

Charles University

Faculty of Science

THEORETICAL INVESTIGATION INTO ZEOLITES VIA NMR: FROM DFT TO MACHINE LEARNING

Doctoral thesis

M. Sc. Chen Lei

Supervisor: Christopher James Heard, Ph.D.

Advisors: doc. RNDr. Filip Uhlík, Ph.D.

Junjie He, Ph.D.

Prague, 2025



Univerzita Karlova
Přírodovědecká fakulta

TEORETICKÉ ZKOUMÁNÍ ZEOLITŮ POMOCÍ NMR: OD DFT PO STROJOVÉ UČENÍ

Disertační práce

M. Sc. Chen Lei

Školitel: Christopher James Heard,
Ph.D.

Konzultanti: doc. RNDr. Filip Uhlík, Ph.D.
Junjie He, Ph.D.

Praha, 2025

Prohlášení

Dizertační práci jsem vypracovala na Přírodovědecké fakultě, Univerzity Karlovy.

Prohlašuji, že jsem závěrečnou práci zpracovala samostatně a že jsem uvedla všechny použité informační zdroje a literaturu. Tato práce ani její podstatná část nebyla předložena k získání jiného nebo stejného akademického titulu.

Declaration

I did my dissertation at the Faculty of Science, Charles University.

I declare that I have prepared the thesis independently and that I have listed all the information sources and literature used. Neither this thesis nor any substantial part of it has been submitted for another or the same academic degree.

Signed:

Date:

Acknowledgments

At this moment, I would like to express my deepest gratitude to my supervisor, Dr. Christopher James Heard, whose expertise, patience, and encouragement have been invaluable in finishing this thesis. I do not doubt that I could not have completed this work without his guidance. His insightful feedback and support helped shape this thesis into its current form, and his kindness and warmth helped me go through the challenging moments along the way.

I also wish to extend my heartfelt thanks to the late Professor Nachtigall, my previous supervisor, who gave me the opportunity to begin my studies and life in Prague and supervised my research. His vast knowledge and way of thinking about scientific questions influenced me deeply.

Additionally, I am sincerely grateful to Dr. Lukáš Grajciar, Dr. Federico Brivio, Dr. Andreas Erlebach, Dr. Carlos Bornes, Dr. Junjie He, and Dr. Filip Uhlík for their advice and guidance as nice colleagues, teachers, and friends. They helped me expand my knowledge, from fundamental theories to technique skills, and their suggestions and kindness helped refine my ideas and approach.

I would also like to thank all the members of our group for their kindness help and friendship. Thanks to Mingxiu Liu, Indranil Saha, Deborah Brako-Amofo, Daniel Willimetz, Tereza Benešová, Kristýna Pokorná, Jakub Szmitek, Denisa Nováková, and Richard Kendra for their willingness to discuss life and science as friends and colleagues. I also want to express my gratitude to my old friends, Mengting Jin, Mingxiu Liu, Dianwei Hou, and Shuo Li, who have accompanied me on this long journey and provided lots of help.

Thanks to the many colleagues at Charles University and collaborators from other institutes, too numerous to list, who helped me with various academic and life matters. I am also grateful to everyone who has contributed to the research in this thesis, directly or indirectly. Your support and encouragement have been greatly appreciated.

Finally, I am deeply grateful to my family for their unwavering support and understanding throughout this long journey.

Abstract

Solid-state nuclear magnetic resonance (ssNMR) spectroscopy is a highly valuable tool for experimentally characterizing zeolites, due to its high sensitivity and the detailed structural insight it provides from the spectra. However, interpreting ssNMR spectra is challenging, and accurately determining the structural features is often impractical, especially for the quadrupolar nuclei. Consequently, computational modelling of ssNMR spectra has become increasingly popular to complement experimental studies. Despite its usefulness, NMR simulations tend to be simplified to limited numbers of static calculations, and there is a lack of thorough studies under realistic conditions, taking into account factors such as temperature variations, dynamic evolution over time, appropriate Si/Al ratios to match experimental samples, and hydration effects.

This thesis focuses on the computational study of ^{27}Al and ^{23}Na NMR related to active acid sites in zeolites, emphasizing the need for *operando* modelling to understand NMR spectra. Two approaches are proposed for *operando* modelling of NMR properties based on density functional theory (DFT) and machine learning (ML) methods. The research contains three main parts.

The first part combined experimental ^{27}Al NMR spectroscopy with *ab initio* calculations to reveal the nature of the octahedral Lewis acid sites (LAS) in zeolites, which become kinetically and thermodynamically stable under wet conditions in the presence of multiple nearby Brønsted acid sites (BAS). The *operando* ^{27}Al NMR modelling established a connection between experimental spectral signals and structures with different Al coordination environments. This finding confirmed a feasible pathway, obtained from biased *ab initio* molecular dynamic (AIMD) calculations, for the formation of framework-associated octahedral LAS sites.

The second part highlighted the complexity of interpreting solid-state ^{27}Al NMR spectra due to the simplifying assumptions in computational models. A systematic evaluation of various models showed that *operando* modelling, which considers water loading, temperature, and charge-compensating cations, is essential for accurately predicting ^{27}Al chemical shifts. The research further demonstrated that the findings obtained from simplified models in simple zeolites, such as high-symmetry CHA, do not readily translate

to more complex zeolites like MOR, leading to potentially incorrect interpretations. Moreover, a simple yet robust relationship between ^{27}Al chemical shielding and two local structural parameters was obtained by using an ML regression method to interpret NMR properties.

The third part tackled the computational limitations of *ab initio* calculations by developing neural network potentials (NNPs) to dynamically sample broad configurational spaces in *operando* modelling of zeolites. By exploring various Al/Na arrangements and Si/Al ratios in sodium-form aluminosilicate, the study found that ^{23}Na NMR spectra of dehydrated high-silica CHA can be used to assess the distribution and pairing of Al atoms. Dynamic simulations revealed that neglecting thermal and dynamical contributions results in significant errors, underscoring the need for long-term simulations, such as those enabled by NNPs. Similar to ^{27}Al chemical shielding regression, a linear regression with seven structural descriptors was also obtained to predict ^{23}Na chemical shielding.

Overall, this work highlighted the importance of sophisticated modelling techniques in accurately characterizing active sites in zeolites and provided new insights into the structure-NMR relationship under experimental conditions.

Abstrakt

Solid-state nuclear magnetic resonance (ssNMR) je vysoce cenný nástroj pro experimentální charakterizaci zeolitů díky své vysoké citlivosti a podrobnému strukturálnímu náhledu, který poskytuje na základě spekter. Interpretace ssNMR spekter je však náročná a přesné určení strukturálních rysů je často nepraktické, zejména u kvadrupolárních jader. Z tohoto důvodu se stalo stále populárnějším využívání výpočetního modelování ssNMR spekter jako doplněk experimentálních studií. Navzdory své užitečnosti jsou simulace NMR často zjednodušovány na omezený počet statických výpočtů a chybí důkladné studie za realistických podmínek, které by zohledňovaly faktory jako jsou teplotní změny, dynamický vývoj v čase, vhodné poměry Si/Al odpovídající experimentálním vzorkům a hydratační efekty.

Tato disertační práce se zaměřila na výpočetní studii ^{27}Al a ^{23}Na NMR vztahující se k aktivním kyselým místům v zeolitech s důrazem na potřebu *operando* modelování pro pochopení NMR spekter. Jsou navrženy dva přístupy pro *operando* modelování NMR vlastností založené na metodách Teorie hustotního funkcionálu (DFT) a strojového učení (ML). Výzkum obsahuje tři hlavní části.

První část kombinovala experimentální ^{27}Al NMR spektroskopii s *ab initio* výpočty k odhalení povahy oktaedrických Lewisových kyselých míst (LAS) v zeolitech, které se stávají kineticky a termodynamicky stabilními ve vlhkých podmínkách za přítomnosti několika blízkých Brønstedových kyselých míst (BAS). *Operando* modelování ^{27}Al NMR vytvořilo spojení mezi signály experimentálních spekter a strukturami s různým Al koordinačním prostředím. Tento nález potvrdil možnou cestu, získanou z ovlivněných AIMD výpočtů, pro vznik oktaedrických LAS míst spojených s kostrou.

Druhá část zdůraznila složitost interpretace ^{27}Al NMR spekter kvůli zjednodušujícím předpokladům ve výpočetních modelech. Systematické zhodnocení různých modelů ukázalo, že *operando* modelování, které zohledňuje vodu, teplotu a kationty kompenzující náboj, je nezbytné pro přesnou předpověď ^{27}Al chemických posunů. Výzkum dále prokázal, že závěry získané ze zjednodušených modelů v jednoduchých zeolitech, jako je vysoce symetrický CHA, nejsou snadno přenositelné na složitější zeolity jako MOR, což může vést k nesprávným interpretacím. Kromě toho byla jednoduchá, ale robustní závislost mezi

chemickým stíněním ^{27}Al a dvěma lokálními strukturálními parametry získána pomocí regresní metody strojového učení pro interpretaci NMR vlastností.

Třetí část se zabývala výpočetními omezeními *ab initio* výpočtů vývojem potenciálů založené na neuronových sítích (NNP) pro dynamické vzorkování širokých konfiguračních prostorů v *operando* modelování zeolitů. Zkoumáním různých uspořádání Al/Na a poměrů Si/Al v aluminosilikátu ve formě sodíku studie zjistila, že ^{23}Na NMR spektra dehydratovaného vysokosilikátového CHA mohou být použita k hodnocení distribuce a párování Al atomů. Dynamické simulace odhalily, že opomíjení tepelných a dynamických příspěvků vede k významným chybám, což zdůrazňuje potřebu dlouhodobých simulací, které umožňují NNP. Podobně jako u regresní analýzy chemického stínění ^{27}Al byla získána lineární regrese se sedmi strukturálními deskriptory pro předpověď chemického stínění ^{23}Na .

Celkově tato práce zdůraznila význam sofistikovaných modelovacích technik pro přesnou charakterizaci aktivních míst v zeolitech a poskytla nové poznatky o vztahu mezi strukturou a NMR při experimentálních podmínkách.

Abbreviations

AIMD	<i>ab initio</i> molecular dynamic
Al(Oh)	Octahedral Aluminum
Al(Td)	Tetrahedral Aluminum
BAS	Brønsted acid sites
BO	Born-Oppenheimer
BOMD	Born-Oppenheimer Molecular Dynamics
CI-NEB	Climbing Image Nudged Elastic Band
DFT	Density functional theory
DFT-D	Dispersion-corrected Density functional theory
<i>d6r</i>	Double Six-ring
EFAL	Extra-framework Aluminum
EFG	Electric Field Gradients
FCC	Fluid Catalytic Cracking
GGA	Generalized Gradient Approximation
IZA	International Zeolite Association
LAS	Lewis Acid Sites
LDA	Local Density Approximation
MAS NMR	Magic Angle Spinning solid-state Nuclear Magnetic Resonance
MLPs	machine learning potentials
MD	Molecular Dynamic
NMR	Nuclear Magnetic Resonance
NNP	Neural Network Potentials

PAW	Projector-Augmented-Wave
PBE	Perdrew–Burke–Ernzerhof
PES	Potential Energy Surface
RT	Room Temperature
<i>s6r</i>	Single Six-ring
SUB	Secondary Building Units
ssNMR	Solid States Nuclear Magnetic Resonance
UC	Unit Cell
VASP	Vienna <i>Ab initio</i> Simulation Package
6MR	6-Member Ring
8MR	8-Member Ring

Contents

Prohlášení.....	II
Declaration.....	II
Acknowledgments.....	III
Abstract.....	IV
Abstrakt.....	VI
Abbreviations.....	VIII
Contents.....	X
Chapter 1 Introduction.....	1
1.1 Zeolites.....	1
1.1.1 Composition and structures of zeolites.....	2
1.1.2 Applications and Properties.....	3
1.1.3 Factors influencing structures and properties.....	6
1.1.4 Characterization of zeolites.....	8
1.1.5 Computational simulations in zeolites.....	11
1.2 Other similar porous materials.....	13
Chapter 2. Theories and Methodology.....	15
2.1. The Potential Energy Surface.....	15
2.2 Born-Oppenheimer approximation.....	16
2.3 Density functional theory (DFT).....	17
2.4 Semi-empirical dispersion-correction.....	19
2.5 Nudged elastic band method.....	20
2.6 Molecular dynamics.....	21
2.7 NMR calculations.....	22
2.8 Machine learning (ML).....	25
Chapter 3. Computational Details.....	28
3.1 Models.....	28
3.1.1 Zeolite chabazite (CHA).....	28
3.1.2 Zeolite mordenite (MOR).....	29
3.2 Methods and computational details.....	30
3.2.1 DFT static calculation.....	30
3.2.2 <i>Operando</i> simulation scheme (AIMD).....	31

3.2.3 NNP-based geometry optimization and MD	32
3.2.4 LASSO: ML analysis for structure- σ relationship	36
3.2.5 From calculated NMR to experimental results.....	36
3.2.6 Spectral simulations.....	39
Chapter 4. Reactive transformations in hydrated protonic zeolites	40
4.1 Motivation	40
4.2 Results	41
4.2.1 ^{27}Al MAS NMR spectra	41
4.2.2 Geometry optimization and the formation of the framework-associated $\text{Al}(\text{O}_\text{h})$	41
4.2.3 ^{27}Al NMR simulation.....	43
4.2.4 Generalization in MOR	45
4.3 Summary	48
Chapter 5. NMR characterization of Al-zeolites with DFT.....	49
5.1 Motivation	49
5.2 Results	49
5.2.1 Geometry optimization.....	49
5.2.2 Effect of the UC size and volume.....	54
5.2.3 Effects of the model complexity.....	58
5.2.4 Effects of dynamics on ^{27}Al chemical shift.....	62
5.2.5 MOR with more Al substitutions.....	66
5.2.6 Interpreting the structure – σ relationship	68
5.3 Summary	72
Chapter 6. ML-assisted simulations of zeolite NMR.....	74
6.1 Motivation	74
6.2 Results	74
6.2.1 Geometrical optimization and energies	74
6.2.2 ^{27}Al NMR	80
6.2.3 ^{23}Na NMR.....	82
6.2.4 Physical Interpretation of ^{23}Na chemical shielding	94
6.2.5 Dipolar coupling and recoupling	99
6.3 Summary	101
Chapter 7. Discussion	103

7.1 Complexity of models	103
7.2 Static vs. dynamic	106
7.3 Development of tools/methods: from <i>ab initio</i> to ML	109
Chapter 8. Conclusions	112
References	114
APPENDIX A	133
APPENDIX B	140
List of Publications	162

Chapter 1 Introduction

1.1 Zeolites

As a class of important inorganic crystalline porous materials, zeolites have now been widely used in chemical industries since they were first found in minerals in 1756 by Swedish chemist Axel F. Cronstedt. Their structure is similar to a sponge that can adsorb small molecules as gas and liquid but exclude large molecules¹⁻² without compromising the integrity of the framework. James W. McBain used "molecular sieve" to describe the ability of zeolites to separate molecules by size.³ Later (in 20th century), with the finding of more properties, such as ion-exchange, and hydrated/dehydrated reversibility, a wide scientific interest and development of zeolites happened.

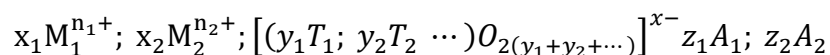
Thanks to the advancement of characterization techniques in modern times, the mystery of mechanisms behind the unique properties of zeolites have been uncovered. The introduction of X-ray crystallography allowed for determining zeolite structures, which suggested zeolites consist of anionic three-dimensional frameworks and the counterbalancing cations and water molecules in extra-framework space.⁴⁻⁵ This finding helped to explain some properties of zeolites, including the capacity for dehydrate/rehydrate, ion exchange, and molecular adsorption.

In 1862, de St. Claire-Deville synthesized levynite in the laboratory, marking the beginning of the development of man-made zeolites. Over the following decades, many analogs of natural zeolites were synthesized.⁶ The works of Richard M. Barrer greatly advanced the development of synthetic zeolites, having synthesized analcite (ANA),⁷⁻⁸ mordenite (MOR),⁹ and zeolite P (KFI).¹⁰⁻¹¹ To date, there are 256 framework types of natural and synthetic zeolites have been recorded in the Structure Commission of the International Zeolite Association (IZA-SC) database,¹² and this number is still increasing. The advancement of computational methods in material science has led to the theoretical prediction of millions of additional zeolite structures,¹³⁻¹⁸ which highlights the potential of this research area for designing new functional porous materials with particular applications.

1.1.1 Composition and structures of zeolites

Zeolites are defined as aluminosilicates with open three-dimensional framework structures composed of corner-sharing TO_4 tetrahedra, where T is Al or Si. Currently, high- or pure-silica (SiO_2) zeolites can also be synthesized with some framework types.¹⁹ The limits of the Si/Al ratio are 0.5 (bicchulite is the only one with $\text{Si/Al} < 1$) and infinite (pure-silica), but there is not a structure which can be synthesized in the whole composition range. Three classes of zeolites are defined: low Si/Al ratios (< 5), medium Si/Al ratios (5-10), and high Si/Al ratios (> 10).

The framework Al introduces negative charges, which need to be compensated by extra framework cations situated in the voids. In general, the composition can be described by the formula:



where the part in square brackets denotes the framework composition; M, compensating cations with charge n; T, elements in the tetrahedra, Si and Al; A, water or molecules in the channels and cavities; and x, y and z, the number of cations, T atoms, and water molecules, respectively.²⁰ Besides, the T site can be isomorphically substituted by other trivalent and tetravalent elements, such as Ge, B, Ga, Zn, P, etc., and the substitution of heteroatoms in the zeolite framework can tune the functions. Also, the charge-balancing cations are exchangeable and extensively used to modify the properties of zeolites, which can be H^+ , NH_4^+ , Na^+ , Co^{2+} and even some charged complex molecules.

To differentiate zeolites and zeolite-like materials from denser tectosilicates, a simple parameter, the framework density (FD), can be used as a criterion. FD is defined as the number of T-atoms per $1000 \text{ \AA}^3$, which correlates with pore volume but does not indicate the size of the pore openings. The FD of zeolites is less than other tectosilicates.²¹ This suggests that the porous structures of zeolites often feature significant surface area (up to $850 \text{ m}^2 \text{ g}^{-1}$) and micropore volumes (up to $0.35 \text{ cm}^3 \text{ g}^{-1}$), which are important characteristics for many applications, such as catalysis to offer more surface for active sites and more space for the reactions.

The zeolite framework types are assigned with three-capital-letter codes based on the name of the zeolite or synthetic type materials by IZA-SC.²² For instance, the code MOR is the natural mineral mordenite and CHA is chabazite. An ideal geometric model for each framework type has been reported by optimizing the structure under the assumption of a silica polymorph with the highest symmetry allowed by its topology.²³ The ideal model is often used to do the computational study.

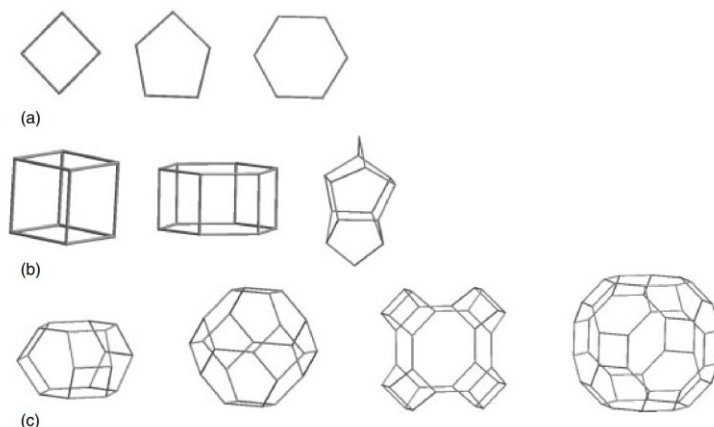


Figure 1.1 Secondary building units (SBUs) in zeolite structures are represented using single lines connecting the position of tetrahedral atom (T-atom). (a) rings; (b) double four-membered rings (D4Rs), double six-membered rings (D6Rs), and pentasil units; and (c) from left to right, cancrinite, sodalite, paulingite, and α -cages. Reproduced with permission.²⁴ Copyright 2010, John Wiley and Sons.

To unambiguously describe different frameworks, secondary building units (SBU) and composite building units (CBU) are defined theoretically as containing more primary building units (TO_4 tetrahedra) in one repeat topological building unit. The entire framework is made of SBU, like 4-, 6-, 8-member rings. Some units, such as double 6-ring, cancrinite cage, alpha cavity, and double crankshaft chain, appear in multiple framework structures and can be used as valuable tools for identifying relationships between framework types. The synergy between the heteroatom effect and zeolite framework types allows the “molecule sieves” to distinguish different types of molecules with a difference of less than 1 Å.

1.1.2 Applications and Properties

The porous structure and various heteroatoms of zeolites bring various unique physical and chemical characteristics, such as large surface areas, well-organized micropore channel systems, exchangeable cationic species, high chemical/thermal stability, and notable

catalytic properties. Thus zeolites have been used industrially in a variety of applications, such as catalysts, absorbents/desiccants, water treatment, molecule separation, and environmental uses. Examples include the first synthesized zeolites mordenite (MOR)⁹, zeolite A (LTA),²⁵⁻²⁶ zeolites X and Y(FAU).²⁷ The varying sizes of the cavities of the framework enable shape selectivity, allowing certain Ca- and Na- exchanged zeolites to selectively adsorb unbranched and branched hydrocarbons.²⁸⁻²⁹ The discovery of highly hydrothermal stable zeolites, e.g. faujasites (zeolite X and Y), started applications as optimal catalysts in petroleum refining,³⁰⁻³² and in fluid catalytic cracking (FCC) processes.³³⁻³⁴ Subsequently, the identification of more zeolites like ZSM-5, known for their high stability and shape-selectivity, expanded their applications in more petrochemical processes,³⁵ including olefin oligomerization,³⁶ methanol to gasoline(MTG) conversion,³⁷⁻³⁹ xylene isomerization,⁴⁰⁻⁴¹ and the conversion of ethylbenzene into xylene.⁴²

Nowadays, elements beyond just silicon and aluminum have been introduced as framework atoms in zeolite, enhancing the flexibility for tuning structural features such as pore size and framework types. This innovation has broadened the scope of applications to address future challenge in sustainable energy resources and environmental improvement. These applications include thermal energy storage, CO₂ capture and conversion, air-pollution remediation, water purification, biomass conversion, and fuel cells.⁴³⁻⁴⁶ Acid zeolites have been widely used over recent decades as catalysts to convert biomass feedstock into high-value biofuels.⁴⁷⁻⁴⁸

The acidity of zeolites is a crucial determinant of their catalytic properties, influenced by several factors including the number and types of acid sites, their strength, location, and accessibility. The acidic sites can be broadly classified into two types: Brønsted acid sites (BAS) and Lewis acid sites (LAS) (Figure 1.2). Brønsted acid sites are typically introduced by ion exchange of the extra-framework cations by H⁺ for the aluminosilicate framework, where Si⁴⁺ ions are substituted by Al³⁺ ions. The resulting species, bridging hydroxyl groups (SiOHAl), are the main source of Brønsted acidity and catalytic activity in zeolites. Lewis acid sites are formed through the introduction of framework heteroatoms, such as titanium, gallium, and tin, as well as the presence of extra-framework species. Extra-

framework aluminum (EFAL) species have been studied as a type of Lewis acid sites in zeolites. Numerous studies have shown that the presence of EFAL species, along with their synergy with Brønsted acid sites, are associated with increased catalytic activity.⁴⁹⁻⁵⁰

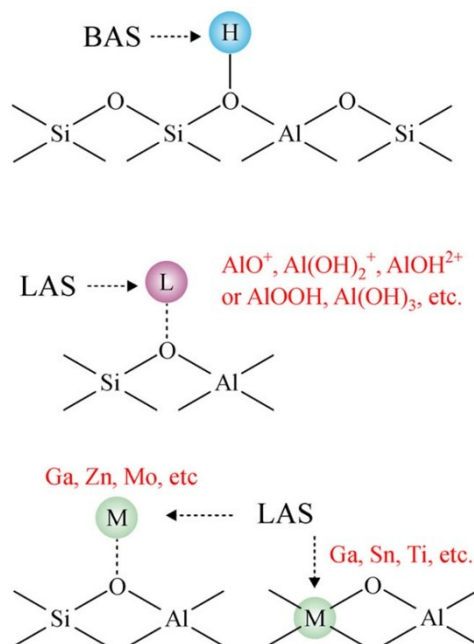


Figure 1.2 Brønsted acid sites (BAS) and Lewis acid sites (LAS) on zeolites. Reproduced with permission.⁵¹ Copyright 2020, Springer Nature.

The structure of Brønsted acid sites is clearly established, but the structures and compositions of Lewis acid sites remain less clearly defined, with several possibilities proposed. Typically, Brønsted has been linked to framework Al, and Lewis acidity has been associated with extra-framework Al species. However, recent studies have indicated that some framework aluminum species can reversibly transition from tetrahedral to octahedral coordination, thereby exhibiting Lewis acidity.⁵²⁻⁵³ In solid acids, the strength, type (Brønsted vs. Lewis), location, and accessibility of the active sites vary significantly depending on the Al distributions. These factors collectively influence the reactivity and selectivity observed during catalysis, making the level of Al substitution and its distribution crucial for determining catalytic activity.

1.1.3 Factors influencing structures and properties

Understanding and controlling the factors that influence the properties of zeolites is essential for tailoring their characteristics to meet specific application requirements. Advances in synthesis techniques, computational modelling, and characterization methods have enhanced our ability to design and utilize zeolites effectively. Below is an examination of the factors that impact the catalytic properties.

Framework types

The zeolite framework determines the main structure features including pore size, porosity, channel systems, and surface area. The pore size and porosity control the type and size of molecules that can be adsorbed or catalyzed and the accessibility of reactants to the active sites. The connectivity and dimensionality of the channels influence the diffusion of molecules and accessibility to active sites. The surface area dominates the availability of active sites for catalysis and the adsorption capacity.

Al substitutions

The Si/Al ratios and Al distributions in the framework significantly affect its acidity, selectivity, and stability/durability in applications.⁵⁴⁻⁵⁶ Higher Si/Al ratios result in more hydrophobic and thermally stable zeolites, while lower Si/Al ratios increase the density of acidic sites. This influence is not merely a single variable effect but results from the synergy among the Si/Al ratio, hydration, and specific Al distributions. The quantity of water within the zeolite channels is highly dependent on the concentration of heteroatoms and/or framework defects, as these show a significantly stronger affinity for water compared to the hydrophobic Si-O-Si bridges. Thus the high silica zeolites are attractive as catalysts because the low density of acidic sites can avoid too rapid deactivation.⁵⁶

The only rule about Al distribution so far obtained from experimental observation, Löwenstein's rule (Al atoms will not occupy neighboring T-sites) is not always respected in some systems, such as aluminosilicate glasses and metastable, disordered phases. The Al distribution is related to the crystallization process kinetically but not energetically

controlled.⁵⁷⁻⁵⁹ It is still a challenge to characterize the Al distribution and connect the structure with the properties.

Besides, the substitution of framework Si or Al with other elements (e.g., Fe, Ti, B, Ge) also can modify the catalytic properties and stability of the zeolite. Similar to Al, Ge substitution often reduces the hydrothermal stability due to the relatively labile nature of Ge–O bonds, which are particularly prone to hydrolysis in the presence of acidic solutions, liquid water, or even air moisture. However, this is a broad topic beyond the scope of this study.

Extra framework cations

The type and distribution of cations (e.g., Na⁺, K⁺, Ca²⁺, Co²⁺, H⁺, NH₄⁺) within the zeolite influence its ion exchange capacity, acidity, and overall reactivity.⁶⁰⁻⁶² The location of cations within the framework can affect the local electrostatic environment and the strength of interactions with adsorbates or reactants. Moreover, the locations of extra framework cations depend on the framework structure and electronic distribution, which partially reflects the framework structure and the heteroatom distribution. This provides a way to detect the Al distributions in zeolites, by combining the cation information with those of framework Al sites spectroscopically.⁶³⁻⁶⁴

Hydration condition

Natural zeolites are characterized as hydrated, and zeolites are exposed to ambient conditions during the synthesis and catalytic processes. In particular, the hydrophilicity increase due to the Al substitution highlights the importance of water loading effects. The removable water molecules in the pores can affect the selective entrance of guest species of suitable size, shape, and polarity.

As shown in Figure 1.3, water molecules can be adsorbed non-reactively or take part in hydrolysis of the framework. The presence of water on zeolites affects their hydrothermal stability,⁶⁵⁻⁶⁶ preferred Al distributions,⁶⁷ dealumination,⁶⁸⁻⁷⁰ desilication,⁷¹ and other related processes.⁷² The water loading lowers the energy barriers of the hydrolysis, as demonstrated by many computational studies. This effect has two aspects. The positive one

is allowing the formation of new zeolites, tuning catalytic or adsorption characteristics by forming defects, such as silanol nests. The negative one is reducing their resistance to degradation at elevated temperatures, which may limit their industrial applications in humid or aqueous environments. Besides, the interaction between water molecules and active sites (BAS/LAS) leads to catalytic behavior that differs from that observed without water loading.⁷³⁻⁷⁴

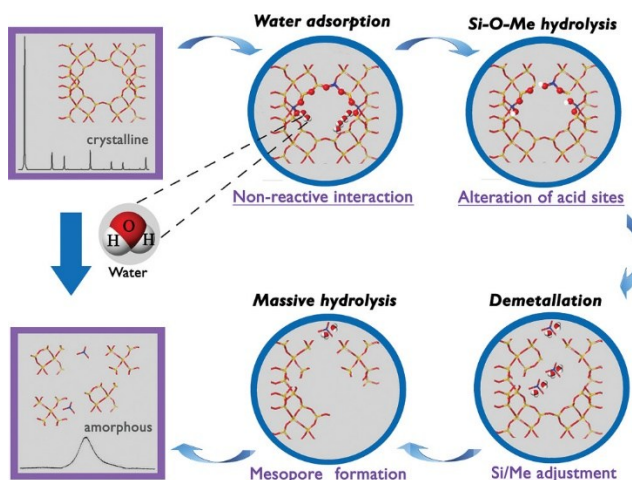


Figure 1.3 The effect of the water loading on the stability of zeolite with the heteroatoms including Al, Ge, Sn, and Ti. The hydrolysis for the increasing extent of the framework degradation starts from nonreactive water adsorption up to the amorphization. Reproduced with permission.⁶⁵ Copyright 2020, John Wiley and Sons.

1.1.4 Characterization of zeolites

In aluminosilicate zeolite, the distribution of Al atoms is related to the mechanism and selectivity of catalytic reactions.⁷⁵⁻⁷⁷ However, a detailed understanding of aluminium distributions and its local environments in zeolites remains one of the major challenges in zeolite science today.⁷⁸⁻⁸¹ In general, neither the distribution of individual Al atoms among crystallographically distinct framework sites nor the relative positions of two Al atoms can be directly determined through experiments. The crystallographic technique, X-ray diffraction (XRD) is a common measurement to get structural information. Although the quantitative determination of framework Al can be achieved by detecting the increase in lattice parameters in Al-rich zeolites, due to the pattern changes from the longer Al-O bonds,⁸² it is challenging to determine all the atomic positions within the crystal structure of zeolites, especially in Si-rich variants. This difficulty arises from three main factors: 1) the unavailability of large single crystals, 2) the similar scattering factors of silicon and

aluminum, making them difficult to distinguish, and 3) the presence of large unit cells and the enormous number of possible ways in which the framework tetrahedra can be linked.

The solid-state nuclear magnetic resonance (ssNMR)⁸³⁻⁸⁴ is a promising technique to deliver critical information about zeolite structure⁸⁵ and aluminium distribution.⁸⁶⁻⁹⁰ Nowadays, there are many ssNMR techniques used in zeolites to improve the resolution of the spectra, such as magic angle spinning (MAS) NMR, cross-polarization (CP) NMR, multiple quantum magic angle spinning (MQMAS) NMR, heteronuclear multiple quantum correlation (HMQC) NMR, etc. Furthermore, computational simulations are introduced to connect the NMR spectra with the exact geometrical structure, which improves the understanding of the spectra. Among these techniques, NMR spectra of both framework atoms, ²⁷Al, ²⁹Si, ¹⁷O, and extra-framework atoms, ²³Na and ¹H, etc., are common to investigate the Al coordination and distribution related to acid properties⁹¹⁻⁹³ (Table 1.1).

Table 1.1 some basic NMR properties of relevant nuclei in zeolites.⁹³

	Description	Chemical Shift Range (ppm)
²⁷ Al (<i>I</i> = 5/2)	Probes aluminum coordination in the zeolite framework.	~50–80 (AlO ₄ , framework Al) ~0–40 (AlO ₅ , AlO ₆ , extra-framework Al)
²⁹ Si (<i>I</i> = 5/2)	Identifies framework connectivity and Si/Al substitution.	-80 to -120 (Si(nAl), n=0–4) ^a
²³ Na (<i>I</i> = 3/2)	Studies Na ⁺ mobility and their interaction with the framework.	Highly variable depending on environment.
¹ H (<i>I</i> = 1/2)	Characterizes hydroxyl groups and Brønsted acidity.	~3–5 (Brønsted acid sites) ~0–3 (Silanol, aluminol)

- a. Si(nAl) represents a SiO₄ tetrahedron bonded to n AlO₄ tetrahedra through shared oxygen atoms within the zeolite framework.

In aluminosilicate zeolites, ²⁹Si NMR has been used to identify variations in the amount of neighbouring Al atoms, which cause different ²⁹Si chemical shifts. However, defects such as SiOH groups can produce ²⁹Si resonances in the same region as Si atoms surrounded by Al atoms, complicating the identification of Al pairs.⁹⁴⁻⁹⁵ The ²⁷Al solid-state NMR is routinely used to directly detect Al sites,^{57, 96} the coordination of Al species (4-, 5- or 6-coordinated), and to provide insight into the decomposition of the framework under reactive or hydrolytic stress by tracing the formation of extra-framework LAS sites, and

extended framework Al species.⁹⁷⁻¹⁰⁰ Moreover, ^{23}Na NMR can also provide information about the Na and Al siting on dehydrated zeolites, such as CHA¹⁰¹ and FER.¹⁰² For example, 2D ^{23}Na - ^{27}Al D-HMQC spectra have been shown to allow an increase in the resolution of ^{27}Al dimension, enabling the separation of Al species in MOR into three groups that overlap in 1D ^{27}Al experiments.¹⁰³ Some examples of the Al distribution characterization with ^{27}Al and ^{23}Na NMR are shown in Figure 1.4. These studies have combined experimental NMR spectra with computational calculations to correlate the NMR signals with specific structural characteristics.

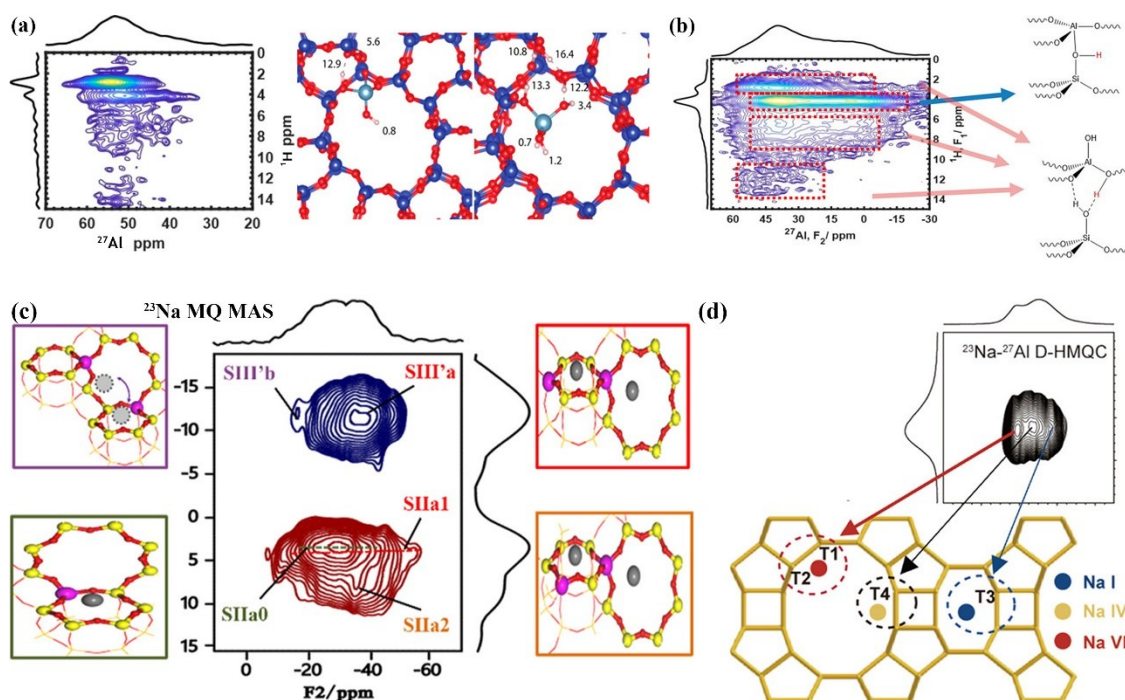


Figure 1.4 Examples of applying NMR spectra to characterizing Al information in zeolites. (a) $^{27}\text{Al}\{^1\text{H}\}$ HMQC NMR spectra for HZSM-5 to detect different types of tetrahedral aluminum. Reprinted (adapted) with permission.⁹⁹ Copyright 2020, American Chemical Society. (b) $^{27}\text{Al}\{^1\text{H}\}$ HMQC NMR spectra for dehydrated HZSM-5 to identify distribution of Al species. Reproduced with permission.¹⁰⁰ Copyright 2021, American Chemical Society. (c) Identify the Al distribution by ^{23}Na MQ MAS NMR for dehydrated Na-SSZ-13 zeolites. Reproduced with permission.¹⁰¹ Copyright 2018, American Chemical Society. (d) ^{23}Na - ^{27}Al D-HMQC spectra for MOR zeolite to improve the ^{27}Al MAS NMR spectra. Reproduced with permission.¹⁰³ Copyright 2022, American Chemical Society.

However, their NMR calculations mostly rely on static calculations and simple models without fitting the real experimental conditions, such as proper Si/Al ratios, hydration, and temperatures. NMR spectra are typically recorded over a timescale of μs -s at room temperature.¹⁰⁴ Therefore, static and short MD calculations significantly simplify real NMR measurements. *Operando* NMR modelling¹⁰⁵ is computationally demanding to agree

with the real NMR spectra. Temperature effects and vibrational averaging of chemical shifts have been studied in organic molecules and molecular crystals, showing good agreement with experimental data.¹⁰⁶⁻¹⁰⁹ Consequently, in the *operando* NMR calculation¹⁰⁵ for zeolite, the models must closely match the experimental composition, including the Si/Al ratio, extra-framework cations, and hydration level. Except for some works from van Speybroeck et al.,¹¹⁰ *operando* modelling has not been performed for ²⁷Al NMR in zeolites. In this thesis, we aim to develop approaches to reproduce the experimental NMR properties fitting the operating conditions, and to investigate the effect of factors influencing the structure and properties of zeolites.

1.1.5 Computational simulations in zeolites

Computational chemistry plays a vital role in NMR characterization to connect the specific spectra with structural features. The generation of fundamental knowledge at the atomic level is key. Over the past decades, theoretical methods have been applied in zeolites research, including molecular modelling of framework structures, prediction of physical and chemical properties, evaluation of stability under varying temperatures and pressures to identify new structures, analysis of adsorption and diffusion of sorbed molecules, computational spectroscopy, and exploration of reaction pathways in catalytic reactions.¹¹¹ These are all crucial to support the *operando* modelling of NMR spectra because NMR are sensitive to the environment around the nuclei of interest, which are not only related to the static structures but also influenced by dynamic behaviours of the structures at different temperatures, such as vibrations, cation migrations, and cation solvation with the presence of water.

The basic contribution of using computational methods is predicting properties and explaining experimental results. The determination of structure is the foundation of further property studies. The static simulation technique, lattice energy minimization approach, has been used to predict the structure and relative stabilities of zeolites. The minimum energy structure is obtained by adjusting atomic positions (constant volume) or both atomic positions and unit cell parameters to eliminate lattice strain (constant pressure). This process yields stable framework structures, cation positions in the cavity, and preferable locations for adsorbed molecules. Based on the stable structures, some observable

properties can be simulated to explain the experimental measurements, such as the XRD patterns, IR spectra, and NMR spectra. This approach offers a better understanding of the experimental results. Recently, *ab initio* calculations such as those that use the DFT method, are the most widely used methods.

Molecular dynamics (MD) simulations are powerful for obtaining information on time-dependent properties of molecular or atomic motion in zeolites. It is used to obtain thermodynamic quantities and detailed dynamical information on sorption and diffusion processes in zeolite systems, such as understanding water-zeolite interaction,¹¹² hydrolysis processes and mechanisms.^{67, 71, 105} Computational studies have shown that NMR parameters calculated using MD simulations align well with experimental results.¹⁰⁶⁻¹¹⁰ However, the huge amount of computer time and memory requirements limits the application of first-principles methods in the study of zeolites, especially for large and complicated systems. The atomistic simulations of zeolite behaviors considering the effects of temperatures and pressures often need a trade-off between accuracy and computational cost: *ab initio* simulations on simple structure models and short timescales or less accurate force field methods with more realistic structure models and longer timescales.¹¹³⁻¹¹⁷ Fortunately, the rapid development of machine learning (ML) methods has opened promising prospects for large-scale simulations that achieve near *ab initio* quality at lower cost, provided they are trained on large, high-quality *ab initio* datasets (Figure 1.5). While constructing such training datasets is costly, the process is adaptable to different materials. The machine learning potentials (MLPs), an advanced form of force fields that interpolate the potential energy surface at the *ab initio* level, have been used in zeolite simulations to predict structures, stabilities, morphology, and acidity, as well as to model catalytic reactions.¹¹⁸⁻¹²¹ These potentials effectively describe both reactive and nonreactive processes in zeolites, including phase transformation,¹²² cation migration,¹²³ water diffusion¹²⁴ and the diffusion of encapsulated metal clusters.¹²⁵

Except for energy-based calculations, ML offers a way to accelerate property prediction with impressive accuracy. Properties of zeolites have been predicted with the regression of geometric descriptors such as the mechanical¹²⁶⁻¹²⁹ and thermal¹³⁰ properties. Meanwhile, the NMR shifts, as a characteristic reflecting the structural information, can be predicted

with atomic position descriptors ML method in glasses¹³¹ and molecular solids.¹³² NMR isotropic shifts of ^{27}Al and ^{23}Na were proved empirically linearly correlating with structural descriptors. Therefore, the double-ML approach, which combines MLPs and ML regression methods, is promising for rapidly and accurately predicting *operando* NMR spectra of zeolites.

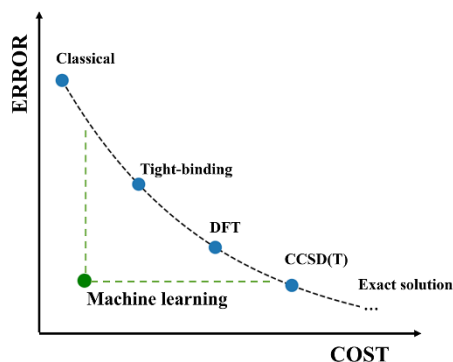


Figure 1.5 The comparison of different methods in computational costs and errors for larger and more complex molecules and materials. Here, the classical method refers to the classical force fields method that disregards quantum mechanics effects.

1.2 Other similar porous materials

There are many porous materials similar to zeolites that have been developed for their functions in catalysis, molecular/heavy metals adsorption, molecular separation, and gas storage etc. Metal-organic frameworks (MOFs) are a class of porous materials with tunable constituents, pore structures, and properties, consisting of uniformly expanded metal-ligand coordination moieties.¹³³ Although MOFs cannot meet the industrial requirements of high stability, long lifetime, and moderate production cost as zeolites yet, higher available pore volume, larger specific surface area, and excellent tailorability determine their promising status in many areas. Interestingly, their porous metal-ligand moieties can be an ideal porous and functional template for the synthesis of zeolite analogues due to their tunable sizes and controllable redox metal species.¹³⁴⁻¹³⁵ Moreover, the flexibility of the organic ligands linking the metal nodes and controlling the distance/distribution of the spin centers (metal atoms, such as Cu, Co, and Fe) leads to their unique magnetic properties, which can be used as magnets,¹³⁶ and catalysts.¹³⁷⁻¹³⁸

Apart from MOFs, many porous analogues of zeolites have attracted significant research interest. Here, only a few types are highlighted as examples. Metal-organic zeolite (MOZs)

are a typical group of coordination polymers that combine the topological and structural advantages of inorganic zeolites and show potential in many applications such as gas adsorption/separation, catalysis, luminescence, and chemical sensing.¹³⁹ Zeolite-like metal-organic frameworks (ZMOFs), a subset of MOFs, exhibit the same topologies as inorganic zeolites and high stability and performance.¹⁴⁰ Additionally, hydrogen bonding frameworks (HOFs), which are porous crystalline materials constructed from organic moieties through hydrogen bonding, can be applied for gas separation.¹⁴¹ These materials highlight the versatility and innovation in the design of zeolite-inspired frameworks.

Chapter 2. Theories and Methodology

2.1. The Potential Energy Surface

The potential energy surface (PES) for a many-body system describes the energy as a function of the positions of the atoms or nuclei. It ideally contains all essential information, including the stable and metastable structures, the atomic forces that drive dynamics at finite temperatures, the transition states and energy barriers that control reactions and structural transitions, as well as the atomic vibrations. The energy function for a system of N components with a general expression $E = E(\mathbf{R}_{3N})$, where the energy E is a continuous function of the coordinate vector $\mathbf{R}$, which is a $3N$ -dimensional vector if x , y , and z components for each of the N atoms are considered in the Cartesian coordinate basis. Each point on the $3N$ dimensional hypersurface PES presents a configuration and the special points correspond to various features (Figure 2.1). The points with zero gradient are stationary. Among the stationary points, the minima (the local minimum) reflect stable geometries (or the possible isomers) of the system, the saddle points represent transition states between the minima, and higher order (greater than one) saddle points can be ignored by the system because they tend to be generally insignificant.¹⁴² The lowest energy point in the local minima is the global minimum which presents the most stable state under a certain condition. The paths that interconvert two minima across the landscape traversing the lowest possible saddle point (minimum energy path, MEP) suggest the mechanism of chemical reactions.

The PES itself cannot be observed but can be obtained by a wide array of methods in computational chemistry. A task of computational chemistry is finding and characterizing stationary points by geometry optimization or energy minimization. These processes provide crucial insights into the stability, reactivity, and mechanisms of chemical systems.¹⁴³ For example, each electronic state of a system corresponds to a distinct PES, and the separation between these surfaces can predict properties, such as NMR shielding and dipole moments, which depend on the response of the energy to applied electric and magnetic fields. Thus, the structure, properties, reactivity, and spectra of a system can be effectively interpreted through potential energy surfaces.

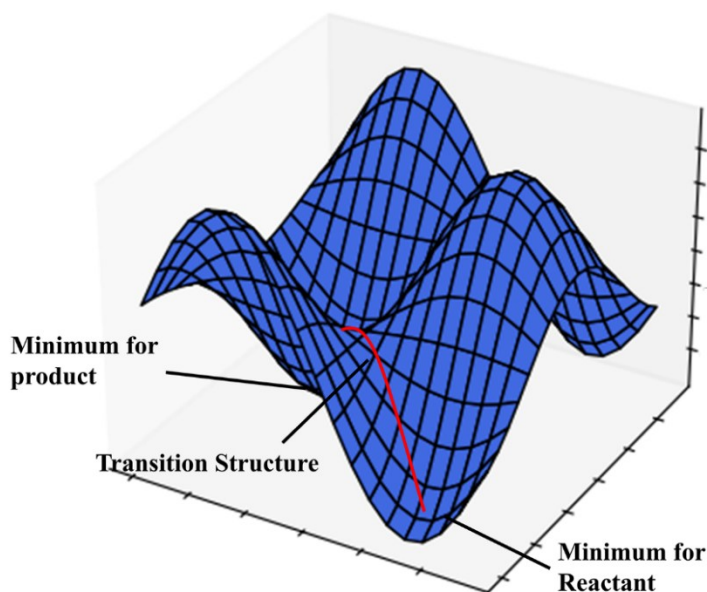


Figure 2.1 A model potential energy surface showing minima, transition states, and reaction paths.

However, it is difficult to find a minimum of the many variables of energy function for a real-life material. An analytic solution is impossible. Optimization often begins with calculating an initial energy and gradients relative to the atomic positions. Then, the atoms are iteratively moved towards coordinates with lower energy until the convergence is achieved. Various methods are available for finding the minimum, with their general differences lying in the strategies they employ to approach the minimum energy configuration.¹⁴⁴ The conjugate gradient (CG)¹⁴⁵ and Broyden-Fletcher-Goldfarb-Shanno (BFGS) methods are two popular methods. CG is a first-order method to select the appropriate descent direction, relying on gradient information based on the previous step to search for an energy minimum. BFGS method is a second-order method using the Hessian (a square matrix of second-order partial derivatives of the energy function) in multivariate optimization to direct the search. Both methods adaptively adjust the direction based on previously taken steps and require relatively modest computational resources, especially in the limited-memory version of BFGS.

2.2 Born-Oppenheimer approximation

Energy calculation is important in computational chemistry. The energetics of a system can be described by solving the Schrödinger equation, $\hat{H}\Psi = E\Psi$, where, $\hat{H}$ is the Hamilton operator representing the total energy, E is the energy of the system, and Ψ is a

wavefunction that contains all information about the physical properties of the system. Unfortunately, with the exception of a few simple cases, there is no strategy to solve the Schrödinger equation exactly for atomic and molecular systems. Therefore, numerical methods are used instead of solving the equation analytically.

To simplify the problem of solving the Schrödinger equation, the Born-Oppenheimer approximation of separating electronic and nuclear was proposed by Max Born and J. Robert Oppenheimer in 1927.¹⁴⁶ The nuclei can be approximated as stationary and the electrons move within their potential field, owing to the fact that nuclei are much heavier than electrons (even the lightest nucleus ^1H , is about 1800 times more massive than an electron) and move at significantly slower speeds. The nuclei move on a PES obtained by solving the electronic problem. But it is still impossible to solve this many-body problem with only electronic information.

2.3 Density functional theory (DFT)

For crystalline systems, the density functional theory (DFT) is used the most widely to predict the structural, chemical, and physical properties because of the practical balance between computational cost and accuracy for medium and large systems. Contrary to *ab initio* methods such as Hartree-Fock or post-Hartree-Fock solving the Schrödinger equation to find the many-electron wave function of the system, DFT solves instead a different set of equations that relate the total energy of the system with the electron density $\rho(\mathbf{r})$. One of the attractive features of the DFT method is that the electron density can be directly and experimentally measured (e.g., through X-ray diffraction). This makes it easier to understand than the concept of wave function. Moreover, electron density is only a function of position defined as the probability of locating an electron within a volume element. Thus, it only depends on the spatial coordinate $\mathbf{r}$, which reduces the dimensionality of an N-electron system from 3N (or 4N for spin polarized system) to 3 (or 4). This makes it much easier to treat mathematically.

