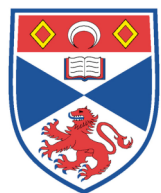


NMR of Microporous Materials

Sharon Ashbrook

School of Chemistry, University of St Andrews

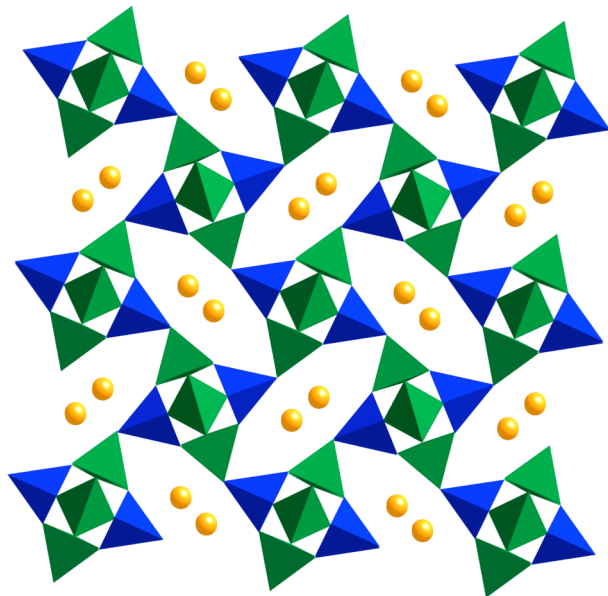


University
of
St Andrews

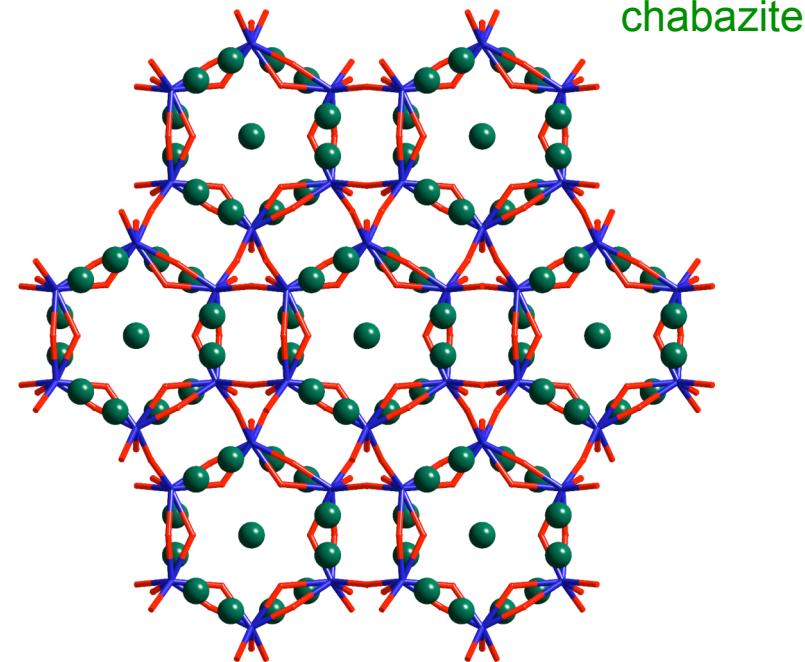


Microporous materials

- Porous open framework solids
- Regular systems of intercrystalline channels and cavities of molecular dimensions
- High surface area
- Typical pore sizes of 4-8 Å



natrolite



chabazite

- Uses are intimately linked to structure

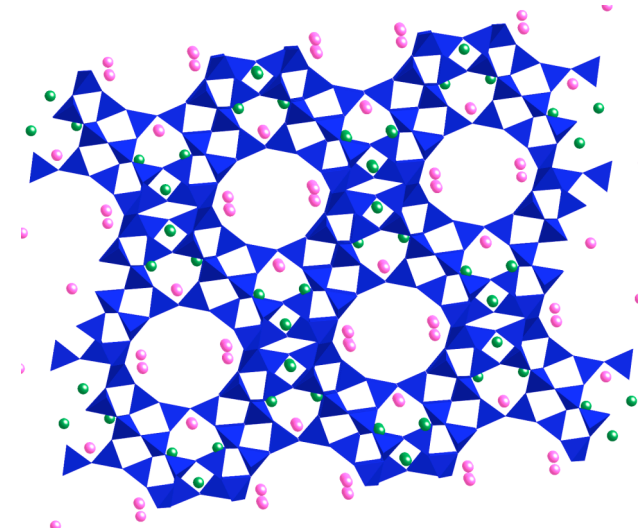
Selective sorption
Cation exchange materials
Catalysis

Zeolites

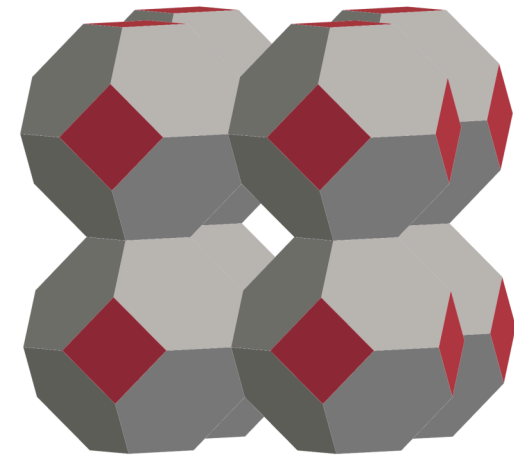
- Porous aluminosilicates built from corner sharing SiO_4^{4-} and AlO_4^{5-} tetrahedra
- Charge balancing cations, typically Na^+
- Channels (up to 50% of volume) usually occupied by water



- 40 species of zeolite minerals ($1 < y/x < 5$) and at least 135 synthetic species
- Ga, Ge, B, Fe and P can substitute into the framework
- Conventionally prepared under mild (60-400°C) hydrothermal conditions in basic media
- Type and concentration of base are important for structure direction
- More recently new methods (fluoride, ionothermal) have been introduced



faujasite

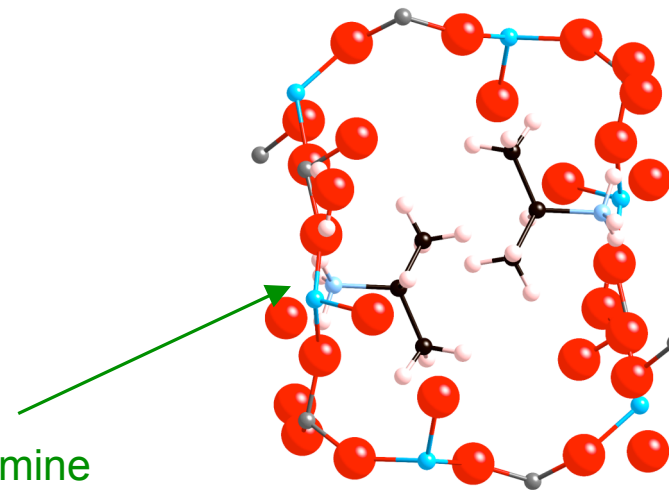
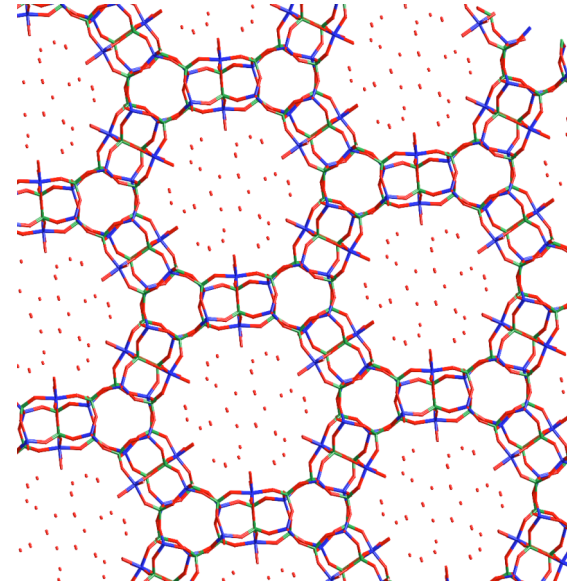


sodalite

AlPOs

- New family of porous solids discovered in 1982
- Alternating AlO_4 and PO_4 tetrahedra
- Some have framework topology of zeolites, others have novel structures
- Incorporation OH groups into the framework and water into the pores
- Structure-directing agent or template
- Incorporation of Si (SAPO), metal (Ga, Mg, Mn, Co etc.,)
- High acidity and potential as catalysts

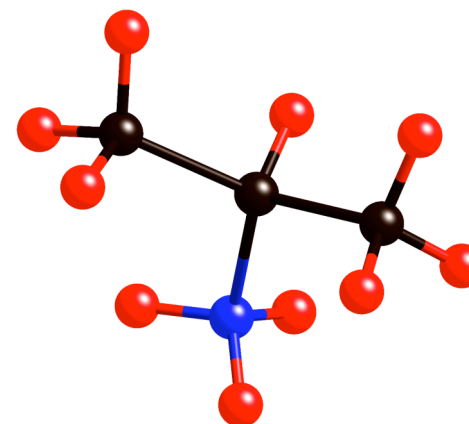
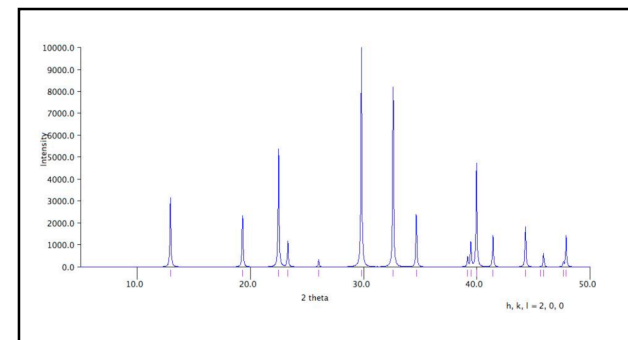
VPI-5



Isopropylamine
template

Structure determination

- Complex structures with large unit cells
- Difficult to grow large single crystals of many phases
- Large volume of free space and high structural flexibility
- Many 10-electron species which are difficult to distinguish by x-ray diffraction (Si^{4+} , Al^{3+} , O^{2-} , Na^{+})
- Cation disorder in the framework
- Presence of template (often amine base)
- Framework OH species and H_2O in pores
- Molecular motion and dynamics



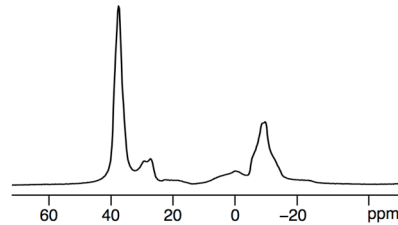
Role of NMR

- NMR is an element-specific probe of local (i.e., atomic scale) structure and dynamics, without any requirement for long-range order
- Confirm/contradict space group and symmetry
- Framework connectivity
- Framework cation order/disorder
- Position and mobility of exchangeable cations
- Interaction and mobility of guest molecules and templates
- Acidity
- Template/water dynamics
- Reactivity (hydration and dealumination)
- Catalysis

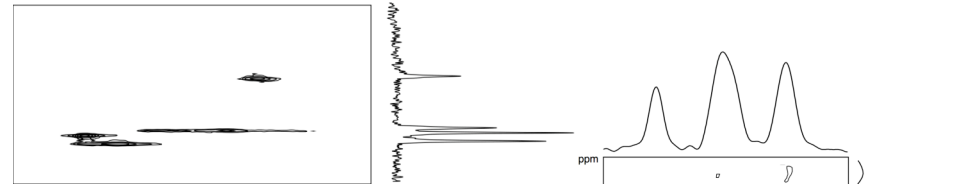
Experimental approaches

- Usually a range of multinuclear experiments is required

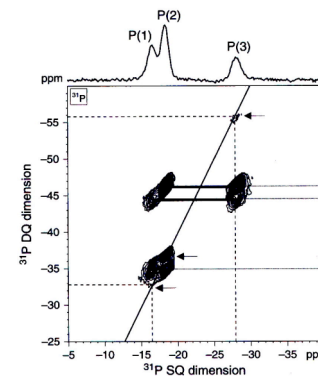
- 1D MAS



- 2D high-resolution experiments

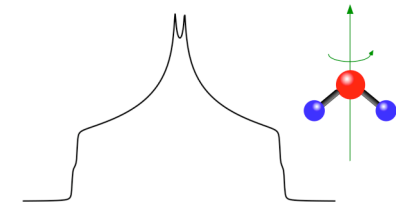


- Heteronuclear correlation experiments (through bond and through space)



- Homonuclear correlation experiments (through bond and through space)

- Experiments to detect dynamics



NMR considerations

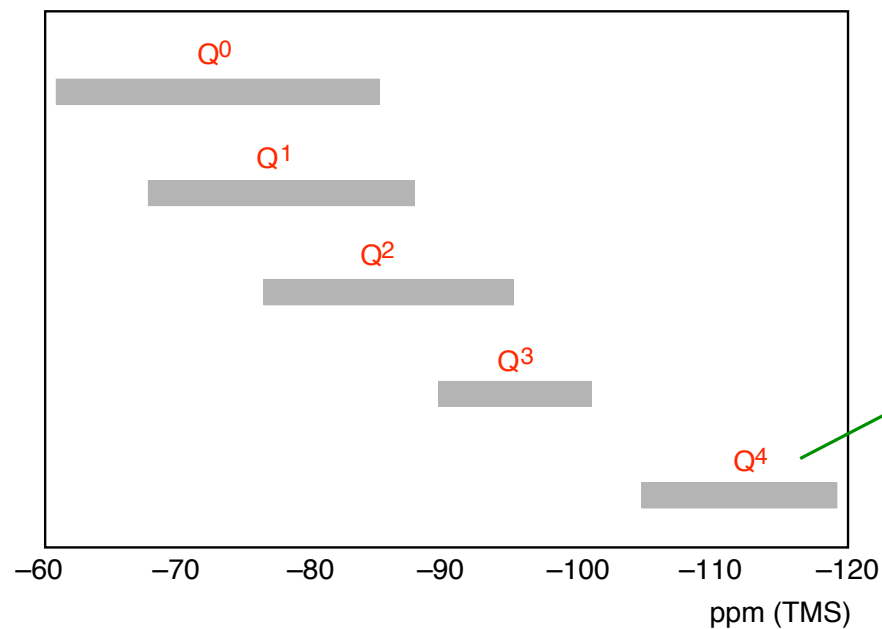
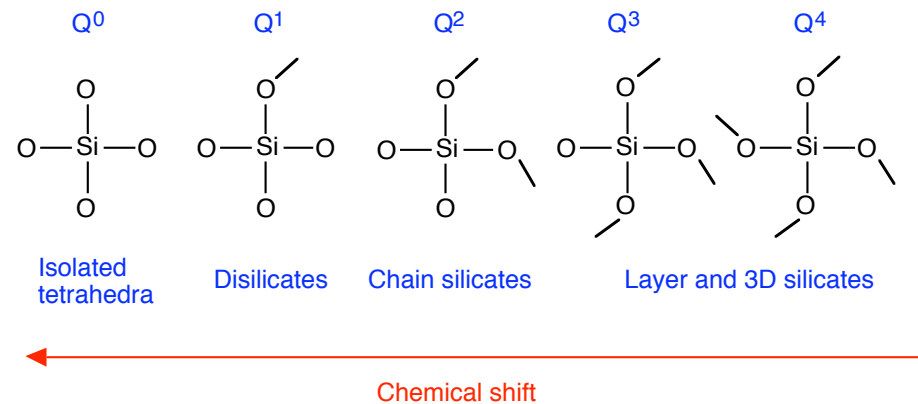
- ^{29}Si $I = 1/2$ 4.7% 79.4 MHz (9.4 T)
 - Found in all zeolites and in SAPOs, strong, well-defined dependence of δ upon environment
- ^{27}Al $I = 5/2$ 100% 104.3 MHz
 - Found in both zeolites and AlPOs, second-order quadrupolar broadening, strong dependence of δ upon coordination number
- ^{31}P $I = 1/2$ 100% 161.3 MHz
 - Found in AlPOs, easy to obtain high-resolution spectra
- ^{17}O $I = 5/2$ 0.037% 54.2 MHz
 - Present in all frameworks, second-order quadrupolar broadening, cost and ease of isotopic enrichment,

