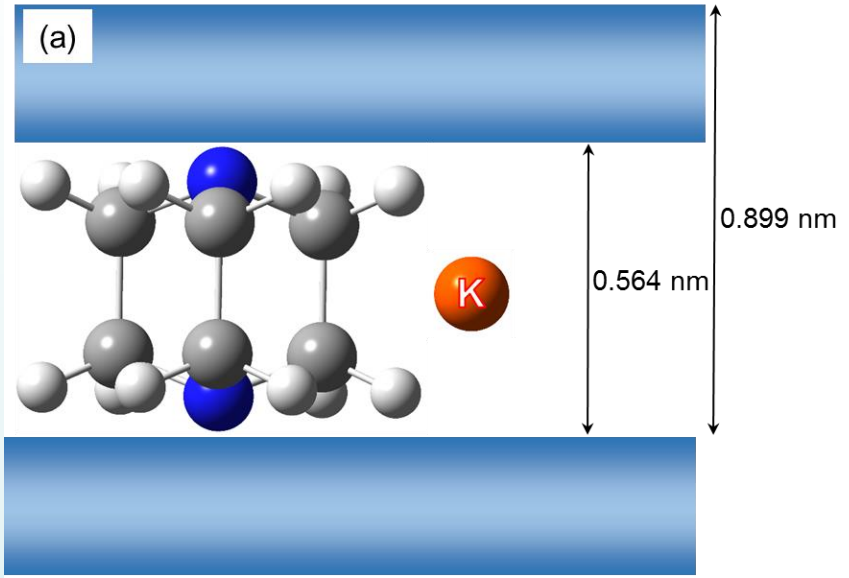
^{2}H NMR

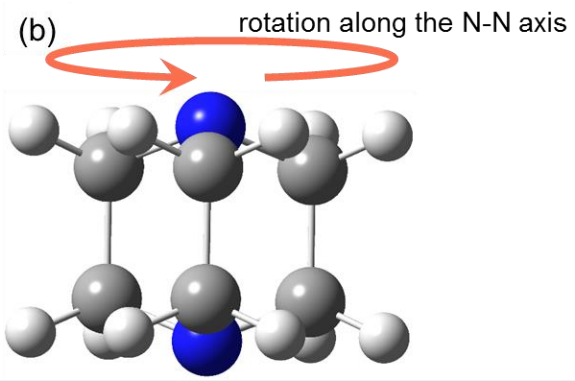
> two components

Broad: qcc= 50

Sharp: width= 2

Nitrogens don't coordinate to K ion.





Thma(d3)-GIC (doesn't contain alkali metal)

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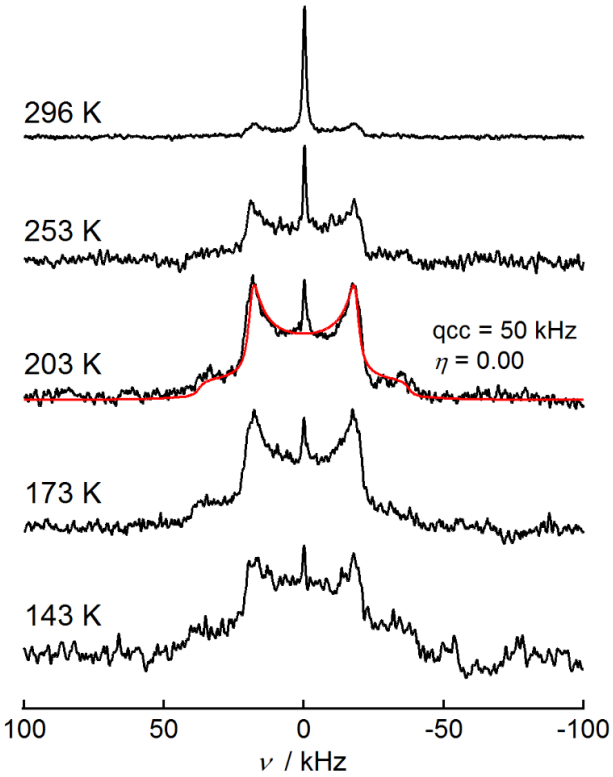
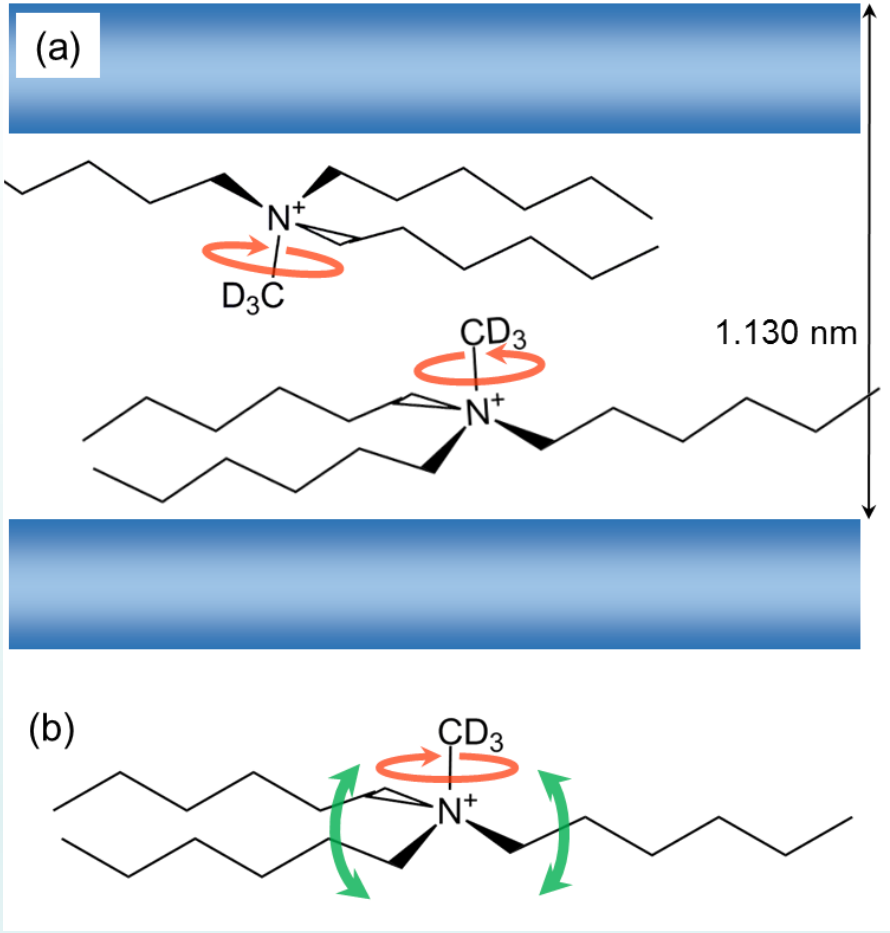
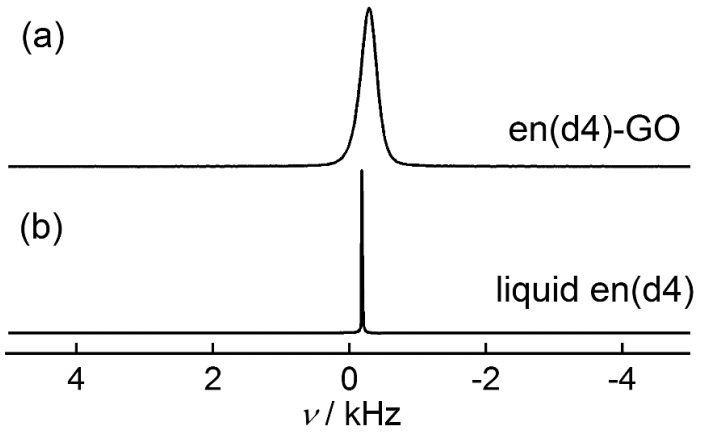
^{2}H NMR
> two components
rotation of CD_3-grops