The theoretical foundations of the DFT method were provided by the work of Hohenberg, Kohn and Sham,¹⁴⁷⁻¹⁴⁸ who demonstrated that the properties of a system can be determined by a functional of the electron density $\rho(\mathbf{r})$. The total energy of the system can be decomposed into the kinetic energy of the electrons and the potential energy of nucleus-

electron and electron-electron interactions, expression for the total energy of the system can be written as a sum of four terms:

$$E = T_k + \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + J[\rho] + E_{xc}[\rho]$$

$$\rho(\mathbf{r}) = N \int \dots \int |\Psi(\mathbf{X}_1, \mathbf{X}_2, \dots, \mathbf{X}_N)|^2 ds_1 d\mathbf{X}_2 \dots d\mathbf{X}_N$$

where T_k is the kinetic energy of the electrons, the second term accounts for the interactions between the nuclei and the electrons, and $J[\rho]$ denotes the term for the static Coulombic self-interaction of the electron cloud. These three terms can be directly calculated using fundamental physical expressions. The exchange-correlation term, E_{xc} , accounts for effects not included in the other terms that cannot be derived directly from fundamental expressions. Specifically, the repulsion between electrons caused by the correlation of their motion, as well as the repulsion of the electrons with the same spin due to the Pauli Exclusion Principle. The xc subscript represents these two contributions: exchange and correlation.

Exchange-correlation functional

In DFT calculation, many different exchange-correlation functionals have been defined because no general analytic formulation of E_{xc} . The most simple and least accurate methods depend only on the value of the electron density at the given spatial position and are known as Local Density Approximation (LDA).¹⁴⁹ It can be written as:

$$E_{xc}^{LDA}[\rho] = \int \rho(\mathbf{r})(\varepsilon_x(\rho(\mathbf{r})) + \varepsilon_c(\rho(\mathbf{r})))d\mathbf{r},$$

where, $\varepsilon_x(\rho(\mathbf{r}))$ and $\varepsilon_c(\rho(\mathbf{r}))$ are the exchange and correlation energies per particle of a uniform electron gas of density $\rho(\mathbf{r})$. The idea of LDA is to divide a multi-electron system into an infinite number of volumetric microelements, assuming that exchange-correlation energy of each microelement is identical to that of a uniform electron gas with the density $\rho(\mathbf{r})$ at a given point. A better solution is the Generalized Gradient Approximation (GGA), which involves both the electron density at the given point and its gradient (the first derivative of the density $\nabla\rho(\mathbf{r})$). This improves the accuracy of the method but slightly increases the expense of computational effort. The Perdew-Berke-Ernzerhof (PBE)

functional¹⁵⁰ is a commonly used example of this type and is a standard functional for the treatment of bulk systems. The GGA functional can be written as:

$$E_{xc}^{GGA}[\rho] = \int f(\rho(\mathbf{r}), \nabla\rho(\mathbf{r}))d\mathbf{r}.$$

Furthermore, meta-GGA functionals improve the computational accuracy further by adding the second derivative of the density, such as the strongly constrained and appropriately normed semi-local density functional (SCAN).¹⁵¹ Another approach to improve the E_{xc} functional is hybrid functionals, which incorporate the exact Hartree-Fock exchange energy into the approximated DFT exchange-correlation energy. While this improves accuracy, it also increases the computational cost significantly. The DFT calculation of zeolites is generally performed at GGA level.

2.4 Semi-empirical dispersion-correction

One shortcoming of DFT methods is the poor description of dispersion interactions. When van der Waals interactions are of interest, one needs to extend DFT to account for the dispersion interactions. Grimme and coworkers devised a simple and computationally inexpensive extension dubbed DFT-D, with currently various parametrization sets available in many DFT codes: D2, D3 and D4.¹⁵²⁻¹⁵⁴ This is one of the most successfully and widely used methods, in which the total energy can be written as:

$$E = E^{DFT} + E^{disp}$$

where E^{DFT} is the energy of DFT calculations, E^{disp} is the empirical dispersion correction term written as a general form:

$$E^{disp} = -\frac{1}{2} \sum_{AB, A \neq B} \sum_{n=6,8,10,\dots} S_n \frac{C_n^{AB}}{R_{AB}^n} f_{damp}(R_{AB})$$

where C_n^{AB} is the coefficient of the nth-order dispersion for the AB pair, R_{AB} is the distance between atom A and B, S_n denotes scaling factors for the individual multipolar contributions, and f_{damp} is called the damping function. The damping function is used to determine the short-range behavior of the dispersion correction and to avoid near-singularities for small R_{AB} and double-counting effects of electron correlation at intermediate distances double-counting effects of electron correlation at intermediate

distance. The Becke-Johnson (BJ) damping used in the DFT-D3 method adopted in this study is¹⁵⁵

$$E_{disp}^{D3(BJ)} = -\frac{1}{2} \sum_{A \neq B} s_6 \frac{C_6^{AB}}{R_{AB}^6 + [f(R_{AB}^0)]^6} + s_8 \frac{C_8^{AB}}{R_{AB}^8 + [f(R_{AB}^0)]^8}$$

with

$$f(R_{AB}^0) = a_1 R_{AB}^0 + a_2$$

where, a_1 and a_2 are free fit parameters introduced by BJ, and $R_{AB}^0 = \sqrt{\frac{C_8^{AB}}{C_6^{AB}}}$.

2.5 Nudged elastic band method

The Nudged Elastic Band (NEB) method¹⁵⁶ is a computational approach to identify transition paths and their associated energy barriers between specified initial and final states. Instead of calculating the time-consuming Hessian, a series of “images” cut from the pathway leading from reactant to product are optimized. Each image seeks the lowest possible energy while preserving equal spacing with its neighboring images. A spring force between images along the band is used to constrain the optimization. The optimization process converts to the minimization of a target function:¹⁴²

$$T = \sum_{i=1}^n E_i + \sum_{i=1}^{n-1} \frac{1}{2} k (X_{i+1} - X_i)^2$$

where X_i denotes the coordinate of each image, the first term E_i is the energy of each single image, and the second term is used to connect the neighboring images with the spring force. This approach keeps images evenly spaced and true forces perpendicular to the tangent to relax the path toward the MEP. The climbing image NEB(CI-NEB)¹⁵⁷ is a small modification to the NEB method, in which a more accurate transition state is determined by defining a “climbing” step. The highest energy image, which is the closest to the transition state, is driven uphill in energy along the path direction while minimizing energy in all other directions. The climbing image does not feel the spring forces along the band. In this way, the computational cost remains nearly unchanged despite the additional climbing steps, but it provides a more precise location of the transition state.

2.6 Molecular dynamics

Unlike static calculations of stationary points on the PES, molecular dynamics (MD) enables the study of particle motion. The evolution of the system over time is determined by solving Newton's equation of motion:

$$F = ma$$

where F is the force acting on a particular atom, m represents its mass and a is its acceleration. Once the position and velocities of each atom are known, the state of the system can be calculated, and the calculation of new positions and velocities is allowed. By repeating this procedure, a trajectory of atomic motions is generated. Various numerical algorithms, such as the Verlet algorithm, the leap-frog algorithm, and the Velocity Verlet algorithm, are used to solve Newton's equations by integration method. The Verlet algorithm is one of the common methods used by the Vienna *Ab initio* Simulation Package (VASP) software.¹⁵⁸⁻¹⁶⁰ This method uses positions and accelerations at time t and the positions from time $t - \Delta t$ to calculate new positions at time $t + \Delta t$. This algorithm is a two-step method because it estimates $r(t + \Delta t)$ from the current position $r(t)$ and the previous position $r(t - \Delta t)$. Therefore, initial positions $r(0)$ and velocities $v(0)$ are not sufficient to begin a calculation, and a backward Euler method must be done at $t = 0$ to get $r(-\Delta t)$.

$$r(t + \Delta t) = r(t) + v(t)\Delta t + \frac{1}{2}a(t)\Delta t^2,$$

$$r(t - \Delta t) = \frac{1}{2}a(t)\Delta t^2 - v(t)\Delta t + r(t),$$

$$r(t + \Delta t) = a(t)\Delta t^2 - r(t - \Delta t)\Delta t + 2r(t),$$

where r represents the spatial coordinates of the given atom, v and a stand for its velocity and acceleration. To observe the phenomenon of interest, the time scale of the trajectory needs to be long enough. For instance, the duration of a diffusion simulation should typically be on the order of nanoseconds. At the same time, the time step must be sufficiently small to accurately capture the vibrational motions of the atoms.

Describing and approximating the interatomic interactions in practice is the core of any molecular dynamics scheme. MD simulations can be broadly classified into three categories: classical MD, *ab initio* molecular dynamics (AIMD), and machine learning

(ML)-based molecular dynamics. In AIMD with BO approximation, the basic idea is to compute the force on the nuclei by treating electrons with quantum mechanism and the nuclei classically. The force is written as,

$$F = -\frac{dE}{dr} = \frac{md^2r}{dt^2},$$

where E is calculated from the electronic structure of the system. DFT is a typical method to compute the forces on atoms. In this case, the Kohn-Sham wave function needs to converge for the calculation of the corresponding forces on atoms. This is accurate for studying systems with complex electronic properties (e.g., chemical reactions). But the expensive computation limits the size of the system (hundreds of atoms) and timescales (picoseconds to nanoseconds).

In ML-based MD, the concept is the same but the force on the atom and the interaction are calculated by a trained model, such as neural network potentials (NNP). The model needs to be trained first on data from high-quality quantum mechanical calculations or classical MD simulations. Once trained, the ML model predicts forces and potential energies with the same accuracy as the training data but much faster, which are then used in molecular dynamics simulations. It is particularly useful for studying systems where detailed electronic interactions are important, while still being able to handle larger systems and longer timescales than AIMD alone.

2.7 NMR calculations

DFT calculations can establish crucial connections between structural models and experimental NMR data, allowing the full potential of NMR spectroscopy to be effectively utilized.¹⁶¹ Previous simulations used the approximation of the infinite periodic solid as a cluster with the nucleus of interest at the center because of the expensive cost of the *ab initio* methods. However, this is not always sufficient for complete spectral assignment. Recently, Pickard and Mauri¹⁶² introduced a plane wave pseudopotential method for calculating NMR parameters with using periodic models, exploiting the high translational symmetry of solids. The gauge including projector-augmented wave (GIPAW) approach,¹⁶³ enabled the calculation of NMR tensors in extended solid systems with all-electron accuracy based on DFT, a plane-wave basis set, pseudopotentials, and the

projector-augmented wave (PAW) approach. This enhances computational efficiency significantly, enabling the simulation of more complex systems within reasonable timescales.

Magnetic Shielding

The nuclear Hamiltonians are the key to describe NMR. When the nucleus interacts with an externally applied field $\mathbf{B}_{\text{ext}}$, the Zeeman interaction between the magnetic field and a set of spin $1/2$ nuclei K is given by:

$$H = -\sum_K \gamma_K \mathbf{I}_K (1 - \vec{\sigma}_K) \mathbf{B}_{\text{ext}} ,$$

where $\hbar \mathbf{I}_K$ is the spin angular momentum and γ_K is the gyromagnetic ratio of nucleus K . The first term is the interaction of the bare nucleus with the applied field $\mathbf{B}_{\text{ext}}$, while the second accounts for the response of the electrons to the field. The absolute magnetic shielding tensor $\vec{\sigma}_K$ reflects the effect of electron around the nucleus, which relates the induced field to the applied field:

$$\mathbf{B}_{\text{in}}(\mathbf{R}_K) = -\vec{\sigma}_K \mathbf{B}_{\text{ext}}.$$

In a diamagnet, the induced field arises solely from orbital currents $j(\mathbf{r})$, induced by the applied field:

$$\mathbf{B}_{\text{in}}(\mathbf{r}) = \frac{1}{c} \int d^3r' j(\mathbf{r}') \times \frac{\mathbf{r}-\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|^3}.$$

The shielding tensor can equivalently be written as a second derivative of the electronic energy of the system:

$$\vec{\sigma}_K = \frac{\partial^2 E}{\partial \mathbf{m}_K \partial \mathbf{B}_{\text{ext}}}.$$

The shielding tensor is a general second-rank tensor that can be decomposed into symmetric and antisymmetric contributions. The antisymmetric components are typically neglected in NMR spectra because they affect spectra to the second-order.¹⁶⁴ The symmetric part of the tensor can be diagonalized to obtain three principal components, σ_{11} , σ_{22} , and σ_{33} . The isotropic part of the shielding tensor $\sigma_{\text{iso}} = 1/3(\sigma_{11} + \sigma_{22} + \sigma_{33})$.

The magnetic shielding causes nuclei in different chemical environments to resonate at frequencies slightly different from the Larmor frequency of the bare nucleus. Instead of directly reporting the change in resonant frequency (which would depend on the operating magnetic field strength), a normalized chemical shift δ is used:

$$\delta = \frac{\sigma_{ref} - \sigma_{sample}}{1 - \sigma_{ref}}.$$

Except for some very heavy elements, $|\sigma_{ref}| \ll 1$, so $\delta \approx \sigma_{ref} - \sigma_{sample}$.

Electric field gradients (EFG)

Quadrupolar nuclei make up more than 75% of NMR active nuclei, with the vast majority being half-integer nuclei. In addition to the magnetic dipole moment, quadrupolar nuclei (nuclear spin $I > 1/2$) possess a nuclear electric quadrupolar moment that arises from a nonspherical distribution of the charge within the nucleus. The electric quadrupole moment interacts with the EFG at the nucleus, significantly influencing the NMR line shape. This interaction is directly related to the nuclear local environment, with the EFG generated by the surrounding nuclei and the electrons.

This interaction can be described by the Hamiltonian:

$$H_{Quadrupolar} = \frac{eQ}{2I(2I-1)\hbar} \mathbf{I} \cdot \mathbf{V} \cdot \mathbf{I},$$

where eQ is the nuclear electric quadrupole moment, I is the spin quantum number, $\mathbf{I}$ is the nuclear spin vector, and $\mathbf{V}$ is a second rank Cartesian tensor describing the EFG. The magnitude of the quadrupolar interaction depends on the size of the nuclear electric quadrupole moment, which is available in the literature,¹⁶⁵ and on the EFG, a tensor obtained based only on the ground-state charge density,

$$\mathbf{V} = \begin{pmatrix} V_{xx} & V_{xy} & V_{xz} \\ V_{yx} & V_{yy} & V_{yz} \\ V_{zx} & V_{zy} & V_{zz} \end{pmatrix},$$

in which a component $V_{\alpha\beta}$ ($\alpha, \beta = x, y, z$) is the α -component of the EFG where the applied magnetic field is in the direction β of the defining frame of reference.

This tensor can be expressed in its principal axis frame, and can be described by a matrix defined by its eigenvectors and its three eigenvalues, V_{xx} , V_{yy} , V_{zz} . Typically, the quadrupolar interaction is often described using the quadrupolar coupling constant C_Q (parameterizing the magnitude) and the asymmetry parameter η where $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$,

$$C_Q = \frac{eQV_{zz}}{h},$$

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}}.$$

The quadrupolar interaction acts as a highly sensitive probe of the local environment and can reasonably be regarded as even more informative than the chemical shift.

2.8 Machine learning (ML)

There are two ML methods used in this study: exploring the PES with neural network potentials (NNP) and correlating the NMR property with geometrical descriptors by ML regression.

Neural Networks Potentials: SchNet

MLPs (machine learning potentials) is an efficient tool for presenting the multidimensional PES by learning the shape of the PES from reference data obtained from an accurate electronic structure calculation. The resulting analytic MLPs represent the atomic interactions, commonly as a function of the atomic positions and nuclear charges, and can then be used without a significant loss in accuracy in large-scale simulations, such as molecular dynamics, that are many orders of magnitude faster than the underlying electronic structure calculations.

Among all classes of MLPs, NNPs have the longest history and the greatest diversity in methods and concepts.¹⁶⁶ The key to generating NNP potentials is mapping the atomic coordinates into structure descriptors and then establishing the linkage between structure descriptors and the total energy. SchNet¹⁶⁷ is a type of representation-learning neural network architecture (Figure 2.2) designed for molecular dynamics and quantum chemistry simulations. It is specifically tailored to predict the properties of molecules and materials with high accuracy by learning from quantum mechanical calculations. A system described with nuclear charges Z and positions R transfers to a tuple of features $X^l = (x_1^l, \dots, x_n^l)$ in

layer 1 through the layers of SchNet. Then interaction blocks add refinements to each atom representation based on pairwise interactions with the surrounding atoms. Finally, a given property of a molecule or material is predicted from the obtained atom-wise representations.

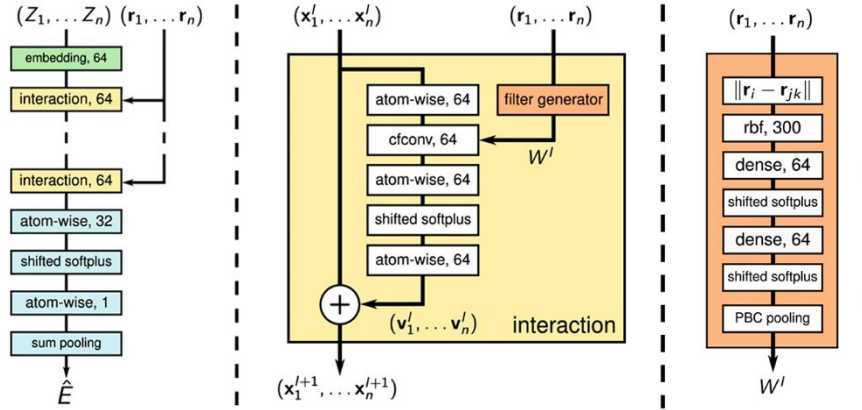


Figure 2.2 Illustrations of the SchNet architecture (left), interaction blocks (middle), and filter-generating network (orange) with atom embedding in green, interaction blocks in yellow, and property prediction network in blue. For each parameterized layer, the number of neurons is given. Reproduced with permission.¹⁶⁷ Copyright 2018, AIP Publishing.

Linear regression

In material science fields, it would be advantageous to predict the properties of a new material using knowledge from similar known materials, rather than conducting new experiments or performing laborious calculations. Easy prediction of these properties enhances the rational design and selection process for new materials with specific functions. The regression analysis, a fundamental concept of supervised ML method, is helpful in establishing a relationship among the variables by estimating how one variable affects the other. Linear regression (LR) is one of the most simple and basic type, yet powerful in creating simplified models despite the presence of a large number of features.

LR is a technique for linearly correlating target dependent variables (y) with independent input variables or features (x). The target property (y) as a linear function:

$$y = f(x) = c_0 + \sum_{i=1}^n c_i \cdot x_i.$$

where c coefficients are the parameters in the model that are adjusted to ensure the model fit the data. This can be achieved by, for example, minimizing a loss function (L) of the

mean squared error of the model with respect to the c coefficients, given by the following equation.

$$L = \frac{1}{n} \sum_{j=1}^n (y_j - f(x_j))^2,$$

where y_j presents the true value of the target property from the training data, $f(x_j)$ is the predicted value from the linear model, n is the number of data points in the training set, and j indexes all training points with features x_j and target values y_j .

An additional term can be introduced to the loss function to penalize redundant features in the linear model, a technique known as regularization. L1 regularization adds the magnitude of the coefficients to the loss function, which is written as:

$$L = \frac{1}{n} \sum_{j=1}^n (y_j - f(x_j))^2 + \lambda (\sum_{i=1}^n |c_i|).$$

The method, least absolute shrinkage and selection operator (LASSO) regression¹⁶⁸ is adopted in this study because it can effectively select relevant features by the removal of irrelevant features, which is done by setting some coefficients exactly to zero. LR models are easy to train and understand. However, their predictions can be less reliable if the key assumption—that a linear relationship exists between the features and the target property—is not met in the data. Because the previous studies empirically correlate the NMR chemical shielding of some nuclei, such as ²⁷Al and ²³Na, with structural features, LR training on a calculated dataset is suitable for defining the structure-property relationship.

It is worth noting that more accurate shielding (tensor) predictions can be achieved using other ML methods in the field of zeolite modelling, such as Kernel Ridge Regression¹⁶⁹ or (equivariant) neural networks.¹⁷⁰⁻¹⁷¹ However, these ML methods use high-dimensional descriptors, making the physical interpretation of the structure- σ correlation difficult. Thus, LASSO regression was adopted to predict σ simply and to facilitate the interpretation of the underlying structure-chemical shielding relationship. Overall, while more complex ML models may offer higher predictive accuracy, the choice of LASSO regression strikes a balance between interpretability and performance, making it a practical choice for understanding structure-chemical shielding relationships in zeolites.

Chapter 3. Computational Details

3.1 Models

3.1.1 Zeolite chabazite (CHA)

Aluminosilicate zeolites with CHA topology have attracted considerable attention from academia and industry owing to their excellent performance in heterogeneous catalysis and their remarkable capabilities in gas adsorption and separation. Zeolite CHA crystallizes in the trigonal space group $R\bar{3}m$, featuring a single type of T site and two types of cell definitions: a primitive rhombohedral cell with 12 T sites and a conventional hexagonal cell with 36 T sites (Figure 3.1). The structure features a distinctive architecture built from 4-, 6-, and 8-membered rings (MR), arranged into a three-dimensional framework that includes small, cage-like cavities interconnected by narrow channels. Its distinctive double six-membered ring (*d6r*) structure enhances its stability and imparts unique properties. Meanwhile, Si/Al ratios of synthesized CHA zeolites vary widely, ranging from less than 3 to infinite.¹⁷² This means sufficient experimental data is available as references for computational studies. Briefly, CHA is an excellent model for computational investigation due to its high symmetry with a single crystallographically independent T site, which simplifies the construction of models with aluminum substitution in the framework, as well as the abundance of experimental results in the literature.

The acidity of the zeolite is determined by the presence and concentration of Al within the framework. The models, spanning Si/Al ratio from 3 to 47 across different unit cell types (12/36 T-site cells) and supercells, are built to match specific experimental data. The ideal siliceous CHA structure was downloaded from the IZA database¹² to build models. Subsequently, the cell parameters were re-optimized for each Si/Al ratio based on experimental data, indicating an increase in unit cell parameters with higher aluminum content in the high-silica CHA material (Si/Al > 5).¹⁷³⁻¹⁷⁴ The optimized lattice parameters will be shown in the specific cases later.

In this work, the cations of Na⁺, H⁺ under both hydrated and dehydrated conditions are considered. There are four independent framework oxygen positions (O1, O2, O3, and O4 shown in Figure 3.1), which can capture H⁺ to form BAS. For the location of Na⁺, 6MR

and 8MR are two stable possibilities (yellow balls SII and SIII in Figure 3.1). In addition, the simple models using background charge to compensate framework charge were sometimes used in order to test its feasibility for *operando* modelling.

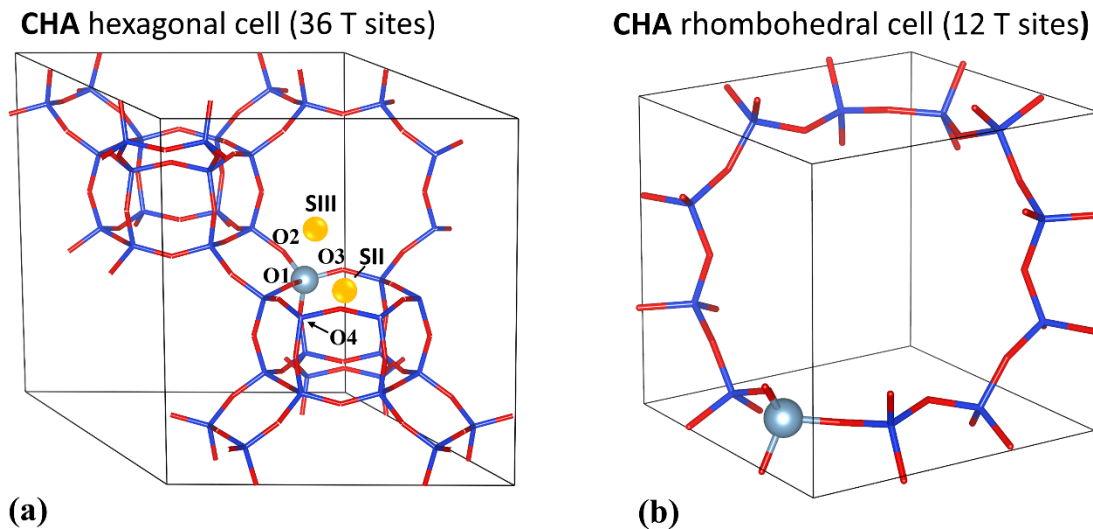


Figure 3.1 The structures of CHA. a) the conventional cell: O1, O2, O3 and O4 are the four independent framework oxygen positions; SII and SIII denote the stable Na⁺ positions considered. b) the primitive cell.

3.1.2 Zeolite mordenite (MOR)

MOR is another industrially important middle-pore zeolite, which is mainly used to extend the study from simple single T site CHA to more complex structures with four types of T sites. It exhibits 8- and 12- rings and side pockets (Figure 3.2a). The idealized silicious structure was also downloaded from IZA database.¹² It crystallized in orthorhombic space group *Cmcm*. To simplify the calculation, the primitive cell with 24 T sites (Figure 3.2b) was used as model, and other supercells were only used for simple validation tests of the model strategy.

Similar to the strategy of the CHA study, MOR with different Si/Al ratios were considered. For the isolated Al systems, a model with Si/Al = 23 was mainly used to systematically investigate the effects of cations and hydration condition, while for the case with Al pairs (Si/Al = 11, 7), only some specific cases were selected as examples to verify the conclusion from the CHA. The lattice parameters of MOR were kept constrained to simplify the calculation.

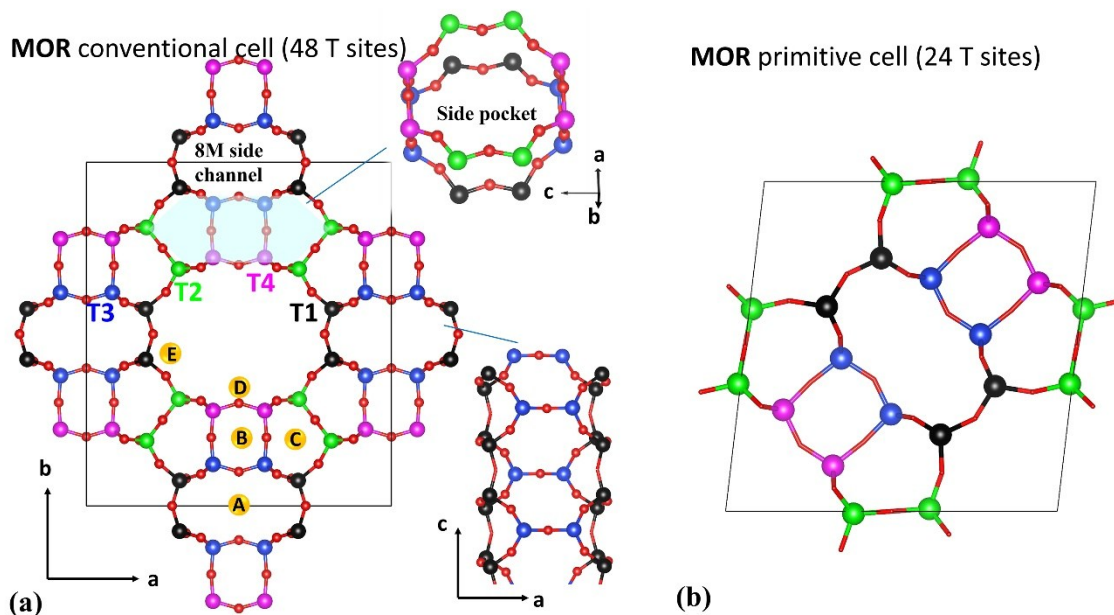


Figure 3.2 The structures of MOR. a) the conventional cell with the five stable Na positions, A, B, C, D, and E. b) the primitive cell. Note: the four types of T sites, T1, T2, T3, and T4 are colored black, green, blue, and pink, respectively.

3.2 Methods and computational details

3.2.1 DFT static calculation

Geometry optimization

The geometry optimizations in this thesis were carried out using *ab initio* calculation in VASP with the projector-augmented wave (PAW) pseudopotentials.¹⁵⁸⁻¹⁶⁰ An energy cutoff of 700 eV was applied, with wave function convergence set to 10^{-6} eV and the force convergence criterion of 10^{-2} eV/Å for geometry optimization. The Brillouin zone was sampled using a $1 \times 1 \times 2$ k-point grid for the MOR primitive cell, which was determined to be sufficient through convergence tests, and the Gamma point was utilized for all CHA models. For the supercell models of MOR in Chapter 5, the k-point grid was adjusted to $1 \times 2 \times 3$ for the $2 \times 1 \times 1$ supercell, and the Gamma point was used for the $1 \times 1 \times 2$ supercell, considering the short lattice parameter in the *c* direction. The general gradient approximation (GGA) Perdew–Burke–Ernzerhof (PBE) functional¹⁵⁰ was used including the description of dispersion forces accordingly to the Becke-Johnson (BJ) damping model¹⁵⁵ (PBE+D3). Although the PBE functional is known for bulk water over-structuring,¹⁷⁵ it performs comparably to other GGA functionals in describing water

clusters, and the accuracy of the description is further improved by the BJ damping correction.¹⁵⁵

NMR calculations

The Magnetic shielding and electric field gradient tensors were all calculated with GIPAW (gauge-including projector augmented-wave) method as implemented in the CASTEP software package.^{163, 176} The PBE functional revised for solids (PBEsol)¹⁷⁷ were used with an energy cutoff of 700 eV. Energy convergence criteria were set to 10^{-8} eV per atom. The Brillouin zone for CHA was sampled using a $1 \times 1 \times 1$ k-point grid for the conventional cell and a $2 \times 2 \times 2$ grid for the primitive cell. For the MOR models, the $1 \times 1 \times 2$ k-point grid was set for both the primitive cell and the $2 \times 1 \times 1$ supercell, while the $1 \times 1 \times 1$ grid was used for the $1 \times 1 \times 2$ supercell models.

3.2.2 Operando simulation scheme (AIMD)

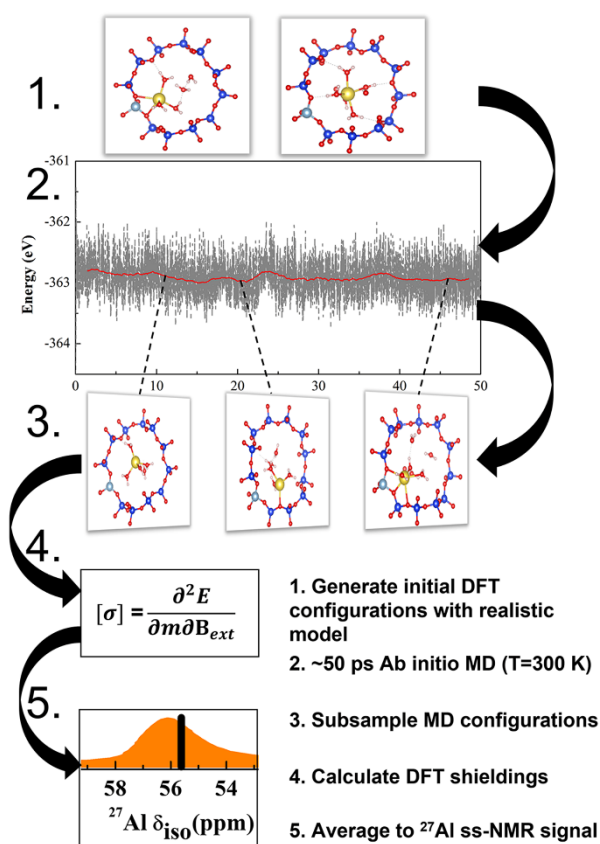


Figure 3.3 The scheme of *operando* modelling of ^{27}Al NMR for zeolites. Such model provides reliable data for analyzing structure-chemical shifts relationship, as well as for understanding effects on solid-state NMR(ssNMR) spectra, such as those arising from zeolite topology and composition, hydration and thermal motion. Reproduced from Ref.¹⁷⁸ with permission from the Royal Society of Chemistry.

The scheme of *operando* simulation strategy is shown in Figure 3.3. Starting from the static optimized configuration, AIMD were performed to generate dynamical trajectories. Then a series of snapshots were sampled from these trajectories to calculate the NMR properties of different configurations. These data were used to get the time-averaged NMR results. Additionally, this dataset obtained from this process offers a good training space for ML analysis to obtain the relationship between NMR shielding/shift and structural features.

The AIMD simulations at room temperature (300 K) were performed with VASP¹⁵⁸⁻¹⁶⁰ with PBE+D3 similar to the static calculations. The trajectories were generated using a plane-wave energy cut-off of 400 eV in the canonical NVT ensemble, with a time step of 0.5 fs (0.75 fs in Chapter 4) and a Nosé-Hoover thermostat. For each system, well-equilibrated trajectories ranging from 20 and 50 ps were performed. To enhance simulation efficiency, the atomic mass of hydrogen was replaced with deuterium (in Chapter 5) and tritium (in Chapter 4).

3.2.3 NNP-based geometry optimization and MD

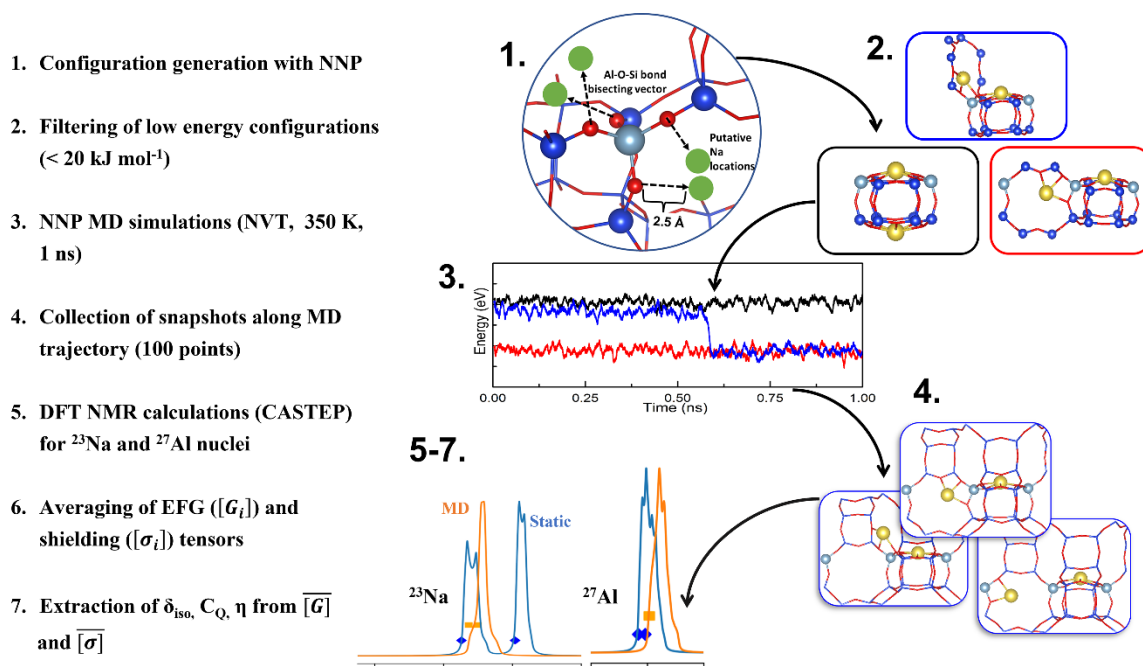


Figure 3.4 Schematic of the computational workflow for the calculation of dynamically averaged NMR spectra for relevant, low-energy configurations with NNP. Reproduced from Ref.¹⁷⁹ with permission from the Royal Society of Chemistry.

To alleviate the main limitations of *ab initio* calculations, a computational approach based on ML was built. The scheme of the modelling process is shown in Figure 3.4. We have

created neural network potentials (NNPs) capable of dynamically exploring extensive configurational and chemical spaces of zeolites while maintaining the accuracy level of the *ab initio* (dispersion-corrected metaGGA) training dataset. Compared to the *ab initio* simulations in the *operando* simulation method shown in section 3.2.2, the introduction of the NNPs enables the simulation of more complex systems over larger time scales (ns). The NMR calculation details are set under the same condition as described in Section 3.2.1.

Neural Network Potential (NNP) for Na-zeolites

Table 2.1 Database index (ID) of the hypothetical zeolite database published in Ref.,¹²² framework density (FD in N_t per nm^3), number of T-sites (N_t), aluminum/sodium atoms (N_{Al} , N_{Na}), and water molecules (N_w) of the initial structures constructed for database creation using existing zeolite topologies (CHA, SOD, MVY), hypothetical frameworks (HYP) and a silica bilayer (BL). Reproduced from Ref.¹⁷⁹ with permission from the Royal Society of Chemistry.

Topology	ID	FD	N_t	$N_{\text{Al}} = N_{\text{Na}}$			N_w			
CHA	-	14.9	12	1	3	6	0	2	6	12
SOD	-	17.8	12	1	3	6	0	2	4	8
MVY	-	20.5	24	2	6	11	0	2	4	6
HYP1	17883	23.2	14	1	4	6	0	1	2	3
HYP2	2251	19.5	16	1	3	5	0	2	4	8
HYP3	17089	20.9	32	1	7	14	0	2	5	10
HYP4	46458	21.5	28	1	5	10	0	1	2	4
HYP5	4552	20.1	32	1	5	10	0	1	3	7
HYP6	9330	19.2	16	1	3	6	0	2	5	10
HYP7	72920	15.8	24	1	5	9	0	5	15	25
BL	-	9.7	24	3	6	9	0	10	25	55

Creating reliable neural network potentials (NNPs) for Na-aluminosilicate zeolites requires a varied dataset in terms of structure. In prior research, our group established a database for protonic aluminosilicate zeolites that covers a wide range of zeolite frameworks, Si/Al ratios, and water loadings to train general NNPs.¹²⁴ We have now applied the same computational method to expand the DFT dataset to include Na-containing zeolites. First, 10 pure silica zeolites and a silica bilayer were utilized to create 132 initial structures (see Table 2.1) with varying Si/Al ratios and water loadings (Materials Studio 2022). The selected silica zeolites (bilayer) were chosen to cover diverse atomic environments in both existing and hypothetical silica frameworks.¹²² All initial configurations were equilibrated

through 10 ps AIMD runs at three temperatures (1200, 2400, 3600 K) using the PBE+D3(BJ) level, Nosé-Hoover thermostat, 1 fs time step, and tritium replacing hydrogen to enhance sampling efficiency.

Table 2.2 Chemical composition of sodium aluminosilicate polymorphs used for DFT dataset creation. Reproduced from Ref.¹⁷⁹ with permission from the Royal Society of Chemistry.

Polymorph	N_{Si}	N_{O}	N_{H}	N_{Na}	N_{Al}
Analcime ¹	32	112	32	16	16
Grumantite ¹	8	24	12	4	0
$\text{Na}_5(\text{Al}(\text{OH})_6)(\text{OH})_2$ ²	0	32	32	20	4
NaOH ²	0	2	2	2	0
Natrolite ¹	24	96	32	16	16
Ussingite ¹	6	18	2	4	2
Carnegieite ¹	4	16	0	4	4
Diaoyudaoite ¹	0	34	0	2	22
Jadeite ¹	8	24	0	4	4
Na_2O ¹	0	4	0	8	0
Natrosilite ¹	8	20	0	8	0
Nepheline ¹	8	32	0	8	8

To reduce the redundancy in similar atomic environments, the AIMD trajectories were subsampled using Farthest Point Sampling (FPS) combined with the smooth overlap of atomic positions (SOAP)¹⁸⁰ kernel. The subsets selected by FPS were then used for single-point calculations at the SCAN+D3(BJ) level. Furthermore, 210 lattice deformations were applied to the 132 initial structures by 70 different lattice vector perturbations (see also previous works of our group^{122, 124} for details) at three strain rates (1.5%, 3%, and 4.5%). These deformations sampled close-to-equilibrium configurations and were also applied to 12 Na-alumino(silicate) and Na-oxide polymorphs such as NaOH and Na_2O (see Table 2.2).

The training and inference of NNPs were conducted using the SchNetPack python package¹⁸¹ and the atomistic simulation environment (ASE).¹⁸² The NNPs¹⁶⁷ employed the SchNet architecture with six interaction blocks, a feature vector size of 128, and 60 Gaussians for the expansion of pairwise distances with a cutoff radius of 6 Å. These

¹available under: <https://rruff.geo.arizona.edu/AMS/amcsd.php>;

²available under: <https://www.crystallography.net/cod/>

parameters have been shown to produce accurate NNPs for related datasets.^{122, 124, 167} Using the extended Na-aluminosilicate database, our colleague Dr. Erlebach retrained an ensemble of six NNPs that were previously developed for H-aluminosilicates. The dataset was randomly into training (80%), validation (10%), and test (10%) sets. The ADAM optimizer with a batch size of four structures was used to minimize the mean squared error of energy per atom and forces. A dynamic learning rate strategy was also applied, decreasing the learning rate from 10^{-4} to 3×10^{-6} by a factor of 0.75 if the validation loss remained unchanged for three consecutive epochs.

The developed NNPs achieved root mean square errors (RMSE) of 5.3 meV/atom for energy and 188 meV/Å for force on the database test set, aligning with other rotationally invariant NNPs capable of DFT quality predictions.^{122, 124} To evaluate their reliability for MD simulations in Na-zeolite systems we concern, energy and force values were recalculated at the SCAN+D3(BJ) level for structures sampled from various MD trajectories. As part of the training domain (in-domain tests), CHA(11), CHA(17), and CHA(35), which closely resemble structures in the training dataset, were analyzed. To further assess the generality of the NNPs, additional zeolite frameworks not in the DFT database were used in out-of-domain tests. MD simulations were performed at 350 K for 1 ns for FER (Si/Al = 35) and MOR (Si/Al = 7 and 11), along with water-loaded FAU (Si/Al = 3). Energy and force errors were subsequently determined using SCAN+D3(BJ) single-point calculations on 100 uncorrelated configurations (50 in the case of FAU) extracted from all MD trajectories. The generalization tests of demonstrated that the NNPs maintained errors within 4.2 meV/atom and 72 meV/Å across different cases which span pore-size, ring diameters, unit cell volume and Si/Al ratios (CHA(11,17,35), MOR(7,11), FER(35), FAU(3)). These results highlight strong transferability of the model across diverse environments and topologies. The observed errors are comparable to those in other reactive MLPs and are not greater than the discrepancies between different (meta)GGA exchange-correlation DFT functionals.¹²⁴ The dataset creation and NNP testing, including AIMD simulations and SCAN+D3(BJ) single-point calculation, were performed using VASP with an energy cutoff of 400 eV, standard PAW potentials, and k-point grids with a linear density of at least 0.1 Å^{-1} .

3.2.4 LASSO: ML analysis for structure- σ relationship

The initial input features and DFT σ values for LASSO regressions were sampled from MD trajectories using various models of MOR and CHA. Structural features calculations were carried out with the Python packages Atomic Simulation Environment (ASE),¹⁸³ and LASSO regression analyses were performed using Scikit-learn.¹⁸⁴

To minimize the objective function L with the error sum of squares over n samples between target values $\sigma_{i,\text{DFT}}$ and a linear model $\sum_{j=1}^p c_j \cdot x_{ij}$ with p coefficients c_j and the structural features x_{ij} :

$$L = \frac{1}{n} \sum_{i=1}^n \left(\sigma_{i,\text{DFT}} - \sum_{j=1}^p c_j \cdot x_{ij} \right)^2 + \lambda \left(\sum_{j=1}^p |c_j| \right) \quad \text{Equation 3-1.}$$

The L1 regularization term $\lambda(\sum_{j=1}^p |c_j|)$ with hyperparameter λ penalizes the coefficients c_j , enabling them to shrink to zero during the minimization of L , thereby facilitating feature selection. For all LASSO regressions, regularization parameters λ were chosen within the range $[10^0, 10^{-3}]$, with 80 % of the DFT calculations used for training and the remaining data points used as test set.

3.2.5 From calculated NMR to experimental results

To calculate chemical shifts, which can be directly comparable to experimental observables, the NMR isotropic shielding tensors need to be first calculated. There are two ways for converting the calculated isotropic chemical shielding (σ) to chemical shift (δ). The first involves using a reference compound with a known, accurate chemical shift. Chemical shielding tensors for both the system of interest and the reference compound are calculated using the same method, with the reference compound providing the conversion standard. The second, more widely accepted approach, is linear regression. In this method, several reference compounds are involved, and their calculated NMR isotropic chemical shielding values are plotted against their experimental chemical shifts. The slope and intercept of the best fit line are then used to convert the calculated isotropic chemical shieldings into chemical shifts. The advantage of this method is that the slope can correct for systematic error, while the intercept provides an alternative to relying on a single reference value. In this thesis, we have chosen the second method, with the conversion of calculated ^{27}Al and

^{23}Na chemical shielding to isotropic chemical shift carried out using linear regression relationships.

Reference of ^{27}Al chemical shifts

In ^{27}Al NMR experiments, the chemical shift is usually referenced relative to aluminum ions in solution. While the solid $\text{Al}(\text{acac})_3$ have been used as a secondary solid reference in ssNMR measurements for zeolites. Also, to limit systematic differences between the reference compounds and the system of interest, single T-site zeolites can serve as suitable reference options. Thus, for the ^{27}Al chemical shift reference, a linear regression was derived using from four reference compounds with experimental measurements, including $\text{Al}(\text{acac})_3$, two types of CHA zeolites with tetrahedral Al and octahedral Al, and AFI zeolite with tetrahedral Al. The experimental ^{27}Al isotropic chemical shift δ^{exp} of $\text{Al}(\text{acac})_3$ were used as -4.2 ppm reference to $\text{Al}(\text{NO}_3)_3$ solution, and that of tetrahedral Al in hydrated protonic zeolites CHA(Si/Al = 30) and AFI(Si/Al = 77) were reported as 59.7 and 55.5 ppm by Holzinger et al.¹⁸⁵ The CHA zeolite with octahedral Al site was used as the last reference, whose chemical shift was reported as 0 ppm.¹⁸⁶

The ^{27}Al chemical shielding of $\text{Al}(\text{acac})_3$ was calculated using the structure downloaded from the Cambridge Crystallographic Data Center (CCDC).¹⁸⁷ Based on the structural files obtained from IZA Database of Zeolite Structures, the 36 T-sites hexagonal cell model of CHA with Si/Al = 35, and the 72 T-sites AFI model of $\sqrt{3}\times\sqrt{3}\times 1$ supercell with Si/Al = 71 were built by substituting one T-site with Al atom to fit the experimental Si/Al ratios. For the hydrated models, five water molecules were loaded close to the Al site. Then the simulation of ^{27}Al NMR (calculations were set as 3.2.2) over 15-20 ps AIMD trajectories were employed to consider the motions of water molecules and protons at room temperature in these systems. The calculated time-averaged chemical shieldings, σ^{cal} , of Al sites in $\text{Al}(\text{acac})_3$, CHA(35), and AFI(71) are 554.00, 494.28 and 500.76 ppm, respectively. The calculated ^{27}Al σ^{cal} of octahedral Al 549.11 ppm was obtained from the static calculation of CHA with Si/Al = 3 with a loading of six water molecules in the 12 T-site cell (as shown in Chapter 4).

From the linear fit of the four point as shown in Figure 3.5, the reference of ^{27}Al chemical shift was given by the equation:

$$\delta^{exp} = -1.11\sigma^{cal} + 609.72 \quad \text{Equation 3-2}$$

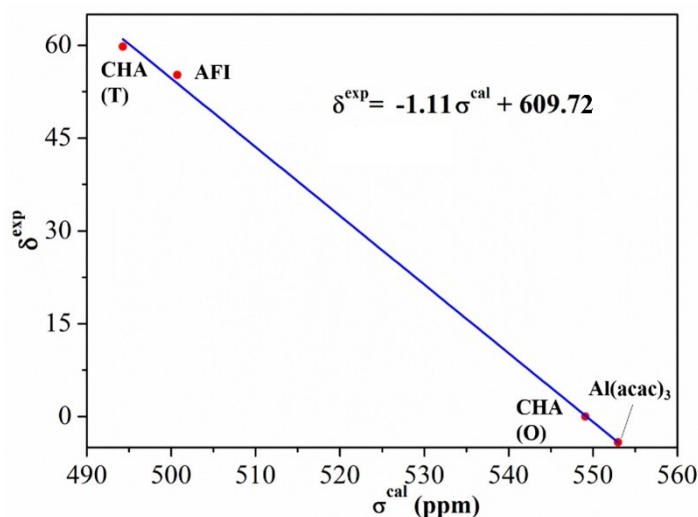


Figure 3.5. The linear regression between the experimental ^{27}Al chemical shift δ^{exp} and calculated chemical shielding σ^{cal} using four reference experimental values. These include tetrahedral framework Al in CHA (CHA(T)) and AFI (AFI(T)),¹⁸⁵ framework-associated octahedral Al sites in CHA (CHA(O)),¹⁸⁶ and octahedral Al in solid aluminum acetylacetonate $\text{Al}(\text{acac})_3$.⁸¹ Reproduced from Ref.¹⁷⁸ with permission from the Royal Society of Chemistry.

Reference of ^{23}Na chemical shifts

Following the strategy of determining a reference for the ^{27}Al chemical shift used above, the reference of ^{23}Na chemical shift was obtained from a linear regression of the experimental chemical shift δ^{exp} and calculated chemical shielding σ^{cal} . To ensure that the regression equation covers the range of ^{23}Na chemical shifts typically observed in zeolites, five compounds with reported experimental NMR data in the range from -12.8 to 23 ppm were selected: Na_2CrO_4 , Na_2SO_4 , NaCl , $\alpha\text{-Na}_2\text{Si}_2\text{O}_5$ and Na_2SiO_3 .

Prior to the calculations, an energy cutoff test of the NMR calculation was performed. Differ to the calculated ^{27}Al chemical shielding, which showed a negligible difference (about 0.1 ppm) between energy cutoffs of 700 and 800 eV, the ^{23}Na chemical shieldings showed a systematical shift around 3 ppm (Figure 3.6). However, this shift is not expected to affect the chemical shifts values, and therefore, the cutoff energy of 700 eV was used, consistent with the ^{27}Al NMR calculations. The chemical shift of ^{23}Na is obtained from the equation:

$$\delta^{exp} = -0.86\sigma^{cal} + 476.68 \quad \text{Equation 3-3.}$$

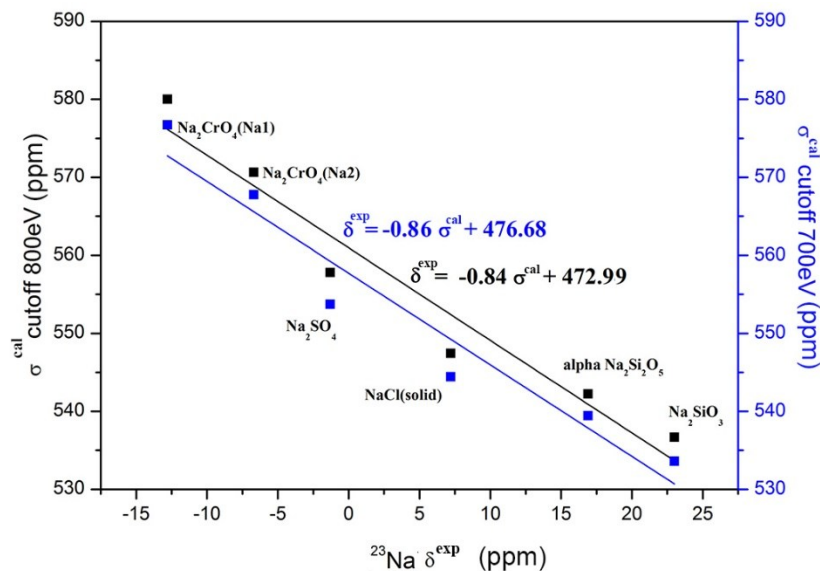


Figure 3.6. The linear regression between the experimental chemical shift δ^{exp} and calculated chemical shielding σ^{cal} based on five compounds with reported experimental δ^{exp} values: Na_2CrO_4 ¹⁸⁸, Na_2SO_4 ¹⁸⁸, NaCl ,¹⁸⁹⁻¹⁹⁰ $\alpha\text{-Na}_2\text{Si}_2\text{O}_5$ ¹⁹¹ and Na_2SiO_3 ¹⁹¹. Note: in ref¹⁸⁸, the original chemical shift values were used the solid NaCl , and we transferred the value to the values refer to NaCl solution to keep the same standard as the ref¹⁸⁹. Reproduced from Ref.¹⁷⁹ with permission from the Royal Society of Chemistry.