NMR considerations

- ^1H $I = 1/2$ 99.99% 400.13 MHz
 - Present as part of the template, water and OH groups, spectra can be broadened by dipolar interactions, study of Bronsted acidity
- ^{23}Na $I = 3/2$ 100% 105.8 MHz
 - Often present as charge balancing cation in zeolites, able to be exchanged with other cations
- ^2H $I = 1$ 0.01% 61.4 MHz
 - Low cost to enrich, selectivity/ease of enrichment, good for studying motion
- ^{129}Xe $I = 1/2$ 26.4% 111.3 MHz
 - Probe of pore volume and shape, large polarizability ensures chemical shift is very sensitive to local environment

^{29}Si NMR

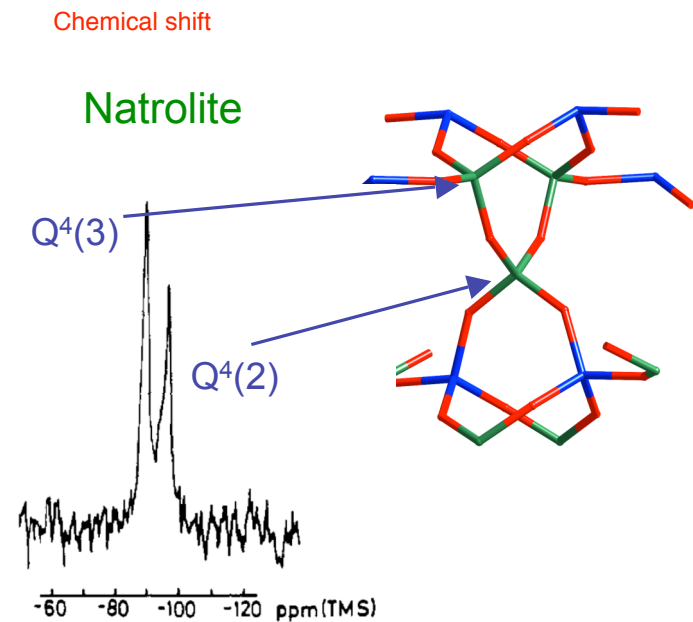
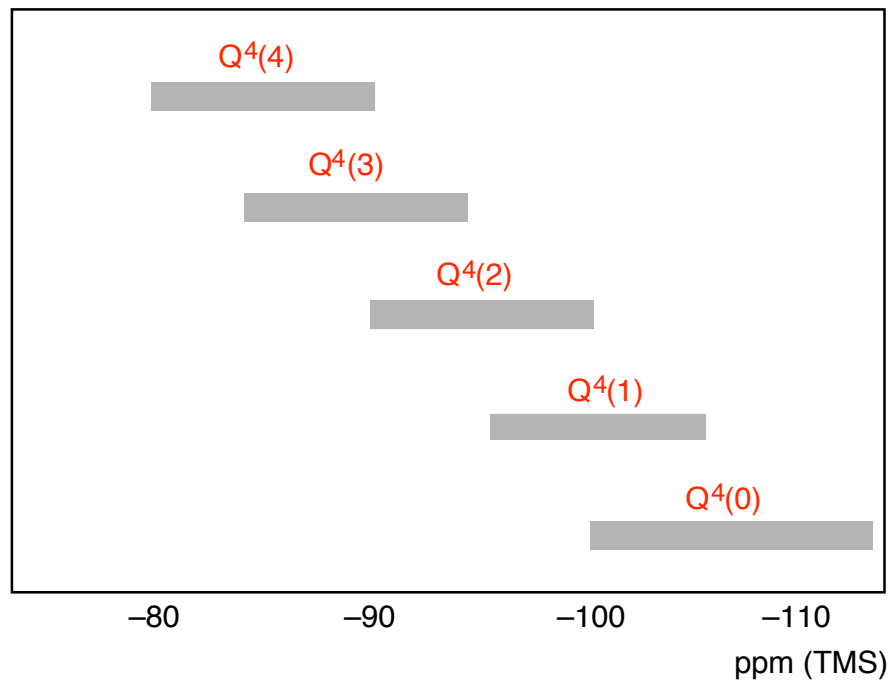
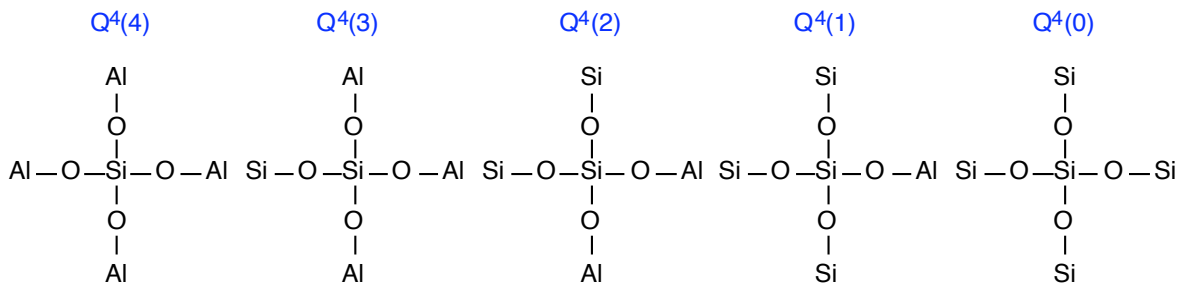
- ^{29}Si chemical shift is extremely sensitive to local environment, with a range of well-known empirical correlations with structural parameters



^{29}Si NMR

- Also sensitive to atoms in the second coordination sphere, e.g., Al

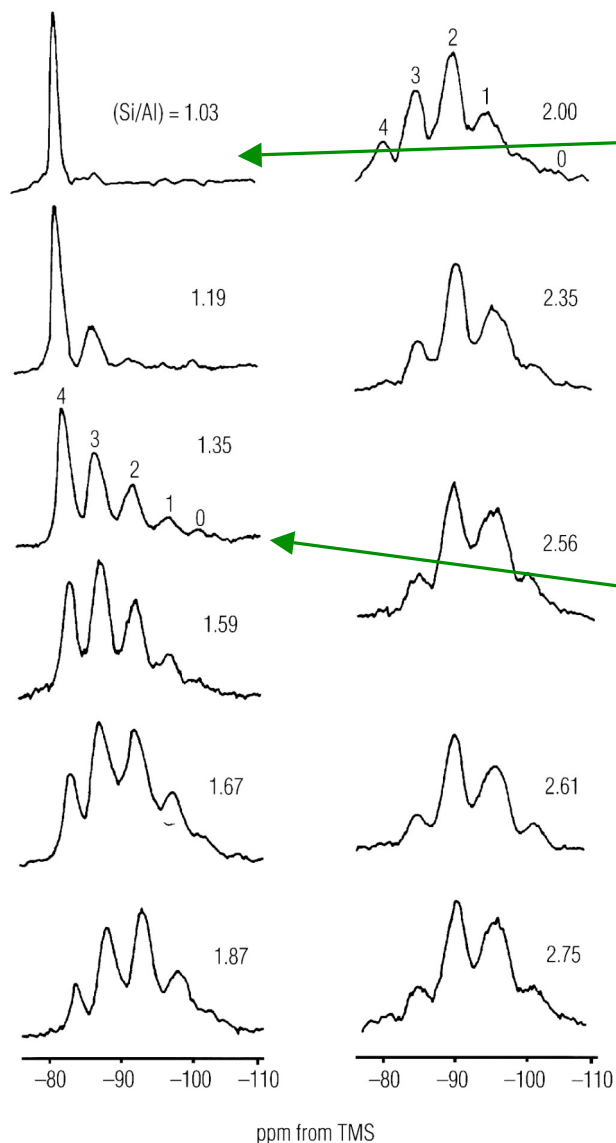
Shift reveals
information on
ordering in the zeolite
framework



Lippmaa et al., *J. Am. Chem. Soc.* **102**, 4889 (1980)

Si/Al ordering in zeolites

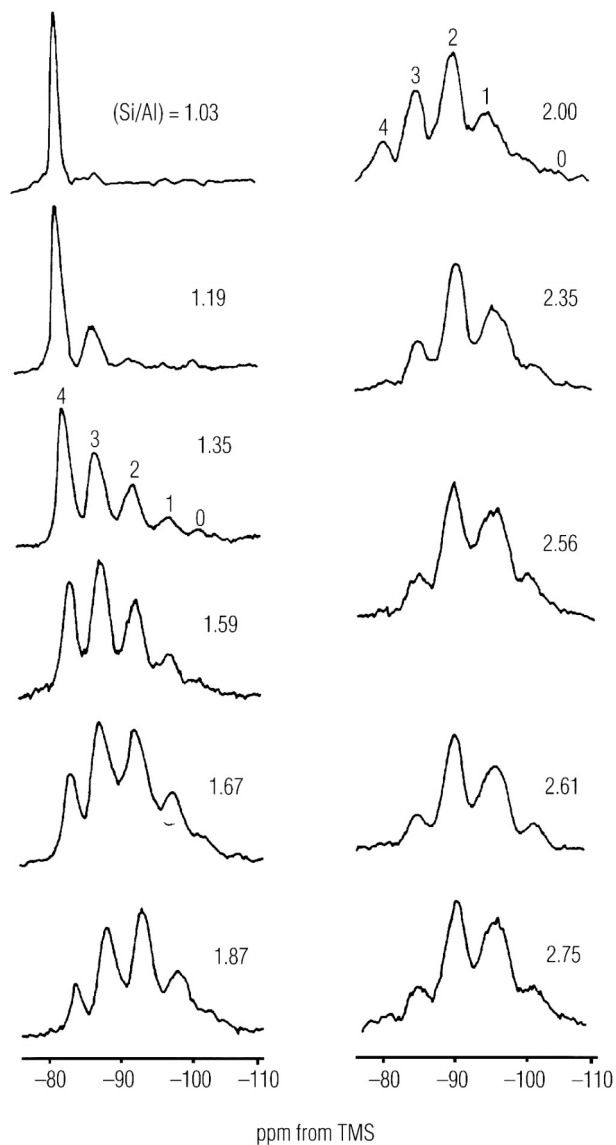
^{29}Si MAS NMR of Na-Y



- At low Si content all Si have the same environment (surrounded by 4 Al)
- Lowenstein's rule (applicable to hydrothermally-prepared zeolites) where Al-O-Al linkages are forbidden
- As the Al content decreases $\text{Q}^4(3\text{Al})$, $\text{Q}^4(2\text{Al})$, etc., appear
- The relative intensities depend upon the Si/Al ratio of the framework

Si/Al ordering in zeolites

^{29}Si MAS NMR of Na-Y



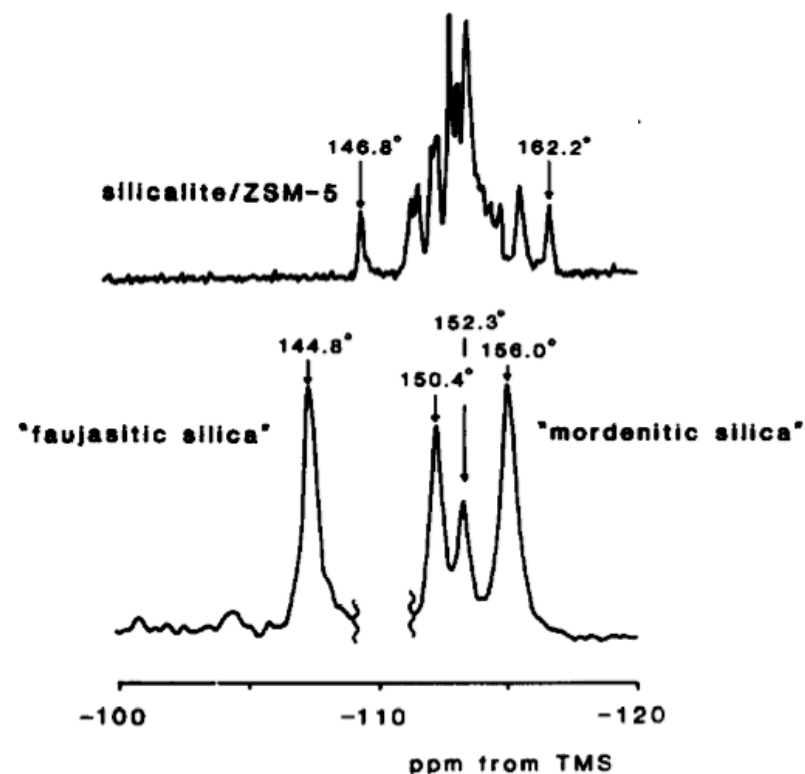
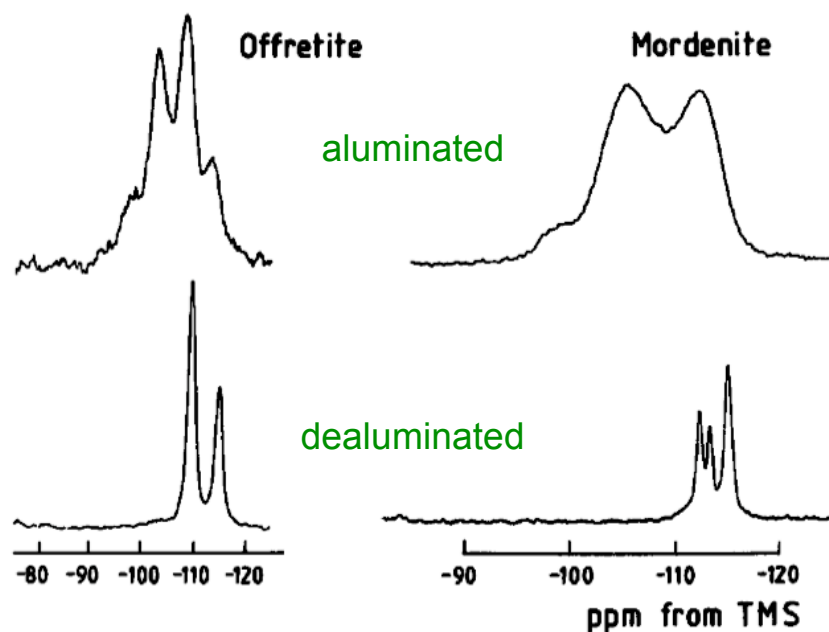
- Using Lowenstein's rule,

$$(\text{Si} / \text{Al})_{\text{NMR}} = \frac{I_4 + I_3 + I_2 + I_1 + I_0}{I_4 + 0.75I_3 + 0.5I_2 + 0.25I_1}$$