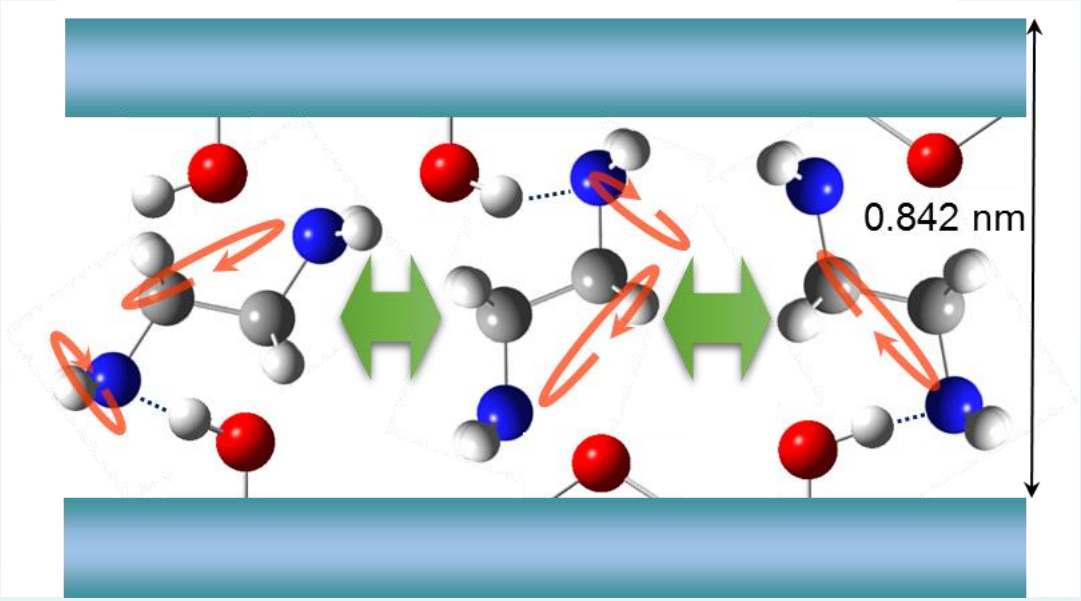


En(d4) - GO



^{2}H NMR
Very sharp signal
(< 0.5 kHz)

isotropic rotation and
diffusion of en in GO



Summery of ^{2}H NMR studies

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◇Diamines and thma in GIC

Each GIC contains two kinds of intercalated molecules;
under isotropic rotation and restricted motion (including rigid state)

- **rigid, coordinating to Na**

  Na-en(d4)-GIC
  Na-thf(d8)-GIC

- **restricted rotation, non-coordinating**

  K-ppz(d10)-GIC
  K-dabco(d12)-GIC
  thma-(d3)-GIC

◇en in GO

en diffuses between layers

- K is softer acid than Na.
  ⇒ lower affinity with amine groups
- The result may concerns stability of donor GICs.
  - **K-en-GIC never synthesized**
  - **K-thf-GIC very unstable**

We firstly explained the coordination structure and the dynamics of intercalated molecules of some ternary GICs, relating to their stability.