3.2.6 Spectral simulations

Simulations of ^{23}Na and ^{27}Al spectra (Chapter 6) were performed using Simpson version 4.2.1.¹⁹²⁻¹⁹³ All simulations were performed at a spinning rate of 40 kHz and a magnetic field of 36 T, except for selected ^{27}Al simulations where the magnetic field was considered as a variable. The powder pattern of each spectrum was generated using 3384 Euler angles by considering 376 α - β pairs based on the Zaremba–Conroy–Wolfsberg (ZCW) algorithm,¹⁹⁴⁻¹⁹⁶ and 9 γ angles. The simulation spin system was defined using σ_{calc} , C_Q , and η_Q parameters obtained from CASTEP NMR calculations, which were converted using the Simpson python package. Only the central transition were considered in all spectra.

For recoupling simulations, a spinning rate of 20 kHz and a magnetic field of 23.5 T were used, with 143 α - β pairs as implemented in ZCW algorithm¹⁹⁴⁻¹⁹⁶ and 15 γ angles. ^{23}Na - ^{27}Al D-HMQC (dipolar heteronuclear multiple-quantum coherence) recoupling simulations were performed using $SR4_1^2$ recoupling scheme,¹⁹⁷ which has been used to recouple other quadrupolar pairs.¹⁹⁸ To prevent recoupling efficiency loss due to frequency offset sensitivity, chemical shift information was omitted when simulating recoupling curves.

Chapter 4. Reactive transformations in hydrated protonic zeolites

4.1 Motivation

Aluminum in protonic zeolites plays a key role in generating Brønsted-acid and Lewis-acid sites (BAS and LAS), which are crucial for catalytic activity. The nature of aluminum in zeolites has been extensively studied through various experimental and theoretical investigations.¹⁹⁹ A BAS in zeolites is linked to a bridging hydroxyl group between framework tetrahedrally coordinated aluminum and silicon in the framework, which is well understood.²⁰⁰ With the water loading in the voids, the BAS can transfer to different types of LAS due to proton solvation and hydrolysis processes. However, the structures and properties of LAS remain not fully established. Several types of LAS have been proposed²⁰¹, including framework LAS,^{86, 100, 202-205} octahedral framework-associated aluminum^{52-53, 97-98, 206-208} and extra-framework aluminum (EFAl).²⁰⁹⁻²¹⁴ The latter two types are characterized by an octahedral coordination of aluminum,²¹⁵ but the octahedral framework-associated aluminum can reversibly switch its coordination between tetrahedral (Al(Td)) and octahedral (Al(Oh)).⁵³ Although ²⁷Al solid-state NMR spectra can identify different Al states (4-, 5- or 6-coordinated) in zeolites,^{97-98, 100} the precise mechanism of the transition between Al(Td) and Al(Oh), the atomistic structures of framework-associated Al(Oh), and the process by which it transforms into a LAS are still not fully understood.

Here the structures of acid sites and the free-energy reaction path connecting the intermediates are investigated using biased AIMD and the thermodynamic integration method. The ²⁷Al NMR simulation is crucial to confirm the reality of computational prediction by connecting the computational structures and the observed experimental NMR signals. Experimental ²⁷Al MAS NMR spectra show that a significant fraction of Al(Td) in acid zeolites can undergo reversible conversion to octahedral Al(Oh) and revert to its original state,⁵²⁻⁵³ even in small-pore zeolite CHA(Si/Al = 3). Since most of the calculations for energetic and transition processes have been conducted by my colleague Mengting Jin, this chapter primarily focuses on simulating ²⁷Al NMR in CHA zeolite, and generalizing

the mechanisms for MOR zeolite, and only includes necessary results briefly from the experiment and previous calculation works related to the ^{27}Al NMR calculations.

4.2 Results

4.2.1 ^{27}Al MAS NMR spectra

^{27}Al NMR spectra were measured under ambient conditions with a spinning speed of 10000 Hz and field strength of 400 MHz (9.4 T). The spectra were collected using a pulse angle of 90 degrees and a recovery delay of 1s, with the chemical shift referenced to $\text{AlNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ at -0.54 ppm. The ^{27}Al NMR spectra of CHA(3) with different cations (NH_4^+ , H^+ , and K^+) shown in Figure 3.1, reveal that only H-CHA-450 resulted in the conversion of $\text{Al}(\text{Td})$ to $\text{Al}(\text{Oh})$ in addition to the formation of a broad shoulder in the range of 50 to 10 ppm. The significant reduction of the $\text{Al}(\text{Oh})$ signal around 0 ppm in NH_4 -(H-CHA-450) due to the NH_4^+ ion exchange shows that a significant fraction of $\text{Al}(\text{Td})$ can reversibly transition to octahedral $\text{Al}(\text{Oh})$ and back, which is a typical characteristic behaviour of acid zeolites.⁵²⁻⁵³ Thus, these results indicate the presence of framework-associated $\text{Al}(\text{Oh})$ in small-pore zeolite CHA(3).

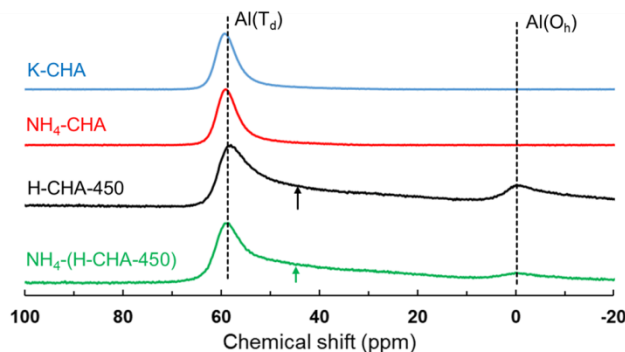


Figure 4.1 The ^{27}Al NMR spectra of K-CHA, NH_4 -CHA, H-CHA-450, and NH_4 -(H-CHA-450). The arrow indicates the broadening of the peak associated with tetrahedral aluminum, which extends toward lower chemical shifts. Note: K-CHA is the sample with K^+ compensated cation; NH_4 -CHA is the NH_4^+ ion exchange of K-CHA; H-CHA-450 is calcination of NH_4 -CHA in the air at 450 °C; NH_4 -(H-CHA-450) is the sample from NH_4^+ ion exchange of H-CHA-450. Reproduced from Ref.¹⁸⁶

4.2.2 Geometry optimization and the formation of the framework-associated $\text{Al}(\text{Oh})$

To fit the experimental conditions, models of protonic zeolites CHA (CHA(11) and CHA(3), with Si/Al ratios of 11 and 3, respectively) and MOR (MOR(47) and MOR(15),

with Si/Al ratios of 47 and 15, respectively) are considered with appropriate water loading, and the lattice parameters are optimized. The water loading of six water molecules per unit cells (UC) was used, corresponding to the water density of 1 g cm^{-3} in the void space of CHA and based on the thermogravimetric analysis. The optimized lattice parameters are $a = b = c = 9.29 \text{ \AA}$, $\alpha = \beta = \gamma = 96.02^\circ$ for CHA. To keep the same hydration level for each Al site, six water molecules are included in the MOR cell as well. The lattice parameters of MOR are kept consistent with the UC from the IZA dataset: $a = 18.26 \text{ \AA}$, $b = 20.53 \text{ \AA}$, $c = 7.54 \text{ \AA}$, $\alpha = \beta = \gamma = 90.00^\circ$, considering the small effect of the low water loading on the lattice parameters. The calculations were then performed by constraining the UC of CHA for both CHA(3) and CHA(11), with compositions $\text{Si}_9\text{Al}_3\text{O}_{24}\text{H}_3 \cdot (\text{H}_2\text{O})_6$ and $\text{Si}_{11}\text{Al}_1\text{O}_{24}\text{H}_1 \cdot (\text{H}_2\text{O})_6$, respectively. Similarly, the lattice parameters of MOR were constrained for MOR(15) and MOR(47), with compositions $\text{Si}_{45}\text{Al}_3\text{O}_{96}\text{H}_3 \cdot (\text{H}_2\text{O})_6$ and $\text{Si}_{47}\text{Al}_1\text{O}_{96}\text{H}_1 \cdot (\text{H}_2\text{O})_6$, respectively.

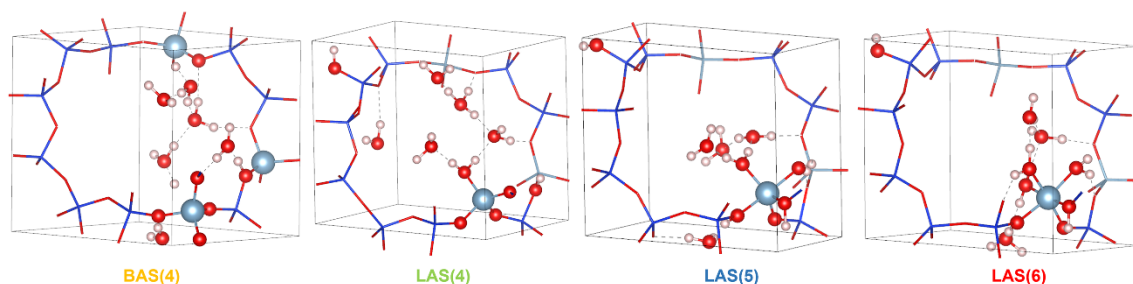


Figure 4.2 Four intermediates found along the path connecting BAS(4) site and framework-associated octahedral LAS(6) sites in CHA(3). Reproduced from Ref.¹⁸⁶

To explain the mechanism of the formation of the octahedral Al, the conversion of the regular framework Al(Td) species into framework-associated Al(Oh) species was investigated by AIMD simulations. The AIMD calculation shows the Al(Td)→Al(Oh) transformation consists of three steps, with each of the four minima on the free-energy surface having its distinct aluminum environment (see Figures 4.2 and 4.3). The initial CHA structure, in which only the tetrahedral framework Al forms Brønsted acid site, is labeled BAS(4). Then a nearly isoenergetic Lewis acid site LAS(4) is a tetrahedral Al site coordinated to three framework oxygen atoms and one oxygen atom of water molecule when an adjacent framework Si-O bond breaks to form a silanol. The second water molecule subsequently attaches to Al to form a penta-coordinated LAS(5) structure, and the two solvated protons also bind to the bridge oxygen of the penta-coordinated Al and

adjacent Si. Finally, one more water molecule can be involved in the first coordination shell of the Al atom to accomplish the octahedral aluminum, denoted also as LAS(6). These four typical structures are shown in Figure 4.2.

Both experimental findings^{54, 97, 216} and computational studies suggest that a specific local concentration of framework aluminum (and Brønsted sites) is required for the formation of octahedral Al(OH) species. Factors such as the Si/Al ratio, the concentration of BAS site, the distance between framework Al atoms (which are interrelated to some extent), and the hydration degree have been shown to play important roles to form Al(OH). This framework-associated octahedral aluminum can form when a sufficient number of BAS sites are located close enough to allow the transfer and stabilization of protons around the to-be-formed octahedral aluminum. The octahedral Al species are typically formed from one of the Al atoms on an Al-pair, where two Al atoms are separated by a single silicon atom in the framework structure.

4.2.3 ²⁷Al NMR simulation

Using the four structures shown in Figure 4.2, the ²⁷Al NMR parameters of each were calculated with the *operando* modelling approach mentioned in Session 3.2.2 based on dynamic trajectories, and compared with the experimental spectra. The strong agreement between the experimental and calculated chemical shifts validates the correspondence between experimentally observed and computationally identified framework-associated Al(OH) (Figure 4.3). The calculated results show the signal at 60 ppm is attributed to the tetrahedral Al of both BAS(4) and LAS(4), and the Al(OH) contributed to the signal at 0 ppm. Additionally, for the shoulder between 50 and 10 ppm can be attributed to three possibilities: 1) the presence of the penta-coordinated Al of the LAS(5), which show an isotropic chemical shift at 30 ppm but is thermodynamically less stable than LAS(6), and may persist for long timescales under conditions of limited water availability (as three water molecules are required to complete the transformation to LAS(6)); 2) the distorted tetrahedrally coordinated aluminum species resulting from irreversible thermal damage as previously reported by van Bokhoven;⁹⁸ 3) the incomplete solvation of protons on BAS(4) sites because all the protons cannot be solvated from the BAS sites at once. The reason for this contribution to the shoulder will be explained in the following part.

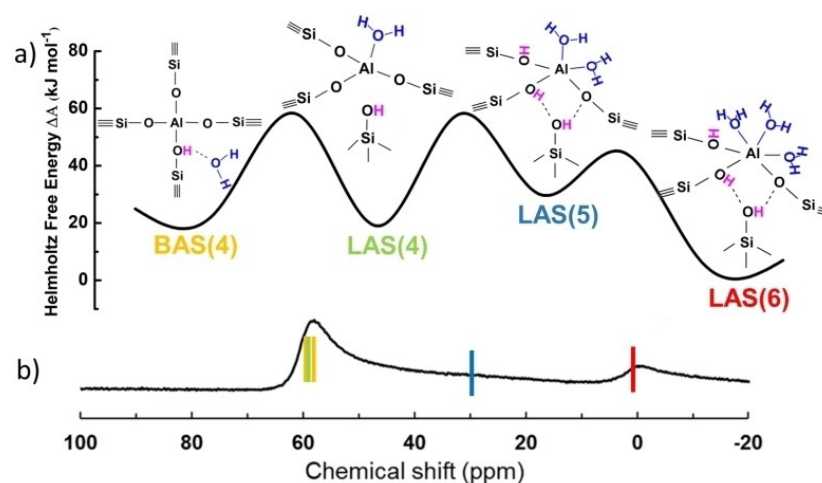


Figure 4.3 Structural, thermodynamic, and NMR characteristics of tetrahedral and octahedral aluminum in zeolites. (a) A schematic representation of the free energy profile connecting Brønsted acid site (BAS) with Lewis acid LAS(*n*) sites, where *n* denotes the number of oxygen atoms surrounding aluminium in its first coordination shell. (b) Calculated chemical shifts for individual framework Al atoms compared with experimental results for the system with the same composition (Si/Al = 3, with 6 water molecules per CHA cage). The colour code is used to distinguish BAS(4) and LAS(*n*) structures in the ^{27}Al NMR spectra. Reproduced from Ref.¹⁸⁶

The effect of water concentration on the relative stability of the Al(OH) structures was investigated for CHA(3) by Mengting Jin and shown in our published work.¹⁸⁶ The study showed that the relative energies between LAS(6) and BAS(4) with three water molecules are similar to that with six water molecules. Therefore, only the high hydration state with six water molecules is considered here.

For the BAS(4) structure, there are three BAS sited in the initial structure, which can be solvated by the six water molecules in the void. However, six water molecule are not enough to solvate all the three proton in BAS sites. According to the AIMD simulations, the BAS sites can be identified three types depend on the proton solvation: the BAS that is never solvated, partially solvated and fully solvated (Figure 4.4). The Al of never solvated BAS is essentially invisible in the NMR spectrum because of the too broad peak, which is also observed in experiments.²¹⁷⁻²¹⁹ The proton attached to the AlO_4^- unit distorts the environment around the Al atom, leading to a large quadrupolar coupling constant for the quadrupolar nucleus of Al, which results in a broad peak in its NMR spectrum. The Al site of the fully solvated BAS results in a narrow peak at around 60 ppm, which is the observed signal for tetrahedral coordinated Al. The simulated spectra shows that the partially solvated BAS (significant time fraction bound to framework oxygen) exhibits a broad peak

(in the range of approx. 35-60 ppm) with the peak maximum at about 40 ppm. Hence, at a high concentration of BAS sites, there should be a fraction of partially solvated protons present in the zeolitic system.

It is notable that NMR calculation along the AIMD trajectories allows the identification of static unstable LAS(5) structure and a further understanding of the broad shoulder in the range of 50 to 10 ppm of the experimental spectra. Thus the *operando* simulation to considering the hydration, cations and the temperature during a time scale is important to the NMR calculations.

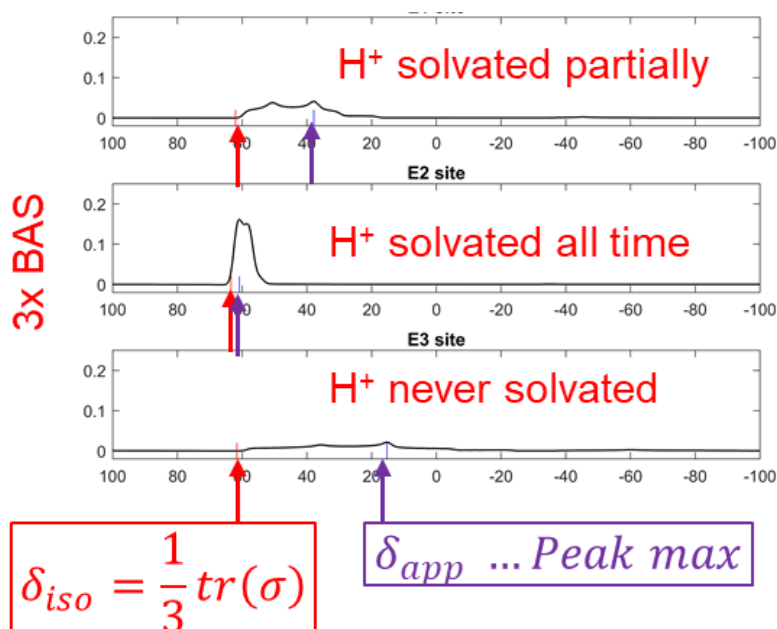


Figure 4.4 The simulated ^{27}Al NMR spectra for H-CHA model ($\text{Si}/\text{Al} = 3$) with three BAS sites (three aluminums) and six waters per unit cell. The spectra depict three types of BAS sites that can be characterized by fully solvated, partially solvated and unsolvated proton in the vicinity of the aluminum. The spectra were obtained from time-averaged chemical shielding tensors with the structures obtained from AIMD simulations. Reproduced from Ref.¹⁸⁶

4.2.4 Generalization in MOR

To evaluate the generality of the results observed in CHA, we also examined whether the framework-associated $\text{Al}(\text{OH})$ species are present in a different zeolite, the proton form of MOR (H-MOR). The existence of framework-associated $\text{Al}(\text{OH})$ in H-MOR has been shown in previous experimental studies.⁹⁷⁻⁹⁸ The results showed that the amount of framework-associated $\text{Al}(\text{OH})$ in H-MOR decreases with increasing Si/Al ratio.⁹⁷ From ^{27}Al MAS NMR spectra of H-MOR the amount of $\text{Al}(\text{OH})$ is almost negligible in the Si-

rich sample with Si/Al = 48, and is up to 10 % relative to total Al in samples with Si/Al $\leq$ 19. This suggests that isolated Al atoms do not form framework-associated Al(OH); instead, two or more Al atoms in close proximity might be required for the generation of framework-associated Al(OH). Our calculations on CHA have already indicated this point. However the phenomenon of reversible tetrahedral–octahedral aluminum coordination in MOR is independent of the Si/Al ratio (in the range of 8.8-19.7).¹⁹⁸

In order to theoretically study the formation of framework-associated Al(OH) species in MOR, models were constructed based on the conventional 48 T-sites cell with Si/Al = 15 (containing three Al atoms in cell and forming one Al-O-Si-O-Al pair) and 47 (isolated Al), incorporating six water molecules per cell. Here, we do not aim to show the formation of all the possible framework-associated Al(OH). Instead, only the framework-associated Al(OH) of T4 site in the main channel is considered as an example, and using two T1 sites as the proximity Al sites to form Al pairs (Figure 4.5). The AIMD trajectories of MOR(15) and MOR(47) are calculated and shown in Figure 4.5 and 4.6, respectively. Similar to CHA, LAS(6) remains kinetically stable in the low-silica MOR model (Si/Al=15). Additionally, the stabilization of the octahedral Al moiety seems to require at least one proton bound to Al(OH)-O-Si bonds, with the system becoming further stabilized by the presence of two protons. These results align with experimental observation. The necessity of protons on Al(OH)-O-Si bridges in MOR was investigated by moving two protons from LAS(6) to BAS(4) oxygen atoms (Figure 4.5). When one proton is moved from LAS(6) to a BAS(4) oxygen, the LAS(6) remains, but the system energy increases by 13 kJ·mol⁻¹, according to AIMD simulations. However, moving both protons from LAS(6) leads to its transformation to LAS(4), accompanied by proton solvation in 15 ps, as shown in Figure 4.6b. Interestingly, this process also causes an energy increase of 14 kJ·mol⁻¹, similar to the effect of moving a single proton. While the energy increase associated with moving protons aligns with that observed in CHA(3), the energy changes differ. In CHA(3), the energy increases by 56 and 19 kJ·mol⁻¹ for moving one and two protons, respectively. These findings suggest that the presence of at least one proton on an Al(OH)-O-Si bridging oxygen atom is crucial for stabilizing the octahedral Al, although the energy required for destruction and transformation varies across different zeolites types.

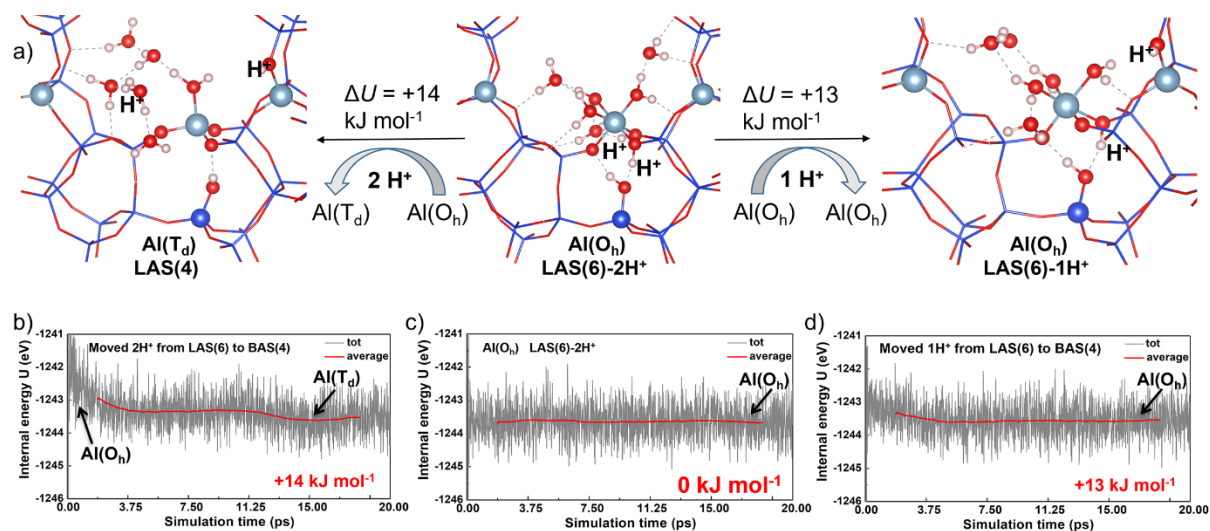


Figure 4.5 (a) Structures and relative internal energies (at 300 K) of framework Al in MOR(Si/Al = 15) with different number of protons attached to the framework oxygen atoms in the first coordination shell of Al. The $\text{Al}(\text{O}_h)$ with two protons is the most thermodynamically stable (middle). The structure with one proton remains octahedral but is the least stable (right). In the absence of proton, the structure reverts to a tetrahedral LAS(4) with a single water molecule bonded to the Al atom (left). (b) The AIMD trajectories for octahedral LAS(6) without protons evolving towards tetrahedral LAS(4) structure. (c) and (d), the AIMD trajectories for octahedral LAS(6) with two protons and with one proton. Note: The LAS(6) is located in the T4 site and is a part of the Al-O-Si-O-Al pair with the second aluminum of the pair residing in T1 site (see the numbering scheme depicted in Figure 4.6a below). Reproduced from Ref.¹⁸⁶

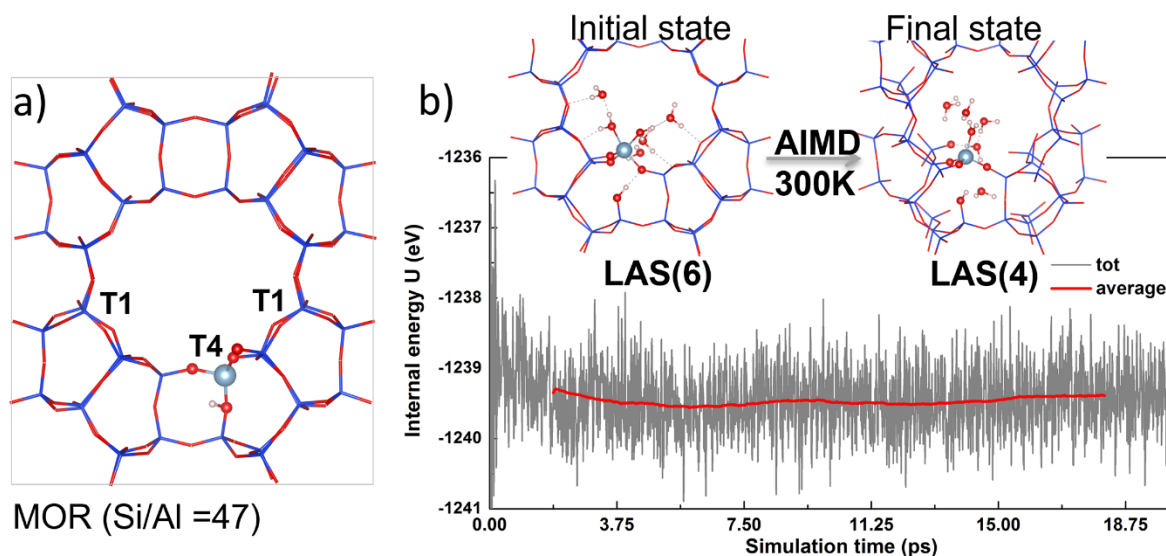


Figure.4.6 (a) The MOR(Si/Al= 47) model with a single BAS site per UC (Al atom located in T4 site). (b) AIMD trajectory depicting the spontaneous evolution of the octahedral LAS(6) towards the tetrahedral LAS(4) structure (the MOR(Si/Al = 47) with six waters in UC is considered) - it shows that the LAS(6) species is unstable in high-silica MOR. Reproduced from Ref.¹⁸⁶

It is notable that framework-associated Al(OH) have a preferred location in the pore structure of MOR zeolite. The proximal aluminum locations are more likely to form in the side-pockets of MOR, which is important for the generation and stabilization of framework-associated Al(OH).²²³ On the other hand, the stronger confinement effect in the side-pocket often leads to relatively stronger acidity of BAS sites compared to those in the main channel.²²⁰ However, the preferred locations of framework-associated Al(OH) species are beyond the scope of this thesis.

4.3 Summary

The structure and formation mechanism of the framework-associated Al(OH) species in CHA have been verified by ²⁷Al NMR calculations and AIMD simulations in combination with experimental NMR spectra. The calculated ²⁷Al NMR of *operando* modelling (Figure 4.3) fits the experimental chemical shifts obtained from MAS NMR ²⁷Al spectra, aligning the signals to different coordinated Al species (BAS(4), LAS(4), LAS(5) and LAS(6)) obtained from biased AIMD. Combining the AIMD with ²⁷Al NMR calculation is crucial for identifying the structure of the acid sites and enhancing the understanding of the spectra, particularly for discovering the mechanism behind the shoulders and peaks. Furthermore, on the example of MOR, it is suggested theoretically that the conditions of framework-associated Al(OH) formation under wet conditions from BAS sites obtained from CHA are general. The conditions for stabilizing framework-associated Al(OH) are: a low Si/Al ratio which offers enough BAS sites in close proximity to allow proton transfer and fixation of protons around the octahedral Al to-be-formed; one of the BAS Al sites is near the Al(OH) forming an Al pair (Al-O-Si-O-Al sequence); and a sufficient number of water molecules can be firmly bound to form the Al(OH) (at least three water molecules for each Al(OH)). This investigation provides further evidence that the framework of acidic zeolites becomes labile under wet conditions, and the partial, reversible hydrolysis of zeolite Si-O-Al and Si-O-Si bonds is kinetically allowed at room temperature. The mechanism behind the reversible transition of framework-associated Al(OH) improves our understanding of Lewis acid sites in zeolites. This insight would allow for greater control over the generation of Lewis acid sites, impacting catalytic applications based on Lewis acidic aluminum and the synergy between Brønsted and Lewis acids.²²¹

Chapter 5. NMR characterization of Al-zeolites with DFT

5.1 Motivation

This chapter establishes the reliability of the *operando* model to more accurately mimic experimental conditions. It demonstrates the influence of each factor in the modelling for accurate and efficient ^{27}Al NMR calculations. On examples of CHA and MOR zeolites, the effects of various factors were investigated, including Si/Al ratios, the topology of the framework, the type of charge compensating cation of the $(\text{AlO}_4)_2^-$ tetrahedron, and the level of hydration of the particular cation. Additionally, based on the dataset collected from the DFT calculated results in the process of *operando* modelling, a machine learning analysis was performed to linearly correlate the ^{27}Al NMR chemical shift with the geometrical features.

5.2 Results

5.2.1 Geometry optimization

To investigate effects of individual model parameters in calculating NMR properties, we conducted a series of calculations using models of increasing complexity. These models were selected to allow for the isolated analysis of specific factors, such as the inclusion of explicit cations, cation solvation in hydration, and framework topology. In a previous systematic study of ^{27}Al ssNMR by Holzinger *et al.*,¹⁸⁵ the influence of key model parameters, such as unit cell (UC) size, and the type of cluster and periodic models, was explored. However, these models did not explicitly account for extra-framework cations, instead using a positive background charge to compensate for the negative charge of the framework in periodic models. Building on the conclusions drawn by Holzinger *et al.*, we also included periodic models that use a background charge to balance the framework charge, referred to here as “background-charge” (bgc) models.

Zeolites CHA and MOR with one Al substituted site in the unit cell, were used as the main model systems. In constructing these models, we considered the charge-compensating ion (Na^+ , H^+ , and background charge (bgc)) and the degree of hydration. The models are

denoted as ABC(*n*)|M|*xw*, in which ABC refers to the zeolite framework, *n* presents the silicon-aluminum ratio (Si/Al), M is the charge-compensating cation, and *x* indicates the number of water molecules in the UC. Detailed description of these models are shown in Figure 5.1.

Models with background charge are labeled as bgc|0w, representing fully dehydrated systems without water. The completely dehydrated Na- and H-forms of zeolites are referred to as Na|0w and H|0w, respectively, while hydrated Na-zeolite and H-zeolites are denoted Na|*xw* and H|*xw*. In these case, *x* is set to 5 or 6. In the Na|*xw* cases, Na⁺ is either partially or fully solvated, as shown in green-framed bottom row of Figure 5.1. Partial Na⁺ solvation means the Na⁺ first coordination shell consists of 2-3 framework oxygen atoms and 3-4 water molecules, and full Na⁺ solvation means the Na⁺ cation moves towards the center of the channel, breaking coordination with framework oxygen atoms, so that its first coordination shell consists only of water molecules. In the H|*xw* cases, the proton is easily solvated, forming an H₃O⁺ group when sufficient water molecules are present.²²² Additionally, two supplementary hydrated MOR models with two and three Al substitutions and five water molecules in the unit cell were included to broaden the scope of the study.

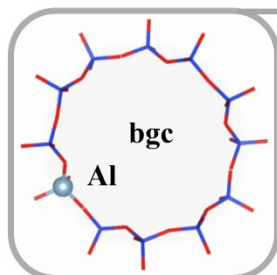
The lattice parameters and atomic position were fully optimized for all CHA cases to investigate the effects of hydration and extra-framework cations on the structures and ²⁷Al NMR properties. The differences in the optimized cells for CHA cases with a single Al substitution showed minimal impact on the ²⁷Al NMR chemical shift, which will be explored in detail in the next section. To isolate the effect of the *operando* modelling, the fixed lattice parameters obtained from optimizing the CHA(11)|Na|5w case were used for all CHA models. These parameters are: *a* = 9.20 Å, *b* = 9.33 Å, *c* = 9.35 Å, *α* = 94.35 °, *β* = 94.17 °, *γ* = 93.05 °, with a volume of 796.35 Å³.

In dehydrated CHA, there are two possible positions for Na⁺, 6MR and 8MR, and four oxygen sites for connecting with proton and forming BAS sites, O1, O2, O3, and O4 (Figure 3.1). The configuration with Na⁺ at the 6MR was used for the CHA(11)|Na|0w case, which is more stable than the configuration with Na⁺ at the 8MR. The most stable CHA(11)|H|0w structure has a proton on O4, while configurations with protons on O1, O2,

and O3 are higher in energy by 7.7, 9.1, and 4.7 kJ·mol⁻¹, respectively. For hydrated cases of Na-CHA, the partially solvated Na⁺ configuration, CHA(11)|Na|5w, is 9.6 kJ·mol⁻¹ less stable than the fully solvated Na⁺ configuration, CHA(11)|Na|5w*.

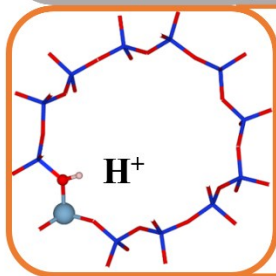
The lattice parameters of the 24 T-sites cell used for all the MOR models are: $a = b = 13.74$ Å, $c = 7.54$ Å, $\alpha = \beta = 90.00$, $\gamma = 83.28$, with volume of 1413.64 Å³. In the MOR(23)|bgc|0w cases, different T-sites (T1, T2, T3 and T4) for Al substitution were explored. The dehydrated MOR(23)|Na|0w model includes a Na⁺ cation, whose position was determined based on geometry optimization of an exhaustive set of initial configurations. The possible Na⁺ locations (A, B, C, D, and E as shown in Figure 3.2) were considered for each Al substitution. The two lowest-energy Na⁺ configurations for each Al substitution in MOR(23)|Na|0w are shown in Figure 5.2. For T1 and T2 Al sites, two different Na⁺ distributions can coexist, with energy differences of only 1 and 3 kJ·mol⁻¹, respectively. In contrast, the energy differences between the second lowest-energy configurations and the lowest energy configurations for T3 and T4 are larger, at 23 and 27 kJ·mol⁻¹, respectively.

The hydrated MOR(23)|Na|6w model features a Na⁺ cation solvated by six water molecules, positioned according to the minimum-energy structure obtained through static geometry optimization. The configurations with partially and fully solvated Na⁺ of MOR(23)|Na|6w cases are denoted T_n and T_n*, respectively (where n = 1–4, corresponding to the T sites) (Figure 5.3). The partially solvated configurations are slightly more stable, with static energy differences of 6.8, 22.2, 28.0, and 23.2 kJ·mol⁻¹ compared to the fully solvated variants for T1, T2, T3, and T4, respectively. Notably, only the solvated configurations of the T1 site, with Na⁺ located in the 12MR channel, were considered, as the confined 8MR channel does not provide enough space for solvation.



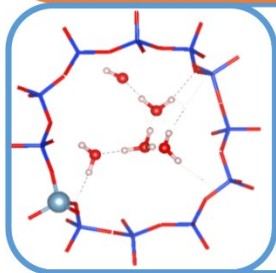
bgc|0w: background charge model

- Not explicitly considering any extra-framework cations
- The negative charge of the framework is compensated by a smeared background charge



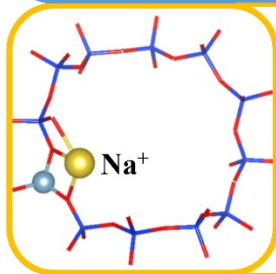
H|0w: dehydrated protonic model

- The negative charge of the framework is compensated by the proton bound to AlO_4
- The presence of proton on one of four oxygen atoms of AlO_4 tetrahedron results in large anisotropy on framework Al
- Different δ expected for each of for oxygen atoms



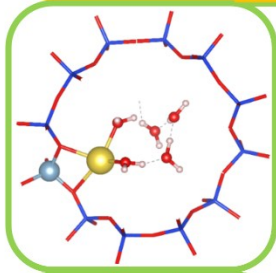
H|nw: hydrated protonic model

- The negative charge of the framework is compensated by the proton solvated in the vicinity of AlO_4
- Such situation occurs when there is sufficient void space with sufficient amount of water
- Charge compensation provided by the hydrogen bond network



Na|0w: dehydrated Na^+ model

- The negative framework charge compensated by Na^+
- There may be more than one position of extra-framework Na^+ cation (depending on zeolite topology), each of them resulting in different δ



Na|nw: hydrated Na^+ model

- The negative framework charge compensated by Na^+ solvated in the vicinity of AlO_4
- Depending on the void space and amount of water in the vicinity of AlO_4 the Na^+ cation can be either partially or fully solvated
- Partial solvation: Na^+ stays coordinated to 2-3 framework oxygen atoms and it has 2-3 water molecules in the first coordination shell
- Full solvation: Na^+ has only water molecules in its first coordination shell and it is farther from AlO_4 tetrahedron

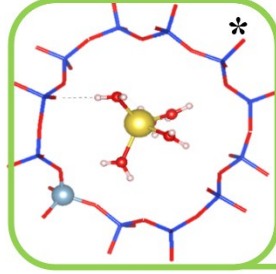


Figure 5.1 The detail of models with considering different cations and water loading. Reproduced from Ref.¹⁷⁸ with permission from the Royal Society of Chemistry.

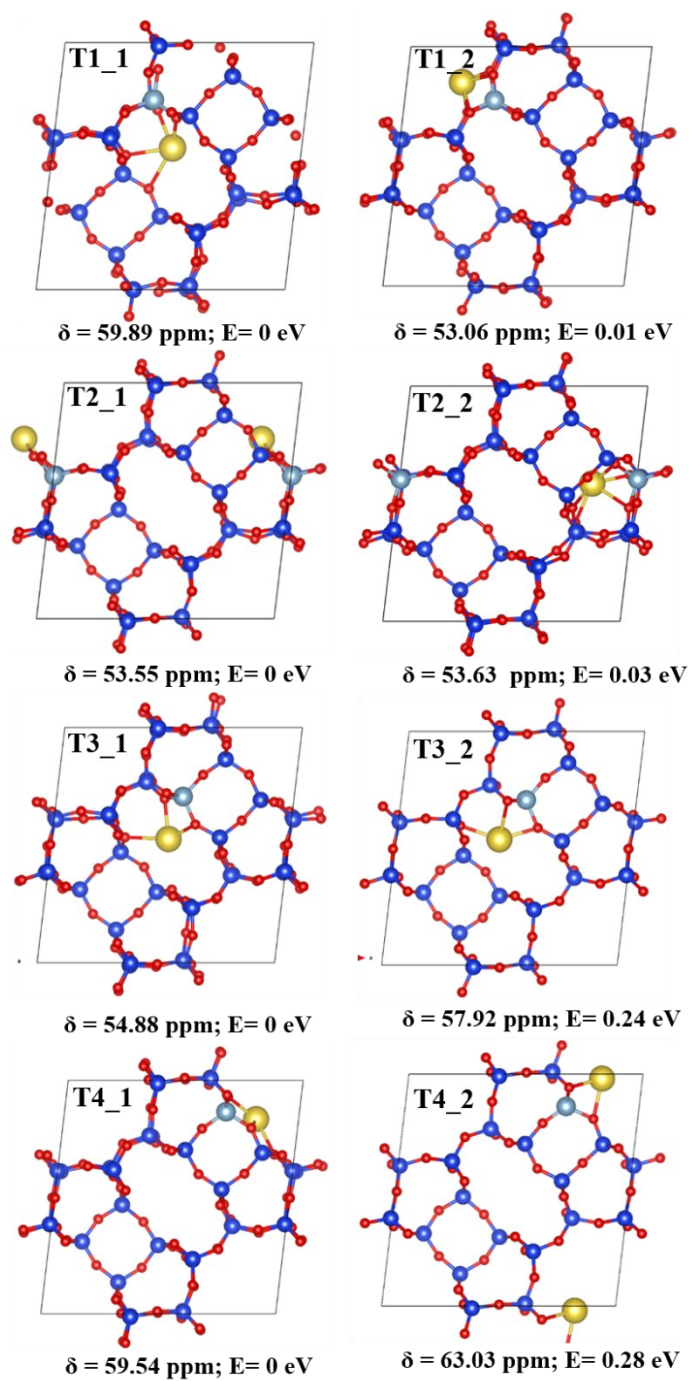


Figure 5.2 Chemical shifts calculated for the two most stable MOR(23)|Na|0w local minimum configurations for each T site. δ and $\langle\delta\rangle$ denote the static and dynamically averaged ^{27}Al chemical shifts, respectively. Reproduced from Ref.¹⁷⁸ with permission from the Royal Society of Chemistry.

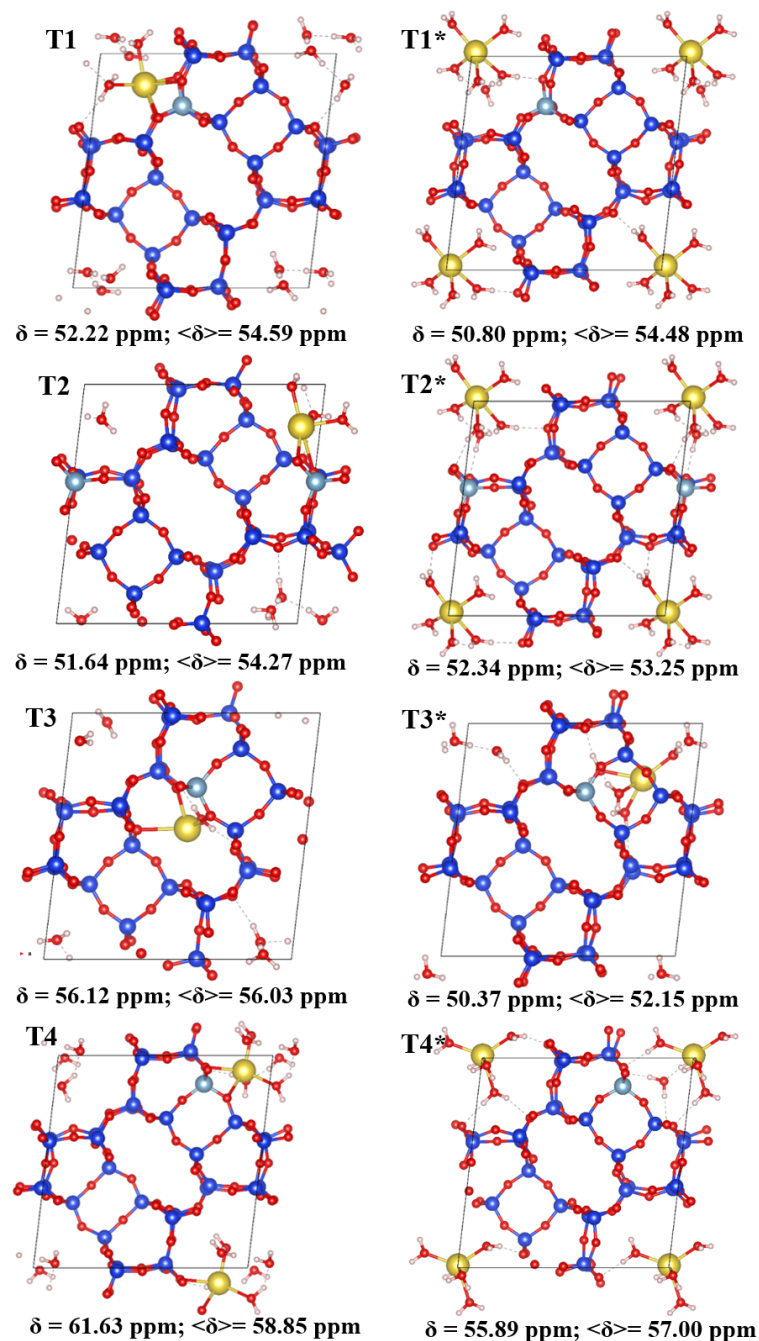


Figure 5.3 Chemical shifts were calculated for partially (left) and fully (right) solvated MOR(23)|Na|6w configurations for each T site. The configurations with solvated and fully solvated Na^+ are shown as T_n and T_n^* , respectively ($n=1-4$). δ and $\langle\delta\rangle$ denote the static and dynamically averaged ^{27}Al chemical shifts, respectively. Reproduced from Ref.¹⁷⁸ with permission from the Royal Society of Chemistry.

5.2.2 Effect of the UC size and volume

The structure is crucial for an accurate calculation of ^{27}Al isotropic chemical shifts of the zeolite. In zeolites, as the Al substitution increases, the UC expands because the

equilibrium Al-O bond length is longer than the Si-O bond. The effect of UC size and volume on structurally sensitive NMR parameters therefore cannot be ignored. To explore this, we optimized the UCs of various CHA(11) models to assess the influence of the extra-framework cations and hydration on the structure and, thereby on NMR parameters.

Compared to the ideal UC from IZA database, the volume change of all the models can reach up to 20 Å³. However, this only results in a maximum 2 ppm shift in the static ²⁷Al isotropic chemical shift (δ), except for the ignorable cases of dehydrated protonic CHA with BAS sites, which are undetectable in the experimental NMR spectra (Figure 5.4a and Table A1). This exception will be explained in Section 5.2.3. The ²⁷Al δ increases slightly with decreasing volume. In the CHA(11)|H|0w case, the values of the structures with BAS on different oxygen atoms do not always follow the tendency of the volume change. For example, CHA(11)|H|0w with BAS on O2 shows a 14 Å³ larger volume and about 2 ppm higher δ compared to the CHA(11)|Na|5w case. This exception may be due to the hydrogen bonding interaction between the proton in the BAS site and adjacent oxygen atoms of the framework,²²³⁻²²⁴ which significantly affects the chemical shifts more than the resulting volume change.

Overall, the volume changes observed between models with a fixed Si/Al ratio in CHA are relatively small, and their effects changes on the chemical shifts is modest, which falls within the range influenced by proton location, cation solvation, and thermal effects.

To systematically evaluate the effect of volume change, the CHA(11)|Na|0w model was used by isotropically varying the UC volume, thereby avoiding the complicated effect of water configuration and the significant effect of the hydrogen bonding from BAS sites. Within the volume range from 810 to 760 Å³, the ²⁷Al δ increases linearly from 61 to 66 ppm with decreasing UC volume (Figure 5.4a), which is consistent with the 10 ppm range found by Goltl et al. for volume changes between 800 and 880 Å³.²²⁵ However, we did not observe a significant volume shift in any of the CHA models, including those with varying Si/Al ratios from 11 to infinity (Table A1 and A2). The volume shift in our models ranges from 794 to 815 Å³, which leads to a deviation of 2 ppm in ²⁷Al δ with an associated energy difference of 5 kJ·mol⁻¹ (Figure 5.4a). This indicates that small volume changes in Si-rich zeolites have no significant effect on ²⁷Al chemical shift.

The geometrical parameters and structural descriptors contributions of to ^{27}Al δ are summarized for $\text{CHA}(11)|\text{Na}|0\text{w}$ with different volumes (Table A3). With the volume decreasing from 810 to 760 $\text{\AA}^3$, the increase in δ is mainly due to the reduction in the Al–O–Si angle (from 143 to 141°) and a slight decrease in the Al–O distance (from 1.742 to 1.736 $\text{\AA}$). The values of C_Q and η_Q change only slightly over the volume range considered, with C_Q increasing by about 0.3 MHz and η_Q decreasing by about 0.1 (Figure 5.4b).

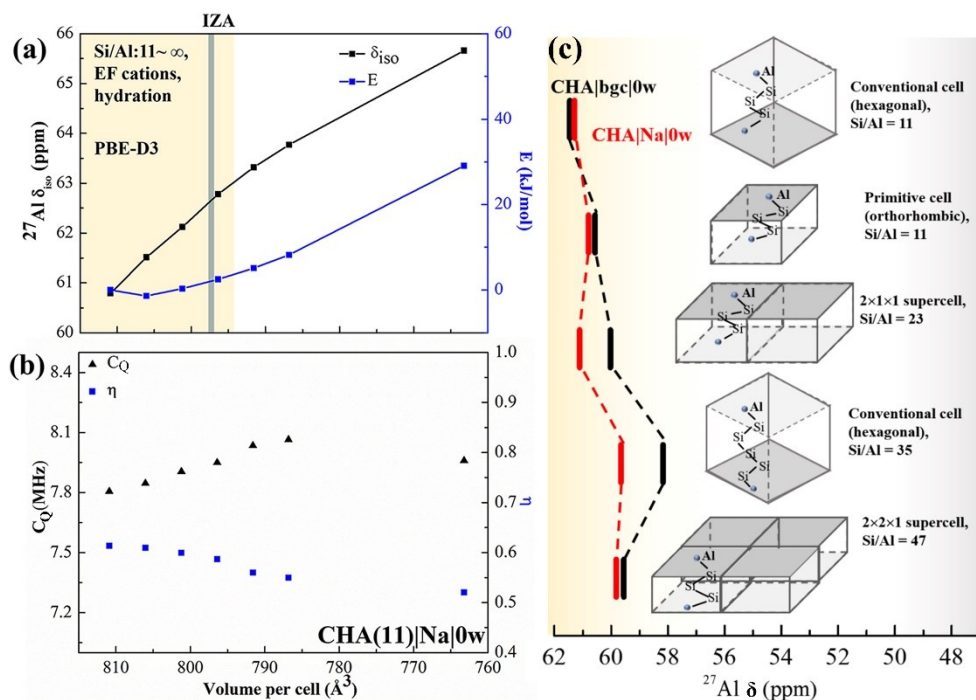


Figure 5.4 The effect of the UC size and parameters on calculated ^{27}Al chemical shifts. (a) The calculated δ as a function of isotropic cell volume variation in $\text{CHA}(11)|\text{Na}|0\text{w}$ along with the relative energy variation. The yellow background covers the full volume range obtained at the PBE-D3 level for CHA with Si/Al from ∞ to 11, including all charge-compensation models and hydration degrees (see also Table A1 and Table A2). The grey bar denotes the volume from the IZA database; (b) Changes of C_Q and η_Q with volume for the same zeolite model. (c) Calculated ^{27}Al chemical shifts in CHA using various supercells, highlighting the importance of local structure and Si/Al ratio over supercell size (the data is also shown in Table A2). Reproduced from Ref.¹⁷⁸ with permission from the Royal Society of Chemistry.