- I_n Intensity of peak corresponding to Si(nAl) unit
- Comparison to chemical analysis (which gives the bulk composition) can reveal amount of extra framework Al
- Not applicable if more than one crystallographic species or if there are framework defects or OH groups

Dealuminated zeolites

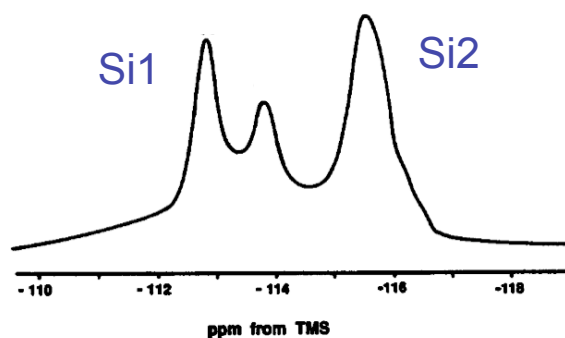
- When Al content is low it is possible to resolve crystallographically distinct Si sites



- ^{29}Si chemical shift depends on the average Si-O-Si angle

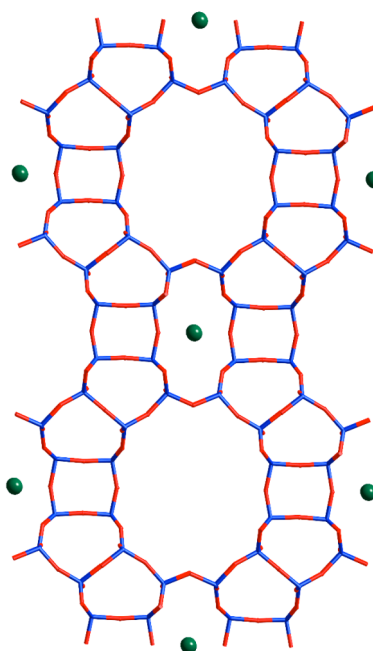
Dealuminated zeolites

- Two-dimensional techniques may also be required to assign the spectra

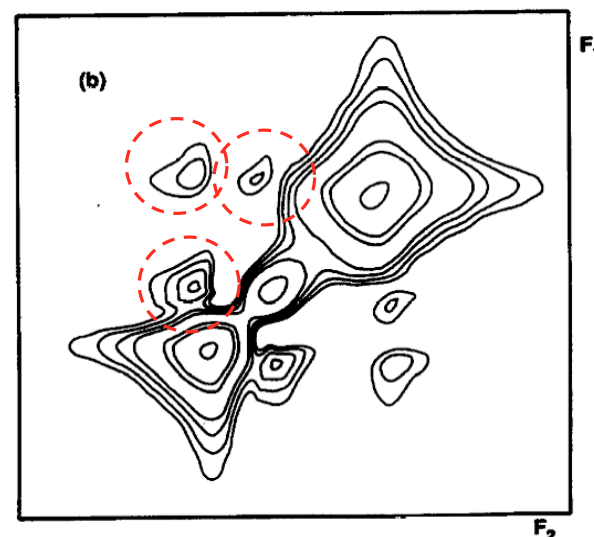


Mordenite contains 4 Si sites in the ratio 2:2:1:1

	No	Neighbours	T-O-T
Si1	1 6	2Si1, Si2, Si3	150.4°
Si2	1 6	Si1, 2Si2, Si4	158.1°
Si3	8	2Si1, Si3, Si4	153.9°
Si4	8	2Si2, Si3, Si4	152.3°



Si1 should have highest δ
Si2 should have lowest δ

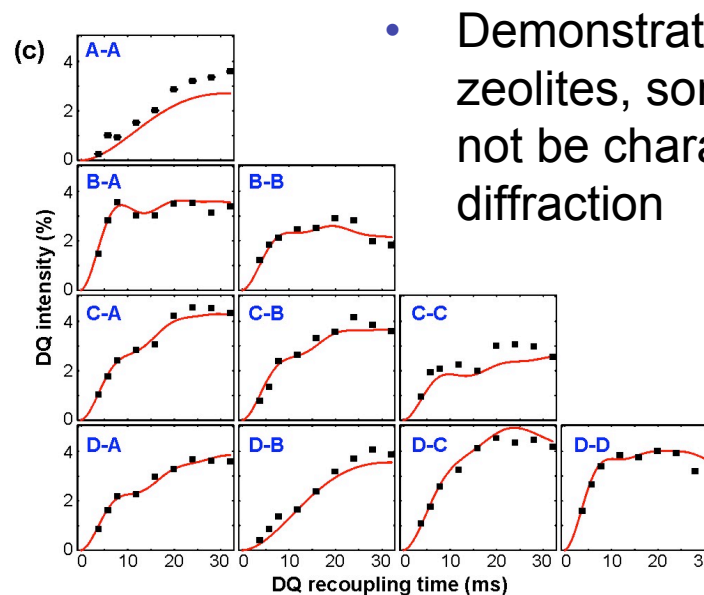
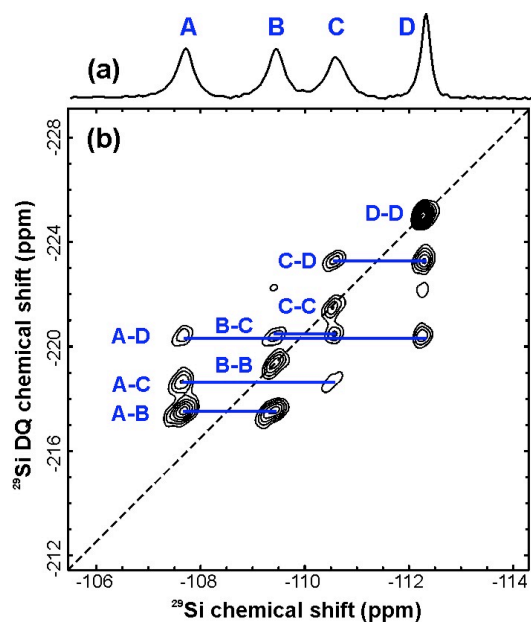


- COSY spectrum
- Spectral assignment as
Si1 Si3 Si2+Si4

Kolodziejewski et al., *J. Chem. Soc. Chem. Commun.* 961 (1991)

Structure determination by NMR

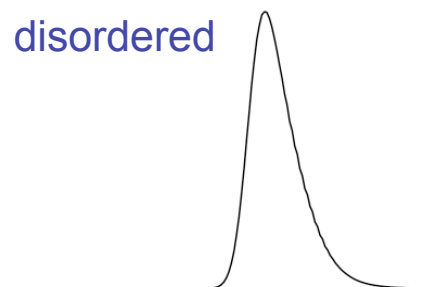
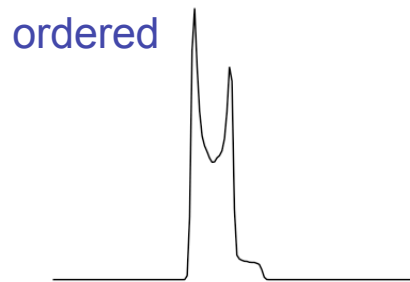
- More recently, ^{29}Si NMR has been used to determine the full framework structure for siliceous zeolites where only space group and unit cell size are known from diffraction
- DQ NMR spectra acquired with varying dipolar recoupling times give information on spatial proximity of Si species
- Used as constraints on possible structural models



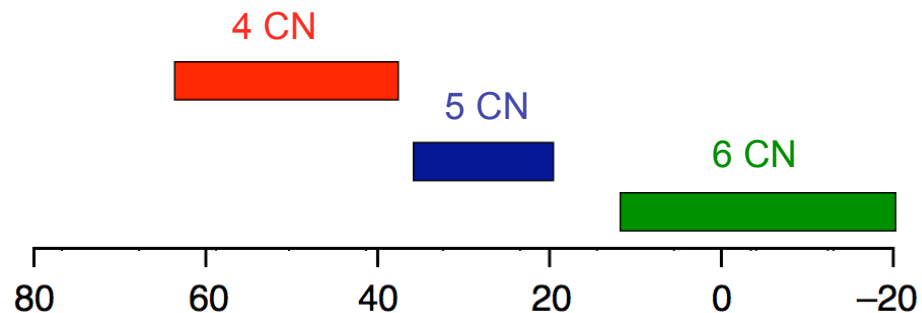
- Demonstrated on a range of zeolites, some of which could not be characterized by diffraction

^{27}Al NMR

- Much less common for study of zeolites than AlPOs owing to quadrupolar broadening and the effects of disorder
- Although all Al are usually coordinated by 4 Si, these Si all have differing environments, leading to a range of chemical shift and quadrupolar parameters

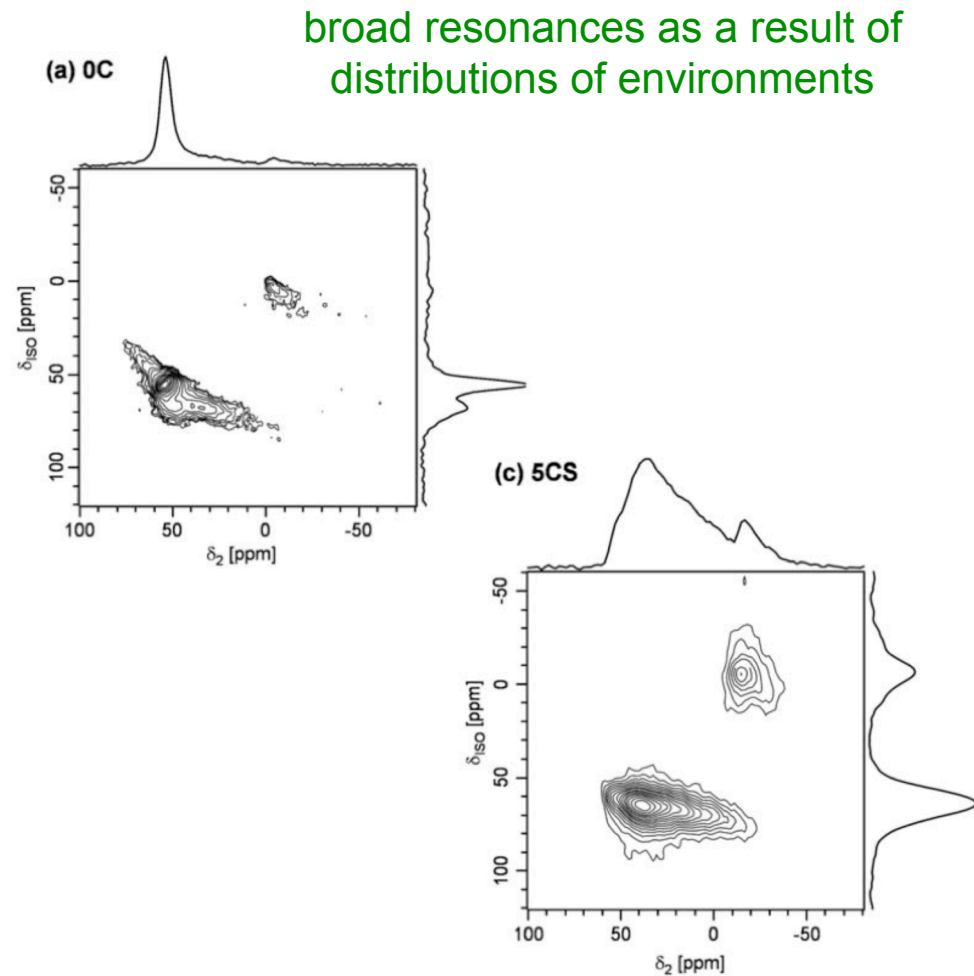
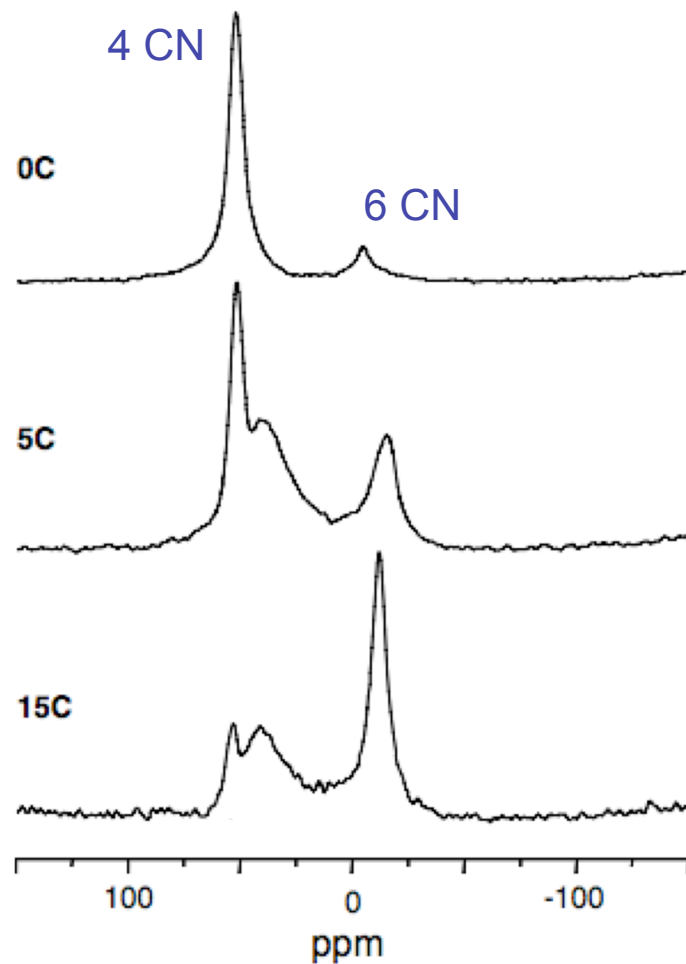


- Large ^{27}Al chemical shift range and strong correlation of δ with coordination number
- Note the isotropic quadrupolar shift can move resonances away from the true δ