The impact of supercell size and Si/Al ratio on the calculated ^{27}Al δ in Si-rich systems was examined using the Na|0w and bgc|0w models. The static ^{27}Al chemical shifts for various CHA structures were considered, including CHA(11) with both conventional and primitive cells, CHA(23) with a $2 \times 2 \times 1$ supercell, CHA(35) with a conventional cell, and CHA(47) with a $2 \times 2 \times 1$ supercell (Figure 5.4c and Table A2). These supercells were constructed based on the primitive cell containing 12 T-sites. The maximum difference in ^{27}Al δ

between the bgc|0w and Na|0w model is 1.5 ppm, observed in the CHA(35) case with the conventional cell. In the Na|0w cases, the ^{27}Al δ varies by less than 1.7 ppm across different cell sizes and Si/Al ratios, ranging from 11 to 47, while in the bgc|0w cases, the shifts exhibit differences of up to 3.3 ppm. This suggests that the simplified model, which uses background charges to balance the negative charge of the framework, may produce NMR chemical shifts that differ from those obtained using real extra-framework cations, even in simple zeolite CHA.

The calculated δ values for the MOR primitive cell (24 T atoms, Si/Al = 23) were compared with those obtained for supercells repeated along the c and a lattice vectors (Si/Al = 47) (Figure 5.5). The δ values from Na|0w models of MOR do not depend on the supercell, except for the T4 Al site calculated with a $1 \times 1 \times 2$ supercell at Si/Al = 47. This effect is attributed to changes in the arrangement of Al atoms, which is often related to the Si/Al ratio. In all MOR(23) models and the MOR(47) of $2 \times 1 \times 1$ supercell model, Al-(O-Si)₂-O-Al sequences are formed due to the short range of the UC in the c direction. However, in the MOR(47) of $1 \times 1 \times 2$ supercell, the cell is expanded in the c direction, resulting in an Al-(O-Si)₃-O-Al sequence, where the Al site can be treated as isolated.⁷⁶ Similar results obtained from the MOR(47) of $2 \times 1 \times 1$ supercell and MOR(23) models further support this finding. Thus, the Si/Al ratio is an essential factor in accurately simulating ^{27}Al δ to match experimental data.

The effect of the supercell on simple background charge models is also shown in Figure 5.5. It is evident that such simplified models can be problematic because a different relative order of δ for individual Al positions was given by using a different supercell. In brief, the pure supercell effect is minimal, while other factors can confound this: 1) the Si/Al ratio, 2) the cell symmetry, and 3) the length of the Al-(O-Si)_n-O-Al sequence. In Si-rich zeolites, Al atoms tend to be isolated,⁷⁶ and the effects of symmetry and Al pairing become negligible. However, the aluminum content at which this threshold is reached depends on the framework topology.

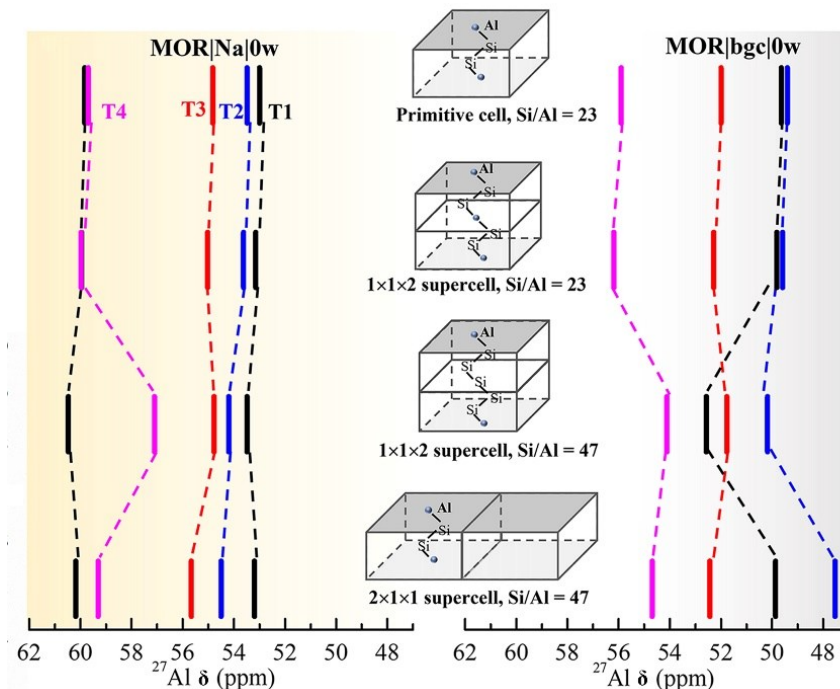


Figure 5.5 The effect of the UC size and Si/Al ratio on calculated ^{27}Al chemical shifts. Reproduced from Ref.¹⁷⁸ with permission from the Royal Society of Chemistry.

5.2.3 Effects of the model complexity

The static ^{27}Al NMR chemical shift (δ) and quadrupolar coupling constant (C_Q) were then calculated based on the low energy structures to examine the effects of cations and hydration. The results of CHA(11) show that, except for dehydrated H-CHA, the calculated ^{27}Al δ values for all CHA models are concentrated around 61 ppm and vary by no more than 2 ppm, which agrees well with experimental results (see Figure 5.6 and Table A4). In the case of dehydrated H-CHA (represented by H|0w), the most stable configuration, where the proton is bonded to O4, gives a ^{27}Al δ value of 65.4 ppm, approximately 5 ppm lower than in other models. The other three BAS sites show values of 56.9, 59.2, and 64.4 ppm for O1, O2, and O3, respectively. The anomalously low chemical shifts observed in dehydrated H-CHA(11) arise from the increased average Al-O bond length and $\alpha_{\text{Al-O-Si}}$ angle at the Brønsted site, which is a consequence of the lack of proton solvation. These peaks are considered "invisible" in experimental observation due to the marked distortion of the AlO_4 tetrahedra at the BAS site caused by the presence of a proton. The highly anisotropic environment of the quadrupolar nucleus results in broad peaks, making them difficult to detect.

Another important parameter in ^{27}Al NMR, C_Q helps characterize the shape of the resonances. In ^{27}Al NMR spectra measurements for zeolites, the hydrated samples are often used to reduce the large quadrupolar couplings, especially for visualizing Al sites in protonic zeolites. The notable effect of water molecules in the voids lies in their ability to solvate charge-compensating cations, which increases the symmetry around the acid sites,²²⁶ thereby leading to a small C_Q . Static calculations (shown in Table A4) reveal that the C_Q values decrease from 6.7 MHz ($P_Q = 7.0$ MHz) for the dehydrated configuration of CHA(11)|Na|0w cases to 3.2 MHz ($P_Q = 3.2$ MHz) for the fully solvated configuration of CHA(11)|Na|5w models. This reduction reflects the increased symmetry of the Al environment upon solvation. Although the precise C_Q values are overestimated, the trend agrees with the experimental results, which show that hydration decreases P_Q^{217} ($C_Q(1 + \eta^2/3)^{1/2}$) from 4.2 MHz to 1.8 MHz.²²⁷ In protonic systems, the value of C_Q for H|0w cases is around 20 MHz, which is consistent with experimental observations that the BAS site Al is undetected in ^{27}Al NMR spectra.²¹⁷⁻²¹⁹ When the proton is solvated in the CHA cage at hydrated condition, the δ and $\langle\delta\rangle$ values of H|5w case are in line with that of other models around 60 ppm and the C_Q values decrease to 1.4 MHz ($P_Q = 1.6$ MHz), thus making the peak visible. By comparison, the experimental quadrupolar product P_Q^{217} , ($C_Q(1 + \eta^2/3)^{1/2}$) is found to be 1-2 MHz for a BAS site in MFI.¹⁰⁰ The results show that considering water and the explicit extra-framework cations improves the accuracy of the C_Q prediction.

To further investigate the effects of modelling factors in more complex zeolites, MOR models, which contains four distinct T-sites, were used to study the ^{27}Al chemical shifts. The static results for MOR with a Si/Al ratio of 23 (Figure 5.7 and Table A5) indicate that the simplified models, MOR(23)|bgc|0w, can produce results that are inconsistent with those obtained from models that more accurately fit the experimental conditions, including explicit cation and water loading. The interpretation of experimental NMR spectra depends heavily on the model used, and using inappropriate models may lead to misleading results. The values of ^{27}Al δ for MOR(23)|bgc|0w models range from 50 to 56 ppm, in which only δ of T4 Al site agrees with experimental results (around 56 ppm⁹⁸) while that of Al in the T1, T2, and T3 positions are too small, showing 49.7, 49.5, and 52.1 ppm, respectively. Because the background charge is often treated as a mean field affecting the entire system, it creates a relatively symmetrical environment for framework Al without local

perturbations by cations. As a result, the C_Q values are around 3.0 MHz, which is lower than other models.

Compared to MOR(23)|bgc|0w models, the presence of the charge-compensating cation Na^+ in MOR(23)|Na|0w models increases the ^{27}Al δ by 3-4 ppm, and increases anisotropy of Al environment, leading to larger C_Q values (above 5 MHz). These effects are attributed to the change of electron density around the Al nucleus due to the attachment of the cation to the oxygen atoms of $(\text{AlO}_{4/2})^-$ tetrahedra. The Na cations located in different channels lead to varying effects on the framework Al, such as different Al-O-Si angles and anisotropic environment. Beyond influencing the δ and symmetry of each T site Al, the presence of Na^+ qualitatively changed the whole spectra: 1) Al in the T1 site can show two signals from the δ values; 2) the order of ^{27}Al δ in individual T sites differs from those obtained with the MOR(23)|bgc|0w models.

In MOR framework, Na^+ cations can approach the $(\text{AlO}_{4/2})^-$ tetrahedron from different channels, leading to different chemical shift values for the same Al site with different positions of Na^+ cations (Figure 5.2). The ^{27}Al δ values for the lowest and second-lowest energy configurations differ by 7, 0, 3, and 3 ppm for the Al sites in T1, T2, T3, and T4, respectively. If such structures with Na^+ in different channels have comparable energies, both configurations could potentially appear in the NMR spectra, provided they do not interchange positions within the time scale of the NMR measurements. Such as the Al in T1 site of the MOR(23)|Na|0w model, shows two isoenergetic Na^+ configurations with distinct different δ values: 53 ppm for Na^+ in the main 12 MR channel and 60 ppm for Na^+ in the limiting 8R channel along [0,0,1]. These two different δ values resulting from a single framework Al atom are denoted as “ δ -doublets”.

Compared to the ^{27}Al isotropic chemical shift of dehydrated MOR(23)|Na|0w cases, cation solvation in hydrated MOR(23)|Na|6w cases widens the range of calculated chemical shifts (from 51 to 62 ppm), shifting the values in different directions. Similar to the CHA(11)|Na|5w case, both partially (Tn) and fully (Tn*) solvation modes of Na^+ in the MOR channels are considered (Figure 5.3). Water molecules surrounding Na^+ weaken its interaction with the framework oxygen atoms of the $(\text{AlO}_{4/2})^-$ tetrahedron, which relaxes Al-O-Si angles and partially reduces the anisotropy of the Al environment. The partially

solvated T3 and T4 cases show lower shifts, while other solvated cases, such as T1 and T2 cases, exhibit higher shifts than their dehydrated counterparts (Figure 5.7 and Table A5). This suggests that the shielding effect of the solvated Na^+ cation is related to the cavities in which it is located. Additionally, solvation of Na^+ induces qualitative shifts in the relative positions of the signals. For instance, T3* has the lowest value in the hydrated model, whereas in the dehydrated models, T1 shows the lowest value. Additionally, cation solvation under hydrated conditions can influence δ -multiplets, representing multiple δ peaks for the same Al sites. For instance, T1 and T2 Al sites show δ -doublets in dehydrated cases, corresponding to two different isoenergetic cation configurations. However, in hydrated cases, cations may adopt different solvation states depending on their local environment, as demonstrated by Maurin et al.²²⁸ All these sites exhibit δ -doublets, which can appear in the NMR spectrum, making it challenging to assign specific peaks to individual Al atoms.

The ^{27}Al C_Q of the T4 Al site for MOR(23)|Na|6w is up to 4 MHz lower than that for MOR(23)|Na|0w (Table A5). Fully solvated cases often display lower C_Q values ($C_Q < 5$ MHz) than partially solvated cases, although the fully solvated T3 case shows a slightly higher C_Q value, possibly due to more hydrogen bonds forming between water molecules and framework oxygen atoms (as shown in the third panel of Figure 5.3).

Previous static calculations^{96, 229} suggest that hydration has a negligible effect on the ^{27}Al isotropic chemical shift in silicon-rich zeolites. Sklenak et al.⁹⁶ found that ZSM-5 with different cations (Na^+ , Li^+ and H^+) exhibits similar ^{27}Al δ , as solvated cations minimize their influence on framework Al. This supports the use of background charge models in Al NMR simulations.^{57, 185, 225, 230} However, this is only true if cations are fully solvated, which depends on topology and Si/Al ratio. Moreover, as Al content and the associated cations increase, water molecules in the voids can only partially solvate the cations.²³¹ Such partially solvated cations affect the chemical shift by influencing the local structure of the framework around Al.

5.2.4 Effects of dynamics on ^{27}Al chemical shift

The ^{27}Al isotropic chemical shifts of the CHA(11) models from the static calculation (δ) and from the time-averaged over the AIMD trajectory ($\langle\delta\rangle$, where the brackets indicate use the averaged results), were compared to identify the effect of the dynamics in NMR calculations (Figure 5.6 and Table A4). The values of $\langle\delta\rangle$ were averaged over a 50 ps MD trajectory for hydrated cases and 40 ps for dehydrated cases, with even sampling every 0.2 ps. Generally, the difference between values of $\langle\delta\rangle$ and corresponding static δ values show a systematic 2 ppm increase, which is not a significant shift to distinguish from the experiments. For the dehydrated cases, the vibration of the framework and the extra-framework cations often exhibit slightly moving behavior at room temperature, the environment around the Al site remains constant during the AIMD simulations.

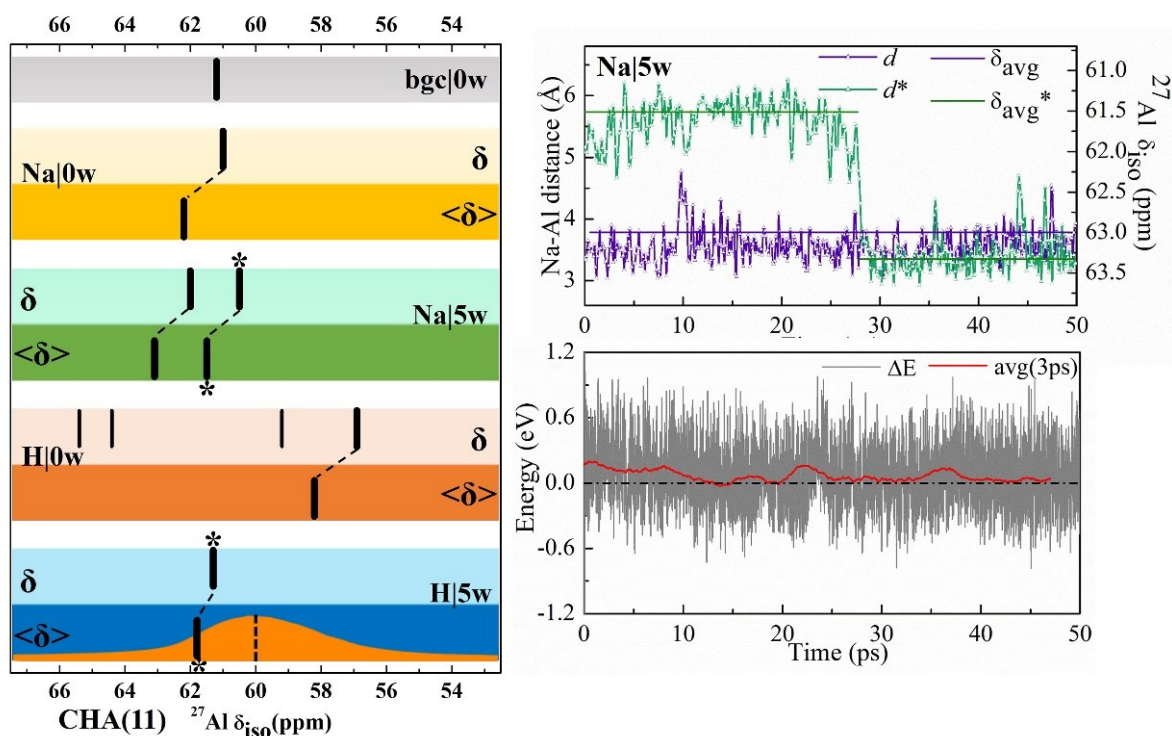


Figure 5.6 Calculated ^{27}Al NMR chemical shifts for CHA(11) zeolite from static calculation and dynamically averaged results (left). Chemical shifts are denoted by black bars. For dehydrated Na-CHA, hydrated Na-CHA, dehydrated H-CHA, and hydrated H-CHA(*), δ values are displayed with a lighter background for static δ and a darker background for averaged $\langle\delta\rangle$ values, represented by colors yellow, green, orange, and blue, respectively. In the CHA(11)|Na|5w models, the fully solvated Na^+ cation is marked with an asterisk. The orange plot in the bottom row corresponds to the experimental MAS NMR⁸¹, while the dotted line refers to the peak maximum of the MQMAS spectrum from Ref²³². The Al-Na distance and energy difference ΔE along the MD trajectory of CHA(11)|Na|5w cases are also shown (right). Here ΔE is defined as the energy difference between fully solvated Na^* models and their partially solvated counterparts. Reproduced from Ref.¹⁷⁸ with permission from the Royal Society of Chemistry.

However, the presence of the water molecules can make a difference because the transformation of different solvation states may happen at room temperature for the cations. In the $\langle \text{CHA}(11)|\text{H}|5\text{w} \rangle^*$ case, the proton at the BAS site keeps steadily on the solvated state, forming hydrated hydronium ions throughout the AIMD simulation with sufficient water loading, which aligns with the findings of Grifoni et al.²²² Thus, the dynamically averaged ^{27}Al chemical shift for $\langle \text{CHA}(11)|\text{H}|5\text{w} \rangle^*$ is similar to the static result of $\text{CHA}(11)|\text{H}|5\text{w}^*$.

The hydrated Na-CHA case is the most complex system, where the Na^+ can be solvated into two interchangeable states at room temperature: fully solvated ($\text{CHA}(11)|\text{Na}|5\text{w}^*$) and partially solvated ($\text{CHA}(11)|\text{Na}|5\text{w}$). Analysis of MD trajectories for the $\text{CHA}(11)|\text{Na}|5\text{w}$ cases reveals the presence of both fully solvated Na^+ and partially solvated Na^+ modes (Figure 5.6). These modes can be distinguished by the Na-Al distance, with about 3.5 Å for the partially solvated state and 5.5 Å for the fully solvated state. Despite a difference of up to 2 Å in Na-Al distance between the two states, the corresponding averaged $\langle \delta \rangle$ values differ by only 1.6 ppm. Moreover, MD analysis of the energies indicates that the average energy $\langle E \rangle$ for fully and partially solvated Na^+ is very similar (Figure 5.6). Therefore, the chemical shielding tensor should be averaged over a sufficiently long simulation to adequately account for both solvation states of Na^+ according to their occupation probabilities. Over the course of the 50 ps MD simulations, the average shift is 62.4 ppm, which does not show a marked difference between those two solvation modes.

The calculated ^{27}Al chemical shifts for CHA(11) cases show minimal sensitivity to the model parameters. Temperature effects, determined by averaging shielding tensors along the MD trajectory, result in an increase in chemical shift of up to 2 ppm. Although the solvation of H^+ has a significant impact, the solvation of the Na^+ charge-compensating cation has little effect on either δ or $\langle \delta \rangle$ values.

Based on the study of CHA, the dynamic effect is minimal on ^{27}Al NMR for dehydrated cases. To verify this for dehydrated MOR, two cases in $\text{MOR}(23)|\text{Na}|0\text{w}$, with Al substituted into the T1 and T3 sites, were selected. The time-averaged $\langle \delta \rangle$ of all the MOR models were obtained over 20 ps MD trajectories. The differences between the dynamically

averaged $\langle\delta\rangle$ and static δ were only 0.7 and 0.4 ppm for T1 and T3, respectively (as shown in Figure 5.7 and Table A5), confirming the minimal dynamic effects on chemical shift.

The dynamic model of the solvated sodium form of MOR, $\langle\text{MOR}(23)|\text{Na}|6\text{w}\rangle$ is a complex case. The comparison between $\langle\text{MOR}(23)|\text{Na}|6\text{w}\rangle$ and $\text{MOR}(23)|\text{Na}|6\text{w}$ models, as illustrated in Figure 5.7, shows that dynamics significantly affect the ^{27}Al chemical shift values, causing shifts ranging from -3 to +4 ppm at 300 K. The calculated ^{27}Al $\langle\delta\rangle$ values for $\langle\text{MOR}(23)|\text{Na}|6\text{w}\rangle$, obtained using the same approach as in the CHA(11) cases over 20 ps AIMD trajectories, fall within the range of 52-59 ppm, which aligns well with the experimental results.

Furthermore, the dynamic effects on chemical shift variations differ between partially and fully solvated Na^+ structures. To examine this, the Na-Al distances were traced along the trajectories for both solvation states, focusing on the Al in the T3 site (Figure 5.7 right). When the Na^+ compensates for Al in the confined 8R channel, it remains close to the Al site due to the lack of space for water molecules to solvate the cation, with the Na-Al distance being about 3 Å. Consequently, Na^+ remains in the same position, exhibiting only vibrational motion throughout the MD simulation, and the Al environment (or ^{27}Al δ) stays unchanged. In contrast, when Na^+ compensates for Al of the T3 site in the more spacious 12MR channel, there is enough space for water molecules to fully solvate it. The Na-Al distances along the MD trajectory indicate that partially and fully solvated states interchange during the simulations (with Na-Al distances exceeding 5 Å). The ^{27}Al $\langle\delta\rangle$ value for cases with Na^+ in the limiting 8MR channel along [001] is 56 ppm, while in the main channel, it is 52 ppm. Although the $\langle\delta\rangle$ values for the two Na^+ solvation states are different, the average energy differences $\langle E\rangle$ over their MD simulations are less than 30 $\text{kJ}\cdot\text{mol}^{-1}$ (Figure 5.8). This demonstrates that the presence of framework Al showing δ -doublets is general, with corresponding cases marked by asterisks in Figure 5.7, indicating $\langle\delta\rangle$ values obtained for fully solvated cases.

Unlike the minimal effect of the model complexity on ^{27}Al δ in the simple CHA zeolite, the results for MOR show that the relative values of ^{27}Al δ for different T-sites qualitatively depend on the model complexity. Therefore, it is evident that models accounting for both experimentally realistic water content and temperature fluctuations are necessary for accurately interpreting experimental spectra, particularly when assigning the positions of framework Al, as demonstrated by the $\langle\text{MOR}(23)|\text{Na}|6\text{w}\rangle$ model.

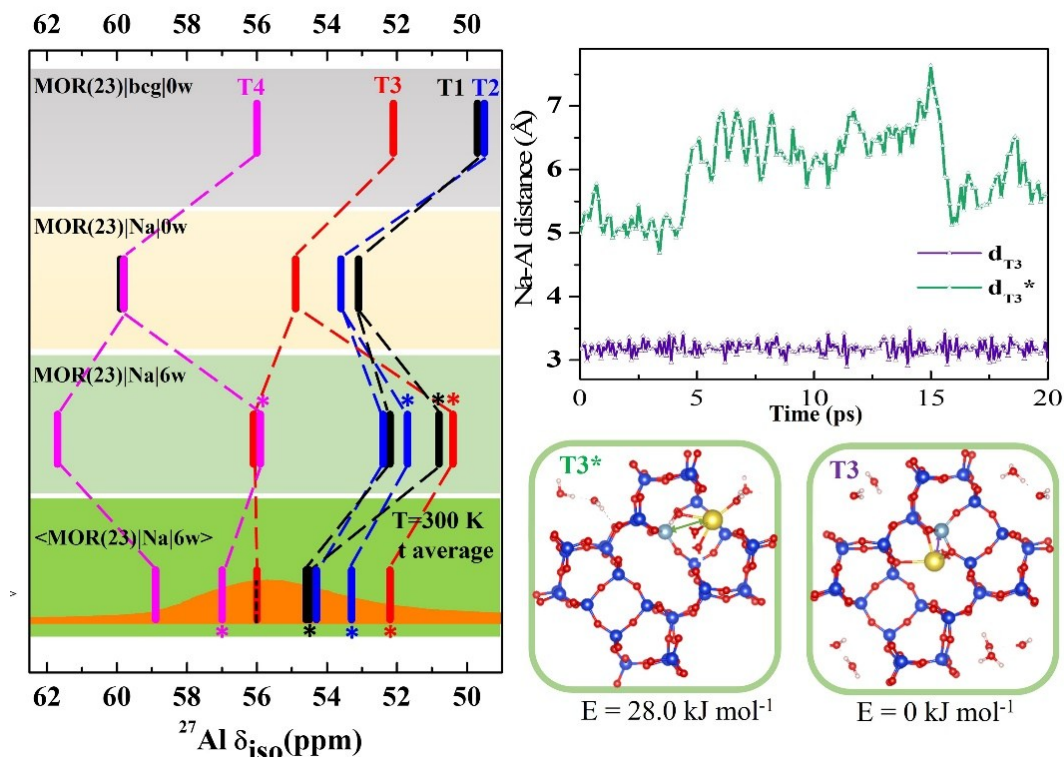


Figure 5.7 Calculated chemical shifts for MOR (Si/Al = 23) using various models. Static results for dehydrated MOR models with bgc and Na^+ are shown on grey and yellow backgrounds, respectively. Static δ and dynamic average $\langle\delta\rangle$ values of the $\text{Na}|\text{MOR}(23)|6\text{w}$ model are shown on lighter and darker green backgrounds, respectively, with the experimental range of MAS-NMR (from Ref⁹⁷⁻⁹⁸) overlaid in orange and the value of the peak maximum from MQMAS NMR, for which the effect of quadrupolar coupling is removed,⁸³ as a dotted line.⁹⁸ Competition between fully and partially solvated cations is given for Al in the T3 position. It is shown that the solvation of Na^+ cation residing on the intersection of the interconnecting cavity and 12R channel (denoted T3*) and in the limiting 8R channel (denoted T3) is rather different and is reflected by a large difference in Na-Al distances. Note: in $\text{MOR}(23)|\text{Na}|6\text{w}$ the fully hydrated Na^+ cation is distinguished with an asterisk (more details are shown in Figure 5.3); there are two T1 configurations in $\text{MOR}(23)|\text{Na}|0\text{w}$ within 1.0 $\text{kJ}\cdot\text{mol}^{-1}$ of each other, so both are shown. Reproduced from Ref.¹⁷⁸ with permission from the Royal Society of Chemistry.

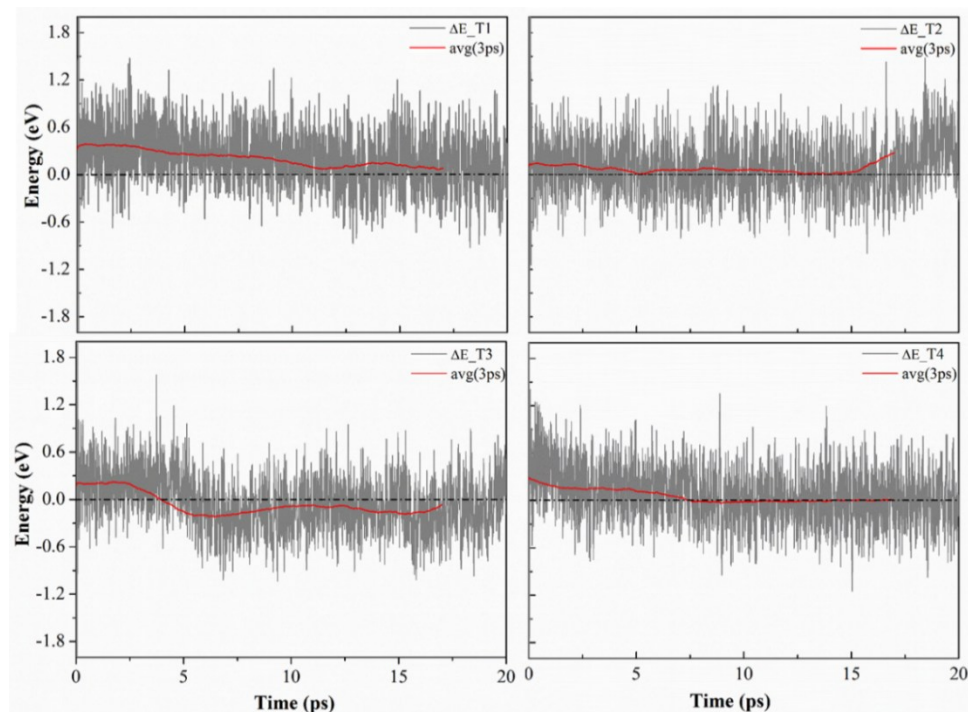


Figure 5.8 The energy difference between the two trajectories of MOR(23)|Na|6w with partially and fully solvated Na. $\Delta E = E_{Tn}^* - \langle E_{Tn} \rangle$, E_{Tn}^* is the energy of each snapshot of trajectory of fully solvated case, $\langle E_{Tn} \rangle$ is the energy average of the partially solvated case. The red line is the moving average of 3 ps. Reproduced from Ref.¹⁷⁸ with permission from the Royal Society of Chemistry.

5.2.5 MOR with more Al substitutions

MOR(11) and MOR(7) models, which contains two and three Al atoms in different T-sites space apart within the UC, were used to examine the effect of *operando* modelling on ^{27}Al NMR for models with different Si/Al ratios and extra-framework cations. In the MOR(11)|Na|5w configuration, one model was considered where Al substitutes into T1 and T3 sites, with Na^+ cations located in the 12MR channel to balance the charge of $(\text{AlO}_4)_2^-$ at T1 and in the 8MR channel to balance the charge of $(\text{AlO}_4)_2^-$ at T3. The MOR(7) model was constructed by substituting the T4 site with Al and adding a Na^+ ion in the 12MR channel, following the CHA(11)|Na|5w model.

The calculated results (Figure 5.9), combined with the MOR(23) results, indicate the following effects: 1) the Si/Al ratio (and the associated concentration of extra-framework cations), 2) the type of cation – Na^+ vs. H^+ , and 3) temperature. Both the $\langle \text{MOR(11)|Na|5w} \rangle$ and $\langle \text{MOR(7)|Na|5w} \rangle$ models produce $\langle \delta \rangle$ values similar to those of the $\langle \text{MOR(23)|Na|6w} \rangle$ model for signals corresponding to partially solvated structures. This similarity occurs because five water molecules are insufficient to fully solvate the three Na^+ cations, leading

to only partial solvation. In the MOR(7)|H|5w case, all three protons can be solvated, resulting in δ values comparable to those of MOR(7)|Na|5w. However, dynamic simulations show a rapid equilibrium between solvated and unsolvated protons at the T1 and T3 sites, causing $\langle\delta\rangle$ to reflect an average of chemical shifts across different solvation states. This results in a qualitatively different peak order compared to the Na-form of MOR. Ultimately, the results of MOR (Figure 5.9) indicate that temperature effects are consistently significant for hydrated zeolites, whereas they are less important in fully dehydrated zeolites, as evidenced by the comparison between the MOR(23)|Na|0w and $\langle\text{MOR(23)|Na|0w}\rangle$ models.

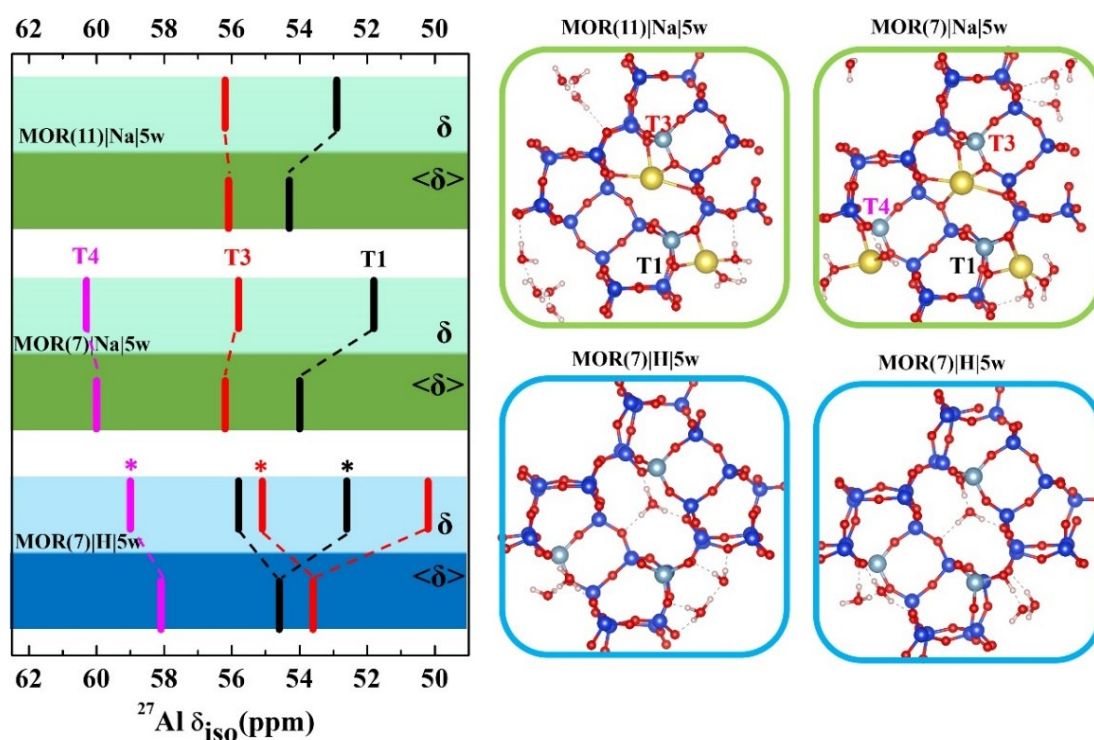


Figure 5.9 The calculated ^{27}Al δ for MOR (Si/Al = 11 and 7, with two and three Al substitution in the cell, respectively). Light-colored frames denote static shifts, and dark-colored frames denote dynamic average results. For MOR(11)|Na|5w, only one model is analyzed, with Al substituted at T1 and T3 sites. In MOR(7), Al is substituted at T1, T3 and T4 sites. In MOR(11)|Na|5w, the Na^+ near T1 is partially solvated, while the one in the 8MR side channel is unsolvated. For MOR(7)|Na|5w, the cations near T1 and T4 are partially solvated, whereas the cation in the 8MR side channel close to T3 is unsolvated. In MOR(7)|H|5w, all three protons initially located at T1, T3 and T4 are preferentially solvated in the static model, but a competing configuration, $+7 \text{ kJ}\cdot\text{mol}^{-1}$ higher in energy, exists where the protons at T1 and T3 are unsolvated. During the MD trajectory, the protons at T1 and T3 rapidly fluctuate between solvated and unsolvated states. Therefore, the structures represent averages over these two accessible states, obtaining intermediate chemical shifts. Fully solvated cases are marked with asterisks in the figure. Reproduced from Ref.¹⁷⁸ with permission from the Royal Society of Chemistry.

5.2.6 Interpreting the structure – σ relationship

Decades ago, Lippmaa²³³ proposed a linear relationship between the ^{27}Al chemical shift and averaged Al-O-Si angle for Al-rich zeolites. This correlation has been widely used in numerous studies, including the assignment of experimental ^{27}Al chemical shifts to Al in specific framework positions (based on T-O-T angles derived from diffraction measurements).^{185, 212, 234} However, it has been demonstrated inaccurate in some studies, especially in high-silica zeolites.^{96, 212, 235}

Considering the chemical shielding (σ) is directly obtained from DFT calculations and can be easily converted to δ , the σ -structure correlation was employed instead of the δ -structure correlation. To test Lippmaa's one-parameter correlation²³³ in our systems, the correlation between σ and average Al-O-Si angles is plotted in Figure 5.11 c and d. It is apparent that this correlation provides only a rough approximation (with $R^2 = 0.36$), even for the simple CHA zeolite, and cannot be used for the assignment of ^{27}Al NMR spectra.

Table 5.1 Local (framework) features considered in LASSO regression including average distances d and angles α as well as the corresponding difference (Δd , $\Delta\alpha$) between minimum and maximum values (spread) of the features in the $(\text{AlO}_4)_2^-$ tetrahedra. Additionally, four average distances to extra-framework atoms were considered. Reproduced from Ref.¹⁷⁸ with permission from the Royal Society of Chemistry.

Framework features	
$d_{\text{Al-O}}$	Mean Al-O distance
$d_{\text{Al-Si}}$	Mean Al-Si distance
$\alpha_{\text{O-Al-O}}$	Mean O-Al-O angle
$\alpha_{\text{Al-O-Si}}$	Mean Al-O-Si angle
$\Delta d_{\text{Al-O}}$	Spread of Al-O distances
$\Delta d_{\text{Al-Si}}$	Spread of Al-Si distances
$\Delta\alpha_{\text{O-Al-O}}$	Spread of O-Al-O angles
$\Delta\alpha_{\text{Al-O-Si}}$	Spread of Al-O-Si angles
Extra-framework features	
$d_{\text{Na-O}}$	Mean Na-O distance (O neighboring Al)
$d_{\text{Al-Na}}$	Mean Al-Na distance
$d_{\text{Na-Ow}}$	Mean Na-O distance (water O neighboring Na)
$d_{\text{Al-Ow}}$	Mean Al-O distance (water O)

Since the electron density around the nucleus is primarily influenced by local geometry, we employed LASSO to identify physically interpretable features, such as bond distances

and angles related to the Al local environment. This approach allowed us to obtain a simple but accurate linear correlation between structural descriptors and σ , facilitating a detailed analysis of the MD trajectories. Twelve structural features (Table 5.1) were calculated for each structure with the corresponding NMR results.

Initially, a small dataset consisting of about 700 DFT NMR calculations of $\langle \text{CHA}(11)|\text{Na}|5\text{W} \rangle$ was used to evaluate the importance of framework descriptors related to $(\text{AlO}_{4/2})^-$ tetrahedra and extra-framework descriptors such as Na-Al distances. The results showed that seven framework features (excluding $\Delta\alpha_{\text{O-Al-O}}$) achieved a coefficient of determination R^2 of 0.85, and incorporating additional descriptors provided negligible improvement (see Figure 5.10a). Subsequently, a second LASSO regression was performed on a larger dataset of 1466 DFT calculations, including dehydrated and H-form CHA and MOR (from the dynamic NMR calculations of $\langle \text{CHA}(11)|\text{Na}|0\text{w} \rangle$, $\langle \text{CHA}(11)|\text{Na}|5\text{w} \rangle$, $\langle \text{CHA}(11)|\text{H}|5\text{w} \rangle$, $\langle \text{CHA}(11)|\text{H}|5\text{w} \rangle$, $\langle \text{CHA}(3)|\text{H}|0\text{w} \rangle$, $\langle \text{CHA}(3)|\text{H}|6\text{w} \rangle$, $\langle \text{MOR}(11)|\text{Na}|1\text{w} \rangle$, $\langle \text{MOR}(11)|\text{Na}|5\text{w} \rangle$). This analysis revealed that the two most significant features, $d_{\text{Al-O}}$ and $\alpha_{\text{Al-O-Si}}$, yielded an R^2 of 0.85, with minimal improvement observed by adding more descriptors (Figure 5.10b). This two factors regression is written as:

$$\sigma = c_1 d_{\text{Al-O}} + c_2 \alpha_{\text{Al-O-Si}} + c_3, \quad \text{Equation 5-1}$$

with coefficients $c_1 = 180.60 \text{ ppm/\AA}$; $c_2 = 0.80 \text{ ppm/degree}$; $c_3 = 64.15 \text{ ppm}$.

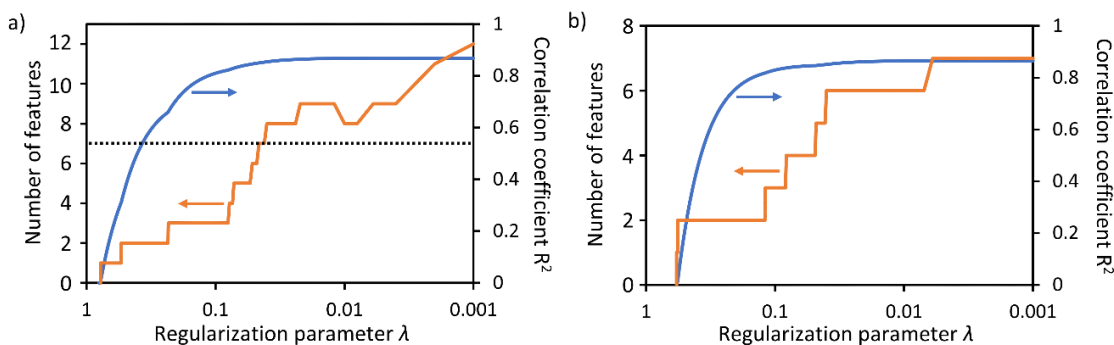


Figure 5.10 The coefficient of determination R^2 of the test set and the number of structural features with non-zero coefficients are plotted as a function of the LASSO regularization parameter λ in two scenarios: (a) the initial LASSO regression using $\langle \text{CHA}(11)|\text{Na}|5\text{W} \rangle$ and all 12 structural features (Table 5.1), and (b) the LASSO regression using data from both hydrated and dehydrated CHA and MOR in H- and Na-form. Reproduced from Ref.¹⁷⁸ with permission from the Royal Society of Chemistry.

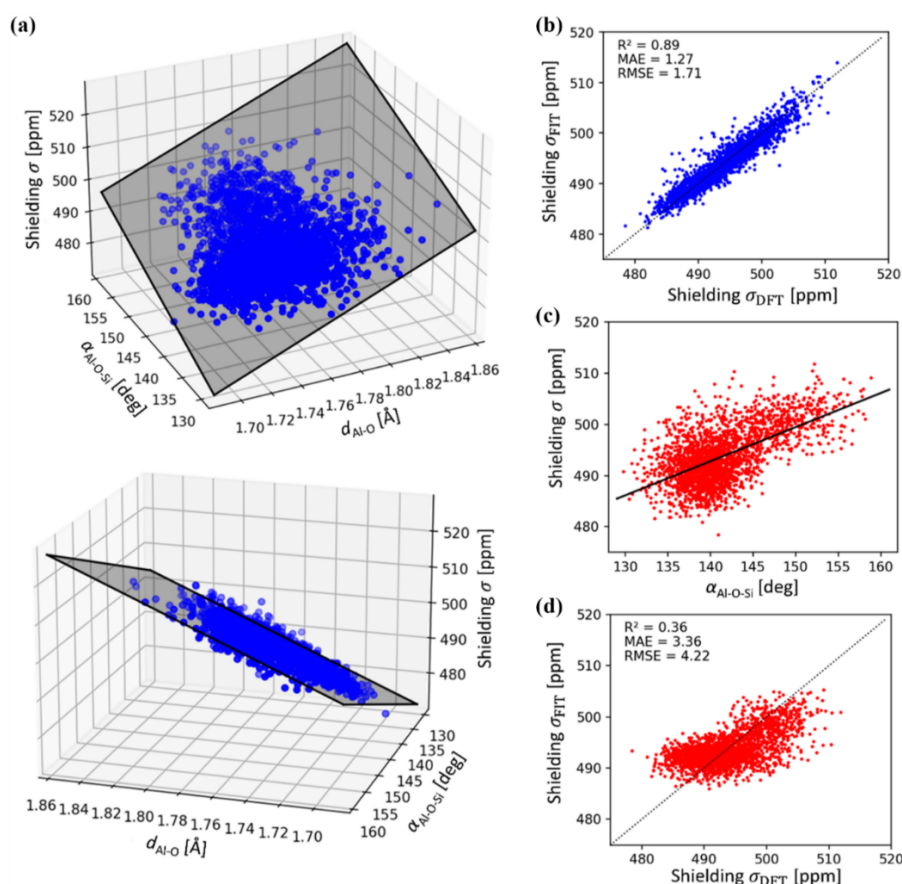


Figure 5.11 (a) ^{27}Al chemical shielding σ as a function of average Al-O distances $d_{\text{Al-O}}$ and Al-O-Si angles $\alpha_{\text{Al-O-Si}}$ of $\text{AlO}_{4/2}$ tetrahedra. Shaded area represents the linear regression model (see eq 4-1). (b) Correlation between LASSO linear regression model (see eq 5-1) and DFT ^{27}Al chemical shieldings ($R^2=0.89$). (c) Correlation between ^{27}Al chemical shielding (σ) with $\alpha_{\text{Al-O-Si}}$ as proposed by Lippmaa,²³³ using DFT reference data (d) Correlation between linear regression model according to Lippmaa,²³³ and DFT ^{27}Al chemical shieldings, showing a weak relationship ($R^2=0.36$). Note, mean absolute (MAE) and root mean squared error (RMSE) are in units of ppm. Reproduced from Ref.¹⁷⁸ with permission from the Royal Society of Chemistry.

Equation 5-1 provides improved results that agree with shieldings obtained from DFT calculations for both tested zeolites, with an R^2 value of 0.89. Its simplicity allows for the interpretation of chemical shieldings in terms of only a few local geometrical descriptors. Additionally, the use of Equation 5-1 reduces the mean absolute errors (MAE) from 3.4 ppm, obtained with the simple correlation, to 1.3 ppm (Figure 5.11). However, it should be noted that averaging over many configurations through dynamical simulations provides a more accurate prediction of the ^{27}Al $\langle\delta\rangle$, whereas predicting δ based on a static model results in greater errors (see Table A6 and A7). This two-parameter prediction formula was applied to the high-silica MFI model to verify its generality in a colleague's thesis from our group.²³⁶

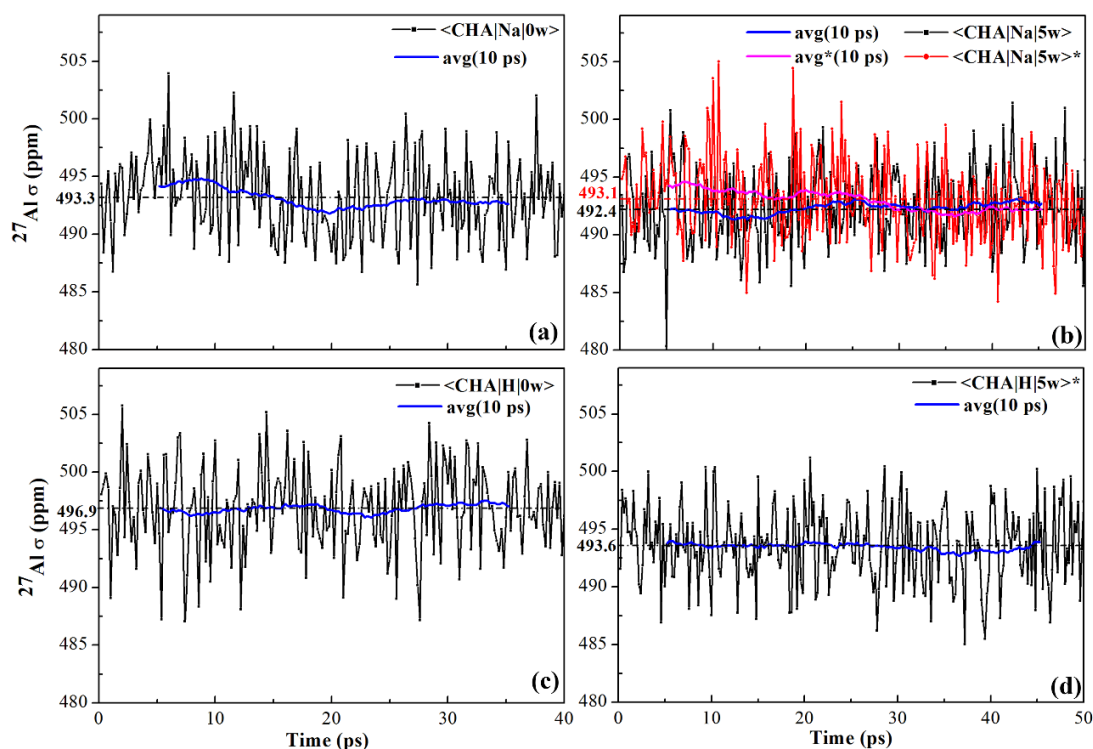


Figure 5.12 The ^{27}Al σ along the MD trajectory of (a) dehydrated Na-CHA, (b) hydrated Na-CHA (the asterisk is used to distinguish the case with the completely solvated Na^+ from the partially solvated Na^+ case), (c) dehydrated H-CHA, and (d) hydrated H-CHA. The dashed line is the average σ value along the trajectory. All predicted average shieldings were within a 0.8 ppm envelope and standard deviations were well within the precision of the method (< 1.5 ppm) over the full range of intervals. The blue solid line denotes the running average of the data in black with 10 ps window, and the pink line is the average of the data in red. Reproduced from Ref.¹⁷⁸ with permission from the Royal Society of Chemistry.

To further understand the impact of dynamic simulations, the ^{27}Al σ values were analyzed along MD trajectories for CHA and MOR, considering various geometrical descriptors. Based on $\langle\text{CHA}(11)|\text{Na}|5\text{w}\rangle$ models (Figure 5.12), the running averages of the ^{27}Al σ over different time windows, ranging from 4 to 14 ps, show convergence around 10 ps, which indicates the 20 ps dynamic simulation sufficiently captures the behavior of the local minima at room temperature.

Analysis of different CHA(11) models shows that the calculated chemical shielding varies significantly along the MD trajectories, with fluctuations depending on the model used (Figure 5.12). The most significant variations are observed in hydrated Na-zeolites, with chemical shift changes of about 20 ppm. In hydrated conditions, Na^+ exhibits greater fluctuations compared to H^+ because of the wider range of partial solvation configurations, which leads to more significant changes in local structural descriptors and, consequently,

greater variations in chemical shielding. In contrast, in the dehydrated cases, Na^+ is more fixed than H^+ because its heavier atomic weight result in smaller fluctuation in local structure. For the MOR(23)|Na|6w cases with Al siting in different T-sites, their behaviours along the trajectories are different (Figure 5.13). Thermal effects are influenced not only by the zeolite framework but also by the size and shape of the channel void space near individual Al atoms. The degree of Na^+ solvation is determined by the zeolite topology and the specific location of framework Al, as also demonstrated in the work of Maurin et al.²²⁸ Consequently, the distance between Al and Na indirectly affects chemical shielding, primarily through variations in the averaged $\alpha_{\text{Al-O-Si}}$ angles (Table A6 and A7).