^{27}Al NMR of zeolites

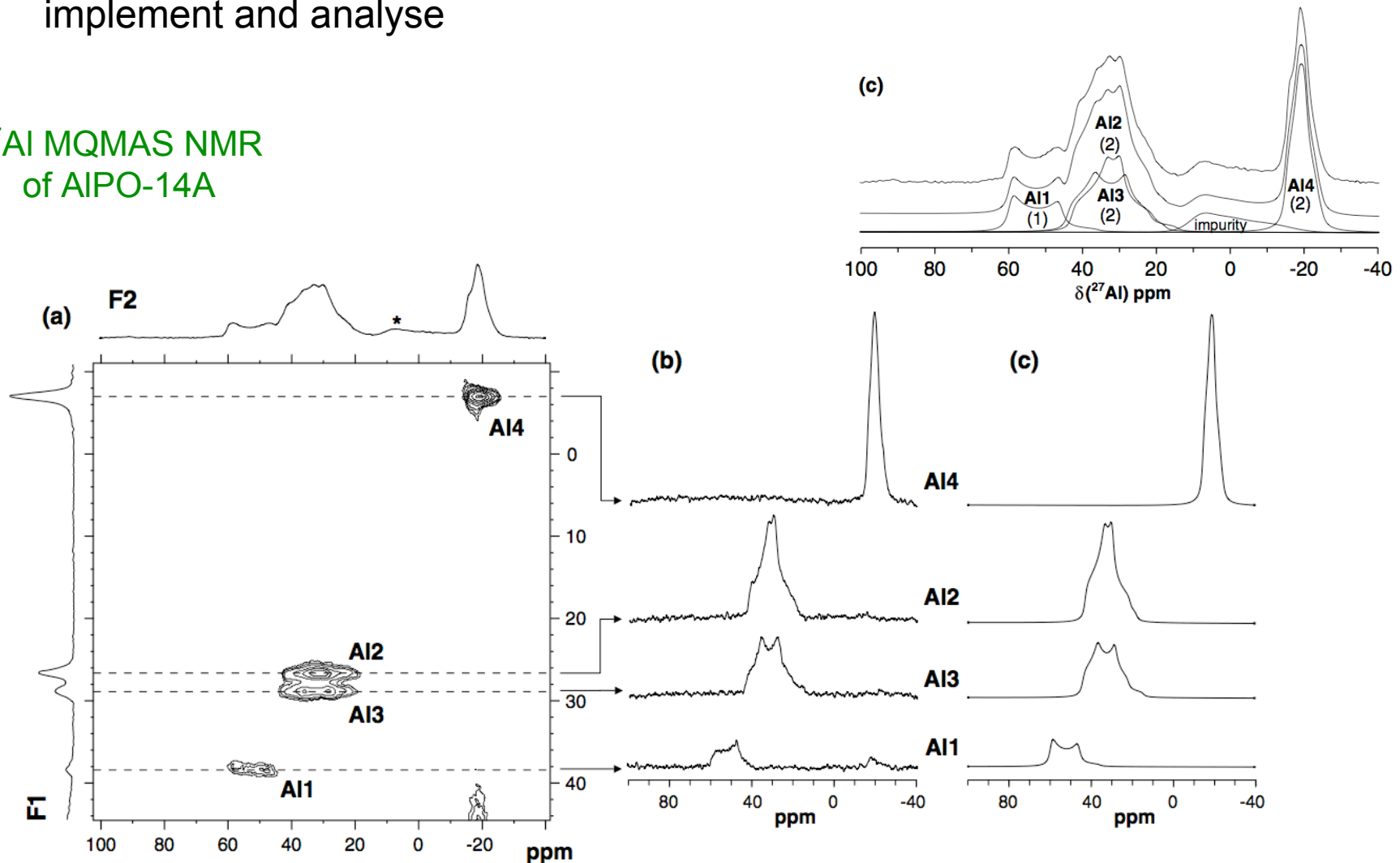
- ^{27}Al MAS and MQMAS of H-ZSM-5 with P substitution



^{27}Al NMR of AIPOs

- Al and P in an AIPO framework are ordered so ^{27}Al NMR is easier to implement and analyse

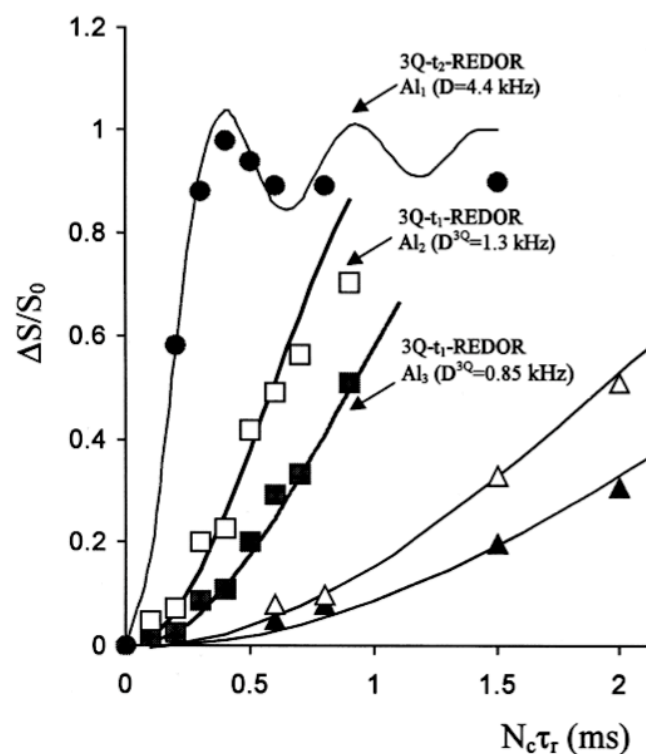
^{27}Al MQMAS NMR of AIPO-14A



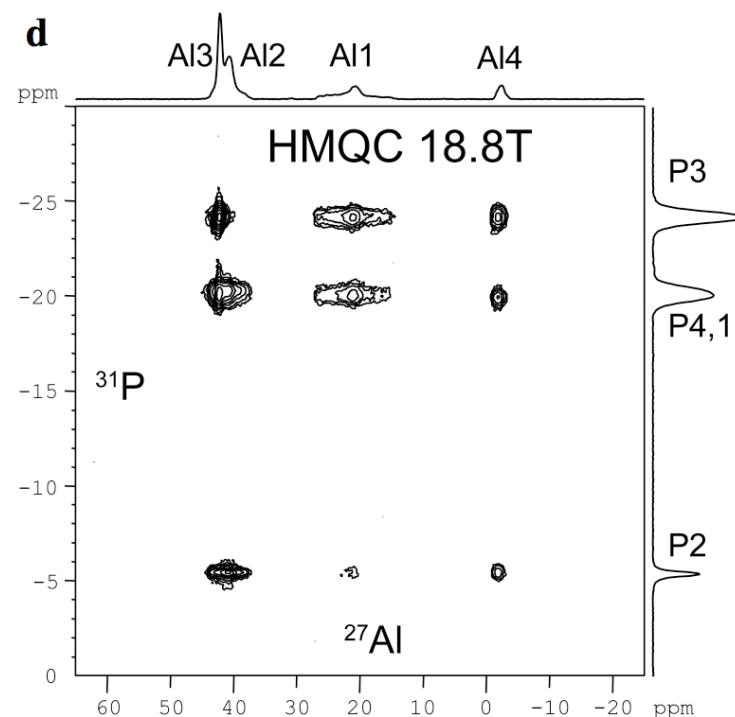
Brouwer et al. *Micro. and Meso. Mater.* **88**, 163 (2006)

$^{27}\text{Al}/^{31}\text{P}$ NMR of AlPOs

- Two 100% abundant nuclei in close proximity in an ordered framework offers great potential for double resonance experiments
- High abundance can lead to problems with quantitative interpretation



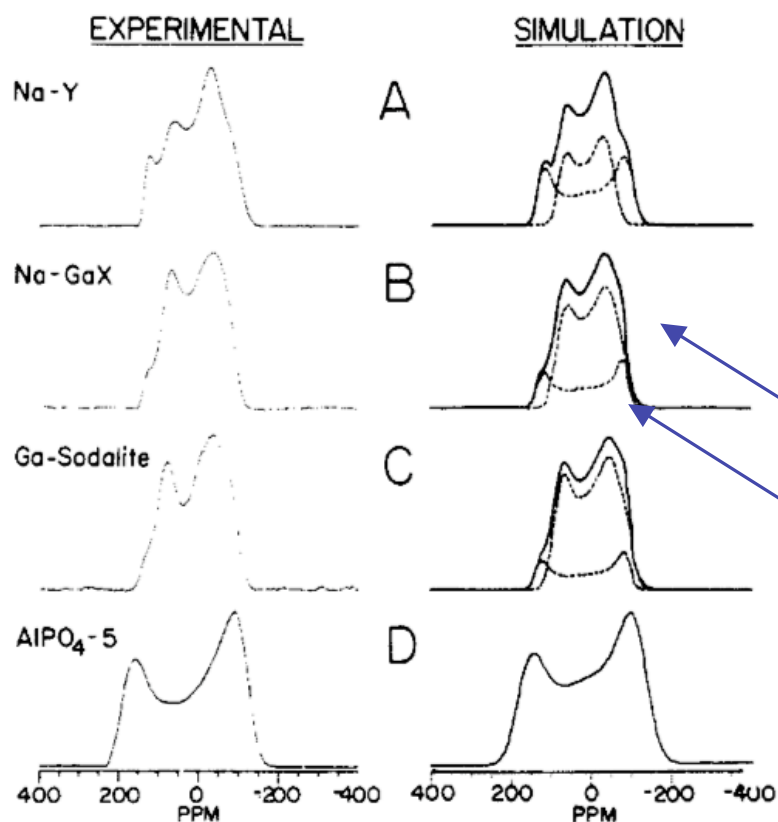
Pruski et al. Chem. Phys. Lett.
307, 35 (1999)



Amoureux et al. J. Magn. Reson.
184, 1 (2007)

^{17}O NMR

- Relatively little use of ^{17}O NMR owing to the need for enrichment
- Often O is the binding site for adsorbed species and the NMR parameters very sensitive to local environment



- Enrichment via hydrothermal exchange for zeolites (often more difficult for AlPOs)
- Care over different reactivity of the linkages when interpreting intensities

Si-O-Al $C_Q = 3-4$ MHz

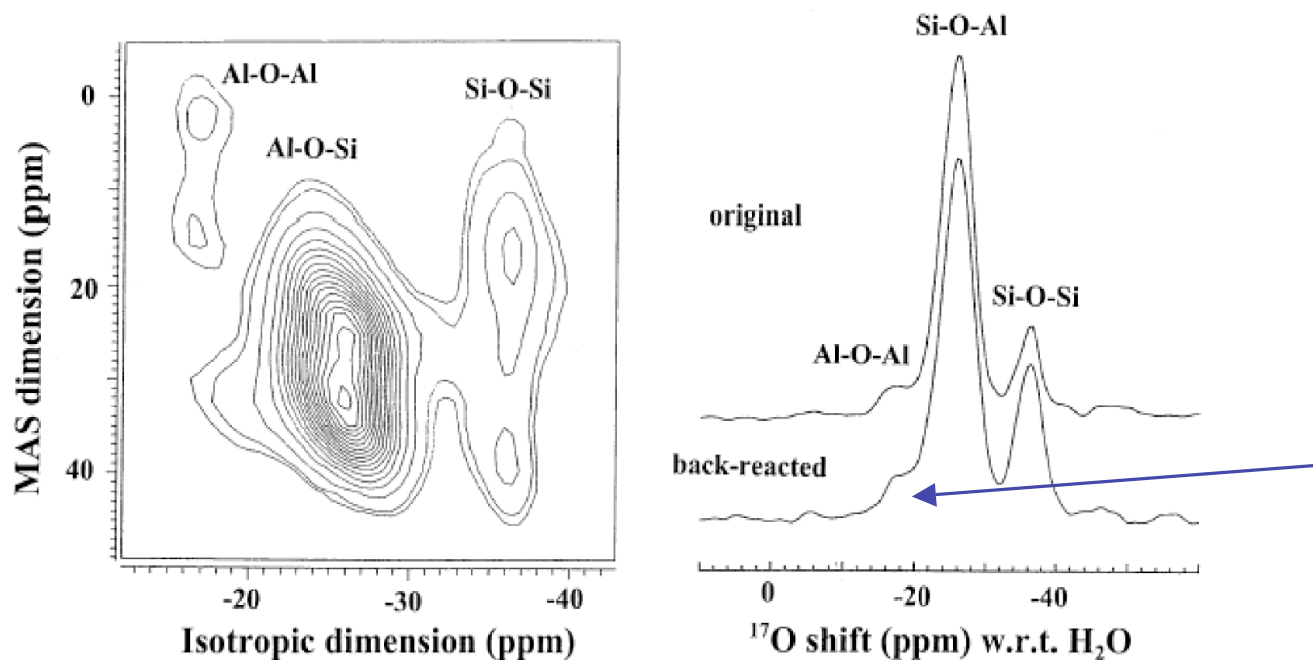
Si-O-Si $C_Q = 5-6$ MHz

^{17}O MAS NMR

Timken et al. *J. Am. Chem. Soc.*
108, 7236 (1986)

^{17}O NMR

- MQMAS/DAS/DOR etc. required to remove quadrupolar broadening and resolve environment types
- Resolution of distinct species often not possible unless siliceous zeolites
- Where distinct sites have been resolved empirical correlations have been observed but shown not to have general validity