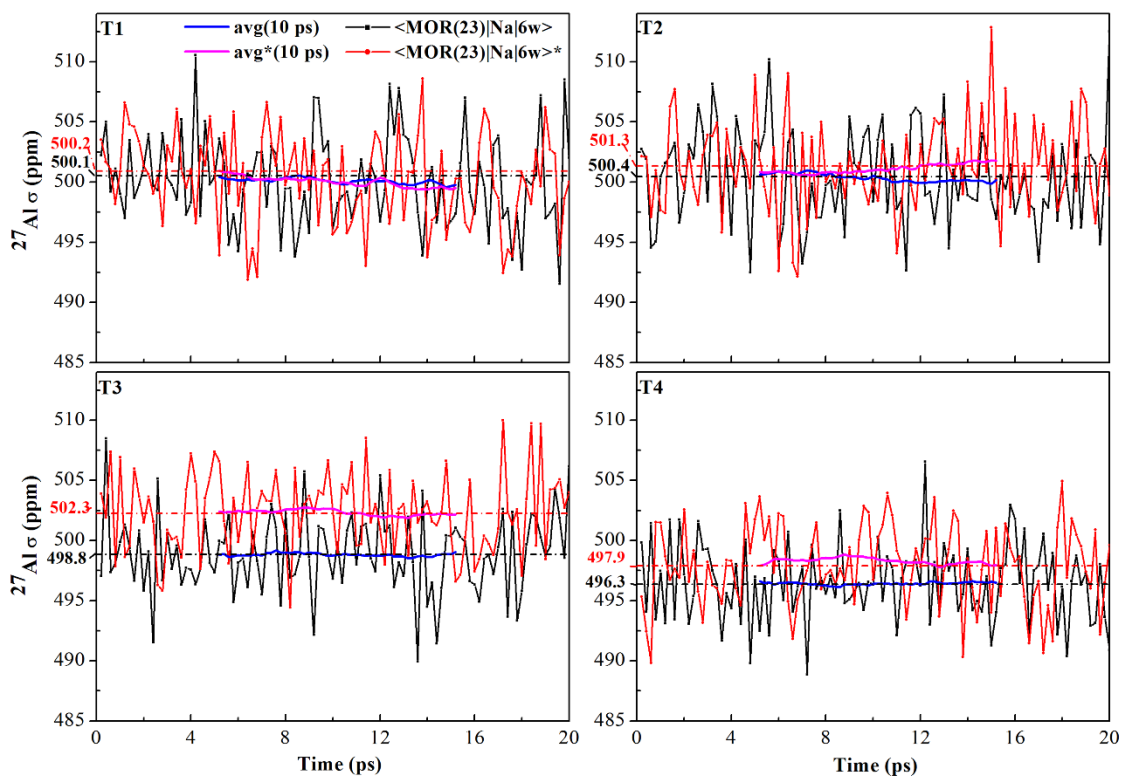


Figure 5.13 The ^{27}Al σ along the MD trajectories of MOR(23)|Na|6w for different Al-substitution sites T1, T2, T3 and T4. The asterisk (*) distinguishes fully solvated Na^+ from partially solvated cases. The dashed line shows the average σ value, while the blue solid line denotes the running average of the data in black with 10 ps window size, and the pink line average of the data in red. Reproduced from Ref.¹⁷⁸ with permission from the Royal Society of Chemistry.

5.3 Summary

In this chapter, the reliability of *operando* modelling of ^{27}Al NMR in zeolites is demonstrated, establishing a robust computational protocol for accurate and efficient NMR calculations. Using CHA and MOR zeolites with varying Si/Al ratios as examples, it is

shown that the position of chemical shift maxima depends not only on the zeolite framework topology but also on the type of charge compensating cations associated with the $(\text{AlO}_{4/2})^-$ tetrahedron, including the hydration level of the specific cation. The results reveal that a single framework Al atom can exhibit two distinct chemical shifts if the charge is compensated by cations located in different channels or if differences in hydration levels or available void space allow for hydration in one channel but not in the other.

Testing model performance on simple zeolites like CHA may lead to incorrect conclusions due to its single T site and rigid small pore framework. For rigid frameworks, the method used to model geometrical parameters has little impact, as no significant changes in ^{27}Al δ are observed. Also, the solvation behavior of cations like Na^+ is limited by the small pore. However, modelling spectra for a specific Al distribution in zeolites, such as MOR, is generally feasible with the appropriate model and method selection. The Al distribution influences how cations coordinate with the framework, while the degree of cation solvation is determined by the water content and the available void space.

The microporous nature of zeolites, along with the presence of water in their channels, highlights the importance of dynamic effect. Predictions must consider the specific composition and temperature effects of the system to be accurate. NMR tensors calculated by averaging over the MD simulation can obtain accurate results for zeolites with varying configurations with Al vibration and cation solvation states due to the temperature effect. The necessity of *operando* modelling for ^{27}Al NMR spectra in zeolites may apply to other elements in the framework and extra-framework (e.g., Si, O, and Na) and even to different solid materials.

Additionally, a LASSO regression was obtained to correlate the ^{27}Al chemical shielding with two structural descriptors, Al-O distance average and Al-O-Si angle average based on the large dataset generated from the *operando* simulations. This regression provides a physical interpretation of the structure-NMR property relationship and offers a faster alternative to the time-consuming DFT NMR calculation, potentially accelerating the prediction of *operando* NMR simulations in the future.

Chapter 6. ML-assisted simulations of zeolite NMR

6.1 Motivation

Owing to the limited resolution, solid-state NMR analysis of the quadrupolar nucleus ^{27}Al is insufficient for identifying the specific locations or distributions of Al atoms within zeolite structures. In this chapter, we focus on ^{23}Na NMR to gain more insight into Al distributions within high-silicon zeolites. Our primary goal was to accurately simulate the NMR spectra using an *operando* modelling approach. To achieve this, we employed NNP to systematically explore the stable Na configurations for various Al distributions and their dynamic behaviours over 1 ns. Numerical simulations of the NMR spectra were performed, taking into account factors such as temperature, dynamics effects, and the impact of Na/Al arrangements by averaging over configurations sampled via NNP-MD. These calculations demonstrate that ^{23}Na NMR can effectively exclude certain Al distributions by analyzing a combination of isotropic chemical shifts, quadrupolar coupling constants, symmetry parameters, and both homo- and heteronuclear dipolar couplings. Additionally, using the dataset from NNP-MD and NMR calculations, a linear regression analysis was performed to establish a relationship between ^{23}Na chemical shielding and various structural descriptors. The ML-assisted approach for predicting the ^{23}Na and ^{27}Al chemical shielding can be built by combining the NNP and the LASSO regression, which offers a potential method to efficiently model the time-averaged NMR characteristics of zeolites.

6.2 Results

6.2.1 Geometrical optimization and energies

To explore the NMR properties of zeolites with varying Al substitutions and Al sequences, we conducted a systematic investigation on high-silicon models using conventional cells (36 T-sites, Figure 3.1a) with Si/Al ratios of 35 and 17 for Na-CHA, denoted as CHA(35) and CHA(17), respectively. Additionally, CHA(11) and CHA(8) models with three and four Al atoms per unit cell were constructed to extend the analysis to lower Si/Al ratios. These configurations were selected as subsets to incorporate additional Na^+ sites and Al

sequences, including 6MR(3Al): Al-Si-Al-Si-Al, 8MR(3Al): Al-Si-Al-Si-Al, and 8MR(3Al): Al-Si₂-Al-Si-Al. Finally, two MOR zeolite models with Si/Al ratios of 11 and 7 were used to test the generalization of the study to a different framework.

There are three low-energy Na⁺ locations for isolated Al sites in CHA(35): one six-member ring geometry (SII) and two different eight-member ring sites (SIII and SIII')²³⁷ (Figure 6.1). For the CHA(11) and CHA(8) cases, only a limited number of configurations were selected. Since the strategy for determining Na/Al configurations is similar, only the configurations for CHA(17) are introduced in detail.

All possible Al distributions of CHA(17) were investigated within the 36 T-sites model. The complete set of Al configurations was systematically evaluated except for those forming the Al-O-Al sequence under the restriction of Löwenstein's rule.²³⁸ Although this rule may not strictly apply in dehydrated H-CHA,²³⁹ it is generally maintained under hydrated conditions⁶⁷ and in the Na-form CHA.²⁴⁰ Here, CHA(17) structures are categorized based on the shortest Al-Si_n-Al (*n* = 1, 2, 3, 4) sequence length within each configuration, labeled as I, II, III, and IV, respectively (as shown in Figure 6.1). Specifically, there are 9 cases with the Al-Si₁-Al sequence, named as I(A)-I(I); 12 configurations with the Al-Si₂-Al sequence, labeled as II(A)-II(L); 8 configurations with the Al-Si₃-Al sequence, named III(A)-III(H); and 2 configurations with the Al-Si₄-Al sequence, named IV(A) and IV(B). For each Al configuration, various potential Na⁺ locations were systematically generated using an automated scheme. The sodium positions were determined by calculating a normalized vector sum, which places the Na⁺ about 2.5 Å from each oxygen atom in the tetrahedron with a bias towards the edges. The vectors $\overrightarrow{AlO}$ and $\overrightarrow{SiO}$ were calculated for each oxygen atom connected to an Al site, where $\overrightarrow{AlO}$ represents the direction from the Al atom to the given oxygen atom, and $\overrightarrow{SiO}$ denotes the vector from the Si atom bonded to the same oxygen. By summing and scaling these vectors, the position of the Na⁺ ion was determined. The resulting projection vector $\vec{P}$ was then added to the Al position thereby defining the Na position.

$$\vec{P} = 2.5 \times \frac{\overrightarrow{AlO} + \overrightarrow{SiO}}{|\overrightarrow{AlO} + \overrightarrow{SiO}|} \quad \text{Equation (6-1).}$$

This algorithm produces 4 potential Na^+ positions per Al site. In CHA zeolite, Na^+ ions are often found positioned near the 6MR and 8MR. These locations are denoted as 6MR($m\text{Al}$): Al-Si_{*n*}-Al or 8MR($m\text{Al}$): Al-Si_{*n*}-Al, where *m* represents the number of the Al substituted sites within the 6MR or 8MR, and *n* defines the length of the Al-Si_{*n*}-Al sequence. This notation helps to describe the distribution and arrangement of Na^+ ions relative to the Al distributions in the zeolite structure.

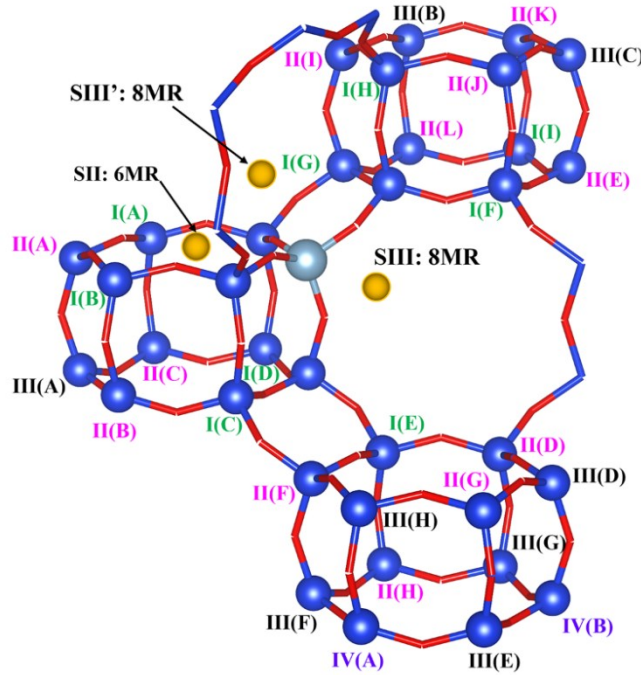


Figure 6.1 The model for the 36 T-site Na-CHA zeolite is illustrated with labels for the configurations of CHA(17). The Al configurations are named with I/II/III/IV(*x*), where I, II, III, and IV represent the shortest Al-Si_{*n*}-Al sequences with *n* = 1, 2, 3, and 4, respectively, and *x* is a letter used to distinguish different sites with the same *n* value. The yellow spheres denote the possible locations of Na^+ ions. SII sites are located on the 6MR windows, and SIII sites are on the 8MR windows, as defined in the previous work.²³⁷ Reproduced from Ref.¹⁷⁹ with permission from the Royal Society of Chemistry.

The cell volumes increase with higher Al content in zeolites, and the changes in lattice parameters are closely linked to the specific Al distributions within the structure. The lattice parameters for each Si/Al ratio were first optimized using a representative low-energy Na/Al configuration. Once determined, these parameters were kept fixed for all subsequent Na/Al configurations to ensure consistency across the calculations. For CHA(35), the lattice parameters are $a = 13.79 \text{ \AA}$, $b = 13.70 \text{ \AA}$, $c = 14.80 \text{ \AA}$, $\alpha = 89.80^\circ$, $\beta = 90.16^\circ$ and $\gamma = 120.19^\circ$, with a volume of $2415.50 \text{ \AA}^3$. For CHA(17) they are $a = 13.83 \text{ \AA}$, $b = 13.63 \text{ \AA}$, $c = 14.89 \text{ \AA}$, $\alpha = 89.80^\circ$, $\beta = 90.35^\circ$ and $\gamma = 120.16^\circ$, with a volume of $2426.69 \text{ \AA}^3$. For CHA(11), they are $a = 13.95 \text{ \AA}$, $b = 13.68 \text{ \AA}$, $c = 14.94 \text{ \AA}$, $\alpha = 89.53^\circ$, $\beta = 90.25^\circ$ and $\gamma =$

121.38°, with a volume of 2434.62 Å³. For CHA(8), they are $a = 13.68$ Å, $b = 13.68$ Å, $c = 15.02$ Å, $\alpha = 89.74^\circ$, $\beta = 90.26^\circ$ and $\gamma = 119.48^\circ$, with a volume of 2445.00 Å³.

All possible permutations were locally relaxed using the NNP to screen the low-energy configurations and gather information on the most favourable configurations. The DFT method was then used to calculate the static energy for selecting low-energetic structures under the energy cutoff 20 kJ·mol⁻¹, which is considered thermally accessible.²⁴¹⁻²⁴⁴ Consequently, the Na configurations within an energy range of 20 kJ·mol⁻¹ from the lowest energy structure for a given Al distribution were chosen for NMR property calculations. Additionally, two specific cases in CHA(17), II(A) and II(B), with energies 22 and 28 kJ·mol⁻¹ above their corresponding lowest energy configuration, were included to investigate unique Al arrangements exhibiting distinct dynamic behaviours: II(A) features an Al-Si₂-Al sequence within a single 6MR, and II(B) contains an Al-Si₂-Al sequence within a double six-ring (*d6r*). For each Al distribution, Na⁺ locations were labeled based to their relative energies; for example, I(A)1 and I(A)2 represent the lowest and second lowest energy configurations with Al arrangement of I(A). This approach ensures a systematic evaluation of both energetically favorable and dynamically significant configurations.

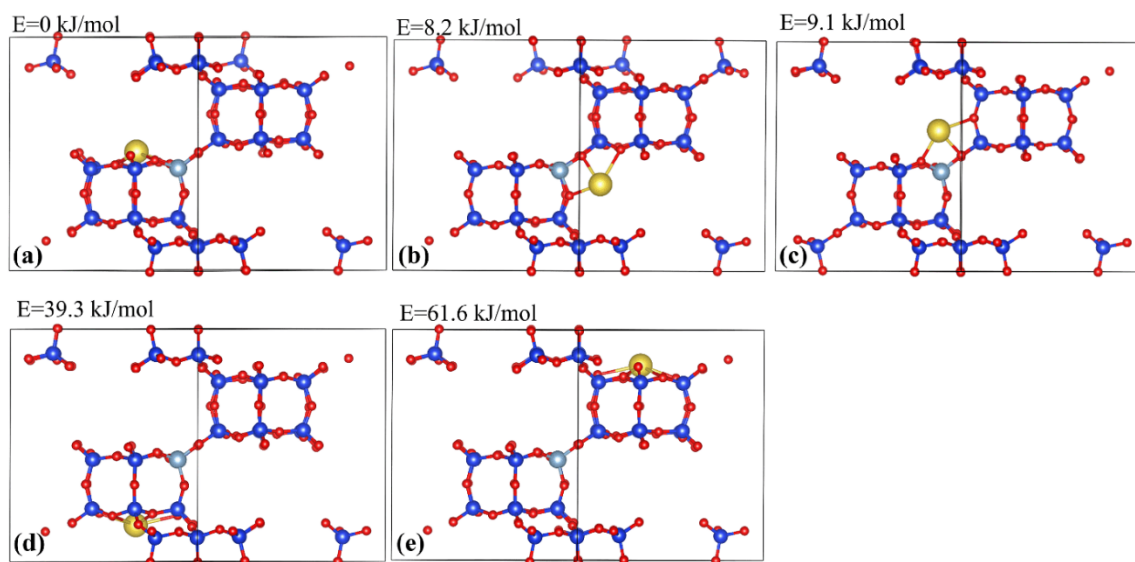


Figure 6.2 The structures of CHA(35) of different Na⁺ configurations. a) the lowest energy case with Na on the 6MR window, b) and c) Na on the 8MR(1Al) window SIII and SIII' sites, d) and e) Na on the all-Si 6MR windows sharing the same *d6r* with Al site and on another all-Si *d6r*, respectively. The energy report here is from DFT static calculations. Reproduced from Ref.¹⁷⁹ with permission from the Royal Society of Chemistry.

In CHA(35) cases, five Na⁺ positions at different SII, SIII, and SIII' were considered to determine stable configurations (Figure 6.2). The Na⁺ ions tend to preferentially bind to positions near Al. Three stable configurations were identified: one 6MR(1Al) above the face of a *d6r*, and two nearly isoenergetic positions at 8MR(1Al), which are higher in energy by 8.2 and 9.1 kJ·mol⁻¹.

In the CHA(17) cases, numerous configurations exist for the more complex Al/Na pair arrangements. Low energy configurations are shown in Figure B1. The results show that stable Na⁺ configurations are closely related to Al distributions. In most cases where two Al atoms are in different 6MR, forming two 6MR(1Al) sites, both Na⁺ cations tend to occupy 6MR(1Al) in the most stable configurations, except for three cases, I(E), I(H) and II(K), where the most stable Na⁺ configuration involves one Na⁺ at 6MR(1Al) and another at 8MR. In instances where two Al substitutions are in a single 6MR, forming Al-Si₁-Al and Al-Si₂-Al sequences (I(A) and II(A)), configurations with one Na⁺ located at a 6MR(0Al) (6MR without Al substitution) are considered plausible. This is supported by the static energies of I(A)3 and II(A)2 configurations, where Na⁺ is located in the 6MR(0Al), showing 14 and 22 kJ·mol⁻¹ higher, respectively, than their corresponding global minimum configurations (Figure 6.3). However, for CHA(35), Na⁺ configurations at 6MR(0Al) display much higher energies as the distance from the Al site increases. The two energetically uncompetitive local minima with Na⁺ at 6MR(0Al) (Figure 6.2 d and e) show 39 and 62 kJ·mol⁻¹ higher energies than the global minimum. A comparison reveals that Na⁺ prefers to be located at a 6MR connected to an Al site within a *d6r* unit. These configurations are also found at other Si/Al ratios, with their relative stability to the global minimum varying with Si/Al ratio. As the Al content increases, the 6MR(0Al) configuration becomes more stable, with the energy difference from the global minimum decreasing from 39 kJ·mol⁻¹ at CHA(35) to 9 kJ·mol⁻¹ at CHA(11) (Figure 6.3). This suggests that such configurations may influence the kinetics and the spectra of Na-CHA.

To test the generalization of the findings from CHA to another framework, two MOR zeolite structures with Si/Al= 11 and 7 were adopted (Figure 6.4). In MOR(11), two Al substitutions are T3 and T4 sites. In MOR(7), three Al substitutions are T1, T3, and T4 sites.

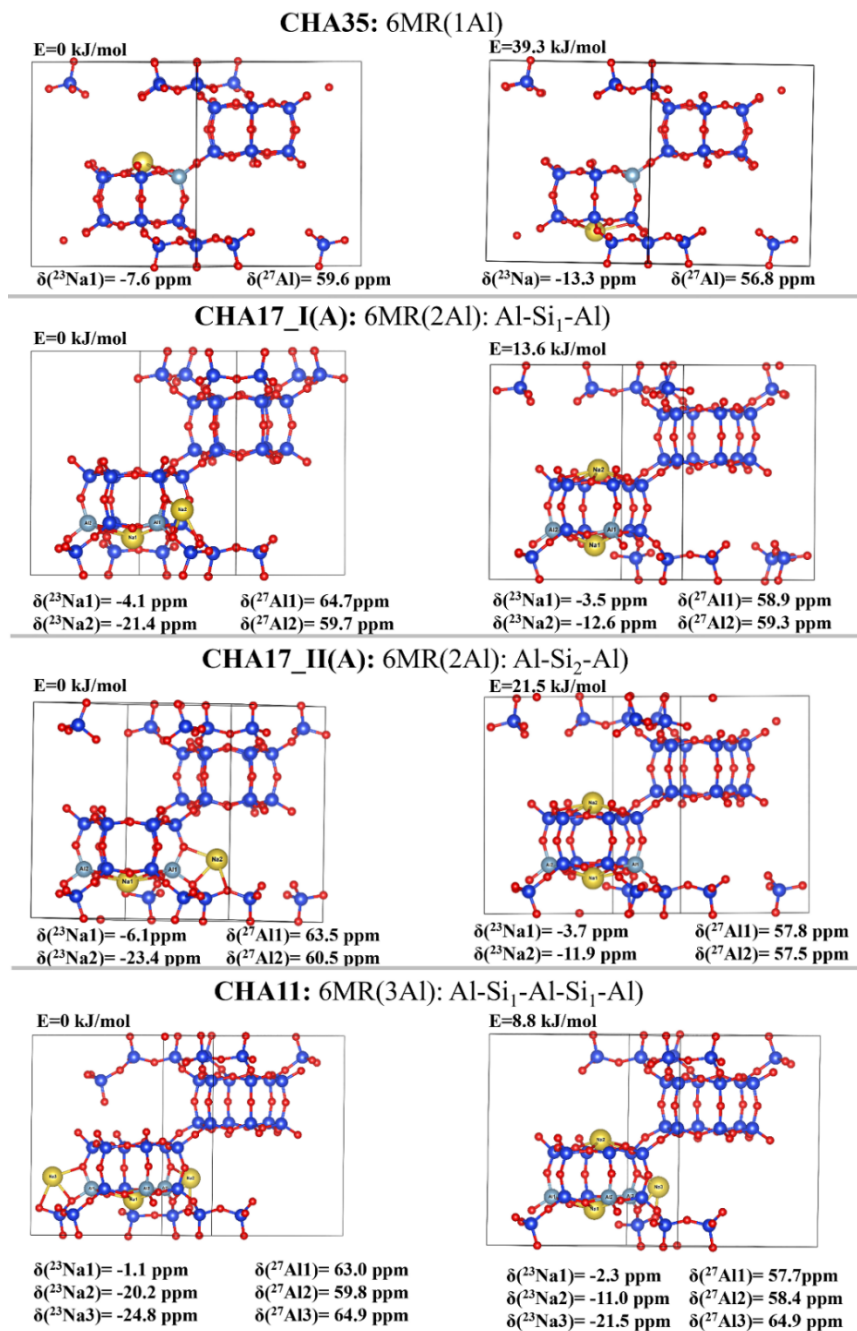


Figure 6.3 Structural and energetic comparison of configurations with Na^+ on siliceous six-rings (6MR(0Al)). Left is the global minimum for a given Al distribution, right is the configuration with a Na^+ in a 6MR(0Al) site. CHA(17) has two Al to form 6MR(2Al):Al-Si_n-Al, $n = 1, 2$; and CHA(11) has three to form 6MR(3Al):Al-Si₁-Al-Si₁-Al. It is notable that the unusual 6MR(0Al) configuration for Na is increasingly competitive with 6MR(1Al) and 6MR(2Al) configurations as the Si/Al ratio decreases. Na^+ on 6MR(0Al) has a distinctive chemical shift at around -12 ppm, which does not significantly vary with Si/Al ratios. Reproduced from Ref.¹⁷⁹ with permission from the Royal Society of Chemistry.

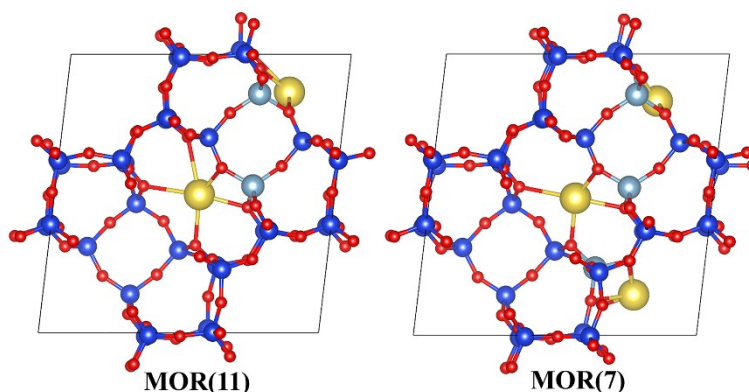


Figure 6.4 The models of MOR with Si/Al ratios of 11 and 7. Reproduced from Ref.¹⁷⁹ with permission from the Royal Society of Chemistry.

6.2.2 ^{27}Al NMR

In dehydrated zeolites, Al sites can produce "invisible" Al species due to significantly distorted environment, appearing as broad resonances that are difficult to observe at modest magnetic fields. However, using a high magnetic field can narrow the ^{27}Al ssNMR peaks, allowing visualization of these resonances (Figure B2). The magnetic field strength corresponding to 1500 MHz ^1H Larmor frequency, was used to simulate NMR spectra here.

The ^{27}Al NMR parameters for all low-energy configurations were calculated, and spectra of a selected subset of CHA(17) were simulated for both static and averaged over 1 ns dynamic trajectories. The values of δ_{iso} , C_Q , and η_Q obtained from static and dynamic calculations are summarized in Figure 6.5, and Table B1 in Appendix B. The static ^{27}Al δ_{iso} values range from 58 to 66 ppm, C_Q values range from 2.5 to 9.0 MHz, and η_Q values range from 0.2 to 1.0. The ^{27}Al chemical shifts are influenced by the vicinity Al sites and the sodium distributions, compared to the isolated Al sites that exhibit 60 ppm and 61(62.6) ppm with Na^+ at 6MR and 8MR, respectively (Chapter 5). Cases involving Al-Si₁-Al and Al-Si₂-Al sequences show significant differences compared to isolated Al sites, which agrees with previous studies by Dědeček et al. about zeolites CHA²⁴⁵ and MFI.²⁴⁶ However, no simple rule correlates these influences with specific structural features. For example, ^{27}Al δ_{iso} exhibits values of about 58 ppm for different sequence lengths I(I)1, II(A)1, and III(A)1 and exceeds 65 ppm in cases such as I(H)2 and II(H)3. C_Q and η_Q values also do not correlate with structural characteristics simply.

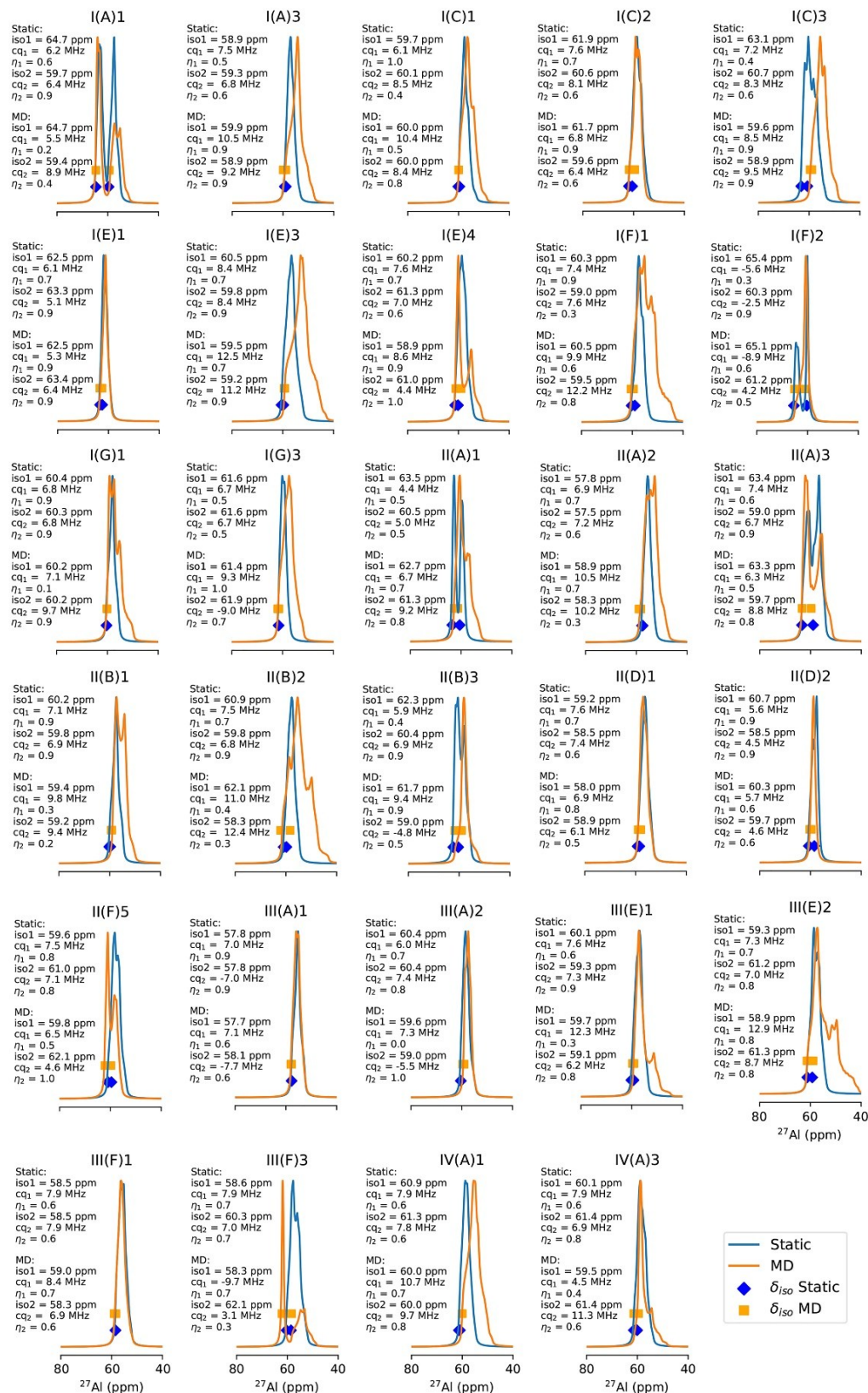


Figure 6.5 Simulated ^{27}Al NMR spectra of static and time-averaged for CHA(17) cases with distinct Na/Al configurations. Reproduced from Ref. ¹⁷⁹ with permission from the Royal Society of Chemistry.

Consistent with the conclusions from Chapter 5 regarding single Al substitution in the cell, the ^{27}Al resonance positions do not significantly change due to dynamic effects. The dynamic effect causes a shift in the peak position by only a few ppm, which agrees with the observations reported by Vanlommel et al.¹¹⁰ for models containing multiple Al atoms per unit cell. The most pronounced difference is observed for the I(C)3 configuration, whose dynamically averaged ^{27}Al δ shifts by about -3.5 ppm compared to its static result; other cases show deviations of about 1 ppm.

Additionally, the ^{27}Al chemical shielding LASSO prediction formula (Equation 5-1) from CHA(11), as described in Chapter 5, was tested on this dataset featuring different Al sequences. The results confirmed that this formula retains high precision, with a mean absolute error (MAE) of 1.25 ppm (Figure 6.6). Analysis of each subset reveals that the prediction performs better in cases with lower Al content. Predictions for CHA(35), CHA(17), and MOR(11) match well with DFT-calculated chemical shieldings, showing R^2 values over 0.85 and MAEs under 1.2 ppm. Although cases with higher Al content exhibit slightly larger errors, the model still performed well, achieving an MAE of 1.7 ppm, thereby demonstrating the generalization capability of the LASSO regression model.

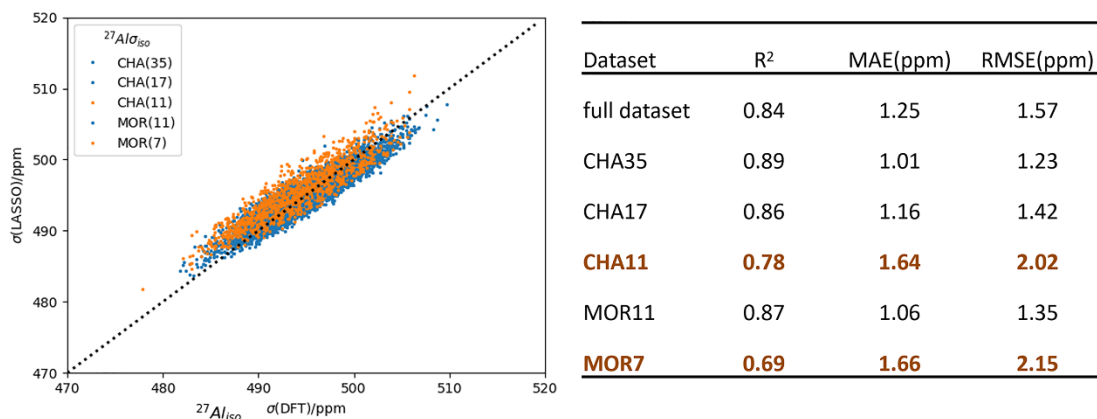


Figure 6.6 Comparison between the DFT calculated ^{27}Al σ and predicted result from the LASSO regression formula (Equation 5-1). Reproduced from Ref.¹⁷⁹ with permission from the Royal Society of Chemistry.

6.2.3 ^{23}Na NMR

6.2.3.1 Static ^{23}Na NMR chemical shift

Static calculations of the ^{23}Na NMR parameters were performed for low-energy configurations. The ^{23}Na chemical shifts for CHA(35) are distinguishable between 6MR sites (-8.5 ppm) and the 8MR sites (-21.5/21.1 ppm) sites, consistent with previous

experimental results.¹⁰¹ However, the nearly-isoenergetic competing 8MR locations cannot be distinguished based on their chemical shift or by C_Q/η_Q parameters. Static calculations show only minor differences of 0.1 MHz in C_Q and 0.1 in η_Q between these two competing sites (Table B2).

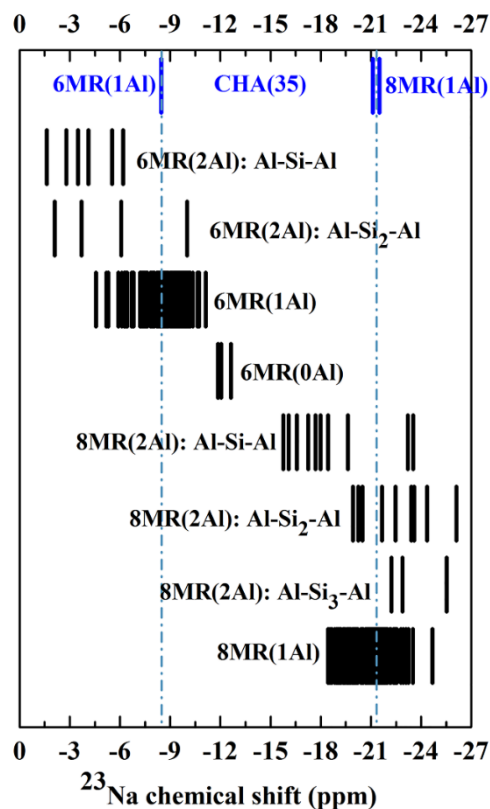


Figure 6.7 Calculated ^{23}Na chemical shifts for all low-energy configurations for CHA(X), (X = 35, 17). Reproduced from Ref.¹⁷⁹ with permission from the Royal Society of Chemistry.

The CHA(17) model introduces additional complexity in determining Na^+ locations by accounting for the proximity of Al atoms to each other and the resulting framework distortions. Static results (Figure 6.7) show that Na^+ cations at the 6MR and 8MR sites can be distinguished by their ^{23}Na chemical shifts: Na^+ cations at 8MR sites are more shielded (more negative δ) compared to those at 6MR sites. The chemical shifts for 6MR sites range between 0 and -15 ppm, while those for 8MR sites fall between -15 and -27 ppm, with minimal overlap between these regions.

Two additional factors can broaden the chemical shift range: the number of Al atoms in the ring, and the distance of two Al atoms. As the number of Al atoms in the ring to which the Na^+ ion is bound increases, the shielding of Na^+ ions decreases. This results in distinct

regions of ^{23}Na chemical shifts which can be used to identify Al distributions. For example, 6MR(1Al) configurations form a broad block centred at -7.9 ppm, which is close to the value observed for the comparable 6MR(1Al) configuration in CHA(35) (-8.5 ppm). The chemical shifts of 6MR(2Al): Al-Si₁-Al configurations cluster with a centre around -3.9 ppm, which is a measurable difference in chemical shift. Similarly, 6MR(0Al) configurations are centred at -12.3 ppm, allowing them to be distinguished from both 6MR(1Al) and 6MR(2Al) configurations.

Another effect influencing ^{23}Na chemical shifts is the distance between two Al atoms, which is defined by the length n of the shortest Al-Si _{n} -Al sequence. We determined that for Al distributions where the Al atoms do not share a $d6r$ unit, an Al-Si₃-Al sequence is sufficiently long to treat the Al atoms as isolated from one another. This conclusion was confirmed for both ^{23}Na and ^{27}Al chemical shifts and aligns with earlier findings by Dědeček on ^{27}Al NMR.²⁴⁶ However, this rule is not followed when both Al atoms are part of the same $d6r$. This deviation is illustrated by the peak at -25.5 ppm for the 8MR(2Al):Al-Si₃-Al configuration in III(A)2, which is shifted relative to the isolated 8MR(1Al) shifts around -21 ppm in CHA(35). Generally, increased shielding correlates with longer sequences, a trend that is most consistently observed in configurations where two Al atoms do not share a $d6r$.

To expand the analysis to models with higher Al substitution, we considered a subset of low-energy configurations for CHA(11) and CHA(8). These models, containing three and four Al sites per unit cell, introduce additional complexities in Na/Al configurations. The predicted static ^{23}Na chemical shifts for these configurations (Figure 6.8) show that the trends observed for CHA(17) are also valid for cases with higher Al contents. Specifically, Na⁺ cations at 6MR sites exhibit lower shielding compared to those at 8MR sites, with no overlap between the two sets, though this overlap decreases as the Si/Al ratio decreases. The 6MR(3Al) configurations display the lowest ^{23}Na chemical shift, followed sequentially by 6MR(2Al), 6MR(1Al), and 6MR(0Al) sites. For 8MR sites, the analysis is more complex due to the wide variety of sequence length combinations, yet clear trends are still observable. For instance, within the 8MR(2Al):Al-Si _{n} -Al class, increasing the sequence length n decreases ^{23}Na chemical shifts. Notably, the ^{23}Na chemical shifts for

6MR(0Al) remain within a narrow range of -11 to -13 ppm across all Si/Al ratios, despite their stabilities increasing with lower Si/Al ratios (Figure 6.3).

Overall, ^{23}Na chemical shifts in CHA can be categorized based on three factors: (1) the location of Na^+ on either 6MR or 8MR, (2) the number of Al atoms in the ring associated with Na, denoted as 6MR($n\text{Al}$) and 8MR($n\text{Al}$) where $n = 0, 1, 2$, and (3) the distance between Al atoms. These three features reveal patterns that can help narrow down possible Al distributions. The ^{23}Na chemical shift thus can provide predictive insight into Al distribution and pairing, extending beyond simply identifying the location of Na^+ ions in 6MR or 8MR positions.

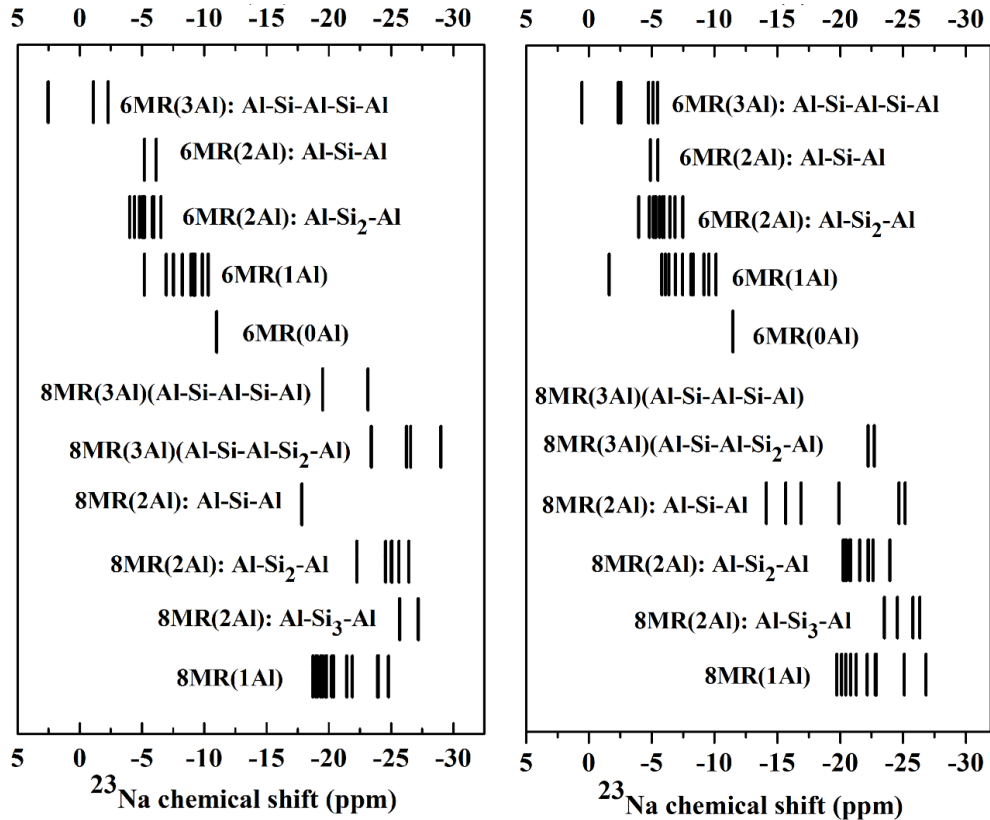


Figure 6.8 Calculated ^{23}Na isotropic chemical shift for CHA(11) (left) and CHA(8) (right) models.

6.2.3.2 Effect of dynamics on ^{23}Na NMR spectra

Based on the thermally accessible Na/Al configurations dataset of CHA(17), the effect of dynamics on ^{23}Na NMR spectra was analyzed by comparison with the static result. The long equilibrium NNP molecular dynamics simulations of 1 ns were performed for a selected subset of the CHA(17) Na/Al distributions with low energy for all $\text{Al-Si}_n\text{-Al}$

sequence lengths. The isotropic chemical shifts δ_{iso} and quadrupolar parameters, C_Q and η_Q , were calculated by averaging over simulations, using 100 snapshots extracted from MD trajectories generated from via DFT. This approach was employed to mimic the averaging effects typically observed in NMR experiments.

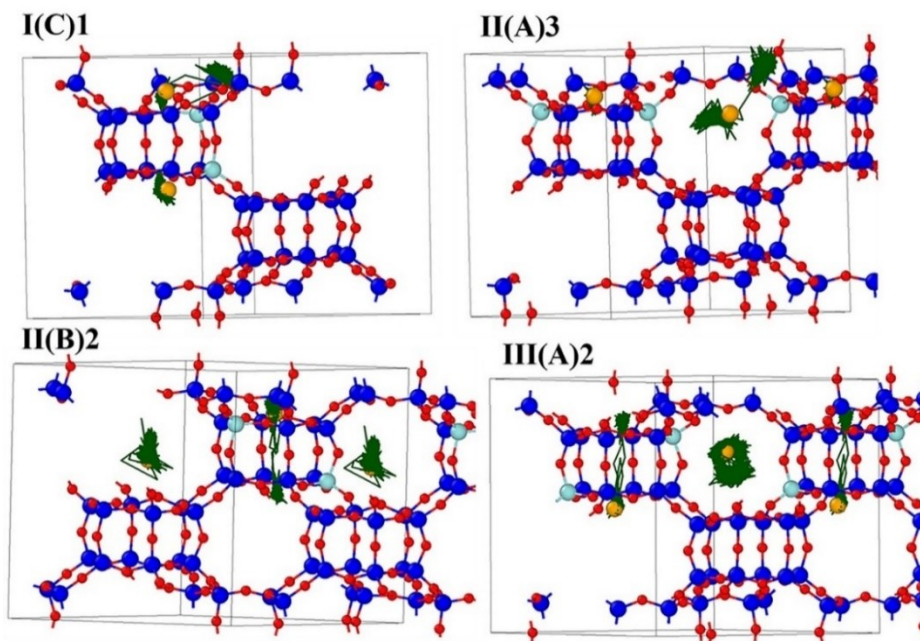


Figure 6.9 The trajectories of the motion of Na of CHA(17) in I(C), II(A), II(B), and III(A) cases, in which the Na^+ migrated to different sites. Note: the trajectory lines are in green. Reproduced from Ref.¹⁷⁹ with permission from the Royal Society of Chemistry.

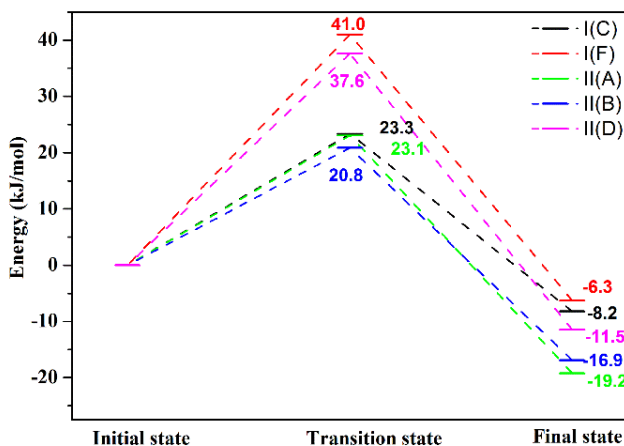


Figure 6.10 The energy barrier of two stated in I(C), I(F), II(A), II(B) and II(D) cases with NNP NEB(nudged elastic band) method. The initial states are the higher energy cases with one 6MR Na^+ and one 8MR(I(C)3, I(F)2, II(A)3, II(B)3 and II(D)2), and the final states are the corresponding minimal state (I(C)1, I(F)1, II(B)1 and II(D)1 with two 6MR Na^+ ; and II(A)1 with one at 6MR and one at a different 8MR). Reproduced from Ref.¹⁷⁹ with permission from the Royal Society of Chemistry.

The motions of the framework and counterions at operating temperature, occurring on the timescale of data collection, can introduce various effects that may alter the spectrum. To assess the movement of Na^+ cations, trajectory analyses were performed for cases I(C)1, II(A)3, II(B)2, and III(A)2 as examples (Figure 6.9). Additionally, energy barriers for certain cases were calculated using the NNP NEB (nudged elastic band) method to get deeper insights into the dynamic behaviors of the system (Figure 6.10). These calculations provide essential context for understanding how dynamic behaviors influence spectral characteristics.

Firstly, local thermal fluctuations can influence bond lengths, angles, and other structural features that affect the chemical shift values. For instance, Na^+ cations at 8MR sites exhibit greater mobility compared to those at 6MR before any migration occurs. Secondly, the localization of thermal energy into the vibrational modes of Na^+ ions can potentially trigger reactive transformations and cause rapid migrations between accessible sites. These transitions may occur on a timescale faster than the NMR acquisition time, leading to dynamic averaging effects. Examples include Na^+ moving from 6MR to 8MR (I(C)1 to I(C)3), migrating between two 8MR sites (II(A)3 to II(A)1), or transferring from 6MR of one side to the opposite side of the *d6r* in II(B)2 and III(A)2. Energy barriers derived from NEB show that migrations in the I(C) and II(A) cases require approximately $23 \text{ kJ}\cdot\text{mol}^{-1}$, which is low to allow migration at room temperature. Lastly, the position and shape of NMR peaks can be influenced by changes in magnetic shielding and electric field gradient tensors resulting from these dynamic effects.

The position and shape of NMR spectra are determined by the combination of chemical shift δ_{iso} , quadrupolar coupling constant C_Q , and the asymmetry parameter η_Q . To investigate the effect of dynamic on the spectrum, these three parameters were compared between static and dynamic results. The chemical shift typically varies by up to 3 ppm between static and dynamic spectra, with most changes shifting to the left, suggesting a deshielding effect due to temperature and time averaging. However, exceptions exist, such as in the case of configuration II(A)2, where two Al substitutions in a 6MR, with one Na^+ located at the 6MR(Al-Si₂-Al) and another at the 6MR(0Al) within the same *d6r* unit. This highlights that dynamical effects do not lead to a simple, systematic shift in the chemical

shift, making a uniform correction impossible. A similar trend is observed for both C_Q and η_Q . Generally, the value of C_Q increases, but exceptions like II(A)2 and certain sodium ions in I(C)1 and I(C)3 are observed. Across the entire dataset shown in Table B3, the average change in C_Q is 0.2 MHz, and the average change in η_Q is 0.1. Therefore, static local minimization does not precisely capture these parameters at thermal equilibrium.

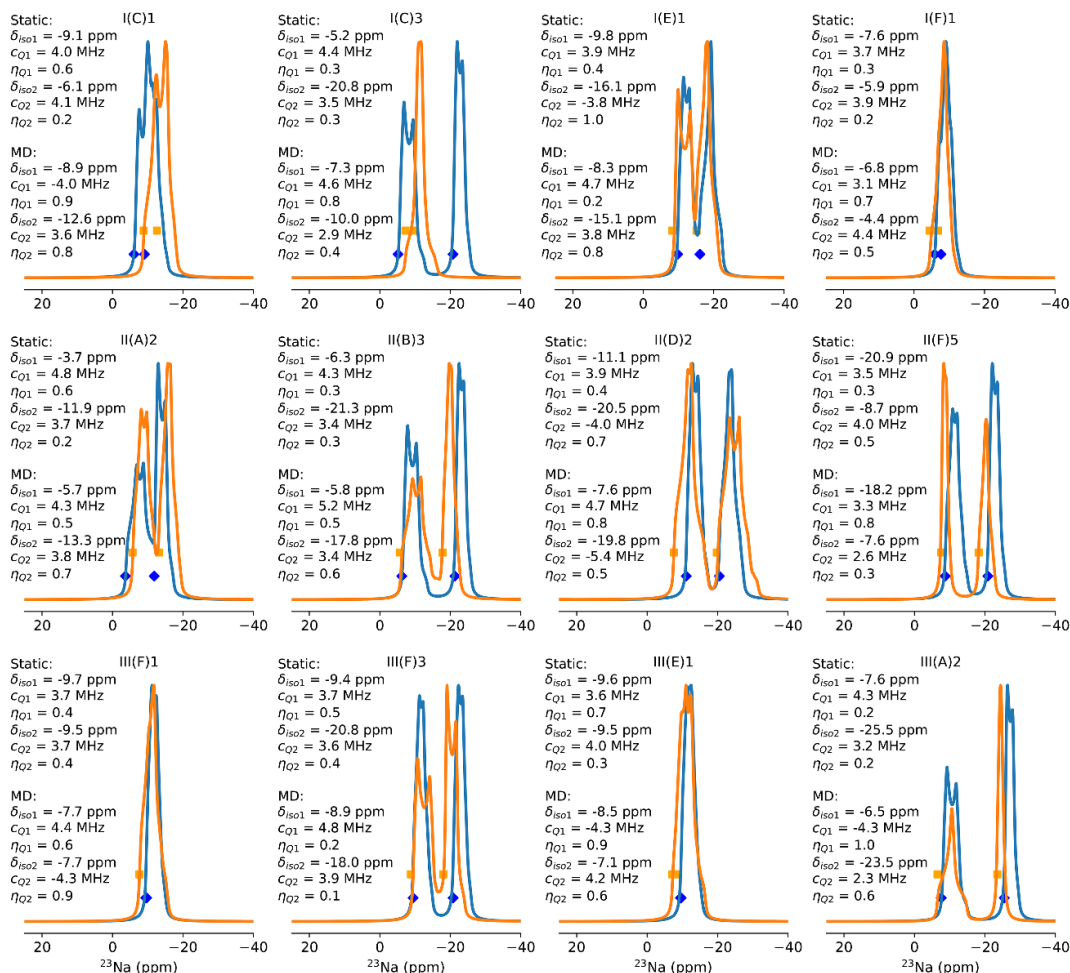


Figure 6.11 Simulated ^{23}Na NMR spectra for selected configurations, comparing static spectra (blue) and dynamical averages (orange). Isotropic chemical shifts are markers, and C_Q / η_Q parameters are included as insets. Top: Configurations with Al-Si₁-Al sequences. Middle: Configurations with Al-Si₂-Al sequences. Bottom: Configurations with the Al-Si₃-Al sequences. Reproduced from Ref.¹⁷⁹ with permission from the Royal Society of Chemistry.

The simulated static and dynamically averaged ^{23}Na NMR spectra for twelve low-energy configurations CHA(17) are shown in Figure 6.11 as examples to demonstrate the influence of dynamic effects. These effects can be categorized into three main classes based on the observed changes in spectral features. The first class includes configurations, such as I(F)1, III(F)1 and III(E)1, where neither the shape nor the position of the spectral peaks changes

significantly. In the second class, which includes configurations like II(D)2, I(E)1, III(F)3, III(A)2 and II(A)2, the peak positions remain relatively stable, but the shape of the spectrum exhibits noticeable changes. The third class includes configurations, such as I(C)1, I(C)3, II(B)3 and II(F)5, where both the spectral shape and peak positions shift significantly. Additionally, the simulated spectra of 17 other configurations, shown in Figure B3 (Appendix B), can also be classified into these three groups, making detailed descriptions of each individual case unnecessary.

In the first class, Na^+ ions remain in their initial position throughout the molecular dynamics simulation, with only short-range thermal vibrations occurring and no long-distance migrations. These configurations typically involve both Na^+ ions occupying 6MR sites. For instance, in the I(F)1 case, in which two Al atoms are positioned in adjacent *d6r* units (one on the top face and one on the bottom) and both Na^+ ions are located at 6MR(1Al) sites, no conversion to the I(F)2 configuration occurs despite their similar energies (differing by about $4 \text{ kJ}\cdot\text{mol}^{-1}$). This is because of the relatively high activation barrier, $41 \text{ kJ}\cdot\text{mol}^{-1}$ (see Figure 6.10). In configurations III(F)1 and III(E)1, the Al atoms are separated by three silicon atoms and located in different *d6r* units, which behave as isolated Al and Na sites, similar to the CHA(35) case. Consequently, the spectra show minimal differences between static and dynamic calculations, with only slight variations resulting from thermal fluctuations of the system. A similar trend is observed in configurations with the longest sequences, IV(A)1 and IV(A)3, where the spectral shape, chemical shift, and Na positions do not change significantly throughout the simulation (Figure B3).

In the second class of configurations, the chemical shifts show only minor changes, but the spectral shapes change significantly due to the influence of dynamics on the local minima occupied by Na^+ ions. These configurations demonstrate that Na^+ ions can occupy both 6MR and 8MR sites. Examples such as II(D)2, I(E)1, III(F)3, and III(A)2 feature Na^+ ions in such arrangements, while II(A)2 has one Na^+ cation at a 6MR(0Al) site. In these cases, significant changes in both C_Q and η_Q are observed for the Na^+ ions. As a result, static predictions perform inadequately for these systems, even though the ions remain within their initial local minima throughout the simulation.

Configurations II(D)2 and the global minima II(D)1 are energetically close ($7 \text{ kJ}\cdot\text{mol}^{-1}$ difference), and can be interconverted by a simple rotation of a Na^+ ion from the top face of a 6MR to a nearby 8MR site. However, this transition does not occur within the 1 ns simulation due to a high activation barrier of $38 \text{ kJ}\cdot\text{mol}^{-1}$ (Figure 6.10). Changes in spectral shape are primarily observed for Na^+ ions at 8MR sites, likely due to their greater flexibility for thermal vibrations and movements. In contrast, in configuration I(E)1, the Na^+ ion at the 6MR site exhibits significant spectral shape modification. Interestingly, in configuration III(F)3, changes in peak shapes are observed for both Na^+ ions, even though they remain in their original local minima at the 6MR and 8MR sites throughout the MD simulation. This lack of a clear pattern in how C_Q or η_Q changes based on the location of Na^+ ions makes it challenging to predict the effects of temperature and dynamical averaging for these configurations. In configuration III(A)2, the Na^+ ion in the 6MR site moves across the *d6r* from one face to another, remaining in the new position for hundreds of picoseconds, while the Na^+ ion in the 8MR site stays in place. Although this dynamic process averages different 6MR Na^+ configurations, the chemical shift changes only slightly, while η_Q changes significantly, likely due to the change in the *d6r* face.

The II(A)2 configuration stands out as an exception in this class. Both Al atoms are positioned on the bottom 6MR of the same *d6r* unit, with one Na^+ at a 6MR(2Al):Al-Si₂-Al site and the other at a 6MR(0Al) site. According to static results (shown in Figure 6.7), these two sites represent the most deshielded and shielded 6MR configurations, respectively. The δ_{iso} values for the 6MR(0Al) Na^+ ion are -11.9 and -13.3 ppm in static and dynamic calculations, respectively, which are close to the lowest values observed for 8MR sites. This configuration is not the most stable II(A) configuration and does not transition to the ground state II(A)1 within the simulation timescale.

For configurations in the third class, the positions of Na^+ cations change during the MD simulation, resulting in the dynamical averaging of all NMR parameters, which reflects contributions from multiple states. For example, in the coupled cases of I(C)1 and I(C)3, both the shape and position of peaks exhibit significant changes. The global minimum I(C)1 has both Na^+ ions located at 6MR(1Al) sites on opposite faces of the same *d6r*, resulting in a broad, overlapping band in the static spectrum. In contrast, I(C)3 features one

Na⁺ in a 6MR(1Al) site and the other in an 8MR(1Al) site, producing distinct, well-separated peaks in the static spectrum. These configurations are connected by a simple rotation of one Na⁺ cation from the 6MR to the 8MR site, as shown in Figure 6.10. Despite a relatively large static energy difference, I(C)1 and I(C)3 interconvert during the simulation, suggesting a low interconversion barrier and a highly dynamic environment. The final equilibrated spectrum represents a weighted average of the two states, though the simulation timescale is insufficient to fully equalize the spectra of I(C)1 and I(C)3. The dynamic spectra are more similar to each other than the static ones, with chemical shifts differing by up to 11 ppm between static and dynamic calculations. Additionally, the C_Q value of the mobile Na ion decreases considerably, a trend also seen in other cases like I(A)1 and I(G)1 (Figure B3).

The II(B)3 configuration, which includes one Na⁺ in a 6MR site and another in an 8MR site, lies 22 kJ·mol⁻¹ above the ground state II(B)1. During the simulation, it converts to II(B)1, where both Na⁺ ions occupy 6MR(1Al) sites, overcoming an energy barrier of 21 kJ·mol⁻¹ (Figure 6.10) and taking 750 ps to complete the transition. This configuration shows unusual dynamic stability. Similarly, II(F)5, with Na⁺ ions in a 6MR and an 8MR site, is 19 kJ·mol⁻¹ higher in energy than the ground state II(F)1 (Figure B1). Over the MD simulation, it converts to another local minimum, II(F)3, but does not reach the ground state within the 1 ns timescale. Although II(F)3 can eventually transition to II(F)1 by rotating the 8MR Na⁺ to a 6MR site, this slow interconversion may lead to spectral contributions from less energetically favourable minima.

In addition, other cases show Na⁺ migrations during the 1ns MD simulation, but there is no obvious rule regarding the types of Na⁺ motion. Migration can happen in configurations with all Al-Si_n-Al sequences, with their effect on the spectra depending on the specific Al/Na arrangement. For example, in configuration II(A)3, Na⁺ migration happens (Figure 6.9), but there is minimal impact on the spectrum (only a 1ppm difference in δ_{iso} of Na atom in 6MR(2Al) site) between static and dynamic results(Figure B3). However, in configuration II(A)2, the spectral shape changes, and a 2 ppm shift of δ_{iso} observed for all the Na atoms, even though the migration does not take place during the MD simulation (Figure 6.11).

Generally, the influence of dynamics on the positions and NMR spectral properties of Na^+ ions is closely related to the interaction between neighboring Al/Na atoms. When the Al-Si_n-Al sequence is long ($n \geq 3$), the sodium ions exhibit minimal interaction with one another, leading to spectra that are similar to those of isolated configurations observed in systems with high Si/Al ratios. For the shorter sequences ($n \leq 3$), analysis becomes more complex due to interactions between aluminum atoms, and the mobility of Na ions depends on the particular arrangement of Al and the identity of the ring to which the Na^+ ion is bound. An exception occurs in cases where $n=3$ and both Al atoms share a *d6r*. In these cases, although the Al sequence is long, the distance between two Al atoms is short.

6.2.3.3 Effect of temperature

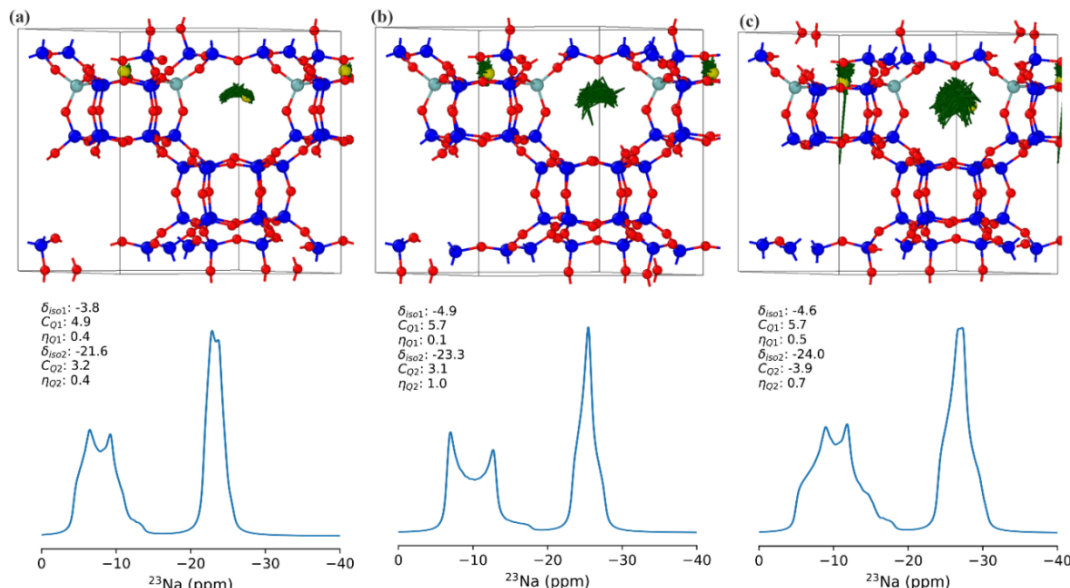


Figure 6.12 Trajectories of Na^+ at different temperatures of CHA(17) with Al-Si₂-Al sequence in 6MR and respective simulated ^{23}Na spectra. (a), (b), and (c) show the trajectories at 150, 350, and 550 K, respectively. The path indicates the Na atom traces, only the initial position of the atoms is shown as a yellow ball. Reproduced from Ref.¹⁷⁹ with permission from the Royal Society of Chemistry.

An additional factor to consider in the simulation is temperature. A temperature of 350 K was selected to match typical experimental solid-state NMR conditions, accounting for the heating effects caused by magic angle spinning. To briefly explore the impact temperature on ^{23}Na NMR, the trajectories and spectra of configuration II(A)1 in CHA(17) were simulated at 150, 350, and 550 K. The results indicate that higher temperatures increase the mobility of Na^+ ions, particularly those at 8MR sites, thereby influencing the calculated δ_{iso} , C_Q , and η_Q parameters (Figure 6.12). In principle, activation energies for transitions

and residence time profiles could be derived from a systematic comparison on MD trajectories at different temperatures, a task made feasible with NNPs. However, this is not the focus of the current study. Future work could explore temperature as a tunable parameter in both MD simulations and experiments to better identify Na/Al siting in zeolites.

6.2.3.4 Effect of hydration

In the hydrated condition, water molecules pull the Na^+ cation from its initial position within the cavity. As a result, the ^{23}Na NMR becomes more influenced by water loading and the available space for the solvation rather than the Al distribution in the framework. This reduces the effectiveness of ^{23}Na NMR for resolving Al distribution. To illustrate the effects of hydration, the ^{23}Na NMR shifts were extracted from the CHA(11)|Na|5w and CHA(11)|Na|0w static and dynamic calculations presented in Chapter 5 (see Table 6.1). In the dehydrated CHA(11), with Na^+ located at the 6MR(1Al) site in an Al-Si₃-Al sequence, the ^{23}Na δ_{iso} is about -12 ppm, in the same range as shown in Figures 6.3 and 6.4. The dynamic effect is negligible, leading to only a 0.7 ppm difference.

In contrast, in the hydrated state, the cation solvation can be at different levels which leads to a wide range of chemical shift changes, and the dynamic effects become significant. The static ^{23}Na δ_{iso} of the partially solvated Na cation is approximately -12.6 ppm, similar to the dehydrated case with Na^+ at 6MR. This suggests that the partially solvated Na^+ bonded to two framework oxygen atoms and two water oxygen atoms can have a comparable electronic environment to that of Na^+ bonded to four framework oxygen atoms in the dehydrated 6MR site. The dynamic average δ_{iso} , however, is -6.0 ppm, which agrees with the experimental results of the Na site at 6MR in hydrated NaY (FAU zeolite).²⁴⁷ The static and dynamically averaged ^{23}Na δ_{iso} values for fully solvated Na^+ are 2.7 ppm and -2.1 ppm, respectively. The static value corresponds to a configuration where the Na^+ is bonded to five water molecules, while the dynamic average also involves configurations where the Na^+ is bonded to four water molecules along the dynamic trajectory. These values, being close to zero, suggest that the electronic environment around Na^+ in a fully hydrated state is similar to that in NaCl solution, which is often used as the reference for ^{23}Na chemical

shifts. This similarity is understandable given the analogous solvation environment in both cases.

A previous study by Deng et al.²⁴⁸ on zeolite omega experimentally investigated the hydration effect on ^{23}Na NMR, revealing a similar difference between partially and fully solvated Na^+ cations. In zeolite omega, the sodium cations in the 12MR channels, which are highly hydrated, exhibit a peak of about -3 ppm in the spectrum. In contrast, the cations in the gmelinite cages, which are less hydrated and bonded to both the water molecules and the framework oxygen atoms, show a lower chemical shift of -8 ppm. These findings are consistent with the trend observed in our computational results, in which water molecules in the system increase the deshielding of Na^+ .

Although the hydration for ^{23}Na NMR is a disadvantageous factor in identifying the Al distribution, it is important to determine the Na distributions because the dehydrated sample is often obtained by calcinating the hydrated sample. The Na distribution of the dehydrated sample is related to the hydration condition, the water loading can lower the diffusion barrier²⁴⁹ and the starting position of the hydrated sample can decide the distribution in dehydrated samples.¹⁰²

Table 6.1 The ^{23}Na NMR chemical shifts (δ_{iso}) from the static calculation and the time-averaged chemical shifts from dynamic calculations for dehydrated and hydrated CHA(11) in Chapter 5. Note: only the static calculation of Na|1w case was performed under the assumption of its dynamic behavior similar to the Na|0w case.

CHA(11)	Static δ_{iso} (ppm)	time-averaged δ_{iso} (ppm)
Na 0w	-12.1	-11.4
Na 5w (partial solvated)	-12.6	-6.0
Na 5w*(full solvated)	2.7	-2.1

6.2.4 Physical Interpretation of ^{23}Na chemical shielding

To gain a deeper understanding of the physical origins of chemical shifts, LASSO regression was employed to obtain the relationship between ^{23}Na chemical shielding and a set of local structural descriptors. The LASSO model was trained on about 6232 DFT data

points generated from dynamical simulations of CHA(17) configurations. The initial feature set included 24 structural parameters, as detailed in Table 6.2.

Table 6.2 Features considered in LASSO regression including average distances d and angles α as well as the corresponding difference (Δd , $\Delta \alpha$) between the minimum and maximum values (spread). Reproduced from Ref.¹⁷⁹ with permission from the Royal Society of Chemistry.

Local features of Na		Cutoff of the neighbor atoms (Å)
CN_{Na-O}	Coordination numbers of the Na-O	3.5
$CN_{Na-O(Al)}$	Coordination numbers of the Na-O connect to Al	
CN_{Na-Si}	Coordination numbers of the Na-Si	5.0
CN_{Na-Al}	Coordination numbers of the Na-Al	4.0
d_{Na-O}	Mean Na-O distance	3.5
$d_{Na-O(Al)}$	Mean Na-O distance with O connected to Al	
d_{Na-Si}	Mean Na-Si distance	5.0
d_{Na-Al}	Mean Na-Al distance	4.0
α_{O-Na-O}	Mean O-Na-O angle	3.5
$\alpha_{Al-Na-Al}$	Mean Al-Na-Al angle	
Δd_{Na-O}	Spread of Na-O distances	
Δd_{Na-Si}	Spread of Na-Si distances	
Δd_{Na-Al}	Spread of Na-Al distances	
$\Delta \alpha_{O-Na-O}$	Spread of O-Na-O angles	
$d_{minNa-O}$	Minimum Na-O distance with O connect to Al	
$d_{minNa-O(Al)}$	Minimum Na-O distance	
$d_{minNa-Si}$	Minimum Na-Si distance	
$d_{minNa-Al}$	Minimum Na-Al distance	
Framework features		
d_{Al-O}	Mean Al-O distance (Al closest to Na)	
$\alpha_{Al-O-Si}$	Mean Al-O-Si angle	
α_{T-O-T}	Mean T-O-T angle (O neighbor to Na)	
Δd_{Al-O}	Spread of Al-O distances	

$\Delta\alpha_{Al-O-Si}$	Spread of Al-O-Si angles
$\alpha_{minT-O-T}$	Minimum T-O-T angle (O neighbor to Na)

Following previous empirical works,²⁵⁰⁻²⁵¹ the one descriptor regressions were tested on our dataset to connect the ^{23}Na chemical shielding with minimum Na-O distance $d_{minNa-O}$ or the distance average d_{Na-O} (Figure 6.13 a, b). The results show that one descriptor is insufficient to predict a ^{23}Na chemical shielding in the zeolite CHA system (with errors greater than 6 ppm from DFT calculations), although the $d_{minNa-O}$ shows a better correlation. The stronger correlation of $d_{minNa-O}$ compared to d_{Na-O} is consistent with the findings of Steinadler et al. for compounds with Na in a pure oxygen environment.²⁵¹ However, the correlation in zeolites is weaker, with an R^2 value of 0.43 and a mean absolute error (MAE) of 6.3 ppm (Figure 6.14b). Subsequently, a correlation involving Na-O distances and O-Na-O angles was tested, as two parameters can achieve a correlation with an R^2 coefficient of about 0.6 (Figure 6.13 d). This approach further improves the regression compared to the single-descriptor regression (Figure 6.13 c).

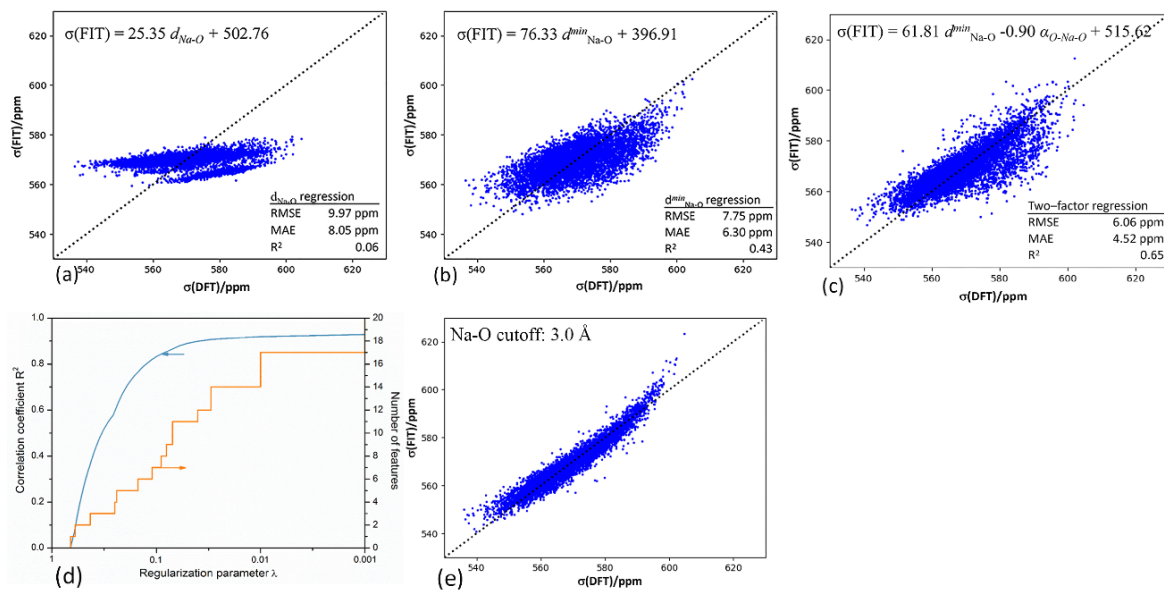


Figure 6.13 (a) Coefficient of determination R^2 of the employed test set and the number of structural features with non-zero coefficients as a function of the LASSO regularization parameter λ . (b) and (c) The one descriptor regression with d_{Na-O} and $d_{Na}^{min}-O$. (d) The two descriptors regression with the two important descriptors selected from LASSO, $d_{Na}^{min}-O$ and α_{O-Na-O} . (e) A test of the LASSO regression model against the training set of chemical shielding of CHA(17) configurations with calculating descriptors about Na-O in 3.0 Å.

It is notable that the definition of the coordination sphere of Na can lead to much difference in chemical shift prediction with structural features in sodium silicate compounds (up to 10 ppm difference).²⁵⁰ Different cutoffs to define the coordination spheres were tested in CHA(17) zeolite. The influence of Na-Si and Na-Al cutoffs are negligible due to their small contribution to ^{23}Na chemical shielding (Table B5), but that of the Na-O cutoff is significant by comparison of 3.0 and 3.5 Å. The correlation with calculating Na-O descriptors in 3.0 Å overestimated the cases with chemical shielding in two ends (Figure 6.14 e). Thus, the features were calculated with the O coordination sphere of Na in 3.5 Å, which agrees with the definition in the work by Koller¹⁸⁸ (3.4 Å).

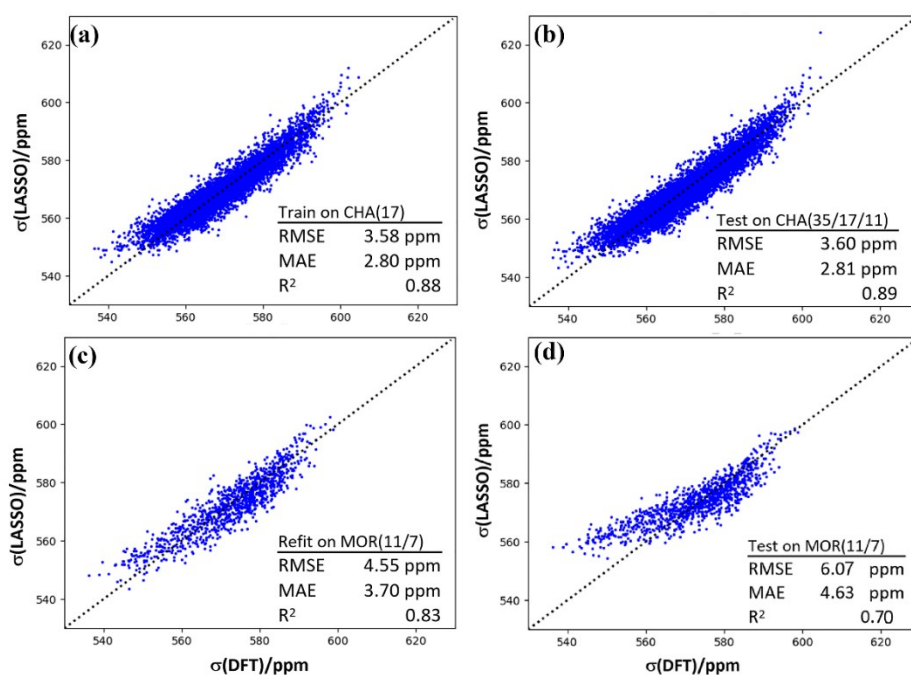


Figure 6.14 (a) Validation of the LASSO regression model against the training set of ^{23}Na chemical shifts of CHA(17) configurations, (b) Generalization test of the LASSO model against CHA(35) and CHA(11) configurations, (c) Performance of the retrained model against MOR(11) data. (d) The test of the seven-factor equation 6-1 on the MOR dataset.

Taking both accuracy and efficiency into account, seven factors were selected from the 24 features to fit the shieldings, resulting in a mean absolute error (MAE) of around 2.5 ppm, and a high Pearson correlation coefficient of 0.88 (Figure 6.14 a). And using additional descriptors provides virtually no improvement (Figure 6.13 d). The final regression formula is written as:

$$\sigma = c_0 + c_1 CN_{Na-O} + c_2 CN_{Na-O(Al)} + c_3 CN_{Na-Si} + c_4 d_{Na-O} + c_5 d_{minNa-O} + c_6 d_{minNa-Si} + c_7 \alpha_{O-Na-O}$$

Equation 6-1

where, coefficients are $c_0 = 383.674$, $c_1 = -5.954$, $c_2 = -2.065$, $c_3 = -0.789$, $c_4 = 40.138$, $c_5 = 45.785$, $c_6 = 11.556$, $c_7 = -0.196$. The surviving parameters identified through LASSO regression include the coordination number between Na and O (with a cutoff of 3.5 Å), the coordination number between Na and O atoms bonded to Al, the coordination number between Na and Si atoms (with a cutoff of 5.0 Å), the average distance between Na and coordinated O atoms (with a cutoff of 3.5 Å), the minimum distance between Na and O atoms, the minimum distance between Na and Si atoms and the average O-Na-O angle.

The seven descriptors in Equation 6-1 and their contributions to the ^{23}Na chemical shielding of CHA(17) for both static and time-averaged results (Tables B4 and B5 of Appendix B) show that the most significant contribution comes from descriptors that describe the oxygen environment around Na. Meanwhile, the Al environment ($CN_{Na-O(Al)}$) plays an important role in describing specific Na positions, such as 6MR(0Al) and 6MR(2Al). In contrast, the descriptors related to Si around Na, such as CN_{Na-Si} and $d_{minNa-Si}$, contribute very little. It is worth noting that the Na-Al distance is absent from Equation 6-1, as are any parameters related to the framework itself, such as Al-O bond lengths or O-Al-O angles.

Furthermore, this LASSO model trained on CHA(17) data was tested on an expanded dataset of CHA structures with lower and higher Al content (1521 points of CHA(35) and CHA(11)), which shows no significant loss of precision (Figure 6.14 b). This generalization test shows that the parameters that control the chemical shielding do not change between Si/Al = 35 and Si/Al = 11. In order to test the transferability of this expression to other topologies, we considered zeolite MOR, which has a more complex pore structure, with both 8 and 12 rings and side pockets. The results show the same parameterization, with the same coefficients as for CHA gave an unsatisfactory result for a combined dataset of MOR(7) and MOR(11) (1005 points), with an R^2 coefficient of 0.70 and an MAE value of 4.6 ppm (shown in Figure 6.14d). However, refitting the coefficients of the LASSO model, while keeping the features identical, recovered a good linear fit, as shown in Figure 6.14c. This result suggests that while the specific regression for one zeolite

does not easily transfer to another, the features included in the fit fundamentally capture the underlying relationship between structure and chemical shielding for other topologies. This finding aligns with the result from Chapter 5 about ^{27}Al chemical shieldings, indicating that insights derived from the simple, rigid CHA do not necessarily apply directly to MOR, making this is a rigorous test of the regression model.

For the derived relationships, we cannot assume a high degree of generalization for the LASSO regression of ^{23}Na chemical shielding. The generalization tests showed that the fit for CHA(17) can be extended to CHA(11) and CHA(35) without loss of precision. However, at lower Si/Al ratios, other factors may become significant. For example, as Na-Al distances reduce and Na-Na interactions become more relevant due to crowding in the unit cell, the optimal unit cell shape and volume will vary. The increased number of Al atoms leads to more significant distortions of the framework, which are highly dependent on their distribution. In the test, LASSO regressions re-trained on alternative frameworks demonstrate good transferability of the features but require new coefficients to achieve optimal linear fits. In addition to the Si/Al ratio, the length of the Al-Si_n-Al sequence plays a significant role in ^{23}Na chemical shifts. This was previously found for ^{27}Al and is also noted for the ^{23}Na chemical shifts, given a particular Na configuration.

6.2.5 Dipolar coupling and recoupling

For quadrupolar nuclei, the quadrupolar interaction can serve as a highly sensitive probe of the local environment, potentially providing more information than the chemical shift. In addition to the parameters C_Q and η_Q , which are crucial for describing resonance shapes in the spectra and can assist in identifying species in experimentally studied zeolites, dipolar coupling, another parameter derived from EFG analysis, also provides insight into the interatomic distances. Although magic angle spinning averages out dipolar coupling, which is proportional to r^{-3} , recoupling methods can reintroduce it, and enable the measurement of interatomic distance information.²⁵²⁻²⁵³ These methods are typically used to recouple spin-1/2 or spin-1/2-quadrupolar pairs,²⁵⁴⁻²⁵⁵ but studies involving quadrupolar-quadrupolar pairs,^{198, 256} including those in zeolites, have also been reported.¹⁰³

To further explore the connection between NMR EFG properties and geometrical characteristics, the ^{23}Na - ^{27}Al heteronuclear, as well as ^{23}Na - ^{23}Na and ^{27}Al - ^{27}Al

homonuclear dipolar couplings, were calculated for the selected CHA(17) cases using both static and dynamic calculations (Figures B4-B6). For the ^{27}Al - ^{27}Al pairs, the values of dipolar coupling align well across static and dynamic calculations for each case and are related to the length of the Al sequences. The agreement of static and dynamic results can be expected because the framework Al atoms remain almost stationary during the dynamic simulations. The largest ^{27}Al - ^{27}Al dipolar couplings are from Al-Si₁-Al moieties, above 40 Hz, and pairs in the same 4MR, such as I(C) and I(G) structures, even exhibiting values above 90 Hz. While the long Al-Si_n-Al ($n \geq 2$) sequences show small coupling, which cannot be distinguished solely by analyzing the coupling between Al pairs. Thus values of ^{27}Al - ^{27}Al coupling might be used to distinguish the short Al sequences.

For ^{23}Na - ^{23}Na pairs, dipolar coupling values vary from static to dynamic calculations, depending on the Al distribution. The high mobility of Na^+ within the cavity along dynamic trajectories can lead to either an increase or decrease of the dipolar coupling compared to static calculations. Conversely, the ^{23}Na - ^{23}Na coupling reflects the distance between Na atoms, which can indicate the motion mobility or whether cation migration happens during the molecular dynamic simulation by comparing static and dynamic results. For example, in the II(A) case, the coupling shows an obvious increase of about 20 Hz from the static to the dynamic average. This increase is attributed to the migrations of one Na^+ from a 6MR to an 8MR, moving further from another Na^+ , as illustrated in the trajectory shown in Figure 6.9.

Similarly, the ^{23}Na - ^{27}Al dipolar couplings reflect the interatomic distances between Na and Al, providing insight into the distribution of Na/Al and cation motions during dynamic simulations. For example, in the II(A)1 case, high couplings are observed between each Na cation and both Al atoms, which indicates the configuration where both Na cations are close to two Al atoms located in the 6MR and 8MR of CHA (Figure B1). Additionally, the $\text{Na}_2\text{-Al}_1$ and $\text{Na}_2\text{-Al}_2$ coupling change in opposite directions from static to dynamic calculations, with $\text{Na}_2\text{-Al}_1$ increasing and $\text{Na}_2\text{-Al}_2$ decreasing. This agrees with the motion of Na_2 in the 8MR(2Al):Al-Si₂-Al site, where Na_2 can be attracted alternately towards Al₁ or Al₂ along the trajectory.

Lastly, a recoupling example is provided to demonstrate its efficiency in identifying Na-Al connectivity and confirming particular Na/Al arrangements. The ^{23}Na NMR spectra of II(A)2 and II(D)2 exhibit two resonances at around -5.7 and -13.3 ppm, and -7.6 and -19.8 ppm, respectively. Although these resonances correspond to distinct Al and Na locations, these spectra are similar, which suggests only 1D spectra cannot determine Al siting and pairing clearly. Numerical simulations of magnetization build-up curves of a recoupling experiment involving ^{23}Na - ^{27}Al pairs (Figure 6.15) show that for model II(D)2, the magnetization of both Na atoms increases rapidly. On the other hand, for model II(A)2, only the Na₁ atom, which is close to two Al atoms, exhibits a rapid magnetization build-up. The Na₂ atom, located at the 6MR(0Al) site, shows a slower magnetization increase and achieves significant magnetization transfer only at longer mixing times.

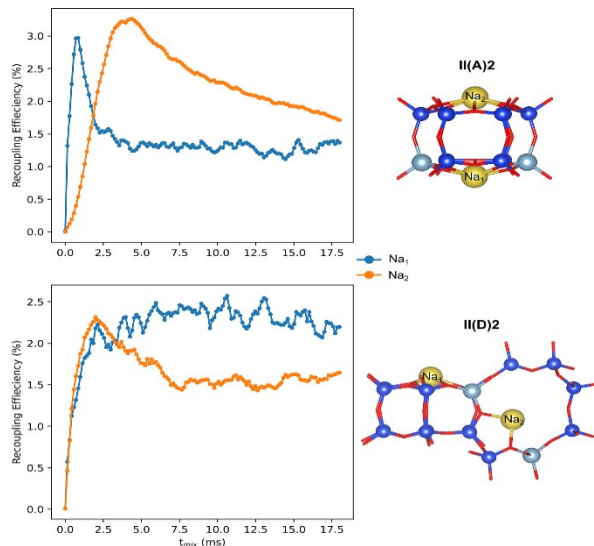


Figure 6.15 Computed ^{23}Na - ^{27}Al recoupling build-up curves and respective structures. Reproduced from Ref.¹⁷⁹ with permission from the Royal Society of Chemistry.

6.3 Summary

This chapter demonstrates the application of a machine-learning-driven approach to simulate $^{23}\text{Na}/^{27}\text{Al}$ solid-state NMR in the zeolite CHA. By enhancing the sampling of the low energy Na/Al configurations in the sodium form of CHA, it was shown that calculated ^{23}Na NMR chemical shifts can significantly narrow down the possible distributions of Al and Na in the sample when combined with asymmetry parameters and dipolar coupling constants. Three key factors were identified to control ^{23}Na chemical shifts: the location of Na^+ ions in 6MR versus 8MR sites, the number of Al atoms in the ring, and the length of the shortest Si_n sequence between Al atoms. Additionally, the critical role of dynamic

sampling was explored, revealing its impact on the position and shape of NMR spectral peaks, as well as on dipolar coupling constants. The extent of this influence depends on the mobility of ion migration at typical NMR acquisition temperatures. By identifying the structural features that govern chemical shifts, a polynomial fit primarily based on Na-O distances, coordination numbers around Na, and O-Na-O angles was developed. This approach, combined with cost-effective ML simulations, offers a promising pathway for accurately predicting chemical shifts without relying on computationally expensive DFT calculations in the future.

Chapter 7. Discussion

7.1 Complexity of models

Modelling ^{27}Al and ^{23}Na NMR properties of zeolites under realistic operating conditions needs to consider factors: Al content, coordination of Al to the framework, framework types, the type and location of cations, and hydration. The effect of Al sequences on ^{27}Al NMR can be significant due to the Al-Al interaction when the length of the Al-Si_{*n*}-Al sequence is short (with $n < 3$). This effect can also influence the ^{23}Na NMR of the extra-framework Na⁺ cations because the locations of cations are determined by the Al distribution. The length of the Al-Si_{*n*}-Al sequence, which is often closely linked to the Si/Al ratios of the framework,⁵⁵ can significantly impact both the ^{23}Na and ^{27}Al chemical shifts. Thus, selecting a Si/Al ratio that matches specific experimental values is crucial for reproducing and aligning the experimental NMR signals. The cations of H⁺ and Na⁺ showed different effects on ^{27}Al NMR due to the different interactions of Na-O and H-O bond with the AlO₄ group. The H-O bond often distorts the AlO₄ group more than the alkali metal cations in the dehydrated condition. The location of the Na⁺ cations, of course, determines ^{23}Na NMR for the different local environments and may lead to various signals of the ^{27}Al NMR for a single Al site in some complex topologies due to isoenergetic cation locations. Finally, hydration is important for quadrupolar nuclei NMR as it reduces the EFG and C_Q , narrowing the peaks, because water molecules can pull the cations to the centre of the channel or cavity, leading to a symmetrization of the electronic environment around the Al atom by weakening the interaction between the cation and the AlO₄ group.

Our simulations show that the use of simple cluster models or periodic bare framework models, which have been used in some previous studies to assign spectral peaks to specific geometrical features, can result in qualitative and quantitative errors when compared to the proper models. The significance of the effect may depend on the framework topologies. The cluster approach can be particularly useful for establishing qualitative correlations between local geometrical parameters and associated properties, such as chemical shifts and EFG. However, the size of the cluster or the charge neutrality at the edge of the cluster can lead to the Al-Si_{*n*}-Al sequence length and the local electronic environment being

different from the real zeolite crystalline structure with cations. The description of the length of the Al-Si_n-Al sequence or the incorrect Si/Al ratio of the crystalline structures is the most disadvantageous aspect of using cluster models. Another simplified model for framework Al atoms that is common, is the periodic approach, using a bare framework and background charge to compensate for the negative charge. This model is superior to the cluster model in the description of the Si/Al ratio, but its effectiveness does not apply to all zeolites. In hydrated silicon-rich zeolites, this model works well because the effect of the hydrated counterion on the local geometry of AlO₄ tetrahedra can be negligible when the cavity or channel near the Al site has enough space to allow water molecules to solvate the counterions centrally, minimizing their interaction with the AlO₄ tetrahedra.⁵⁷ However, this assumption breaks down in zeolites with more complex porous structures, such as MOR zeolites, which feature large channels and confined small cavity structures. The counterions located in the limited channels are impossible to be fully solvated, the effect of the cations on the ²⁷Al NMR cannot be overlooked. In addition, some Al sites can be compensated iso-energetically from cations in different voids, which can produce more than one different chemical shift for one Al site (δ -multiplet), which is usually ignored in the simple models.

For ²⁷Al NMR simulations, the solvation of the extra-framework cation plays an important role in the NMR spectra in the hydrated condition. The solvation of cations results in a higher symmetrical environment around the Al nucleus, characterized by a small C_Q and EFG. Specifically, in hydrated H-zeolites, the presence of water molecules tends to promote the deprotonation of BAS, which significantly decreases quadrupolar coupling and enables the detection of signals from Al site in BAS that are otherwise invisible under dehydrated conditions. Furthermore, the calculated ²⁷Al isotropic chemical shifts of the hydrated Si-rich CHA models show differences from dehydrated BAS cases up to about ± 4 ppm (Figure 5.6). In hydrated Si-rich Na-zeolites, the solvated is more complex than in protonic cases because the Na⁺ cations can exist in different solvation states: a partially solvated state, where Na⁺ forms Na-O bonds with both framework oxygen and water molecules; and a fully solvated state, where Na⁺ forms Na-O bonds only with water molecules. These two states have different effects on the environment around the Al nucleus, leading to variations in NMR properties. The differences are influenced by the

confinement of the framework topology. In the case of the small pore, rigid, single T-site CHA structure, the framework's confinement limits the variation of the Na motion thereby the difference of ^{27}Al chemical shift between different solvated states, with even dehydrated Na-CHA is only a few ppm. However, in the case of MOR with diverse channels/cavities, solvation effects can result in chemical shift differences of up to 6 ppm (Figure 5.7 and Table A5). Besides, Al-Si_n-Al sequences can also shift the ^{27}Al chemical shift by a few ppm. The range of the discrepancy increases as the value of n decreases, and the Al can be considered isolated for sequences with $n \geq 3$.

The ^{23}Na NMR properties under dry conditions are particularly valuable for detecting Na⁺ locations and, subsequently, for understanding the Al distribution around the Na atoms. The complexity of Al distributions and the Na locations become significant when considering relative Al pairing. This is because the Al distribution cannot be determined based on energetic stability, and the number of possible Na locations with similar static energies for each Al distribution can be vast. In the CHA(17) cases, the ^{23}Na chemical shift variation of the Na site at a ring can exceed 10 ppm depending on the Al content and the length of Al-Si_n-Al sequences in the ring (Figure 6.7). Thus, achieving a Si/Al ratio model systematically with all the possible Al distribution and corresponding low energy Na locations is necessary to align the ^{23}Na NMR signals to the correct structural features, such as the Na locations, Al contents, and Al-Si_n-Al sequences.

In addition to the direct effect of Al content on NMR properties, specifically through Al sequences, Al substitutions have two additional effects. Firstly, Al substitution in zeolite structures also increases the volume/lattice parameters of UC, leading to changes in NMR properties. The UC expands with increasing Al content due to the longer Al-O bond length compared to the Si-O bond length. Calculating NMR parameters using an optimized structure is generally more accurate than relying on the ideal structures obtained directly from XRD method.²⁵⁷⁻²⁵⁸ However, it is well known that the DFT tends to overestimate the lattice dimensions for zeolites.²⁵⁹ In Si-rich zeolites, this effect on ^{27}Al NMR parameters is fairly insignificant because the slight change leads to only a change of few ppm in the chemical shifts, which are indistinguishable from experiments (Figure 5.4a). By contrast, cell optimization for Al-rich zeolites requires caution, as the large volume change may lead

to significant differences in NMR properties. For example, the ^{27}Al δ increases almost linearly with the cell volume decrease, and the change is up to 10 ppm when the volume expands by 10%.²²⁵ Secondly, for hydrated Al-rich cases, the solvation of the cation can be limited by the available water loading in the frameworks. Grifoni et al.²²² presented that increasing the water count to three per BAS completely destabilizes the non-solvated BAS state. This suggests the BAS site cannot be deprotonated for too high Al content due to the lack of a sufficient number of water molecules. For example in the CHA(3)|H|6w case (Figure 4.4), we observe that six water molecules are not enough to solvate three BAS sites.

7.2 Static vs. dynamic

Dehydrated conditions

The dynamic effect in dehydrated cases is primarily dominated by thermal vibrations without the influence of the water loading. This effect on ^{23}Na NMR is more significant than on framework ^{27}Al NMR because extra-framework cation Na^+ exhibits greater mobility compared to the relatively rigid framework Al atoms.²⁶⁰ As a result, the chemical shift of ^{27}Al in dehydrated cases of both CHA and MOR shows a slight difference between static and dynamic average results. For the framework Al site under anhydrous conditions, the time-averaged ^{27}Al δ is very similar to the result obtained from the corresponding static stable structure independent of the framework topology and extra-framework cations, exhibiting only around 1 ppm discrepancy (Table A1, A4, B1, and Figure 6.11). However, the chemical shielding fluctuates by up to about 20 ppm along the trajectories (see Figure 5.12), which suggests the structural descriptors related to the ^{27}Al shielding change along the trajectory, but the average is similar to the static stable structures. The extent of these fluctuations is related to the cation types, with Na^+ being more fixed than H^+ , resulting in smaller fluctuations.

For the ^{23}Na NMR in the case with isolated Al, such as the CHA($\text{Si}/\text{Al} = 35, 17$, and 11) cases with Al-Si_{*n*}-Al ($n \geq 3$) sequences, the difference of chemical shift between the time-averaged and static calculations is related to the initial position of the Na^+ in the static configuration. The dynamic effect on ^{23}Na δ of Na^+ confined within small rings is less pronounced compared to Na^+ in larger rings and voids. For example, the maximum

difference between static and dynamically averaged results is about 0.5 ppm for Na^+ in the center of 6MR, and about 2 ppm for Na^+ in an 8MR. Notably, the ^{23}Na chemical shieldings of snapshots along the trajectories exhibit greater fluctuation than those of ^{27}Al shieldings due to the more flexible movement of Na^+ compared to the relatively rigid framework, even though the difference between the dynamic average and the static result is not very significant.

When cases involve more Al substitutions and Na^+ cations in a single cell, they exhibit a greater number of possible configurations and more complex interactions between nearby Na and Al atoms. This can lead to the cation migration between different positions driven by the thermal energy within the simulation timescale of 1 ns at room temperature. The energy barrier between two sites decreases with increasing Al numbers in the intermediate rings and is related to the Al positions.²⁶¹ The presence of the Al pairs in CHA(17), e.g. Al-Si₁-Al and Al-Si₂-Al sequences, determines the accessible locations of Na cations at static energy levels and establishes different energy barriers for transformation between these local minima. The dynamic effect on ^{23}Na spectra in the presence of Al pairs depends on the proximity and configuration of surrounding Al and Na atoms for each specific Na atom. The difference between the dynamic and static shift can be as large as 10 ppm when Na^+ migration can happen during the simulation timescale due to the moderate energy barrier. The accessible energy minima for Na locations vary significantly depending on the specific Al distribution, and the ease of transformation between these minima for a given Al distribution further influences the observed dynamic effects on the spectra.

Hydrated conditions

Water loading is ubiquitous in many thermal treatments and reaction conditions of zeolites, playing various roles in their properties and reaction processes.²⁶² The influence of dynamic simulations on NMR properties under hydrated conditions varies between cationic and protonic zeolites due to their different hydration effects. In cationic zeolites, such as Na-zeolites, the transition between the partially and fully solvated states at room temperature results in time-averaged NMR properties that reflect the average of these distinct solvation states. In contrast, in protonic zeolite, where Al sites typically form BAS under dehydrated conditions, the presence of water molecules can lead not only to

protonation, similar to Na-zeolites, but also to hydrolysis of the framework. The hydrolysis can change the coordination of Al from tetrahedral Al to other states, such as the octahedral Al, which significantly impacts the ^{27}Al NMR spectra of H-zeolites.

The impact of dynamically simulated results also depends on the zeolite topology, Si/Al ratios, and hydration levels because extra-framework metal cation behavior varies with water loading and Al distribution.^{228, 263-265} For small-pore zeolites like CHA, which has a simple single T-site structure, the dynamic effect may be minimal (e.g., around 1 ppm shift in ^{27}Al δ from static to dynamic results, as shown in Table A4) due to the confinement that reduces differences between solvation states (resulting in only about a 1.5 ppm difference in ^{27}Al δ , Table A4). However, in more complex topologies with multiple T-sites and large channels and pores, such as the four T-sites zeolite MOR, the proximity of Na^+ to different Al sites can lead to different migration and solvation behaviors as a function of water content.²²⁸ The dynamic effects are reflected in NMR properties, with a variety of shifts in ^{27}Al δ for different Al substitution sites (ranging from -3 to +4 ppm, as shown in Table A5). The dynamic effect on ^{23}Na δ is obvious, the dynamically averaged results for CHA(11)|Na|5w agree better with the experimental result which shows up to 6 ppm difference from the static result (Table 6.1). Therefore, modelling in a simple framework topology may be misleading when assessing the dynamic effects in NMR simulations of zeolites.

In hydrated H-zeolites cases, the dynamic simulation is crucial to fit experimental NMR spectra describing the protonation of BAS over time, which is related to the Si/Al ratios, and water content in the framework. The coordination of Al in zeolite and the protonation degree are affected by the water content in systems and the Al siting in the framework.²⁶⁶⁻²⁶⁷ There can be three solvation states for the BAS proton over time without considering the hydrolysis reaction: solvated at all times (protonated state all time along the trajectory), partially solvated (exchange between to BAS and solvated state), and never solvated (staying at BAS site). For the case with sufficient water loading (more than three water molecules per acid site), the proton of a BAS site located in voids with ample space to accommodate these water molecules becomes solvated, forming H_3O^+ groups, and remains in this state throughout the simulation duration. The dynamic average ^{27}Al NMR shows

negligible difference from the static results, such as the CHA(11)|H|5w case (Table A1 and A4). For the high Al content cases, the water loading is not enough to solvate all the BAS sites and the ^{27}Al chemical shift over the dynamic simulation results from the average of different protonation forms. The dynamic average results of course differ from the simplified static results, as proton forms significantly influence the Al environments. As shown in Figure 4.4, in the CHA zeolite with $\text{Si}/\text{Al} = 3$, three acid sites with loading six water molecules per UC, there are three different proton forms along the dynamic trajectories which are reflected by different ^{27}Al NMR spectra. Similar phenomena were observed in the MOR(7)|H|5w case (Figure 5.9). Furthermore, the framework hydrolysis process, such as the reversible tetrahedral–octahedral aluminum coordination transfer, can happen at room temperature when the Al distributions fit the requirement of Al pairs, and water loadings. In this case, the dynamic process is important to search for some thermodynamically and kinetically feasible states that may be ignored in static calculations as shown in Chapter 4. Particularly, the LAS(5) structure is thermodynamically unstable with respect to LAS(6) but cannot be overlooked to understand the shoulder of the ^{27}Al experimental spectra.

In general, the various effects of dynamics on ^{27}Al and ^{23}Na NMR cannot be summarized as a simple rule, but give rise to particular phenomena and observables that cannot be reliably obtained with high accuracy using static calculations alone.

7.3 Development of tools/methods: from *ab initio* to ML

To perform the *operando* modelling of NMR, an approach was developed by combining the *ab initio* molecular dynamic and static DFT NMR calculation. In this process, the MD calculation properly describes the vibration of the atoms and the accessible reactive transformation at practical measurement temperature, usually room temperature, instead of the stable structure from the static and athermal calculations. Then a series of configurations are sampled evenly along the MD trajectory to cover various local environments of the specific atom for NMR calculation over a while. Finally, the NMR tensors are obtained and averaged over all the sampled configurations to mimic the data collection process in the NMR measurement. The benefit of this *ab initio*-based method lies in its precise depiction of dynamic behaviour and accurate prediction of NMR

properties. However, the high cost of AIMD restricts calculations to a short timescale on the order of picoseconds, and the system size is also limited. Additionally, the need for a large number of static DFT NMR calculations to get time-averaged results significantly increases the computational cost. Combining MD calculations with NMR calculations requires several orders of magnitude more computing power than performing a single NMR calculation on a single optimized structure.²⁶⁸

Machine learning, as a useful tool to advance computational efficiency, has recently been introduced into NMR simulations.^{131-132, 269} An important aspect of improving *operando* modelling of NMR properties in zeolites is accelerating the search for structurally low-energy equilibrium configurations and thermodynamically accessible configurations at room temperature. NNP has been developed and applied in zeolites to describe the behaviors of various conditions for different zeolites to expand the MD timescale to a nanosecond range but with DFT accuracy. Our NNPs have demonstrated their capability to describe both the structural and dynamical behaviour of various Na-zeolites, spanning from fully siliceous frameworks to the Löwenstein rule-limited Si/Al ratio of 1. The process allows observation of the transition of local minimum that occurs on long time scales, to avoid possible misleading results from too short MD simulations. For example, in the cases of CHA(17) with some specific Al distributions, Na cations transfer to other iso-energetic or thermodynamically accessible states after a few hundreds of picoseconds, which can be described properly with NNP-MD method. The NNP is a useful method to accelerate the process of the PES search of complex models for both static and MD calculations.