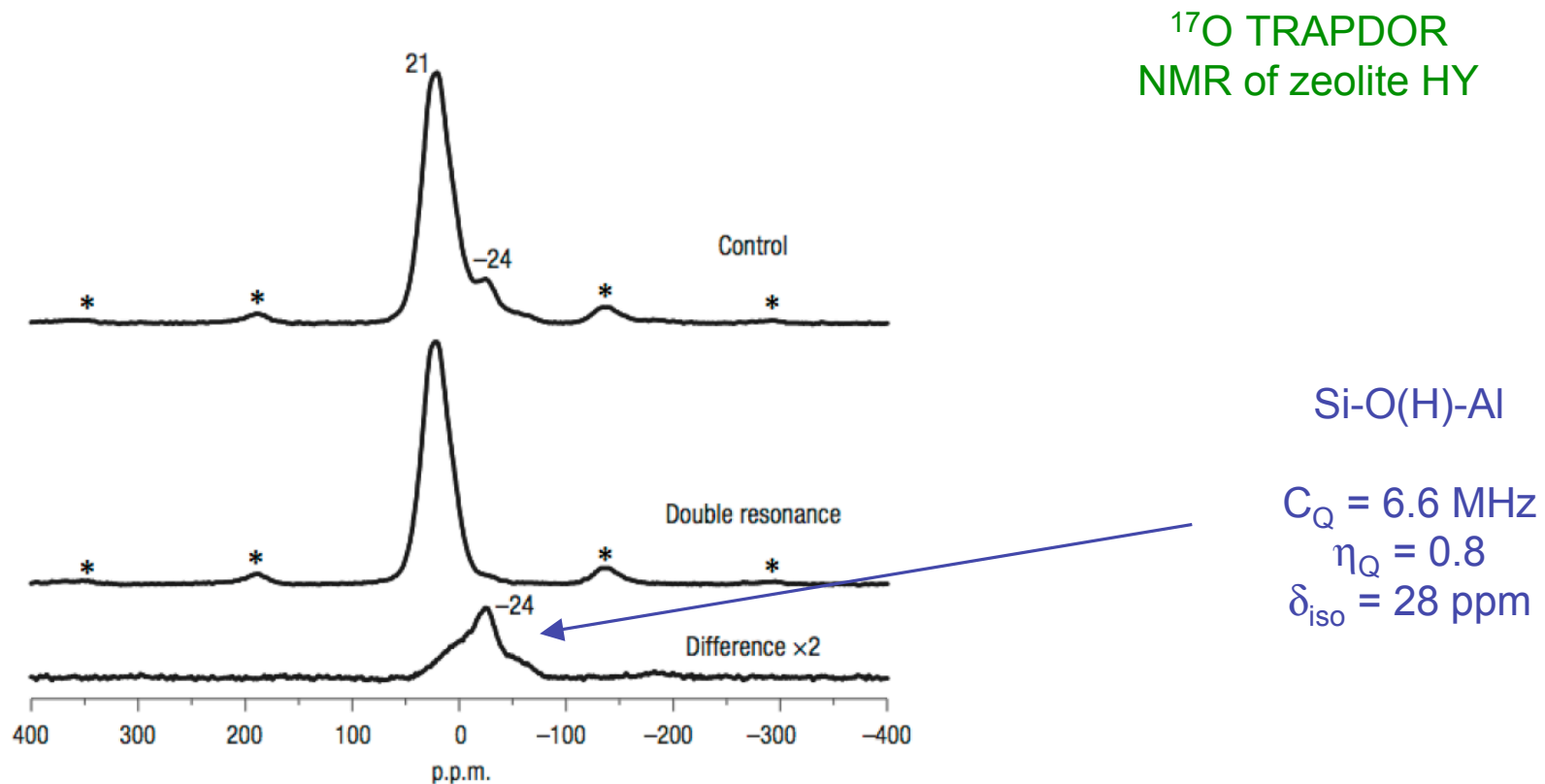


^{17}O MQMAS NMR
of stilbite

Reactivity of Al-O-Al
species

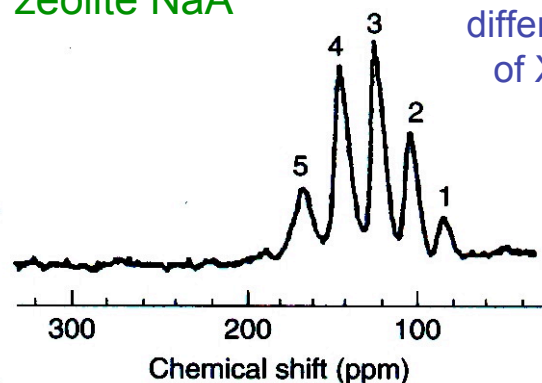
Bronsted acidity

- Catalytic properties often centre on acidic sites within a structure
- Direct detection of Si-O(H)-Al Bronsted acid sites via double resonance ($^1\text{H}/^{17}\text{O}$) experiments
- Parameters very different to Si-O-Al sites



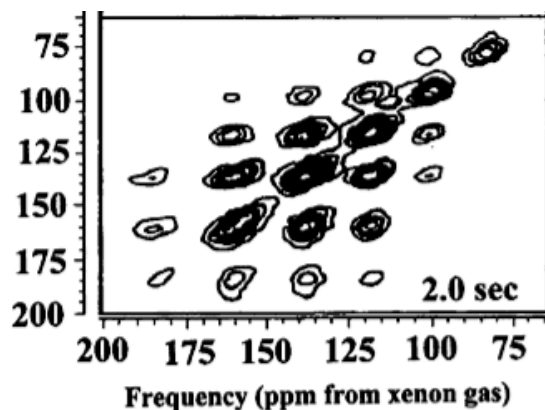
Alternative nuclei

^{129}Xe NMR of
zeolite NaA



different numbers
of Xe in cages

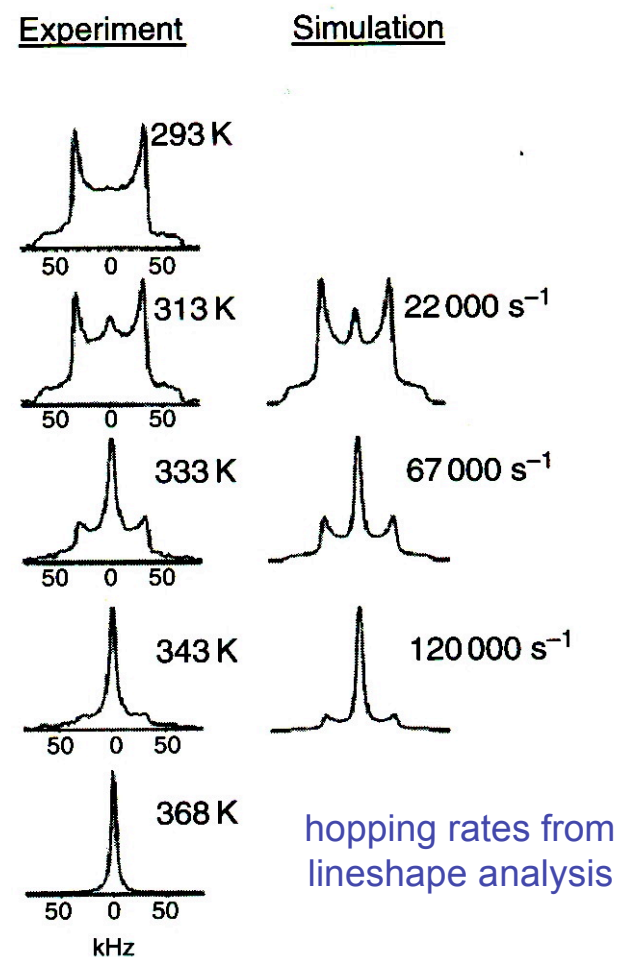
Large polarizability results in
sensitivity of chemical shift to
local environment



diffusion between
cages from
NOESY/EXSY

Huet et al. *Magn. Reson.
Chem.* **37**, S1 (1999)

^2H NMR of benzene
in zeolite Ag-Y



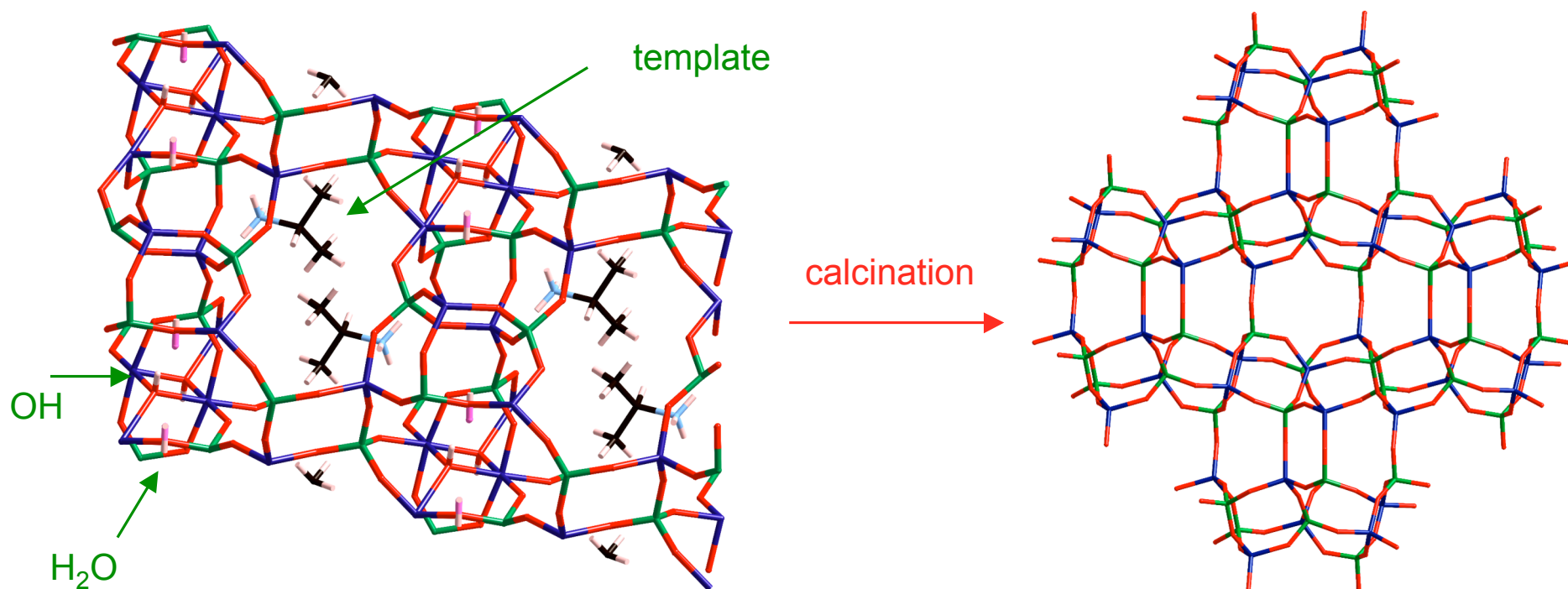
Gedeon et al. *J. Phys.
Chem. A* **103**, 6691 (1999)

High-Resolution NMR of AIPO-14

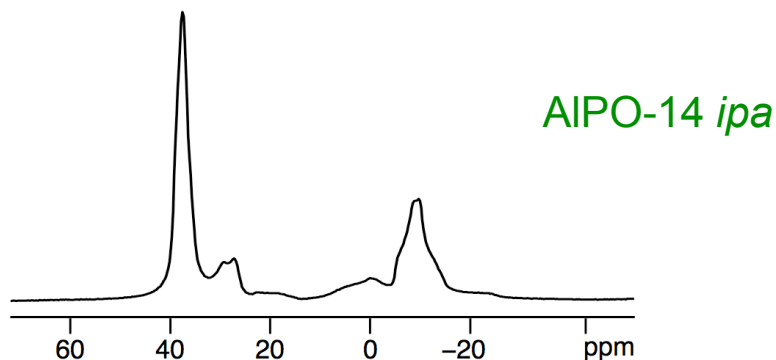
Dr Richard Walton (University of Warwick)
Professor Steve Wimperis (University of Glasgow)
Marica Cutajar (University of Glasgow)
Dr Chris Pickard (University of St Andrews)
Dr John Griffin (University of St Andrews)

NMR of AIPO-14

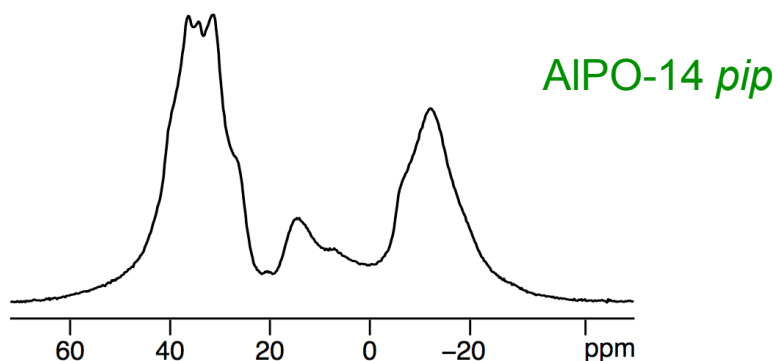
- One of the first structures studied by Wilson in 1982
- Initial confusion over spectral assignment in the literature as AIPO-14 can be prepared with a number of different templates
- Four distinct Al and four distinct P species
- Synthesized with isopropylamine (*ipa*) and piperidine (*pip*) templates
- As-synthesized forms contain framework OH increasing the Al coordination



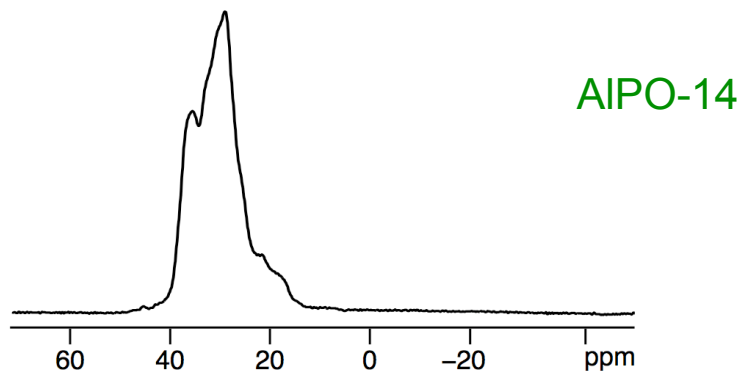
NMR of AIPO-14



- AIPO-14 *ipa* has 4-, 5- and 6-coordinate Al

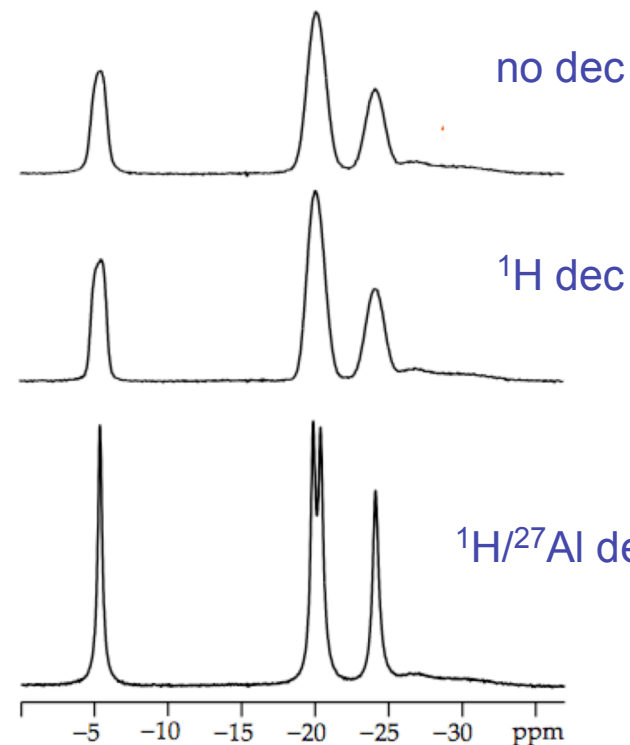
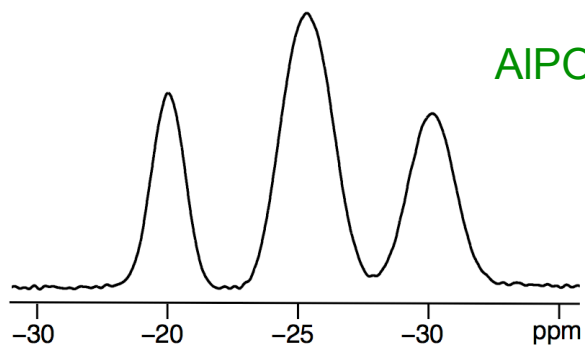
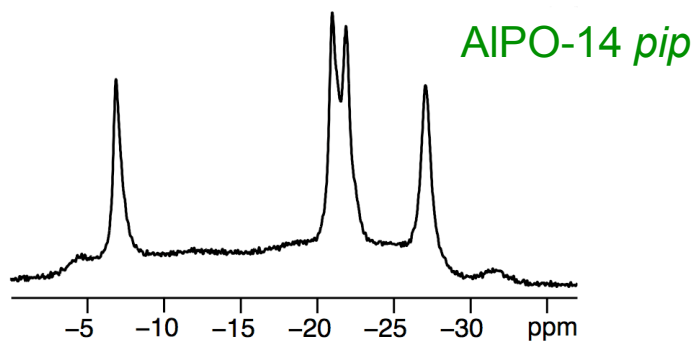
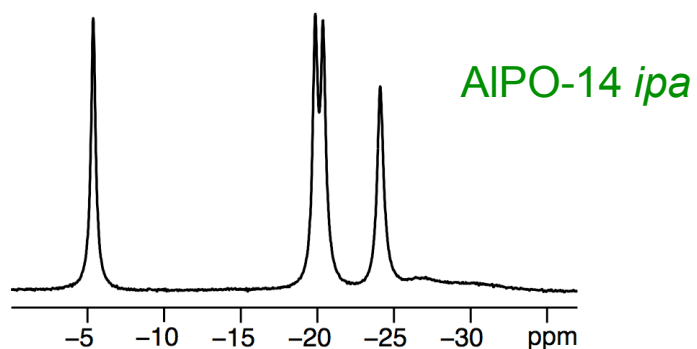