Inspired by the previous empirical linear correlation of the NMR chemical shift about simple local structural descriptors, such as bond lengths and angles, the efficient feature selection ML method LASSO regression has been used to correlate the chemical shift of ²⁷Al and ²³Na by training on the large dataset of DFT NMR calculations obtained from the *operando* simulation process. The correlation can predict the chemical shifts along the whole MD trajectories almost by nothing to replace the DFT NMR calculation. The ²⁷Al chemical shift of the framework Al is correlated with only two descriptors, resulting in an MAE of about 2 ppm. In contrast, the ²³Na chemical shift is related to seven descriptors

with an MAE of about 2.5 ppm. This correlation aids in understanding the structure-NMR property relationship. Besides simple structural descriptors measurable from experiments or directly readable from the structural files, more sophisticated descriptors, such as the SOAP descriptors, may improve the accuracy of NMR chemical shift prediction due to their better capture of the local atomic environment. For example, the previous work showed that the linear ridge regression of SOAP descriptors can predict ^{27}Al and ^{23}Na chemical shifts of aluminosilicate glasses with deviations from DFT NMR results of only about 1.5 ppm and 1.4 ppm, respectively.¹³¹ There are various ML methods that may predict chemical shifts accurately, and handle parameters with nonlinear relationships to descriptors, e.g., Kernel Ridge Regression, gradient boosting regressor models¹⁶⁹ or (equivariant) neural networks.¹⁷⁰⁻¹⁷¹ However, these methods are computationally more expensive and make it difficult to interpret the relationship between the input features and prediction compared to LASSO.

Despite this thesis focusing only on NMR isotropic chemical shieldings/shifts, it is feasible to extend this approach to other NMR parameters (such as C_Q and η) and tensorial properties (shielding tensors, EFG tensors) as shown in recent works.²⁷⁰ It is therefore promising in this direction to expand the scope of the “Double ML” scheme to *operando* NMR simulations for other elements of interest, such as ^1H , ^{17}O and ^{29}Si .

Chapter 8. Conclusions

In this thesis, we developed approaches based on DFT and ML to perform *operando* modelling of ^{27}Al and ^{23}Na NMR for zeolites and to interpret the structure-NMR property relationships. The effects of various factors that align with real measurement conditions, such as hydration, temperature, and the presence of extra-framework cations, on the NMR parameters were systematically studied to clarify the necessity and accuracy compared to experimental results. Also linear correlations between the chemical shielding and local structural features were obtained to interpret the mechanism of NMR chemical shift in zeolites and predict the NMR chemical shift easily reducing the need for costly DFT calculations.

Firstly, the DFT calculation of the ^{27}Al NMR property was performed for a series of snapshots obtained along AIMD trajectories (room temperature) of zeolite CHA to reproduce and further understand the experimental spectra. This approach aligned the experimental NMR spectra with the theoretically predicted structures of intermediate states for reversible transformation between tetrahedral Al(Td) species and framework-associated octahedral Al(Oh) species in zeolites. The NMR simulations considering the time evolution of Al coordination states in zeolites under wet conditions at room temperature, are more accurate to fit the experimental results. Especially, the presence of the kinetically unstable penta-coordinated LAS(5) which provides a signal around 30 ppm in the shoulder of the ^{27}Al MAS NMR spectra, can be missed without the dynamic simulations. In brief, the *operando* NMR simulation demonstrated the pathway from Brønsted acid site (BAS) via tetrahedral Lewis acid sites (LAS) to the octahedral Al(Oh) species and back.

Then, *operando* modelling of ^{27}Al for Si-rich zeolites, CHA(11) and MOR(23) with a single Al site in the UC, has been performed using AIMD and DFT NMR calculations. The results show that to achieve accurate qualitative and quantitative ^{27}Al NMR results for complex zeolites like MOR, it is required to consider factors, such as Si/Al, cation type, and hydration degree. Relying on simple zeolites like CHA for testing can lead to misleading conclusions, particularly when dealing with

frameworks that are relatively symmetric and stiff, with well-defined extra-framework cation positions, such as those in zeolites with a *d6r* unit. In rigid frameworks, model complexity has little effect on geometrical parameters thereby on NMR results, and cations like Na^+ tend to occupy positions in 6MRs, with cation solvation only occurring when a significant amount of water is available. The findings highlight that modelling spectra for a particular Al distribution in zeolites is generally straightforward, provided the appropriate model and method are selected. Al distribution determines the cation coordination to the framework (whether a metal cation or proton), and the water content in the sample determines the cation's solvation degree. To achieve highly accurate NMR calculations across a wide range of zeolite motifs, NMR tensors need to be obtained as an average taken over the course of an MD simulation using proper models. The simple two-parameter correlation of ^{27}Al chemical shifts obtained from LASSO regression can replace DFT calculations along the MD trajectory, which significantly reduces computational demand. Thus, the primary challenge of *ab initio* computation becomes the AIMD simulation, which is currently limited to tens of picoseconds, which can be solved by the machine learning potentials (MLPs) method.

Lastly, *operando* modelling of ^{23}Na and ^{27}Al NMR for dehydrated Si-rich zeolites, including CHA and MOR with various Si/Al ratios and multiple Al sites per cell, was performed by using NNP-MD and DFT NMR calculations. The introduction of neural network potentials (NNPs) significantly accelerates the screening of stable configurations in systems requiring numerous Al configurations and cation positions and extends available timescales by several orders of magnitude compared to the AIMD. This advancement alleviates the challenges that currently hinder dynamical simulations for large systems and long timescales. Although the dynamic effect of ^{27}Al NMR in dehydrated CHA with compensated Na^+ has been shown to be slight, dynamic sampling greatly influences the position and shape of peaks in the ^{23}Na NMR spectrum as well as the dipolar coupling constants, due to the feasible ion migrations at a standard NMR acquisition temperature. Similar to the ^{27}Al chemical shift LASSO regression with structure features, we obtained a fitted polynomial of primarily coordination numbers of Na with O, Na-O distance and O-Na-O angle

parameters which can be used to reproduce ^{23}Na chemical shifts without the need for DFT calculations. It is promising to develop the ML-driven “double ML” approach which combines NNP-MD and ML property prediction, to achieve accurate ^{23}Na and ^{27}Al NMR cost-effectively in the future.

So far, we have mainly focused on the Si-rich zeolites. NMR calculations for Al-rich zeolites require further work and collaboration between experimental and theoretical approaches for systematic investigation in the future. Firstly, determining accurate cell parameters is crucial because significant cell changes due to high Al content can lead to substantial differences in NMR parameters,²²⁵ especially for flexible frameworks. However, the commonly used DFT methods are not sufficiently accurate for optimizing lattice parameters.²⁵⁹ Secondly, as the amount of framework Al increases, modelling these systems becomes more challenging due to the larger number of possible configurations, such as various types of Al pairs and the corresponding cation locations, since there is no simple rule for Al distribution.⁵⁷⁻⁵⁸ Finally, the water content in the channels and its distribution are influenced by the Al content and distributions in high Al zeolites, which can even affect hydrolysis processes, such as the reversible tetrahedral–octahedral aluminum coordination occurring at room temperature. It is anticipated that the ML method will play a pivotal role in the future of these fields.

References

1. Grandjean, F., Étude optique des solutions de vapeurs lourdes dans certaines zéolithes. *Bulletin de Minéralogie* **1910**, 5-32.
2. Friedel, G., Sur quelques propriétés nouvelles des zéolithes. *Bulletin de Minéralogie* **1896**, 94-118.
3. McBain, J. W., *The sorption of gases and vapours by solids*. G. Routledge: London, 1932.
4. Taylor, W. H., I. The structure of analcite ($\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$). *Zeitschrift für Kristallographie - Crystalline Materials* **1930**, 74 (1-6), 1-19.
5. Pauling, L., The structure of some sodium and calcium aluminosilicates. *Proceedings of the National Academy of Sciences* **1930**, 16 (7), 453-459.
6. Morey, G. W.; Ingerson, F. E., The pneumatolytic and hydrothermal alteration and synthesis of silicates. *Economic Geology* **1937**, 32 (5_Suppl), 607-761.
7. Barrer, R. M., Preparation of synthetic quartz. *Nature* **1946**, 157 (3996), 734-734.

8. Barrer, R. M.; White, E. A. D., 286. The hydrothermal chemistry of silicates. Part II. Synthetic crystalline sodium aluminosilicates. *Journal of the Chemical Society (Resumed)* **1952**, (0), 1561-1571.
9. Barrer, R. M., 435. Syntheses and reactions of mordenite. *Journal of the Chemical Society (Resumed)* **1948**, (0), 2158-2163.
10. Barrer, R. M., 33. Synthesis of a zeolitic mineral with chabazite-like sorptive properties. *Journal of the Chemical Society (Resumed)* **1948**, (0), 127-132.
11. Barrer, R. M.; Riley, D. W., 34. Sorptive and molecular-sieve properties of a new zeolitic mineral. *Journal of the Chemical Society (Resumed)* **1948**, (0), 133-143.
12. Database of Zeolite Structures <http://www.iza-structure.org/databases/>.
13. Pophale, R.; Cheeseman, P. A.; Deem, M. W., A database of new zeolite-like materials. *Physical Chemistry Chemical Physics* **2011**, 13 (27), 12407-12412.
14. Woodley, S. M.; Catlow, C. R. A.; Battle, P. D.; Gale, J. D., The prediction of inorganic crystal framework structures using excluded regions within a genetic algorithm approach. *Chemical Communications* **2004**, 4 (1), 22-23.
15. Li, Y.; Yu, J.; Xu, R., FraGen: a computer program for real-space structure solution of extended inorganic frameworks. *Journal of Applied Crystallography* **2012**, 45 (4), 855-861.
16. Li, Y.; Li, X.; Liu, J.; Duan, F.; Yu, J., In silico prediction and screening of modular crystal structures via a high-throughput genomic approach. *Nature Communications* **2015**, 6 (1), 8328.
17. Li, Y.; Yu, J., Genetic engineering of inorganic functional modular materials. *Chemical Science* **2016**, 7 (6), 3472-3481.
18. Mellot Draznieks, C.; Newsam, J. M.; Gorman, A. M.; Freeman, C. M.; Férey, G., De Novo Prediction of Inorganic Structures Developed through Automated Assembly of Secondary Building Units (AASBU Method). *Angewandte Chemie International Edition* **2000**, 39 (13), 2270-2275.
19. Mi, Z.; Lu, T.; Zhang, J.-N.; Xu, R.; Yan, W., Synthesis of Pure Silica Zeolites. *Chemical Research in Chinese Universities* **2022**, 38 (1), 9-17.
20. Weitkamp, J.; Puppe, L., *Catalysis and zeolites: fundamentals and applications*. Springer Science & Business Media: 1999.
21. Baerlocher, C.; McCusker, L. B.; Olson, D. H., *Atlas of zeolite framework types*. Elsevier: 2007.
22. Barrer, R., Chemical nomenclature and formulation of compositions of synthetic and natural zeolites. *Pure and Applied Chemistry* **1979**, 51 (5), 1091-1100.
23. Baerlocher, C., Kristallograph; Hepp, A.; Meier, W. M., Kristallograph, Schweiz, *DLS-76 : a program for the simulation of crystal structures by geometric refinement*. Institute of crystallography and petrography - ETH: Zürich, 1978.
24. Cejka, J.; Corma, A.; Zones, S., *Zeolites and catalysis: Synthesis, reactions and applications*. John Wiley & Sons: 2010.
25. Breck, D. W.; Eversole, W. G.; Milton, R. M.; Reed, T. B.; Thomas, T. L., Crystalline zeolites. I. The properties of a new synthetic zeolite, type A. *Journal of the American Chemical Society* **1956**, 78 (23), 5963-5972.

26. Reed, T. B.; Breck, D. W., Crystalline Zeolites. II. Crystal Structure of Synthetic Zeolite, Type A. *Journal of the American Chemical Society* **1956**, 78 (23), 5972-5977.
27. Barrer, R. M.; Baynham, J. W.; Bultitude, F. W.; Meier, W. M., 36. Hydrothermal chemistry of the silicates. Part VIII. Low-temperature crystal growth of aluminosilicates, and of some gallium and germanium analogues. *Journal of the Chemical Society (Resumed)* **1959**, (0), 195-208.
28. Weisz, P. B.; Frillette, V. J., Intracrystalline and Molecular-Shape-Selective Catalysis by Zeolite Salts. *The Journal of Physical Chemistry* **1960**, 64 (3), 382-382.
29. Weisz, P. B.; Frillette, V. J.; Maatman, R. W.; Mower, E. B., Catalysis by crystalline aluminosilicates II. Molecular-shape selective reactions. *Journal of Catalysis* **1962**, 1 (4), 307-312.
30. Kerr, G. T., Intracrystalline rearrangement of constitutive water in hydrogen zeolite Y. *The Journal of Physical Chemistry* **1967**, 71 (12), 4155-4156.
31. Kerr, G. T., Chemistry of crystalline aluminosilicates. VI. Preparation and properties of ultrastable hydrogen zeolite Y. *The Journal of Physical Chemistry* **1969**, 73 (8), 2780-2782.
32. Kerr, G. T., Hydrogen zeolite Y, ultrastable zeolite Y, and aluminum-deficient zeolites. In *Molecular Sieves*, American Chemical Society: 1973; Vol. 121, pp 219-229.
33. Cerqueira, H. S.; Caeiro, G.; Costa, L.; Ramôa Ribeiro, F., Deactivation of FCC catalysts. *Journal of Molecular Catalysis A: Chemical* **2008**, 292 (1), 1-13.
34. Chapter 5 - FCC catalysts. In *Fluid Catalytic Cracking Handbook (Fourth Edition)*, Sadeghbeigi, R., Ed. Butterworth-Heinemann: 2020; pp 83-110.
35. Chen, N.-Y., *Shape selective catalysis in industrial applications*. Second Edition, (2nd ed.) ed.; CRC press: 2023.
36. Garwood, W. E., Conversion of C₂-C₁₀ to higher olefins over synthetic zeolite ZSM-5. In *Intrazeolite Chemistry*, American Chemical Society 1983; Vol. 218, pp 383-396.
37. Meisel, S. L., Gasoline from methanol in one step. *CHEMTECH; (United States)* **1976**, 6:2, Medium: X; Size: Pages: 86-89 2009-12-17.
38. New process changes methanol into gasoline. [By Mobil Oil]. *Nation's Bus.; (United States)* **1978**, 66:5, Medium: X; Size: Pages: 74F-74H 2009-12-17.
39. Chakraborty, J. P.; Singh, S.; Maity, S. K., Chapter 6 - Advances in the conversion of methanol to gasoline. In *Hydrocarbon Biorefinery*, Maity, S. K.; Gayen, K.; Bhowmick, T. K., Eds. Elsevier: 2022; pp 177-200.
40. Demikhova, N. R.; Rubtsova, M. I.; Vinokurov, V. A.; Glotov, A. P., Isomerization of Xylenes (a Review). *Petroleum Chemistry* **2021**, 61 (11), 1158-1177.
41. Bauer, F.; Chen, W.-H.; Ernst, H.; Huang, S.-J.; Freyer, A.; Liu, S.-B., Selectivity improvement in xylene isomerization. *Microporous and Mesoporous Materials* **2004**, 72 (1), 81-89.
42. Tsai, T.-C.; Wang, I.; Huang, C.-K.; Liu, S.-D., Study on ethylbenzene and xylene conversion over modified ZSM-5. *Applied Catalysis A: General* **2007**, 321 (2), 125-134.
43. Li, Y.; Li, L.; Yu, J., Applications of Zeolites in Sustainable Chemistry. *Chem* **2017**, 3 (6), 928-949.

44. Sherman, J. D., Synthetic zeolites and other microporous oxide molecular sieves. *Proceedings of the National Academy of Sciences* **1999**, *96* (7), 3471-3478.
45. Pera-Titus, M., Porous Inorganic Membranes for CO₂ Capture: Present and Prospects. *Chemical Reviews* **2014**, *114* (2), 1413-1492.
46. Yu, N.; Wang, R. Z.; Wang, L. W., Sorption thermal storage for solar energy. *Progress in Energy and Combustion Science* **2013**, *39* (5), 489-514.
47. Gomes, G. J.; Zalazar, M. F.; Padilha, J. C.; Costa, M. B.; Bazzi, C. L.; Arroyo, P. A., Unveiling the mechanisms of carboxylic acid esterification on acid zeolites for biomass-to-energy: A review of the catalytic process through experimental and computational studies. *Chemosphere* **2024**, *349*, 140879.
48. Ennaert, T.; Van Aelst, J.; Dijkmans, J.; De Clercq, R.; Schutyser, W.; Dusselier, M.; Verboekend, D.; Sels, B. F., Potential and challenges of zeolite chemistry in the catalytic conversion of biomass. *Chemical Society Reviews* **2016**, *45* (3), 584-611.
49. Li, S.; Zheng, A.; Su, Y.; Zhang, H.; Chen, L.; Yang, J.; Ye, C.; Deng, F., Brønsted/Lewis acid synergy in dealuminated HY zeolite: a combined solid-state NMR and theoretical calculation study. *J Am Chem Soc* **2007**, *129* (36), 11161-71.
50. Almutairi, S. M. T.; Mezari, B.; Filonenko, G. A.; Magusin, P. C. M. M.; Rigutto, M. S.; Pidko, E. A.; Hensen, E. J. M., Influence of extraframework aluminum on the Brønsted acidity and catalytic reactivity of faujasite zeolite. *ChemCatChem* **2013**, *5* (2), 452-466.
51. Xingling Zhao, J. X., Feng Deng, Solid-state NMR for metal-containing zeolites: from active sites to reaction mechanism. *Front. Chem. Sci. Eng.* **2020**, *14* (2), 159-187.
52. Ravi, M.; Sushkevich, V. L.; van Bokhoven, J. A., Towards a better understanding of Lewis acidic aluminium in zeolites. *Nat. Mater.* **2020**, *19* (10), 1047-1056.
53. Bourgeat-Lami, E.; Massiani, P.; Di Renzo, F.; Espiau, P.; Fajula, F.; Des Courières, T., Study of the state of aluminium in zeolite-β. *Applied Catalysis* **1991**, *72* (1), 139-152.
54. Abraham, A.; Lee, S.-H.; Shin, C.-H.; Bong Hong, S.; Prins, R.; van Bokhoven, J. A., Influence of framework silicon to aluminium ratio on aluminium coordination and distribution in zeolite Beta investigated by ²⁷Al MAS and ²⁷Al MQ MAS NMR. *Physical Chemistry Chemical Physics* **2004**, *6* (11).
55. Li, J.; Gao, M.; Yan, W.; Yu, J., Regulation of the Si/Al ratios and Al distributions of zeolites and their impact on properties. *Chemical Science* **2023**, *14* (8), 1935-1959.
56. Palčić, A.; Valtchev, V., Analysis and control of acid sites in zeolites. *Applied Catalysis A: General* **2020**, *606*, 117795.
57. Sklenak, S.; Dedeczek, J.; Li, C.; Wichterlova, B.; Gabova, V.; Sierka, M.; Sauer, J., Aluminum siting in silicon-rich zeolite frameworks: a combined high-resolution ²⁷Al NMR spectroscopy and quantum mechanics / molecular mechanics study of ZSM-5. *Angew Chem Int Ed Engl* **2007**, *46* (38), 7286-7289.
58. Han, O. H.; Kim, C.-S.; Hong, S. B., Direct evidence for the nonrandom nature of Al substitution in zeolite ZSM-5: An investigation by ²⁷Al MAS and MQ MAS NMR. *Angewandte Chemie International Edition* **2002**, *41* (3), 469-472.
59. Bae, J.; Dusselier, M., Synthesis strategies to control the Al distribution in zeolites: thermodynamic and kinetic aspects. *Chem Commun (Camb)* **2023**, *59* (7), 852-867.

60. Beerdsen, E.; Smit, B.; Calero, S., The influence of non-framework sodium cations on the adsorption of alkanes in MFI- and MOR-type zeolites. *The Journal of Physical Chemistry B* **2002**, *106* (41), 10659-10667.
61. Beerdsen, E.; Dubbeldam, D.; Smit, B.; Vlugt, T. J. H.; Calero, S., Simulating the effect of nonframework cations on the adsorption of alkanes in MFI-type zeolites. *The Journal of Physical Chemistry B* **2003**, *107* (44), 12088-12096.
62. Civalieri, B.; Ferrari, A. M.; Llundell, M.; Orlando, R.; Mérawa, M.; Ugliengo, P., Cation selectivity in alkali-exchanged chabazite: An *ab initio* periodic study. *Chemistry of Materials* **2003**, *15* (21), 3996-4004.
63. Mlekodaj, K.; Dedecek, J.; Pashkova, V.; Tabor, E.; Klein, P.; Urbanova, M.; Karcz, R.; Sazama, P.; Whittleton, S. R.; Thomas, H. M.; Fishchuk, A. V.; Sklenak, S., Al Organization in the SSZ-13 Zeolite. Al Distribution and Extraframework Sites of Divalent Cations. *Journal of Physical Chemistry C* **2019**, *123* (13), 7968-7987.
64. Dědeček, J.; Kaucký, D.; Wichterlová, B.; Gonsiorová, O., Co²⁺ ions as probes of Al distribution in the framework of zeolites. ZSM-5 study. *Physical Chemistry Chemical Physics* **2002**, *4* (21), 5406-5413.
65. Heard, C. J.; Grajciar, L.; Uhlík, F.; Shamzhy, M.; Opanasenko, M.; Čejka, J.; Nachtigall, P., Zeolite (in)stability under aqueous or steaming conditions. *Advanced Materials* **2020**, *32* (44), 2003264.
66. Ravenelle, R. M.; Schüßler, F.; D'Amico, A.; Danilina, N.; van Bokhoven, J. A.; Lercher, J. A.; Jones, C. W.; Sievers, C., Stability of zeolites in hot liquid water. *The Journal of Physical Chemistry C* **2010**, *114* (46), 19582-19595.
67. Heard, C. J.; Grajciar, L.; Nachtigall, P., The effect of water on the validity of Lowenstein's rule. *Chemical Science* **2019**, *10* (22), 5705-5711.
68. Nielsen, M.; Hafreager, A.; Brogaard, R. Y.; De Wispelaere, K.; Falsig, H.; Beato, P.; Van Speybroeck, V.; Svelle, S., Collective action of water molecules in zeolite dealumination. *Catalysis Science & Technology* **2019**, *9* (14), 3721-3725.
69. Silaghi, M.-C.; Chizallet, C.; Sauer, J.; Raybaud, P., Dealumination mechanisms of zeolites and extra-framework aluminum confinement. *Journal of Catalysis* **2016**, *339*, 242-255.
70. Silaghi, M.-C.; Chizallet, C.; Petracovschi, E.; Kerber, T.; Sauer, J.; Raybaud, P., Regioselectivity of Al–O Bond Hydrolysis during Zeolites Dealumination Unified by Brønsted–Evans–Polanyi Relationship. *ACS Catalysis* **2015**, *5* (1), 11-15.
71. Jin, M.; Liu, M.; Nachtigall, P.; Grajciar, L.; Heard, C. J., Mechanism of zeolite hydrolysis under basic conditions. *Chemistry of Materials* **2021**, *33* (23), 9202-9212.
72. Jin, M.; Veselý, O.; Heard, C. J.; Kubů, M.; Nachtigall, P.; Čejka, J.; Grajciar, L., The role of water loading and germanium content in germanosilicate hydrolysis. *The Journal of Physical Chemistry C* **2021**, *125* (43), 23744-23757.
73. Liu, Q.; van Bokhoven, J. A., Water structures on acidic zeolites and their roles in catalysis. *Chemical Society Reviews* **2024**, *53* (6), 3065-3095.
74. Zornes, A.; Abdul Rahman, N. B.; Das, O. R.; Gomez, L. A.; Crossley, S.; Resasco, D. E.; White, J. L., Impact of Low-Temperature Water Exposure and Removal on Zeolite HY. *Journal of the American Chemical Society* **2024**, *146* (1), 1132-1143.

75. Corma, A., From microporous to mesoporous molecular sieve materials and their use in catalysis. *Chemical Reviews* **1997**, 97 (6), 2373-2420.
76. Dědeček, J.; Sobalík, Z.; Wichterlová, B., Siting and Distribution of Framework Aluminium Atoms in Silicon-Rich Zeolites and Impact on Catalysis. *Catalysis Reviews-Science and Engineering* **2012**, 54 (2), 135-223.
77. Dedecek, J.; Tabor, E.; Sklenak, S., Tuning the Aluminum Distribution in Zeolites to Increase their Performance in Acid-Catalyzed Reactions. *Chemsuschem* **2019**, 12 (3), 556-576.
78. Nimlos, C. T.; Hoffman, A. J.; Hur, Y. G.; Lee, B. J.; Di Iorio, J. R.; Hibbitts, D. D.; Gounder, R., Experimental and Theoretical Assessments of Aluminum Proximity in MFI Zeolites and Its Alteration by Organic and Inorganic Structure-Directing Agents. *Chemistry of Materials* **2020**, 32 (21), 9277-9298.
79. Knott, B. C.; Nimlos, C. T.; Robichaud, D. J.; Nimlos, M. R.; Kim, S.; Gounder, R., Consideration of the aluminum distribution in zeolites in theoretical and experimental catalysis research. *ACS Catalysis* **2018**, 8 (2), 770-784.
80. Heard, C. J.; Grajciar, L.; Nachtigall, P., The effect of water on the validity of Löwenstein's rule. *Chemical Science* **2019**, 10 (22), 5705-5711.
81. Heard, C. J.; Grajciar, L.; Rice, C. M.; Pugh, S. M.; Nachtigall, P.; Ashbrook, S. E.; Morris, R. E., Fast room temperature lability of aluminosilicate zeolites. *Nature Communications* **2019**, 10 (1), 4690.
82. Karge, H. G.; Hunger, M.; Beyer, H. K., Characterization of Zeolites — Infrared and Nuclear Magnetic Resonance Spectroscopy and X-Ray Diffraction. In *Catalysis and zeolites: Fundamentals and applications*, Weitkamp, J.; Puppe, L., Eds. Springer Berlin Heidelberg: Berlin, Heidelberg, 1999; pp 198-326.
83. Fernandez, C.; Pruski, M., Probing quadrupolar nuclei by solid-state NMR spectroscopy: Recent advances. In *Solid State NMR*, Chan, J. C. C., Ed. Springer Berlin Heidelberg: Berlin, Heidelberg, 2012; pp 119-188.
84. Ashbrook, S. E.; Griffin, J. M.; Johnston, K. E., Recent advances in solid-state nuclear magnetic resonance spectroscopy. *Annual Review of Analytical Chemistry* **2018**, 11 (1), 485-508.
85. Brouwer, D. H.; Darton, R. J.; Morris, R. E.; Levitt, M. H., A solid-state NMR method for solution of zeolite crystal structures. *Journal of the American Chemical Society* **2005**, 127 (29), 10365-70.
86. Xin, S.; Wang, Q.; Xu, J.; Chu, Y.; Wang, P.; Feng, N.; Qi, G.; Trebosc, J.; Lafon, O.; Fan, W.; Deng, F., The acidic nature of "NMR-invisible" tri-coordinated framework aluminum species in zeolites. *Chem Sci* **2019**, 10 (43), 10159-10169.
87. Dib, E.; Mineva, T.; Veron, E.; Sarou-Kanian, V.; Fayon, F.; Alonso, B., ZSM-5 zeolite: Complete Al bond connectivity and implications on structure formation from solid-state NMR and quantum chemistry calculations. *The Journal of Physical Chemistry Letters* **2018**, 9 (1), 19-24.
88. Al-Nahari, S.; Dib, E.; Cammarano, C.; Saint-Germes, E.; Massiot, D.; Sarou-Kanian, V.; Alonso, B., Impact of mineralizing agents on aluminum distribution and acidity of ZSM-5 zeolites. *Angewandte Chemie International Edition* **2023**, 62 (7), e202217992.

89. Wang, W. Y.; Xu, J.; Deng, F., Recent advances in solid-state NMR of zeolite catalysts. *Natl. Sci. Rev.* **2022**, *9* (9), 23.
90. Yakimov, A. V.; Ravi, M.; Verel, R.; Sushkevich, V. L.; van Bokhoven, J. A.; Copéret, C., Structure and Framework Association of Lewis Acid Sites in MOR Zeolite. *Journal of the American Chemical Society* **2022**, *144* (23), 10377-10385.
91. Li, S.; Deng, F., Chapter One - Recent Advances of Solid-State NMR Studies on Zeolites. In *Annual Reports on NMR Spectroscopy*, Webb, G. A., Ed. Academic Press: 2013; Vol. 78, pp 1-54.
92. Zheng, M.; Chu, Y.; Wang, Q.; Wang, Y.; Xu, J.; Deng, F., Advanced solid-state NMR spectroscopy and its applications in zeolite chemistry. *Progress in Nuclear Magnetic Resonance Spectroscopy* **2024**, *140-141*, 1-41.
93. Paul, G.; Bisio, C.; Braschi, I.; Cossi, M.; Gatti, G.; Gianotti, E.; Marchese, L., Combined solid-state NMR, FT-IR and computational studies on layered and porous materials. *Chemical Society Reviews* **2018**, *47* (15), 5684-5739.
94. Lippmaa, E.; Maegi, M.; Samoson, A.; Tarmak, M.; Engelhardt, G., Investigation of the structure of zeolites by solid-state high-resolution silicon-29 NMR spectroscopy. *Journal of the American Chemical Society* **1981**, *103* (17), 4992-4996.
95. Klinowski, J., Solid-state NMR studies of molecular sieve catalysts. *Chemical Reviews* **1991**, *91* (7), 1459-1479.
96. Sklenak, S.; Dedecek, J.; Li, C.; Wichterlova, B.; Gabova, V.; Sierka, M.; Sauer, J., Aluminium siting in the ZSM-5 framework by combination of high resolution ^{27}Al NMR and DFT/MM calculations. *Phys Chem Chem Phys* **2009**, *11* (8), 1237-1247.
97. Ravi, M.; Sushkevich, V. L.; van Bokhoven, J. A., Lewis Acidity Inherent to the Framework of Zeolite Mordenite. *The Journal of Physical Chemistry C* **2019**, *123* (24), 15139-15144.
98. Ravi, M.; Sushkevich, V. L.; van Bokhoven, J. A., On the location of Lewis acidic aluminum in zeolite mordenite and the role of framework-associated aluminum in mediating the switch between Brønsted and Lewis acidity. *Chemical Science* **2021**, *12* (11), 4094-4103.
99. Chen, K.; Horstmeier, S.; Nguyen, V. T.; Wang, B.; Crossley, S. P.; Pham, T.; Gan, Z.; Hung, I.; White, J. L., Structure and Catalytic Characterization of a Second Framework Al(IV) Site in Zeolite Catalysts Revealed by NMR at 35.2 T. *J Am Chem Soc* **2020**, *142* (16), 7514-7523.
100. Chen, K.; Gan, Z.; Horstmeier, S.; White, J. L., Distribution of Aluminum Species in Zeolite Catalysts: ^{27}Al NMR of Framework, Partially-Coordinated Framework, and Non-Framework Moieties. *Journal of the American Chemical Society* **2021**, *143* (17), 6669-6680.
101. Zhao, Z.; Xing, Y.; Li, S.; Meng, X.; Xiao, F.-s.; McGuire, R.; Parvulescu, A.-N.; Müller, U.; Zhang, W., Mapping Al Distributions in SSZ-13 Zeolites from ^{23}Na Solid-State NMR Spectroscopy and DFT Calculations. *The Journal of Physical Chemistry C* **2018**, *122* (18), 9973-9979.
102. Klein, P.; Dedecek, J.; Thomas, H. M.; Whittleton, S. R.; Klimes, J.; Brus, J.; Kobera, L.; Bryce, D. L.; Sklenak, S., NMR Crystallography of Monovalent Cations in

Inorganic Matrices: Na⁺ Siting and the Local Structure of Na⁺ Sites in Ferrierites. *Journal of Physical Chemistry C* **2022**, *126* (26), 10686-10702.

103. Fan, B.; Zhang, W.; Gao, P.; Hou, G.; Liu, R.; Xu, S.; Wei, Y.; Liu, Z., Quantitatively mapping the distribution of intrinsic acid sites in mordenite zeolite by high-field ²³Na solid-state nuclear magnetic resonance. *The Journal of Physical Chemistry Letters* **2022**, *13* (23), 5186-5194.

104. Bryant, R. G., The NMR time scale. *Journal of Chemical Education* **1983**, *60* (11), 933.

105. Grajciar, L.; Heard, C. J.; Bondarenko, A. A.; Polynski, M. V.; Meeprasert, J.; Pidko, E. A.; Nachtigall, P., Towards operando computational modeling in heterogeneous catalysis. *Chemical Society Reviews* **2018**, *47* (22), 8307-8348.

106. Dračinský, M.; Bouř, P.; Hodgkinson, P., Temperature Dependence of NMR Parameters Calculated from Path Integral Molecular Dynamics Simulations. *Journal of Chemical Theory and Computation* **2016**, *12* (3), 968-973.

107. Dračinský, M.; Hodgkinson, P., A molecular dynamics study of the effects of fast molecular motions on solid-state NMR parameters. *CrystEngComm* **2013**, *15* (43), 8705-8712.

108. Dračinský, M.; Bouř, P., Vibrational averaging of the chemical shift in crystalline α -glycine. *Journal of Computational Chemistry* **2012**, *33* (10), 1080-1089.

109. Folliet, N.; Roiland, C.; Bégu, S.; Aubert, A.; Mineva, T.; Goursot, A.; Selvaraj, K.; Duma, L.; Tielens, F.; Mauri, F.; Laurent, G.; Bonhomme, C.; Gervais, C.; Babonneau, F.; Azaïs, T., Investigation of the Interface in Silica-Encapsulated Liposomes by Combining Solid State NMR and First Principles Calculations. *Journal of the American Chemical Society* **2011**, *133* (42), 16815-16827.

110. Vanlommel, S.; Hoffman, A. E. J.; Smet, S.; Radhakrishnan, S.; Asselman, K.; Chandran, C. V.; Breynaert, E.; Kirschhock, C. E. A.; Martens, J. A.; Van Speybroeck, V., How Water and Ion Mobility Affect the NMR Fingerprints of the Hydrated JBW Zeolite: A Combined Computational-Experimental Investigation. *Chemistry* **2022**, *28* (68), e202202621.

111. Van Speybroeck, V.; Hemelsoet, K.; Joos, L.; Waroquier, M.; Bell, R. G.; Catlow, C. R., Advances in theory and their application within the field of zeolite chemistry. *Chem Soc Rev* **2015**, *44* (20), 7044-111.

112. Stanciakova, K.; Louwen, J. N.; Weckhuysen, B. M.; Bulo, R. E.; Göttl, F., Understanding Water–Zeolite Interactions: On the Accuracy of Density Functionals. *The Journal of Physical Chemistry C* **2021**, *125* (37), 20261-20274.

113. Peral, I.; Íñiguez, J., Amorphization Induced by Pressure: Results for Zeolites and General Implications. *Physical Review Letters* **2006**, *97* (22), 225502.

114. Wondraczek, L.; Pan, Z.; Palenta, T.; Erlebach, A.; Misture, S. T.; Sierka, M.; Micoulaut, M.; Hoppe, U.; Deubener, J.; Greaves, G. N., Kinetics of Decelerated Melting. *Advanced Science* **2018**, *5* (5), 1700850.

115. Greaves, G. N.; Meneau, F.; Sapelkin, A.; Colyer, L. M.; ap Gwynn, I.; Wade, S.; Sankar, G., The rheology of collapsing zeolites amorphized by temperature and pressure. *Nature Materials* **2003**, *2* (9), 622-629.

116. Greaves, G. N.; Meneau, F.; Kargl, F.; Ward, D.; Holliman, P.; Albergamo, F., Zeolite collapse and polyamorphism. *Journal of Physics: Condensed Matter* **2007**, *19* (41), 415102.
117. Cruciani, G., Zeolites upon heating: Factors governing their thermal stability and structural changes. *Journal of Physics and Chemistry of Solids* **2006**, *67* (9), 1973-1994.
118. Friederich, P.; Häse, F.; Proppe, J.; Aspuru-Guzik, A., Machine-learned potentials for next-generation matter simulations. *Nature Materials* **2021**, *20* (6), 750-761.
119. Behler, J.; Csányi, G., Machine learning potentials for extended systems: a perspective. *The European Physical Journal B* **2021**, *94* (7), 142.
120. Ma, S.; Liu, Z.-P., Machine learning potential era of zeolite simulation. *Chemical Science* **2022**, *13* (18), 5055-5068.
121. Kulichenko, M.; Smith, J. S.; Nebgen, B.; Li, Y. W.; Fedik, N.; Boldyrev, A. I.; Lubbers, N.; Barros, K.; Tretiak, S., The rise of neural networks for materials and chemical dynamics. *The Journal of Physical Chemistry Letters* **2021**, *12* (26), 6227-6243.
122. Erlebach, A.; Nachtigall, P.; Grajciar, L., Accurate large-scale simulations of siliceous zeolites by neural network potentials. *npj Computational Materials* **2022**, *8* (1), 174.
123. Bocus, M.; Goeminne, R.; Lamaire, A.; Cools-Ceuppens, M.; Verstraelen, T.; Van Speybroeck, V., Nuclear quantum effects on zeolite proton hopping kinetics explored with machine learning potentials and path integral molecular dynamics. *Nature Communications* **2023**, *14* (1), 1008.
124. Erlebach, A.; Šípka, M.; Saha, I.; Nachtigall, P.; Heard, C. J.; Grajciar, L., A reactive neural network framework for water-loaded acidic zeolites. *Nature Communications* **2024**, *15* (1), 4215.
125. Heard, C. J.; Grajciar, L.; Erlebach, A., Migration of zeolite-encapsulated subnanometre platinum clusters via reactive neural network potentials. *Nanoscale* **2024**.
126. Evans, J. D.; Coudert, F.-X., Predicting the Mechanical Properties of Zeolite Frameworks by Machine Learning. *Chemistry of Materials* **2017**, *29* (18), 7833-7839.
127. Kim, N.; Min, K., Accelerated discovery of zeolite structures with superior mechanical properties via active learning. *The Journal of Physical Chemistry Letters* **2021**, *12* (9), 2334-2339.
128. Gaillac, R.; Chibani, S.; Coudert, F.-X., Speeding up discovery of auxetic zeolite frameworks by machine learning. *Chemistry of Materials* **2020**, *32* (6), 2653-2663.
129. Kim, N.; Min, K., Optimal machine learning feature selection for assessing the mechanical properties of a zeolite framework. *Physical Chemistry Chemical Physics* **2022**, *24* (44), 27031-27037.
130. Ducamp, M.; Coudert, F.-X., Prediction of Thermal Properties of Zeolites through Machine Learning. *The Journal of Physical Chemistry C* **2022**, *126* (3), 1651-1660.
131. Chaker, Z.; Salanne, M.; Delaye, J.-M.; Charpentier, T., NMR shifts in aluminosilicate glasses via machine learning. *Physical Chemistry Chemical Physics* **2019**, *21* (39), 21709-21725.
132. Paruzzo, F. M.; Hofstetter, A.; Musil, F.; De, S.; Ceriotti, M.; Emsley, L., Chemical shifts in molecular solids by machine learning. *Nature Communications* **2018**, *9* (1), 4501.

133. Valtchev, V.; Mintova, S., Zeolites and MOFs? Dare to Know Them! In *Zeolites and Metal-Organic Frameworks*, Blay, V.; Bobadilla, L. F.; García, A. C., Eds. Amsterdam University Press: 2018; pp 13-24.
134. Ye, J.; Tang, J.; Zhao, Y.-J.; Wu, C.-D., Synthesis and Catalytic Properties of Porous Metal Silica Materials Templated and Functionalized by Extended Coordination Cages. *Inorganic Chemistry* **2020**, *59* (1), 767-776.
135. Chen, Y.-Z.; Zhang, R.; Jiao, L.; Jiang, H.-L., Metal–organic framework-derived porous materials for catalysis. *Coordination Chemistry Reviews* **2018**, *362*, 1-23.
136. Thorarinsdottir, A. E.; Harris, T. D., Metal–Organic Framework Magnets. *Chemical Reviews* **2020**, *120* (16), 8716-8789.
137. Yadav, S.; Dixit, R.; Sharma, S.; Dutta, S.; Solanki, K.; Sharma, R. K., Magnetic metal–organic framework composites: structurally advanced catalytic materials for organic transformations. *Materials Advances* **2021**, *2* (7), 2153-2187.
138. Nadar, S. S.; Rathod, V. K., Magnetic-metal organic framework (magnetic-MOF): A novel platform for enzyme immobilization and nanozyme applications. *International Journal of Biological Macromolecules* **2018**, *120*, 2293-2302.
139. Huang, W.-H.; Zhang, X.-X.; Zhao, Y.-N., Recent progress and perspectives on the structural design on metal–organic zeolite (MOZ) frameworks. *Dalton Transactions* **2021**, *50* (1), 15-28.
140. Liu, X.; Liu, Y., Recent progress in the design and synthesis of zeolite-like metal–organic frameworks (ZMOFs). *Dalton Transactions* **2021**, *50* (10), 3450-3458.
141. Yabushita, M.; Osuga, R.; Yokoi, T.; Muramatsu, A., Zeolite-based catalysts for oxidative upgrading of methane: design and control of active sites. *Catalysis Science & Technology* **2023**, *13* (14), 4020-4044.
142. Jensen, F., *Introduction to computational chemistry*. John Wiley & sons: 2017.
143. Wales, D. J., Exploring Energy Landscapes. *Annual Review of Physical Chemistry* **2018**, *69* (Volume 69, 2018), 401-425.
144. Kochenderfer, M. J.; Wheeler, T. A., *Algorithms for optimization*. Mit Press: 2019.
145. Teter, M. P.; Payne, M. C.; Allan, D. C., Solution of Schrödinger's equation for large systems. *Phys Rev B* **1989**, *40* (18), 12255-12263.
146. Born, M.; Oppenheimer, R., Zur Quantentheorie der Molekeln. *Annalen der Physik* **1927**, *389* (20), 457-484.
147. Hohenberg, P.; Kohn, W., Inhomogeneous electron gas. *Physical Review* **1964**, *136* (3B), B864-B871.
148. Kohn, W.; Sham, L. J., Self-consistent equations including exchange and correlation effects. *Physical Review* **1965**, *140* (4A), A1133-A1138.
149. Perdew, J. P.; Zunger, A., Self-interaction correction to density-functional approximations for many-electron systems. *Phys Rev B* **1981**, *23* (10), 5048-5079.
150. Perdew, J. P.; Burke, K.; Ernzerhof, M., Generalized Gradient Approximation Made Simple. *Physical Review Letters* **1996**, *77* (18), 3865-3868.
151. Sun, J.; Ruzsinszky, A.; Perdew, J. P., Strongly Constrained and Appropriately Normed Semilocal Density Functional. *Physical Review Letters* **2015**, *115* (3), 036402.

152. Grimme, S., Semiempirical GGA-type density functional constructed with a long-range dispersion correction. *Journal of Computational Chemistry* **2006**, 27 (15), 1787-1799.
153. Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H., A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *The Journal of Chemical Physics* **2010**, 132 (15), 154104.
154. Caldeweyher, E.; Ehlert, S.; Hansen, A.; Neugebauer, H.; Spicher, S.; Bannwarth, C.; Grimme, S., A generally applicable atomic-charge dependent London dispersion correction. *The Journal of Chemical Physics* **2019**, 150 (15).
155. Grimme, S.; Ehrlich, S.; Goerigk, L., Effect of the damping function in dispersion corrected density functional theory. *Journal of Computational Chemistry* **2011**, 32 (7), 1456-1465.
156. Mills, G.; Jónsson, H., Quantum and thermal effects in H₂ dissociative adsorption: Evaluation of free energy barriers in multidimensional quantum systems. *Physical Review Letters* **1994**, 72 (7), 1124-1127.
157. Henkelman, G.; Uberuaga, B. P.; Jónsson, H., A climbing image nudged elastic band method for finding saddle points and minimum energy paths. *The Journal of Chemical Physics* **2000**, 113 (22), 9901-9904.
158. Kresse, G.; Hafner, J., Ab initio molecular dynamics for open-shell transition metals. *Phys Rev B* **1993**, 48 (17), 13115-13118.
159. Kresse, G.; Furthmüller, J., Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set. *Phys Rev B* **1996**, 54 (16), 11169-11186.
160. Kresse, G.; Furthmüller, J., Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Computational Materials Science* **1996**, 6 (1), 15-50.
161. Bonhomme, C.; Gervais, C.; Babonneau, F.; Coelho, C.; Pourpoint, F.; Azais, T.; Ashbrook, S. E.; Griffin, J. M.; Yates, J. R.; Mauri, F.; Pickard, C. J., First-principles calculation of NMR parameters using the gauge including projector augmented wave method: a chemist's point of view. *Chem Rev* **2012**, 112 (11), 5733-79.
162. Pickard, C. J.; Mauri, F., Calculations of Magnetic Resonance Parameters in Solids and Liquids Using Periodic Boundary Conditions. In *Calculation of NMR and EPR Parameters*, 2004; pp 265-277.
163. Pickard, C. J.; Mauri, F., All-electron magnetic response with pseudopotentials: NMR chemical shifts. *Phys Rev B* **2001**, 63 (24), 245101.
164. Mehring, M.; Weberruß, V. A., 7 - Spin Interactions and Spectra. In *Object-Oriented Magnetic Resonance*, Mehring, M.; Weberruß, V. A., Eds. Academic Press: London, 2001; pp 147-180.
165. Meyers, R., Encyclopedia of Analytical Chemistry: Applications, Theory, and Instrumentation. **2011**.
166. Käser, S.; Vazquez-Salazar, L. I.; Meuwly, M.; Töpfer, K., Neural network potentials for chemistry: concepts, applications and prospects. *Digital Discovery* **2023**, 2 (1), 28-58.

167. Schütt, K. T.; Saucedo, H. E.; Kindermans, P.-J.; Tkatchenko, A.; Müller, K.-R., SchNet – A deep learning architecture for molecules and materials. *The Journal of Chemical Physics* **2018**, *148* (24).
168. Tibshirani, R., Regression Shrinkage and Selection Via the Lasso. *Journal of the Royal Statistical Society: Series B (Methodological)* **1996**, *58* (1), 267-288.
169. Gaumard, R.; Dragún, D.; Pedroza-Montero, J. N.; Alonso, B.; Guesmi, H.; Malkin Ondik, I.; Mineva, T., Regression machine learning models used to predict DFT-computed NMR parameters of zeolites. *Computation* **2022**, *10* (5), 74.
170. Venetos, M. C.; Wen, M.; Persson, K. A., Machine Learning Full NMR Chemical Shift Tensors of Silicon Oxides with Equivariant Graph Neural Networks. *The Journal of Physical Chemistry A* **2023**, *127* (10), 2388-2398.
171. Cuny, J.; Xie, Y.; Pickard, C. J.; Hassanali, A. A., Ab Initio quality NMR parameters in solid-state materials using a high-dimensional neural-network representation. *Journal of Chemical Theory and Computation* **2016**, *12* (2), 765-773.
172. Chen, G.; Zhao, N.; Chen, Y.; Zhao, J.; Zhu, R.; Hong, M., Recent advances in synthetic strategies and physicochemical modifications of SSZ-13 zeolites: A review. *Materials Today Catalysis* **2024**, *4*, 100037.
173. Eilertsen, E. A.; Nilsen, M. H.; Wendelbo, R.; Olsbye, U.; Lillerud, K. P., Synthesis of high silica CHA zeolites with controlled Si/Al ratio. In *Studies in Surface Science and Catalysis*, Gédéon, A.; Massiani, P.; Babonneau, F., Eds. Elsevier: 2008; Vol. 174, pp 265-268.
174. Eilertsen, E. A.; Arstad, B.; Svelle, S.; Lillerud, K. P., Single parameter synthesis of high silica CHA zeolites from fluoride media. *Microporous and Mesoporous Materials* **2012**, *153*, 94-99.
175. Gillan, M. J.; Alfe, D.; Michaelides, A., Perspective: How Good is DFT for Water? *The Journal of Chemical Physics* **2016**, *144* (13), 130901.
176. Yates, J. R.; Pickard, C. J.; Mauri, F., Calculation of NMR chemical shifts for extended systems using ultrasoft pseudopotentials. *Phys Rev B* **2007**, *76* (2), 024401.
177. Csonka, G. I.; Perdew, J. P.; Ruzsinszky, A.; Philipsen, P. H. T.; Lebègue, S.; Paier, J.; Vydrov, O. A.; Ángyán, J. G., Assessing the performance of recent density functionals for bulk solids. *Phys Rev B* **2009**, *79* (15), 155107.
178. Lei, C.; Erlebach, A.; Brivio, F.; Grajciar, L.; Tošner, Z.; Heard, C. J.; Nachtigall, P., The need for operando modelling of ^{27}Al NMR in zeolites: the effect of temperature, topology and water. *Chemical Science* **2023**, *14* (34), 9101-9113.
179. Lei, C.; Bornes, C.; Bengtsson, O.; Erlebach, A.; Slater, B.; Grajciar, L.; Heard, C. J., A machine learning approach for dynamical modelling of Al distributions in zeolites via $^{23}\text{Na}/^{27}\text{Al}$ solid-state NMR. *Faraday Discussions* **2024**.
180. Bartók, A. P.; Kondor, R.; Csányi, G., On representing chemical environments. *Phys Rev B* **2013**, *87* (18), 184115.
181. Schütt, K. T.; Kessel, P.; Gastegger, M.; Nicoli, K. A.; Tkatchenko, A.; Müller, K. R., SchNetPack: A Deep Learning Toolbox For Atomistic Systems. *Journal of Chemical Theory and Computation* **2019**, *15* (1), 448-455.