- Although a different spectrum, AIPO-14 *pip* also 4-, 5- and 6-coordinate Al



- Calcination of both *ipa* and *pip* produces a material with only 4-coordinate Al

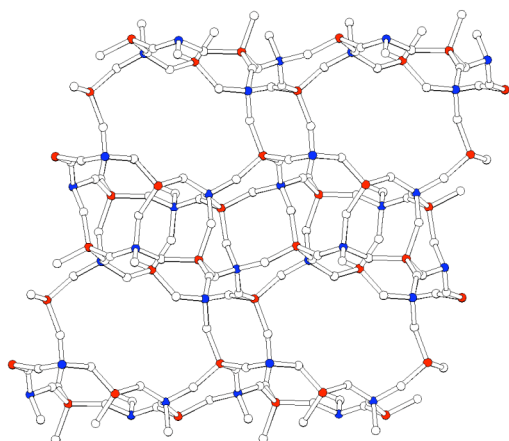
NMR of AIPO-14



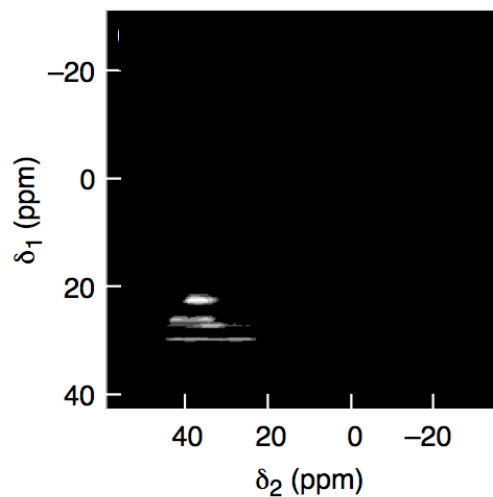
- For ^{31}P NMR both ^1H (70 kHz) and ^{27}Al (6 kHz) decoupling is required
- Only low power decoupling is needed (avoiding $\omega_R \approx \omega_1$)

NMR of AIPO-14

AIPO₄-14 calcined

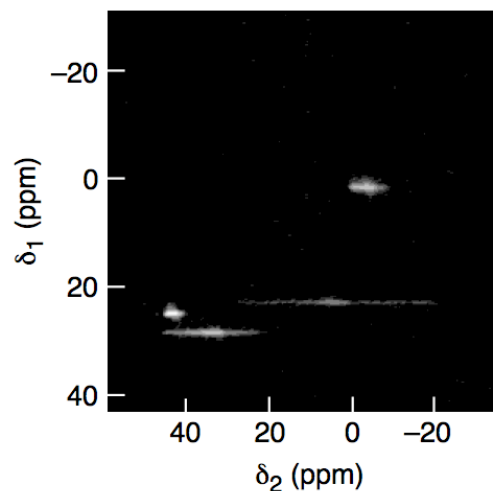
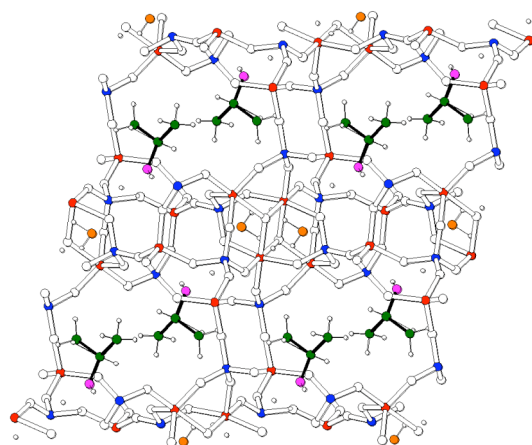


MQMAS



δ_{iso} (ppm)	C_Q / MHz	η_Q
45	4.9	0.3
43	4.0	0.8
43	3.4	0.2
38	2.5	0.6

AIPO₄-14 *ipa*

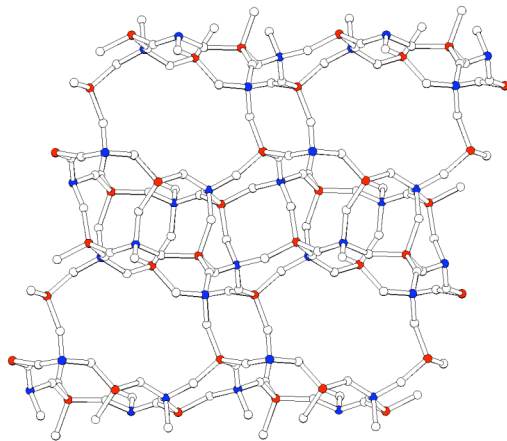


δ_{iso} (ppm)	C_Q / MHz	η_Q
27	5.6	1.0
44	4.1	0.8
43	1.7	0.6
-1	2.6	0.7

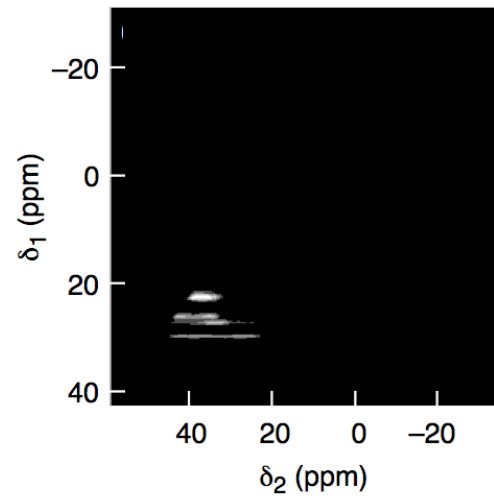
Antonijevic et al. *J. Am. Chem. Soc.* **128**, 8054 (2006)

NMR of AIPO-14

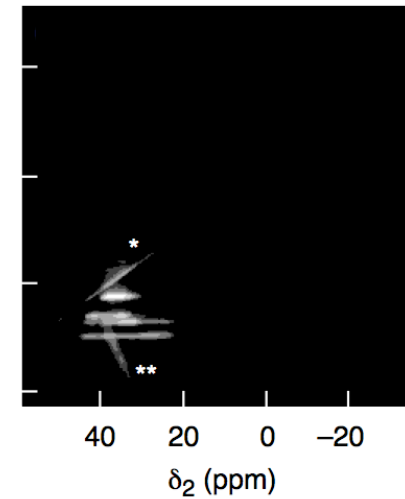
AIPO₄-14 calcined



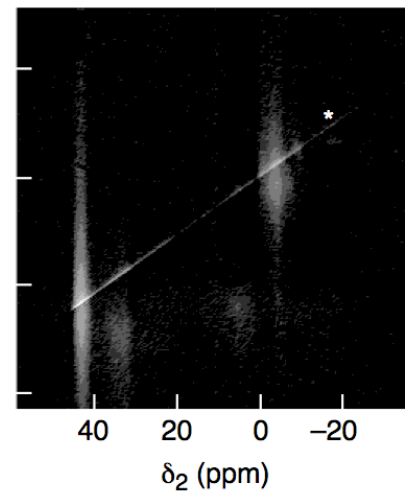
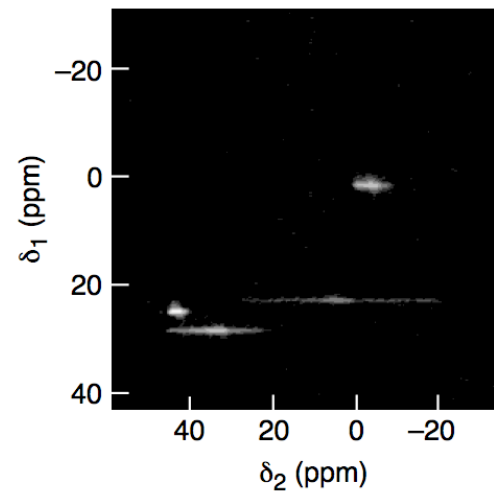
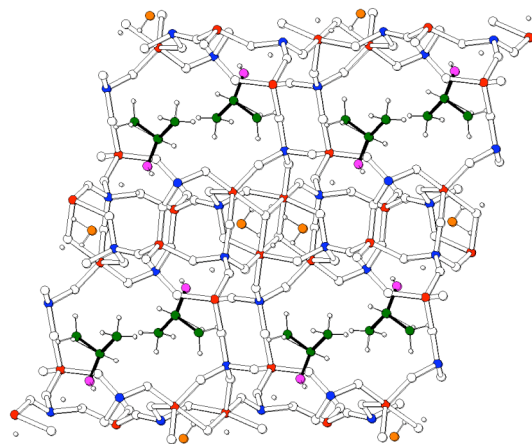
MQMAS



STMAS

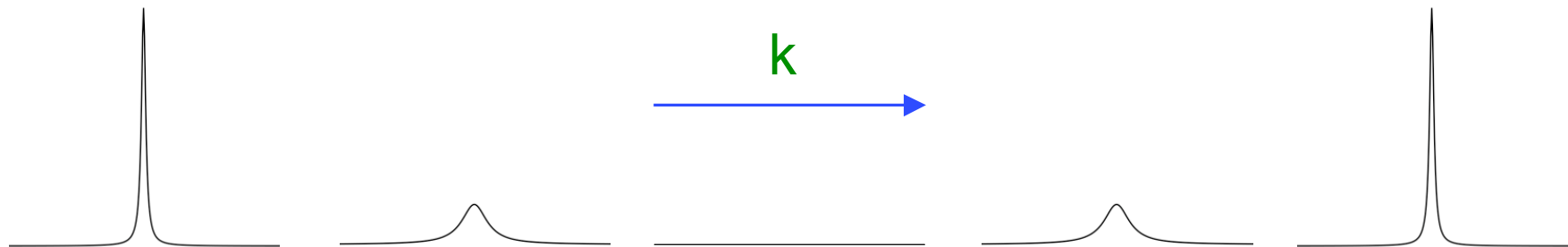


AIPO₄-14 *ipa*



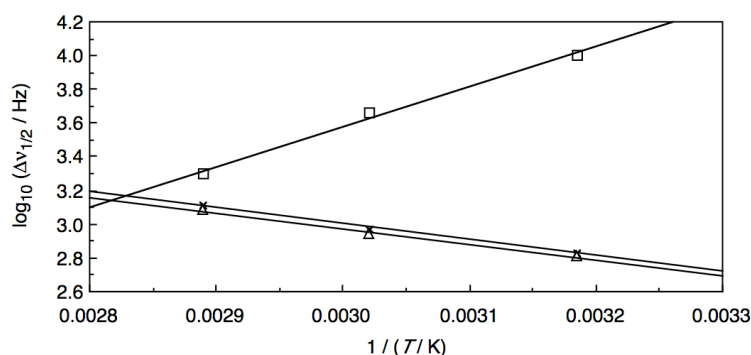
NMR of AIPO-14

- Satellite transitions experience a first-order quadrupolar interaction (removed from the spectrum by rotor-synchronized MAS)
- Sensitive to motion and dynamics on the μs timescale
- Motion during the rotor period interrupts the MAS averaging and prevents formation of rotary echoes leading to broadening

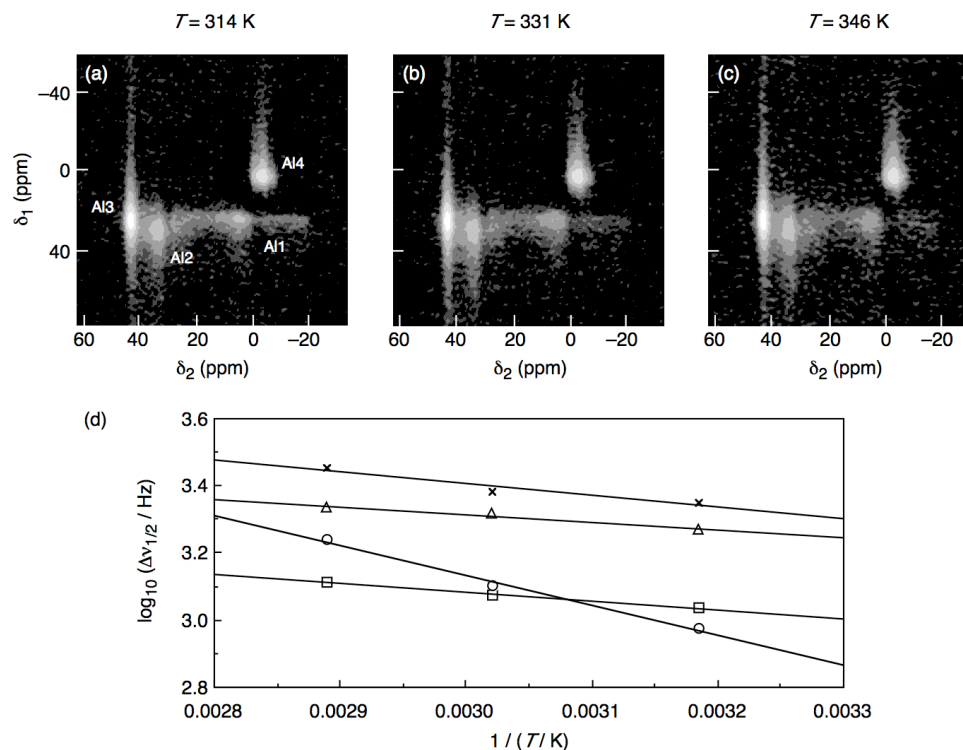


NMR of AIPO-14

- No effect on calcined material
- All 4 Al affected
- Broadening is temperature dependent
- E_A of 4-17 kJ mol⁻¹ (*ipa*) and 18-45 kJ mol⁻¹ (*pip*)
- Not bond breaking but conformational change
- Not a single motional process
- Both template and water molecules contribute



AIPO-14 *ipa*



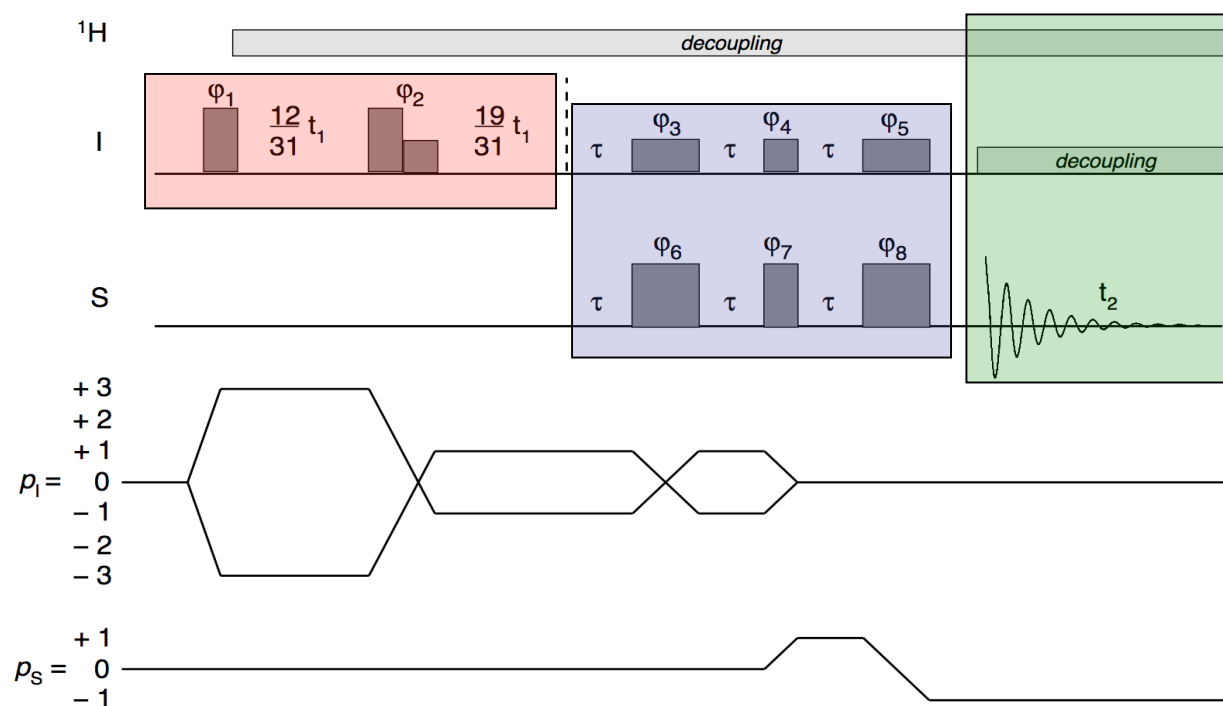
AIPO-14 *pip*

Antonijevic et al. J. Am. Chem. Soc. **128**, 8054 (2006)

NMR of AIPO-14

- To fully understand this motion we need to be able to assign the Al spectra (and understand the effect upon each different type of Al)

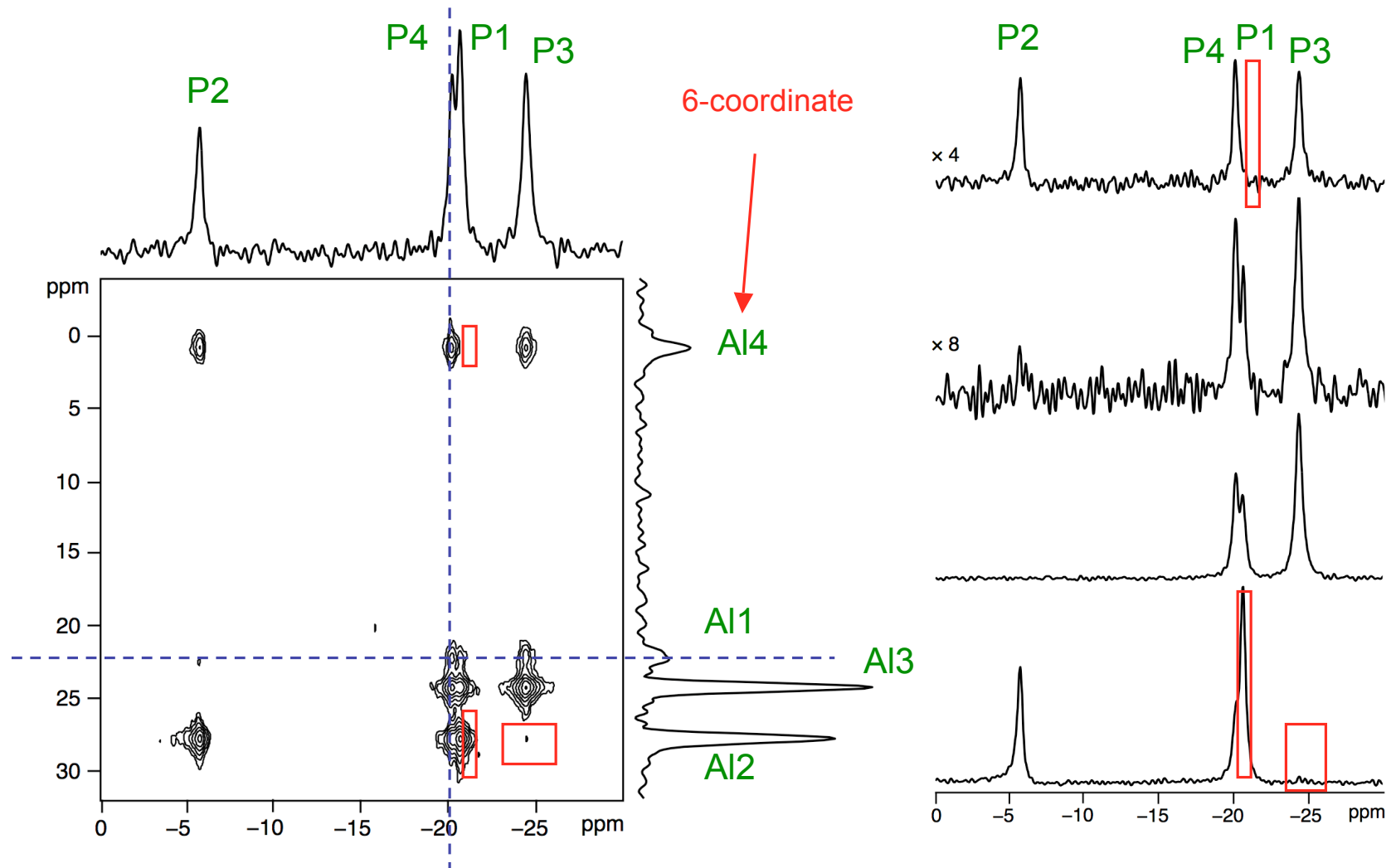
MQ-J-HETCOR



	P 1	P 2	P 3	P 4
Al1	X	X	X	X
Al2	XX	X		X
Al3	X		XX	X
Al4		XX	X	X

AlPO-14 *ipa*

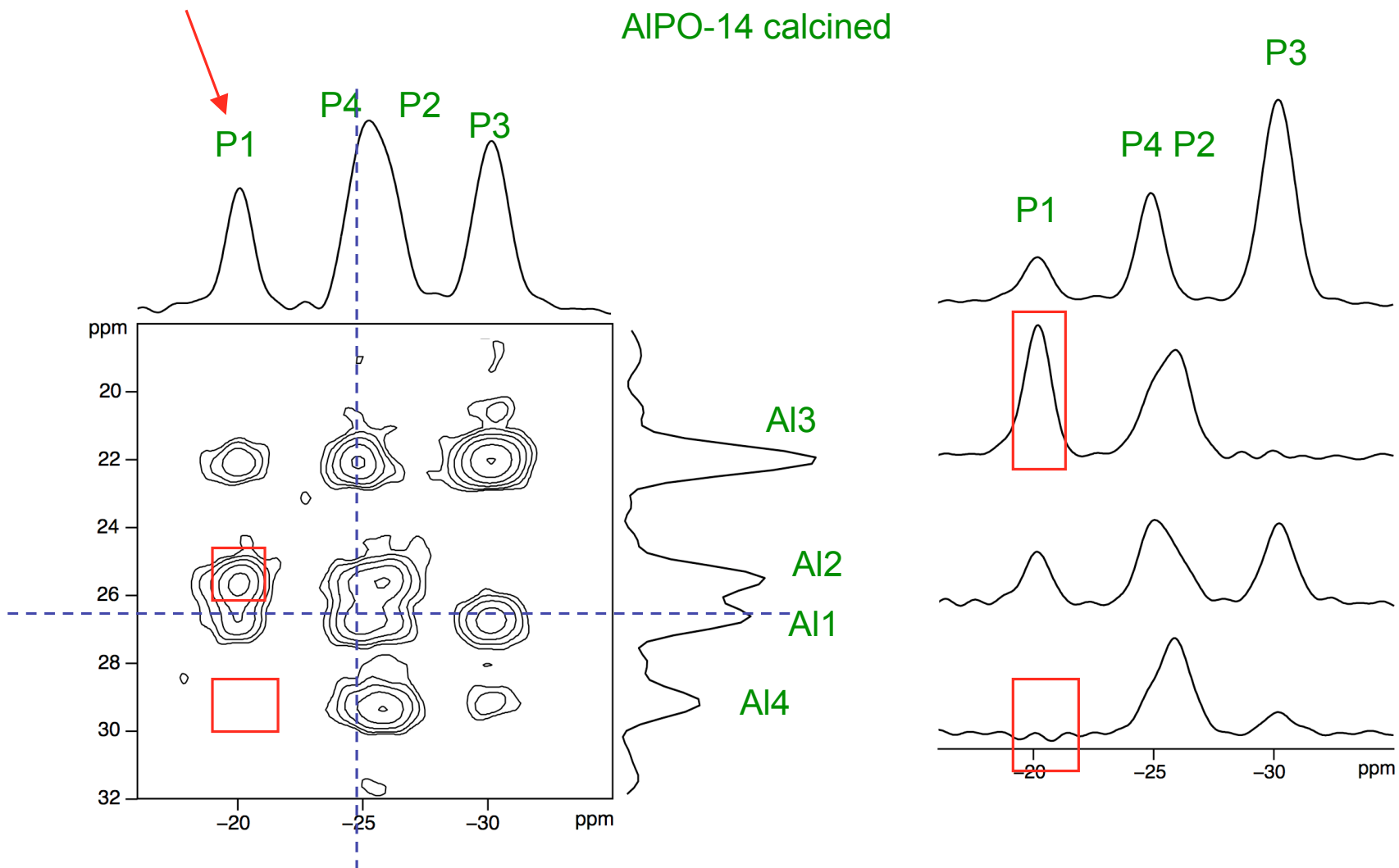
NMR of AlPO-14



NMR of AIPO-14

Smallest O-P-O
angle

AIPO-14 calcined



NMR of AIPO-14

- Can we use calculations (CASTEP) to support these assignments?

Experimental				AIPO-14 calcined				Calculated			
	δ_{iso} (ppm)	C_Q / MHz	η_Q					δ_{iso} (ppm)	C_Q / MHz	η_Q	
Al1	43	4.0	0.8					Al1	38.5	5.30	0.08
Al2	43	3.4	0.2					Al2	48.6	9.69	0.26
Al3	38	2.5	0.6					Al3	40.3	5.55	0.74
Al4	45	4.9	0.3					Al4	55.9	7.04	0.57
P1	-21.4							P1	-33.5		
P2	-26.7							P2	-24.0		
P3	-31.5							P3	-35.7		
P4	-26.7							P4	-35.8		

- Poor agreement and does not support assignments

NMR of AIPO-14

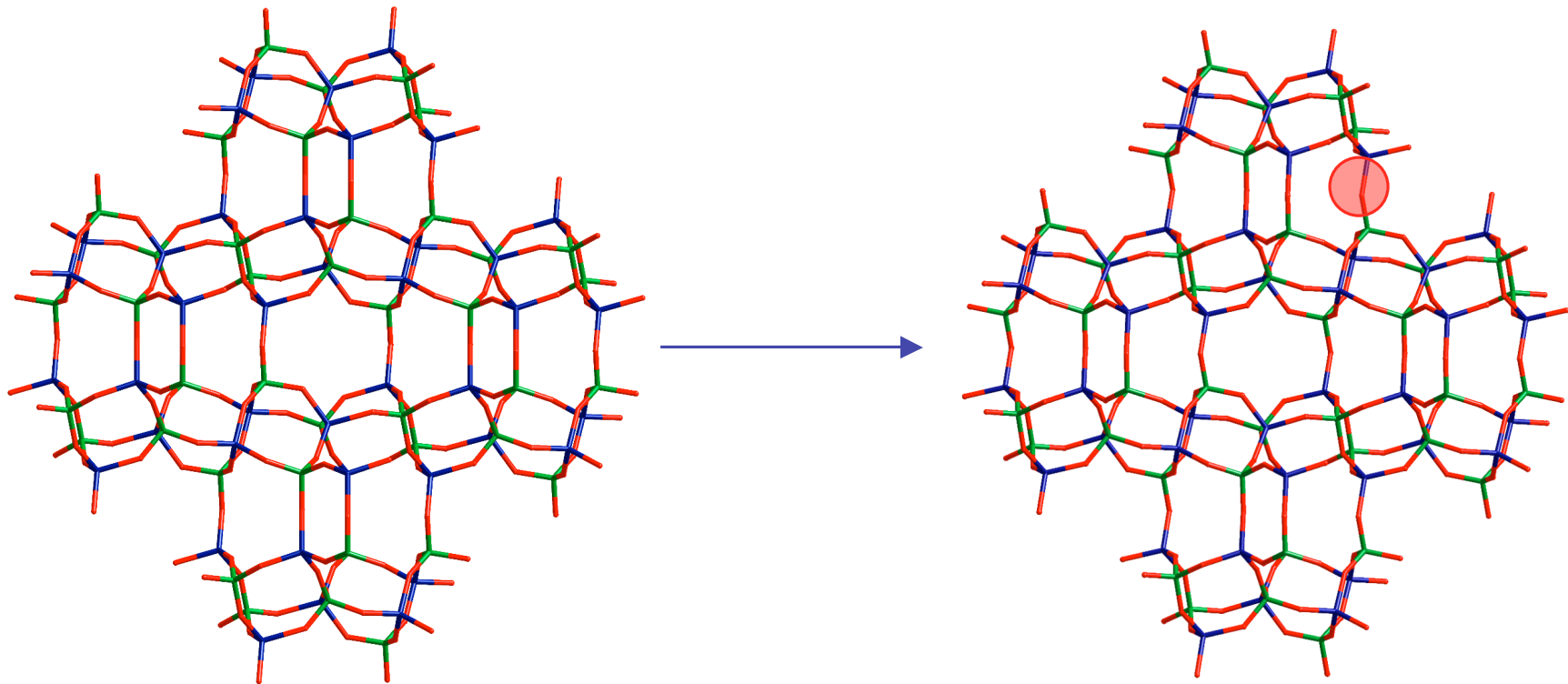
- Use geometry optimization?

Atoms but no cell				AIPO-14 calcined				Atoms and cell			
	δ_{iso} (ppm)	C_Q / MHz	η_Q						δ_{iso} (ppm)	C_Q / MHz	η_Q
Al1	46.5	3.72	0.95					Al1	43.2	4.54	0.74
Al2	46.8	3.44	0.48					Al2	43.8	3.57	0.25
Al3	41.8	2.22	0.37					Al3	38.0	2.80	0.71
Al4	48.7	4.5	0.27					Al4	46.6	4.96	0.26
P 1	-19.3							P 1	-21.4		
P 2	-25.6							P 2	-26.6		
P 3	-30.3							P 3	-32.9		
P 4	-24.5							P 4	-25.3		

- Agreement is better and best when cell is also varied
- Supports the assignment

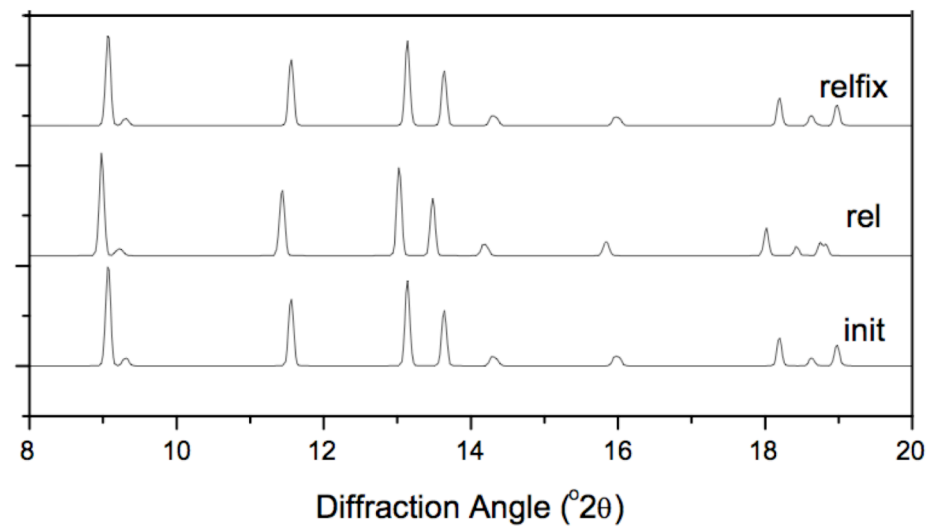
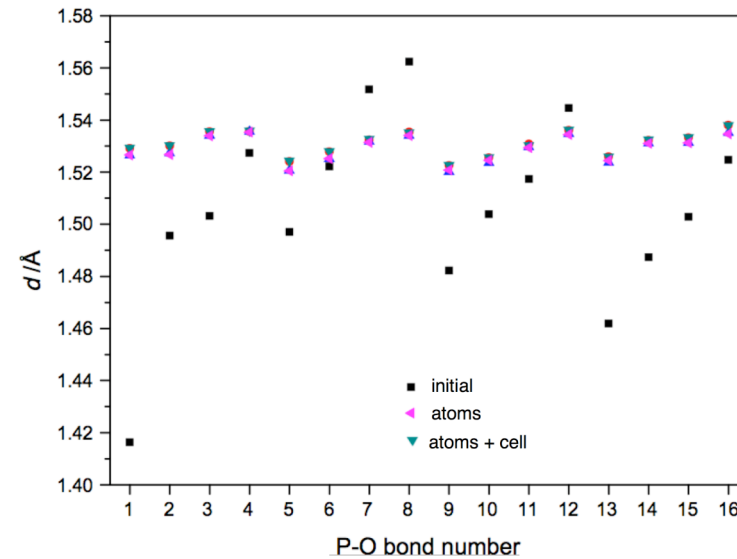
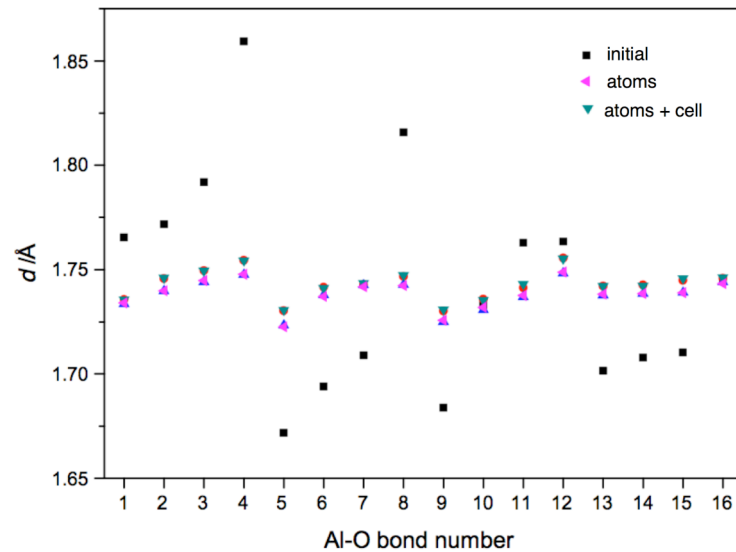
NMR of AIPO-14

- So how much have we changed the structure? Is this realistic?



NMR of AIPO-14

- So how much have we changed the structure? Is this realistic?



NMR of AIPO-14

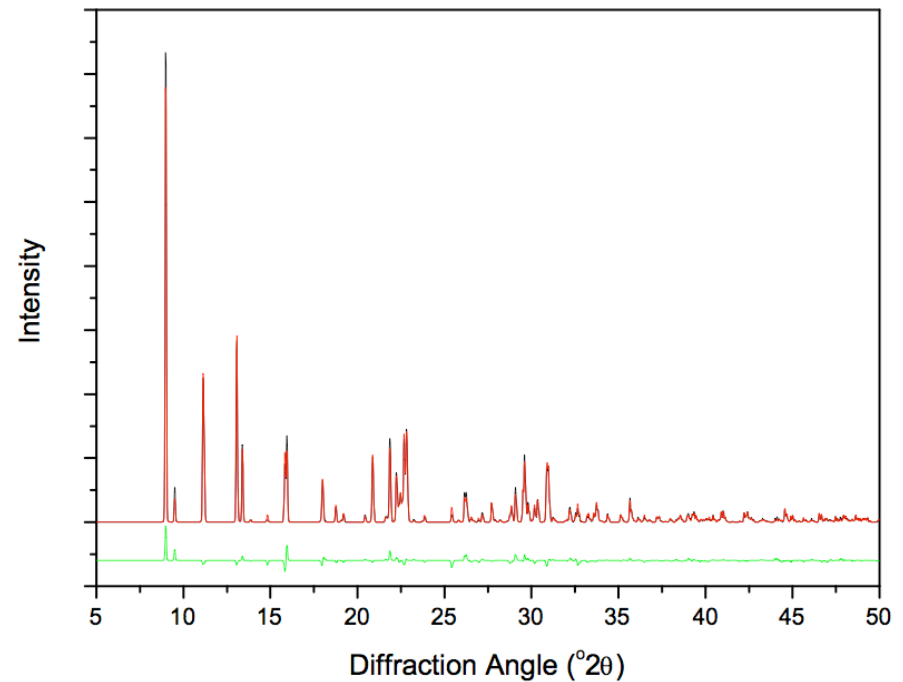
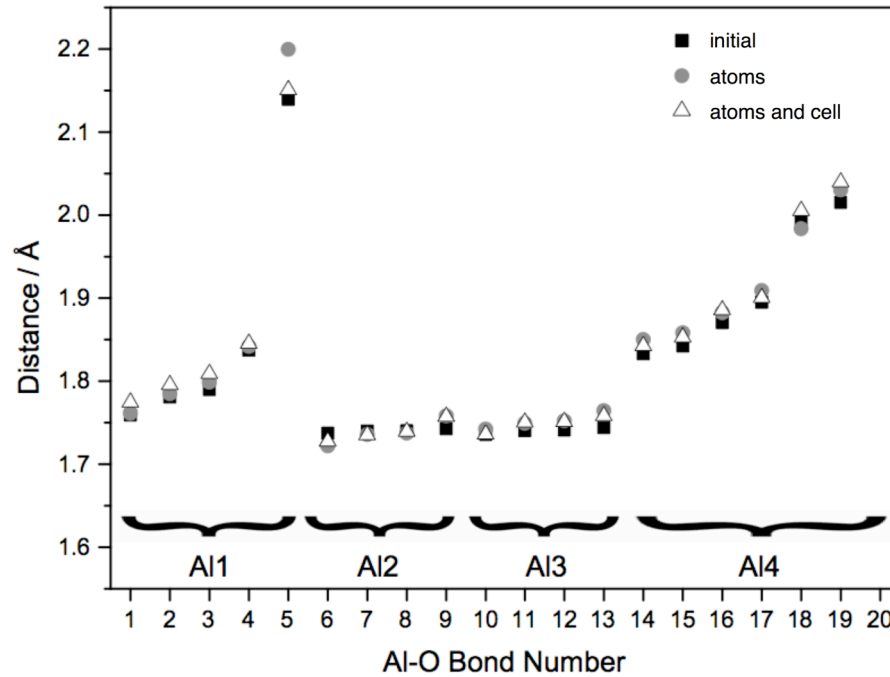
AIPO-14 *ipa*

Experimental				Calculated				Atoms and cell			
	δ_{iso} (ppm)	C_Q / MHz	η_Q		δ_{iso} (ppm)	C_Q / MHz	η_Q		δ_{iso} (ppm)	C_Q / MHz	η_Q
Al1	27	5.6	1.0	Al1	35.9	10.5	0.73	Al1	29.5	6.01	0.92
Al2	44	4.1	0.8	Al2	41.6	6.5	0.74	Al2	44.8	3.98	0.94
Al3	43	1.7	0.6	Al3	41.7	3.78	0.59	Al3	42.6	2.27	0.98
Al4	-1	2.6	0.7	Al4	6.3	1.98	0.85	Al4	1.4	2.42	0.56
P 1	-20.6			P 1	-17.5			P 1	-19.9		
P 2	-5.8			P 2	3.2			P 2	-1.1		
P 3	-24.3			P 3	-19.6			P 3	-22.3		
P 4	-20.1			P 4	-16.0			P 4	-17.0		

- Agreement not as good (^1H , template, water, motion....)
- But assignment is supported

NMR of AIPO-14

AIPO-14 *ipa*

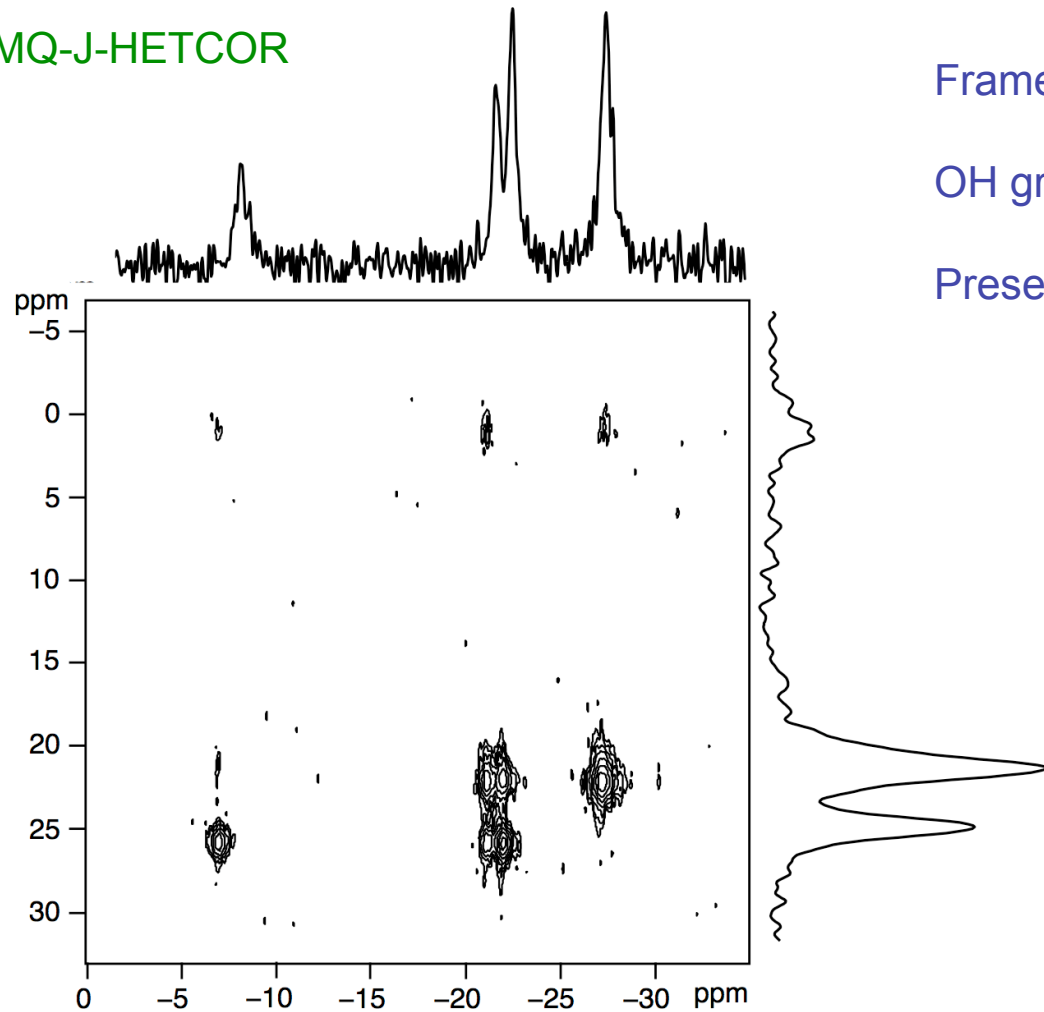


- Much smaller changes than for the calcined material
- NMR parameters remain extremely sensitive to these differences

NMR of AIPO-14

- For AIPO-14 *pip* there is no crystal structure

MQ-J-HETCOR



Framework connectivity is the same

OH groups attached at same Al species

Presence of water molecules

Conclusions

- MAS and MQMAS techniques to obtain high-resolution NMR spectra of microporous aluminophosphates
- Use of MQ-*J*-HETCOR experiments to probe through-bond correlation
- Suggested assignments supported by first-principles calculations
- Detection of microsecond timescale dynamics using STMAS offers a probe of host guest interactions