182. Hjorth Larsen, A.; Jørgen Mortensen, J.; Blomqvist, J.; Castelli, I. E.; Christensen, R.; Duřak, M.; Friis, J.; Groves, M. N.; Hammer, B.; Hargus, C.; Hermes, E. D.; Jennings, P. C.; Bjerre Jensen, P.; Kermode, J.; Kitchin, J. R.; Leonhard Kolsbjerg, E.; Kubal, J.; Kaasbjerg, K.; Lysgaard, S.; Bergmann Maronsson, J.; Maxson, T.; Olsen, T.; Pastewka, L.; Peterson, A.; Rostgaard, C.; Schiøtz, J.; Schütt, O.; Strange, M.; Thygesen, K. S.; Vegge, T.; Vilhelmsen, L.; Walter, M.; Zeng, Z.; Jacobsen, K. W., The atomic simulation environment—a Python library for working with atoms. *Journal of Physics: Condensed Matter* **2017**, 29 (27), 273002.
183. Hjorth Larsen, A.; Jørgen Mortensen, J.; Blomqvist, J.; Castelli, I. E.; Christensen, R.; Dulak, M.; Friis, J.; Groves, M. N.; Hammer, B.; Hargus, C.; Hermes, E. D.; Jennings, P. C.; Bjerre Jensen, P.; Kermode, J.; Kitchin, J. R.; Leonhard Kolsbjerg, E.; Kubal, J.; Kaasbjerg, K.; Lysgaard, S.; Bergmann Maronsson, J.; Maxson, T.; Olsen, T.; Pastewka, L.; Peterson, A.; Rostgaard, C.; Schiøtz, J.; Schütt, O.; Strange, M.; Thygesen, K. S.; Vegge, T.; Vilhelmsen, L.; Walter, M.; Zeng, Z.; Jacobsen, K. W., The atomic simulation environment—a Python library for working with atoms. *Journal of Physics: Condensed Matter* **2017**, 29 (27), 273002.
184. Fabian, P.; Gael, V.; Alexandre, G.; Vincent, M.; Bertrand, T.; Olivier, G.; Mathieu, B.; Peter, P.; Ron, W.; Vincent, D.; Jake, V.; Alexandre, P.; David, C., Scikit-learn: Machine Learning in Python. *Journal of Machine Learning Research* 12 (85), 2825-2830.
185. Holzinger, J.; Nielsen, M.; Beato, P.; Brogaard, R. Y.; Buono, C.; Dyballa, M.; Falsig, H.; Skibsted, J.; Svelle, S., Identification of Distinct Framework Aluminum Sites in Zeolite ZSM-23: A Combined Computational and Experimental ²⁷Al NMR Study. *The Journal of Physical Chemistry C* **2019**, 123 (13), 7831-7844.
186. Jin, M.; Ravi, M.; Lei, C.; Heard, C. J.; Brivio, F.; Tošner, Z.; Grajciar, L.; van Bokhoven, J. A.; Nachtigall, P., Dynamical equilibrium between Brønsted and Lewis sites in zeolites: Framework-associated octahedral aluminum. *Angewandte Chemie International Edition* **2023**, 62 (31), e202306183.
187. Shirodker, M.; Borker, V.; Nather, C.; Bensch, W.; Rane, K. S., Synthesis and structure of tris(acetylacetonato aluminum(III)). *Indian Journal of Chemistry* **2010**, 49, 1607-1611.
188. Koller, H.; Engelhardt, G.; Kentgens, A. P. M.; Sauer, J., ²³Na NMR spectroscopy of solids: interpretation of quadrupole interaction parameters and chemical shifts. *The Journal of Physical Chemistry* **1994**, 98 (6), 1544-1551.
189. Kundla, E.; Samoson, A.; Lippmaa, E., High-resolution NMR of quadrupolar nuclei in rotating solids. *Chemical Physics Letters* **1981**, 83 (2), 229-232.
190. Harris, R. K.; Nesbitt, G. J., Cross polarization for quadrupolar nuclei—Proton to sodium-23. *Journal of Magnetic Resonance (1969)* **1988**, 78 (2), 245-256.
191. Xue, X.; Stebbins, J. F., ²³Na NMR chemical shifts and local Na coordination environments in silicate crystals, melts and glasses. *Physics and Chemistry of Minerals* **1993**, 20 (5), 297-307.
192. Bak, M.; Rasmussen, J. T.; Nielsen, N. C., SIMPSON: a general simulation program for solid-state NMR spectroscopy. *Journal of Magnetic Resonance* **2000**, 147 (2), 296-330.

193. Juhl, D. W.; Tošner, Z.; Vosegaard, T., Chapter One - Versatile NMR simulations using SIMPSON. In *Annual Reports on NMR Spectroscopy*, Webb, G. A., Ed. Academic Press: 2020; Vol. 100, pp 1-59.
194. Zaremba, S. K., Good lattice points, discrepancy, and numerical integration. *Annali di Matematica Pura ed Applicata* **1966**, 73 (1), 293-317.
195. Conroy, H., Molecular Schrödinger equation. VIII. A new method for the evaluation of multidimensional integrals. *The Journal of Chemical Physics* **1967**, 47 (12), 5307-5318.
196. Cheng, V. B.; Suzukawa, H. H., Jr.; Wolfsberg, M., Investigations of a nonrandom numerical method for multidimensional integration. *The Journal of Chemical Physics* **1973**, 59 (8), 3992-3999.
197. Brinkmann, A.; Kentgens, A. P. M., Proton-selective ^{17}O – ^1H distance measurements in fast magic-angle-spinning solid-state NMR spectroscopy for the determination of hydrogen bond lengths. *Journal of the American Chemical Society* **2006**, 128 (46), 14758-14759.
198. Dorn, R. W.; Paterson, A. L.; Hung, I.; Gor'kov, P. L.; Thompson, A. J.; Sadow, A. D.; Gan, Z.; Rossini, A. J., Dipolar heteronuclear correlation solid-state NMR experiments between half-integer quadrupolar nuclei: The case of ^{11}B – ^{17}O . *The Journal of Physical Chemistry C* **2022**, 126 (28), 11652-11666.
199. Weckhuysen, B. M.; Yu, J., Recent advances in zeolite chemistry and catalysis. *Chem. Soc. Rev.* **2015**, 44 (20), 7022-7024.
200. Haag, W.; Lago, R.; Weisz, P., The active site of acidic aluminosilicate catalysts. *Nature* **1984**, 309 (5969), 589-591.
201. Chizallet, C., Toward the atomic scale simulation of intricate acidic aluminosilicate catalysts. *Acs Catalysis* **2020**, 10 (10), 5579-5601.
202. Phung, T. K.; Busca, G., On the Lewis acidity of protonic zeolites. *Appl. Catal. A-Gen.* **2015**, 504, 151-157.
203. Coster, D.; Blumenfeld, A. L.; Fripiat, J. J., Lewis acid sites and surface aluminum in aluminas and zeolites: A high-resolution NMR study. *The Journal of Physical Chemistry* **1994**, 98 (24), 6201-6211.
204. Dapsens, P. Y.; Mondelli, C.; Pérez-Ramírez, J., Highly selective Lewis acid sites in desilicated MFI zeolites for dihydroxyacetone isomerization to lactic acid. *ChemSusChem* **2013**, 6 (5), 831-839.
205. Woolery, G. L.; Kuehl, G. H.; Timken, H. C.; Chester, A. W.; Vartuli, J. C., On the nature of framework Brønsted and Lewis acid sites in ZSM-5. *Zeolites* **1997**, 19 (4), 288-296.
206. Omegna, A.; van Bokhoven, J. A.; Prins, R., Flexible aluminum coordination in aluminosilicates. Structure of zeolite H-USY and amorphous silica-alumina. *J. Phys. Chem. B* **2003**, 107 (34), 8854-8860.
207. van Bokhoven, J. A.; Sambe, H.; Ramaker, D.; Koningsberger, D., Al K-edge near-edge X-ray absorption fine structure (NEXAFS) study on the coordination structure of aluminum in minerals and Y zeolites. *J. Phys. Chem. B* **1999**, 103 (36), 7557-7564.

208. Abraham, A.; Lee, S.-H.; Shin, C.-H.; Hong, S. B.; Prins, R.; van Bokhoven, J. A., Influence of framework silicon to aluminium ratio on aluminium coordination and distribution in zeolite Beta investigated by ^{27}Al MAS and ^{27}Al MQ MAS NMR. *Phys. Chem. Chem. Phys.* **2004**, 6 (11), 3031-3036.
209. Lohse, U.; Löffler, E.; Hunger, M.; Stöckner, J.; Patzelova, V., Hydroxyl groups of the non-framework aluminium species in dealuminated Y zeolites. *Zeolites* **1987**, 7 (1), 11-13.
210. Almutairi, S. M. T.; Mezari, B.; Filonenko, G. A.; Magusin, P. C.; Rigutto, M. S.; Pidko, E. A.; Hensen, E. J., Influence of extraframework aluminum on the Brønsted acidity and catalytic reactivity of faujasite zeolite. *ChemCatChem* **2013**, 5 (2), 452-466.
211. Liu, C.; Li, G.; Hensen, E. J. M.; Pidko, E. A., Nature and Catalytic Role of Extraframework Aluminum in Faujasite Zeolite: A Theoretical Perspective. *ACS Catalysis* **2015**, 5 (11), 7024-7033.
212. Holzinger, J.; Beato, P.; Lundegaard, L. F.; Skibsted, J., Distribution of aluminum over the tetrahedral sites in ZSM-5 zeolites and their evolution after steam treatment. *The Journal of Physical Chemistry C* **2018**, 122 (27), 15595-15613.
213. Silaghi, M. C.; Chizallet, C.; Sauer, J.; Raybaud, P., Dealumination mechanisms of zeolites and extra-framework aluminum confinement. *Journal of Catalysis* **2016**, 339, 242-255.
214. Yi, X.; Liu, K.; Chen, W.; Li, J.; Xu, S.; Li, C.; Xiao, Y.; Liu, H.; Guo, X.; Liu, S.-B.; Zheng, A., Origin and Structural Characteristics of Tri-coordinated Extra-framework Aluminum Species in Dealuminated Zeolites. *Journal of the American Chemical Society* **2018**, 140 (34), 10764-10774.
215. Jiao, J.; Kanellopoulos, J.; Wang, W.; Ray, S. S.; Foerster, H.; Freude, D.; Hunger, M., Characterization of framework and extra-framework aluminum species in non-hydrated zeolites Y by ^{27}Al spin-echo, high-speed MAS, and MQMAS NMR spectroscopy at $B_0 = 9.4$ to 17.6 T. *Physical Chemistry Chemical Physics* **2005**, 7 (17), 3221-3226.
216. Di Iorio, J. R.; Gounder, R., Controlling the Isolation and Pairing of Aluminum in Chabazite Zeolites Using Mixtures of Organic and Inorganic Structure-Directing Agents. *Chemistry of Materials* **2016**, 28 (7), 2236-2247.
217. Grey, C. P.; Vega, A. J., Determination of the Quadrupole Coupling Constant of the Invisible Aluminum Spins in Zeolite HY with $^1\text{H}/^{27}\text{Al}$ TRAPDOR NMR. *Journal of the American Chemical Society* **1995**, 117 (31), 8232-8242.
218. Kentgens, A. P. M.; Iuga, D.; Kalwei, M.; Koller, H., Direct observation of Brønsted acidic sites in dehydrated zeolite H-ZSM5 using DFS-enhanced ^{27}Al MQMAS NMR spectroscopy. *Journal of the American Chemical Society* **2001**, 123 (12), 2925-2926.
219. Ernst, H.; Freude, D.; Wolf, I., Multinuclear Solid-State Nmr-Studies of Bronsted Sites in Zeolites. *Chemical Physics Letters* **1993**, 212 (6), 588-596.
220. Yi, X.; Xiao, Y.; Li, G.; Liu, Z.; Chen, W.; Liu, S.-B.; Zheng, A., From One to Two: Acidic Proton Spatial Networks in Porous Zeolite Materials. *Chemistry of Materials* **2020**, 32 (3), 1332-1342.
221. Ravi, M.; Sushkevich, V. L.; van Bokhoven, J. A., Towards a better understanding of Lewis acidic aluminium in zeolites. *Nature Materials* **2020**, 19 (10), 1047-1056.

222. Grifoni, E.; Piccini, G.; Lercher, J. A.; Glezakou, V.-A.; Rousseau, R.; Parrinello, M., Confinement effects and acid strength in zeolites. *Nature Communications* **2021**, *12* (1), 2630.
223. Schroeder, C.; Siozios, V.; Muck-Lichtenfeld, C.; Hunger, M.; Hansen, M. R.; Koller, H., Hydrogen Bond Formation of Bronsted Acid Sites in Zeolites. *Chemistry of Materials* **2020**, *32* (4), 1564-1574.
224. Hack, J. H.; Dombrowski, J. P.; Ma, X.; Chen, Y.; Lewis, N. H. C.; Carpenter, W. B.; Li, C.; Voth, G. A.; Kung, H. H.; Tokmakoff, A., Structural characterization of protonated water clusters confined in HZSM-5 zeolites. *Journal of the American Chemical Society* **2021**, *143* (27), 10203-10213.
225. Goltl, F.; Love, A. M.; Schuenzel, S. C.; Wolf, P.; Mavrikakis, M.; Hermans, I., Computational Description of Key Spectroscopic Features of Zeolite SSZ-13. *Physical Chemistry Chemical Physics* **2019**, *21* (35), 19065-19075.
226. Zhu, L.; Seff, K.; Olson, D. H.; Cohen, B. J.; Von Dreele, R. B., Hydronium Ions in Zeolites. 1. Structures of Partially and Fully Dehydrated Na₃H₃O-X by X-ray and Neutron Diffraction. *The Journal of Physical Chemistry B* **1999**, *103* (47), 10365-10372.
227. Klein, P.; Pashkova, V.; Thomas, H. M.; Whittleton, S. R.; Brus, J.; Kobera, L.; Dedecek, J.; Sklenak, S., Local Structure of Cationic Sites in Dehydrated Zeolites Inferred from ²⁷Al Magic-Angle Spinning NMR and Density Functional Theory Calculations. A Study on Li-, Na-, and K-Chabazite. *The Journal of Physical Chemistry C* **2016**, *120* (26), 14216-14225.
228. Maurin, G.; Bell, R. G.; Devautour, S.; Henn, F.; Giuntini, J. C., Modeling the Effect of Hydration in Zeolite Na⁺-Mordenite. *The Journal of Physical Chemistry B* **2004**, *108* (12), 3739-3745.
229. Sarv, P.; Fernandez, C.; Amoureux, J.-P.; Keskinen, K., Distribution of Tetrahedral Aluminium Sites in ZSM-5 Type Zeolites: An ²⁷Al (Multiquantum) Magic Angle Spinning NMR Study. *The Journal of Physical Chemistry* **1996**, *100* (50), 19223-19226.
230. Dedecek, J.; Lucero, M. J.; Li, C. B.; Gao, F.; Klein, P.; Urbanova, M.; Tvaruzkova, Z.; Sazama, P.; Sklenak, S., Complex Analysis of the Aluminum Siting in the Framework of Silicon-Rich Zeolites. A Case Study on Ferrierites. *Journal of Physical Chemistry C* **2011**, *115* (22), 11056-11064.
231. Saha, I. E., A.; Nachtigall, P.; Heard, C. J.; Grajciar, L. Reactive Neural Network Potential for Aluminosilicate Zeolites and Water: Quantifying the Effect of Si/Al Ratio on Proton Solvation and Water Diffusion in H-FAU *ChemRxiv* [Online], 2022.
232. Fan, B.; Zhu, D.; Wang, L.; Xu, S.; Wei, Y.; Liu, Z., Dynamic evolution of Al species in the hydrothermal dealumination process of CHA zeolites. *Inorganic Chemistry Frontiers* **2022**, *9* (14), 3609-3618.
233. Lippmaa, E.; Samoson, A.; Magi, M., High-resolution ²⁷Al NMR of aluminosilicates. *Journal of the American Chemical Society* **1986**, *108* (8), 1730-1735.
234. Huntley, G. M.; Luck, R. L.; Mullins, M. E.; Newberry, N. K., Hydrochloric acid modification and lead removal studies on naturally occurring zeolites from Nevada, New Mexico, and Arizona. *Processes* **2021**, *9* (7), 1238.

235. Kučera, J.; Nachtigall, P., A simple correlation between average T–O–T angles and ^{27}Al NMR chemical shifts does not hold in high-silica zeolites. *Microporous and Mesoporous Materials* **2005**, *85* (3), 279-283.
236. Willimetz, D. Theoretical investigation of ^{27}Al chemical shifts dependence on water amount and temperature in zeolite MFI. Bachelor's thesis, Charles university, Prague, 2023.
237. Smith, L. J.; Eckert, H.; Cheetham, A. K., Site Preferences in the Mixed Cation Zeolite, Li,Na-Chabazite: A Combined Solid-State NMR and Neutron Diffraction Study. *Journal of the American Chemical Society* **2000**, *122* (8), 1700-1708.
238. Loewenstein, W., The distribution of aluminum in the tetrahedra of silicates and aluminates. *American Mineralogist* **1954**, *39* (1-2), 92-96.
239. Fletcher, R. E.; Ling, S.; Slater, B., Violations of Löwenstein's rule in zeolites. *Chemical science* **2017**, *8* (11), 7483-7491.
240. Fant, M.; Ångqvist, M.; Hellman, A.; Erhart, P., To every rule there is an exception: A rational extension of Loewenstein's rule. *Angewandte Chemie International Edition* **2021**, *60* (10), 5132-5135.
241. Navrotsky, A.; Trofymuk, O.; Levchenko, A. A., Thermochemistry of Microporous and Mesoporous Materials. *Chemical Reviews* **2009**, *109* (9), 3885-3902.
242. Navrotsky, A.; Tian, Z.-R., Systematics in the Enthalpies of Formation of Anhydrous Aluminosilicate Zeolites, Glasses, and Dense Phases. *Chemistry – A European Journal* **2001**, *7* (4), 769-774.
243. Piccione, P. M.; Laberty, C.; Yang, S.; Cambor, M. A.; Navrotsky, A.; Davis, M. E., Thermochemistry of Pure-Silica Zeolites. *The Journal of Physical Chemistry B* **2000**, *104* (43), 10001-10011.
244. Henson, N. J.; Cheetham, A. K.; Gale, J. D., Theoretical calculations on silica frameworks and their correlation with experiment. *Chemistry of Materials* **1994**, *6* (10), 1647-1650.
245. Dědeček, J.; Sklenak, S.; Li, C.; Gao, F.; Brus, J.; Zhu, Q.; Tatsumi, T., Effect of Al/Si substitutions and silanol nests on the local geometry of Si and Al framework sites in silicone-rich zeolites: A combined high resolution ^{27}Al and ^{29}Si NMR and density functional theory/molecular mechanics study. *The Journal of Physical Chemistry C* **2009**, *113* (32), 14454-14466.
246. Dědeček, J.; Sklenak, S.; Li, C.; Wichterlová, B.; Gábová, V.; Brus, J.; Sierka, M.; Sauer, J., Effect of Al–Si–Al and Al–Si–Si–Al pairs in the ZSM-5 zeolite framework on the ^{27}Al NMR spectra. A combined high-resolution ^{27}Al NMR and DFT/MM study. *The Journal of Physical Chemistry C* **2009**, *113* (4), 1447-1458.
247. Hu, K.-N.; Hwang, L.-P., The influence of adsorbed molecules on Na-sites in NaY zeolite investigated by triple-quantum ^{23}Na MAS NMR spectroscopy. *Solid State Nuclear Magnetic Resonance* **1998**, *12* (4), 211-220.
248. Deng, F.; Du, Y.; Ye, C.; Wang, K.; Chen, T.; Ding, D.; Wang, J.; Li, H., Characterization of sodium cations in zeolite omega by solid-state ^{23}Na NMR spectroscopy. *Applied Magnetic Resonance* **1994**, *6* (4), 537-547.

249. Kim, H.; Deng, W.-Q.; Goddard, W. A., III; Jang, S. S.; Davis, M. E.; Yan, Y., Sodium diffusion through aluminum-doped zeolite BEA system: Effect of water solvation. *The Journal of Physical Chemistry C* **2009**, *113* (3), 819-826.
250. Charpentier, T.; Ispas, S.; Profeta, M.; Mauri, F.; Pickard, C. J., First-principles calculation of ^{17}O , ^{29}Si , and ^{23}Na NMR spectra of sodium silicate crystals and glasses. *The Journal of Physical Chemistry B* **2004**, *108* (13), 4147-4161.
251. Steinadler, J.; Zeman, O. E. O.; Bräuniger, T., Correlation of the Isotropic NMR Chemical Shift with Oxygen Coordination Distances in Periodic Solids. *Oxygen* **2022**, *2* (3), 327-336.
252. Hodgkinson, P.; Emsley, L., The accuracy of distance measurements in solid-state NMR. *Journal of Magnetic Resonance* **1999**, *139* (1), 46-59.
253. De Paëpe, G., Dipolar Recoupling in Magic Angle Spinning Solid-State Nuclear Magnetic Resonance. *Annual Review of Physical Chemistry* **2012**, *63* (Volume 63, 2012), 661-684.
254. Tricot, G.; Trébosc, J.; Pourpoint, F.; Gauvin, R.; Delevoye, L., Chapter Four - The D-HMQC MAS-NMR Technique: An Efficient Tool for the Editing of Through-Space Correlation Spectra Between Quadrupolar and Spin-1/2 (^{31}P , ^{29}Si , ^1H , ^{13}C) Nuclei. In *Annual Reports on NMR Spectroscopy*, Webb, G. A., Ed. Academic Press: 2014; Vol. 81, pp 145-184.
255. Ji, Y.; Liang, L.; Bao, X.; Hou, G., Recent progress in dipolar recoupling techniques under fast MAS in solid-state NMR spectroscopy. *Solid State Nuclear Magnetic Resonance* **2021**, *112*, 101711.
256. Zheng, M.; Xin, S.; Wang, Q.; Trébosc, J.; Xu, J.; Qi, G.; Feng, N.; Lafon, O.; Deng, F., Through-space ^{11}B – ^{27}Al correlation: Influence of the recoupling channel. *Magnetic Resonance in Chemistry* **2021**, *59* (9-10), 1062-1076.
257. Vasconcelos, F.; Cristol, S.; Paul, J.-F.; Montagne, L.; Mauri, F.; Delevoye, L., First-principles calculations of NMR parameters for phosphate materials. *Magnetic Resonance in Chemistry* **2010**, *48* (S1), S142-S150.
258. Harris, R. K.; Hodgkinson, P.; Pickard, C. J.; Yates, J. R.; Zorin, V., Chemical shift computations on a crystallographic basis: some reflections and comments. *Magnetic Resonance in Chemistry* **2007**, *45* (S1), S174-S186.
259. Fischer, M.; Evers, F. O.; Formalik, F.; Olejniczak, A., Benchmarking DFT-GGA calculations for the structure optimisation of neutral-framework zeotypes. *Theoretical Chemistry Accounts* **2016**, *135* (12), 257.
260. Blanco, C.; Auerbach, S. M., Nonequilibrium molecular dynamics of microwave-driven zeolite–guest systems: Loading dependence of athermal effects. *The Journal of Physical Chemistry B* **2003**, *107* (11), 2490-2499.
261. Ramsahye, N. A.; Bell, R. G., Calculating the energy barriers to sodium cation motion through the six-rings of zeolite Y. *Microporous and Mesoporous Materials* **2008**, *109* (1), 405-412.
262. Resasco, D. E.; Crossley, S. P.; Wang, B.; White, J. L., Interaction of water with zeolites: a review. *Catalysis Reviews* **2021**, *63* (2), 1-61.

263. Lee, Y.; Vogt, T.; Hriljac, J. A.; Parise, J. B.; Hanson, J. C.; Kim, S. J., Non-framework cation migration and irreversible pressure-induced hydration in a zeolite. *Nature* **2002**, 420 (6915), 485-489.
264. Abrioux, C.; Coasne, B.; Maurin, G.; Henn, F.; Jeffroy, M.; Boutin, A., Cation behavior in faujasite zeolites upon water adsorption: A combination of Monte Carlo and molecular dynamics simulations. *The Journal of Physical Chemistry C* **2009**, 113 (24), 10696-10705.
265. de S. Vilhena, F.; Serra, R. M.; Boix, A. V.; Ferreira, G. B.; de M. Carneiro, J. W., DFT study of Li^+ and Na^+ positions in mordenites and hydration stability. *Computational and Theoretical Chemistry* **2016**, 1091, 115-121.
266. van Bokhoven, J. A.; van der Eerden, A. M. J.; Koningsberger, D. C., Flexible aluminium coordination of zeolites as function of temperature and water content, an in-situ method to determine aluminium coordinations. In *Studies in Surface Science and Catalysis*, Aiello, R.; Giordano, G.; Testa, F., Eds. Elsevier: 2002; Vol. 142, pp 1885-1890.
267. Vener, M. V.; Rozanska, X.; Sauer, J., Protonation of water clusters in the cavities of acidic zeolites: $(\text{H}_2\text{O})_n\cdot\text{H}$ -chabazite, $n = 1-4$. *Physical Chemistry Chemical Physics* **2009**, 11 (11), 1702-1712.
268. Mazurek, A. H.; Szeleszczuk, Ł.; Pisklak, D. M., A Review on Combination of Ab Initio Molecular Dynamics and NMR Parameters Calculations. *Int J Mol Sci* **2021**, 22 (9), 4378.
269. Gao, P.; Zhang, J.; Peng, Q.; Zhang, J.; Glezakou, V.-A., General protocol for the accurate prediction of molecular $^{13}\text{C}/^1\text{H}$ NMR chemical shifts via machine learning augmented DFT. *Journal of Chemical Information and Modeling* **2020**, 60 (8), 3746-3754.
270. Grisafi, A.; Wilkins, D. M.; Csányi, G.; Ceriotti, M., Symmetry-adapted machine learning for tensorial properties of atomistic systems. *Physical Review Letters* **2018**, 120 (3), 036002.

APPENDIX A

Appendix for Chapter 5

Table A1 ^{27}Al calculated NMR chemical shifts (δ) of CHA with Si/Al = 11 with optimized cell shape and atomic positions.

CHA	σ ($\langle\sigma\rangle$) (ppm)	δ ($\langle\delta\rangle$) (ppm)	Volume ($\text{\AA}^3$)
bgc 0w ^a	494.33	60.94	810.90
Na 0w ^b	494.46 (494.74)	60.79(60.48)	810.90
Na 0w ^c	493.05	62.36	805.82
H(O1) 0w	497.71	57.19	811.79
H(O2) 0w	491.58	64.00	810.00
H(O3) 0w	493.15	62.24	811.42
H(O4) 0w ^d	499.55 (498.41)	55.14 (56.41)	815.12
Na 1w	494.51	60.74	807.59
H(O1) 1w	497.04	57.93	811.56
H(O2) 1w	493.13	62.27	800.52
H(O3) 1w	494.89	60.32	810.62
H(O4) 1w	499.44	55.26	807.93
Na 5w ^e	493.44 (492.42)	61.93 (63.06)	796.35
Na 5w*	494.84 (493.09)	60.37 (62.31)	796.35
H 5w*	493.06 (493.09)	62.34 (62.32)	794.65

^a The framework negative charge is compensated with a homogeneous positive background charge; both the lattice parameters and atomic coordinates optimized with the CHA(11)|Na|0w model. ^b Na^+ located in the 6MR site. ^c Na^+ located in the 8MR site. ^d The most stable structure is the one with proton on O4. ^e Na|5w denotes the partially solvated Na^+ , while Na|5w* and H|5w* denotes the fully solvated cations. The rows in bold are the stable cases and on which MD calculations were performed.

Table A2 Calculated ^{27}Al NMR chemical shifts (δ) and quadrupole coupling (C_Q) of dehydrated Na-CHA with Si/Al = 47, 35 23 and 11.

	Na 0w				bgc (Vol= 802.05)		
Si/Al	σ (ppm)	δ (ppm)	C_Q (MHz)	Volume ($\text{\AA}^3$)	σ (ppm)	δ (ppm)	C_Q (MHz)
∞	-	-	-	802.05			
47	495.33	59.83	7.46	804.90	495.58	59.55	3.58
35	495.48	59.66	7.57	803.89	496.82	58.17	2.95
23	494.17	61.12	7.50	807.52	495.15	60.03	3.47
11	494.46	60.79	7.81	810.90	494.66	60.57	2.54
11(hex) ^a	494.01	61.30	7.74	811.57	493.87	61.45	2.55

a. This is the CHA(11)|Na|0w model with conventional hexagonal cell.

Table A3 The geometric descriptors and their contributions to the chemical shielding for the CHA|Na|0w model with varying volumes. The definitions of all the descriptors are given in Table 5.1.

	Geometrical descriptors					Contribution to the ^{27}Al σ (ppm)		^{27}Al δ (ppm)	
V(Å ³)	d _{Al-O} (Å)	Δ d _{Al-O} (Å)	d _{Al-Si} (Å)	$\alpha_{\text{Al-O-Si}}$ (°)	$\alpha_{\text{O-Al-O}}$ (°)	$\sigma(\text{d}_{\text{Al-O}})$	$\sigma(\alpha_{\text{Al-O-Si}})$	$\delta(\text{FIT})$	$\delta(\text{DFT})$
810.90	1.742	0.069	3.706	143.26	109.40	314.7	114.6	62.0	60.8
806.04	1.741	0.070	3.699	142.97	109.39	314.5	114.3	62.5	61.6
801.20	1.741	0.068	3.695	142.71	109.38	314.3	114.1	62.9	62.2
796.39	1.740	0.066	3.689	142.47	109.37	314.2	113.9	63.3	62.8
791.59	1.739	0.064	3.683	142.28	109.36	314.0	113.8	63.6	63.4
786.81	1.738	0.062	3.678	142.11	109.36	313.9	113.6	63.9	63.8
763.21	1.736	0.046	3.652	141.28	109.35	313.5	113.0	65.1	65.7

Table A4 Calculated ^{27}Al NMR parameters of CHA (Si/Al=11) with a fixed volume of $796.35 \text{ \AA}^3$, which is the optimal volume for the Na|5w model.

CHA	σ (ppm)	δ (ppm)	C_Q (MHz)	$\langle\sigma\rangle$ (ppm)	$\langle\delta\rangle$ (ppm)
bgc 0w	494.20	61.2	2.75	-	-
Na 0w	494.39	61.0	6.70	493.25	62.2
Na 5w	493.44	62.0	5.31	492.42	63.1
Na 5w*	494.85	60.5	3.19	493.81	61.5
H 0w	498.06	56.9	19.51	496.87	58.2
	495.98	59.2	20.70		
	491.32	64.4	17.31		
	490.35	65.4	16.29		
H 5w	494.04	61.3	1.44	493.59	61.8

*The case with completely-solvated Na^+ case. Its energy is only $9.6 \text{ kJ}\cdot\text{mol}^{-1}$ lower than the Na|5w case with partially solvated Na^+ ; the $\langle\sigma\rangle$ is obtained from the trajectory with fully solvated (as shown in Figure 5.6). The four static cases of CHA|H|0w models are ordered by increasing energy, with H^+ at the O4, O1, O3, and O2 BAS sites, as defined according to the convention in reference². The relative energy differences of O1, O3, and O2 from the stable O4 are 7.3 , 9.1 , and $10.2 \text{ kJ}\cdot\text{mol}^{-1}$, respectively. The first case, with the lowest energy at the O4 BAS, was used to calculate time-averaged result as an example.

² Heard, C. J.; Grajciar, L.; Rice, C. M.; Pugh, S. M.; Nachtigall, P.; Ashbrook, S. E.; Morriss, R. E., Fast room temperature lability of aluminosilicate zeolites. *Nature Communications* **2019**, *10* (1), 7.

Table A5 ^{27}Al NMR parameters of MOR. The model for MOR with Si/Al=11 has Al in T1 and T3 sites. The model for MOR with Si/Al=7 has Al in T1, T3 and T4 sites.

Models	δ (ppm)				C_Q (MHz)				$\langle\delta\rangle$ (ppm)			
	T1	T2	T3	T4	T1	T2	T3	T4	T1	T2	T3	T4
MOR(47) bcg 0w	52.6	50.2	51.8	54.1	3.26	2.72	2.43	3.05				
MOR(23) bcg 0w	49.7	49.5	52.1	56.0	2.71	2.71	2.82	3.33				
MOR(23) Na 0w	53.1	53.6	54.9	59.8	5.86	6.72	5.41	5.60			55.3	
	59.9 ^a	53.7 ^a			5.65 ^a	6.29 ^a			59.3			
MOR(23) Na 6w	52.2	51.6	56.1	61.7	4.98	2.56	3.86	7.71	54.6	54.3	56.0	58.9
MOR(23) Na 6w*	50.7	52.4	50.4	55.9	3.78	2.24	4.74	2.15	54.5	53.3	52.2	57.0
MOR(11) Na 5w	52.9		56.2		4.62		5.17		54.3		56.1	
MOR(7) Na 1w	53.8		57.7	61.4	4.20		5.16	6.99	53.2		56.2	61.5
MOR(7) Na 5w	51.8		55.8	60.3	4.24		4.57	3.23	54.0		56.2	60.0
MOR(7) H 5w ^b	55.8		50.2	57.7	13.29		8.91	3.24				
MOR(7) H 5w* ^b	52.6		55.1	59.0	5.97		4.23	6.97	54.6		53.6	58.1

Note: MOR(23)|Na|6w and MOR(23)|Na|6w* denote the states of the Na^+ are partial solvated and completely-solvated as shown in Figure 5.6; C_Q are from the static calculation. $\langle\delta\rangle$ refers to the chemical shift averaged over the MD trajectory. C_Q is the quadrupolar coupling constant from static calculations. a: two nearly isoenergetic configurations for Na were found for Al at T1 in MOR(23)|Na|0w and Al at T2 in MOR(23)|Na|0w. Static chemical shifts and C_Q values were calculated for both configurations. For dehydrated Na-MOR, dynamic simulations were not run, as tests showed the effect of dynamics was small, due to the lack of Na motion during the simulations. b: in MOR(7)|H|5w, all three protons originating at T1, T3 and T4 are preferentially solvated in the static model(MOR(7)|H|5w*), but there is a competing configuration at +7 $\text{kJ}\cdot\text{mol}^{-1}$ (MOR(7)|H|5w), in which T1 and T3 protons are unsolvated. The protons at T1 and T3 rapidly fluctuate between solvated and unsolvated configurations along the MD trajectory.

Table A6 The geometric descriptors and their contribution to the NMR chemical shielding of CHA with the fixed volume (796.35 Å³) based on the LASSO analysis. Note: all the CHA|H|0w case in here are used the same model with BAS site on O4.

Models	Geometrical descriptors					²⁷ Al σ (ppm)		²⁷ Al δ (ppm)	
CHA(11)	d _{Al-O} (Å)	Δd _{Al-O} (Å)	d _{Al-Si} (Å)	α _{Al-O-Si} (°)	α _{O-Al-O} (°)	σ(d _{Al-O})	σ(α _{Al-O-Si})	δ (DFT)	δ(FIT)
bgc 0w	1.742	0.028	3.677	141.78	109.472	314.5	113.4	61.1	63.5
Na 0w	1.743	0.075	3.679	141.551	109.464	314.7	113.2	60.9	63.5
<Na 0w>	1.745	0.103	3.628	141.650	109.367	315.1	113.3	62.2	62.9
Na 5w	1.745	0.051	3.676	141.526	109.470	315.1	112.3	62.0	64.0
<Na 5w>	1.752	0.070	3.623	139.493	109.385	315.9	111.7	63.1	63.9
Na 5w*	1.745	0.051	3.676	141.526	109.470	315.1	113.2	60.4	63.0
<Na 5w>*	1.752	0.090	3.623	139.493	109.385	316.4	111.6	62.4	63.4
H 0w	1.760	0.211	3.422	143.318	108.798	317.9	114.7	56.9	58.4
<H 0w>	1.765	0.238	3.551	142.402	108.729	318.8	113.9	58.2	58.2
H 5w	1.749	0.037	3.676	140.858	109.470	315.9	112.7	61.3	62.8
<H 5w>	1.751	0.086	3.625	140.232	109.383	316.2	112.2	61.8	63.0

Table A7. The geometric descriptors and their contribution to the ^{27}Al NMR σ parameters for static and average MD NMR calculation in MOR.

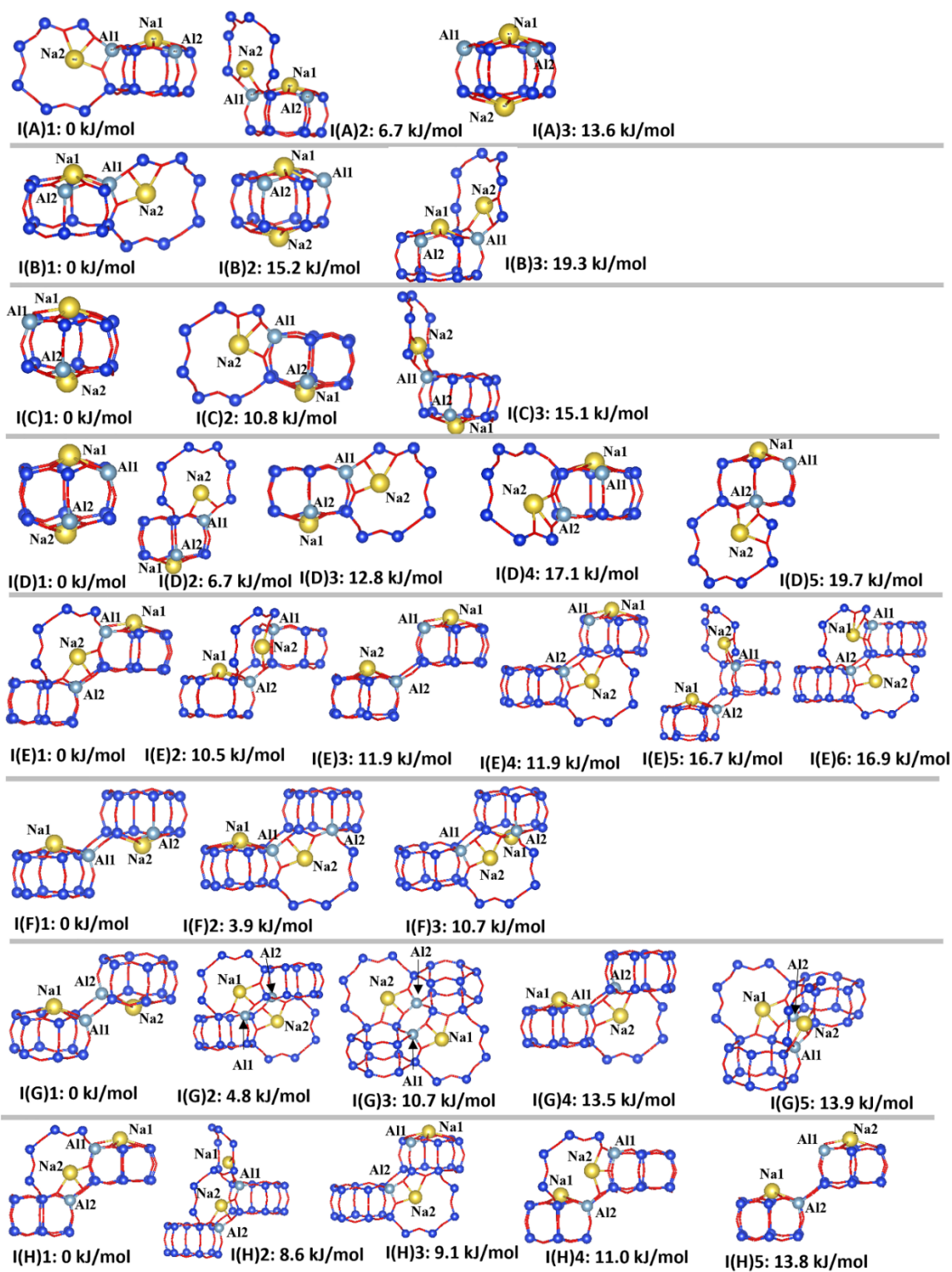
Models		$d_{\text{Al-O}}(\text{\AA})$	$\Delta d_{\text{Al-O}}(\text{\AA})$	$d_{\text{Al-Si}}(\text{\AA})$	$\alpha_{\text{Al-O-Si}}(^{\circ})$	$\alpha_{\text{O-Al-O}}(^{\circ})$	$\sigma(d_{\text{Al-O}})$ (ppm)	$\sigma(\alpha_{\text{Al-O-Si}})$ (ppm)	$\delta(\text{ML})$ (ppm)	$\delta(\text{DFT})$ (ppm)
T1	MOR(23)Na 0w	1.751	0.060	3.43	153.29	109.36	316.2	122.6	51.4	53.1
	MOR(23)Na 6w	1.751	0.048	3.42	153.17	109.39	316.2	122.5	51.5	52.2
	<MOR(23)Na 6w>	1.754	0.105	3.43	150.04	109.35	316.8	120.0	53.6	54.6
	MOR(23)Na 6w*	1.750	0.054	3.44	152.51	109.46	316.0	122.0	52.3	50.8
	<MOR(23)Na 6w>*	1.751	0.094	3.43	149.01	109.39	316.3	119.2	55.1	54.4
	MOR(23)Na 0w ^(a)	1.754	0.072	3.40	141.05	109.28	316.7	112.8	61.7	59.9
	MOR(7)H 5w	1.756	0.147	3.44	149.20	109.24	317.1	119.4	54.1	55.8
	MOR(7)H 5w*	1.752	0.074	3.44	151.41	109.39	316.4	121.1	52.9	52.6
	<MOR(7)H 5w>	1.760	0.152	3.45	149.16	109.23	317.8	119.3	53.3	54.6
T2	MOR(23)Na 0w	1.754	0.063	3.62	148.52	109.05	316.8	118.8	54.9	53.5
	MOR(23)Na 6w	1.746	0.032	3.74	152.01	109.39	315.3	121.6	53.5	51.6
	<MOR(23)Na 6w>	1.752	0.092	3.60	149.90	109.32	316.4	119.9	54.2	54.3
	<MOR(23)Na 6w>*	1.747	0.086	3.62	151.89	109.38	315.4	121.5	53.5	53.2
T3	MOR(23)Na 0w	1.751	0.049	3.44	147.40	109.36	316.2	117.9	56.6	54.9
	MOR(23)Na 6w	1.750	0.042	3.62	146.65	109.43	316.1	117.3	57.4	56.1
	<MOR(23)Na 6w>	1.757	0.093	3.55	146.44	109.36	317.2	117.2	56.3	56.0
	<MOR(23)Na 6w>*	1.752	0.085	3.52	149.49	109.38	316.4	119.6	54.5	52.2

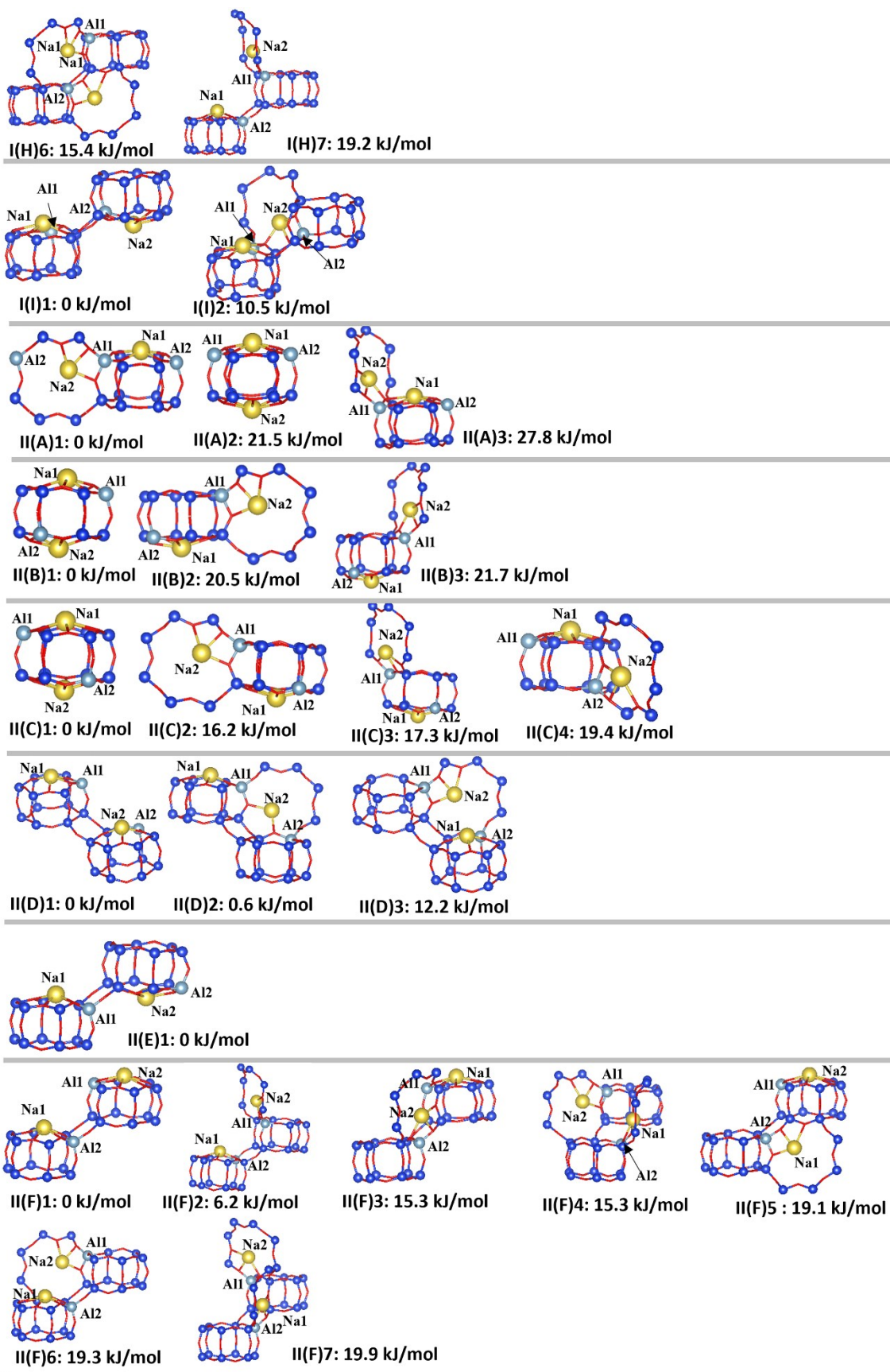
	MOR(7) H 5w	1.753	0.111	3.60	149.89	109.28	316.6	119.9	54.0	50.2
	MOR(7) H 5w*	1.748	0.088	3.39	146.51	109.31	315.7	117.2	58.0	55.1
	<MOR(7) H 5w>	1.755	0.137	3.56	146.99	109.21	316.9	117.6	56.2	53.6
T4	MOR(23) Na 0w	1.745	0.051	3.17	144.63	109.33	315.1	115.7	60.2	59.5
	MOR(23) Na 6w	1.742	0.123	3.15	142.91	109.19	314.7	114.3	62.3	61.6
	<MOR(23) Na 6w>	1.752	0.088	3.38	143.85	109.36	316.3	115.1	59.6	59.0
	<MOR(23) Na 6w>*	1.752	0.086	3.37	144.84	109.38	316.4	115.9	58.7	57.0
	MOR(7) H 5w*	1.750	0.057	3.42	143.77	109.44	316.0	115.0	60.1	59.0
	<MOR(7) H 5w>	1.757	0.101	3.39	143.44	109.37	317.2	114.7	59.0	58.1

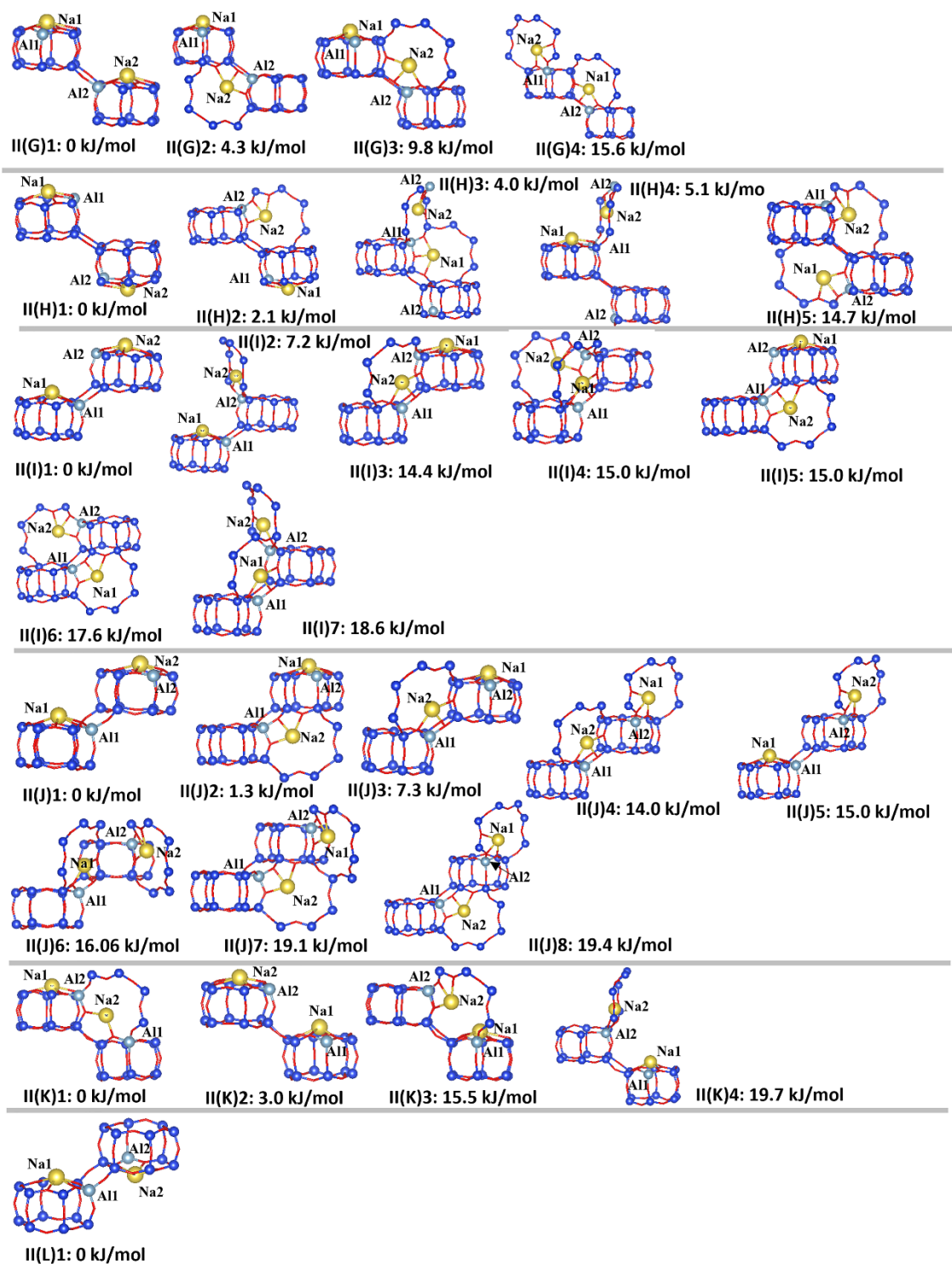
MOR(23)|Na|6w and MOR(23)|Na|6w* denote the states of the Na⁺ are partially solvated and completely solvated. In MOR(7)|H|5w, all three protons originating at T1, T3 and T4 are preferentially solvated in the static model(MOR(7)|H|5w*), and there is a competing configuration at +7 kJ·mol⁻¹ (MOR(7)|H|5w), in which T1 and T3 protons are unsolvated.

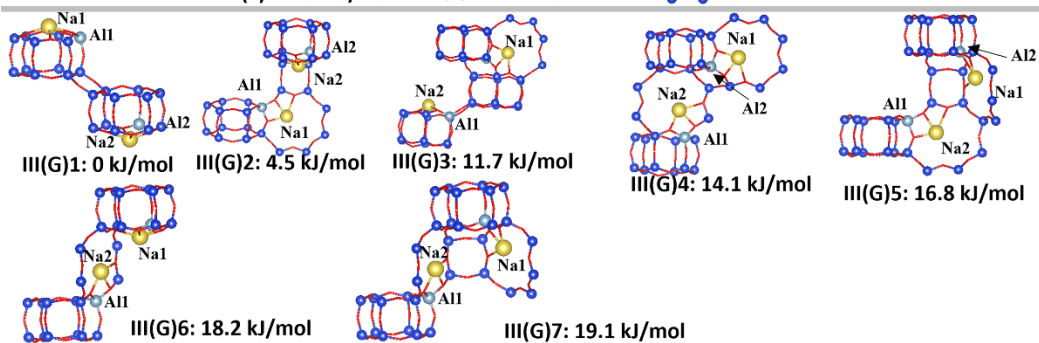
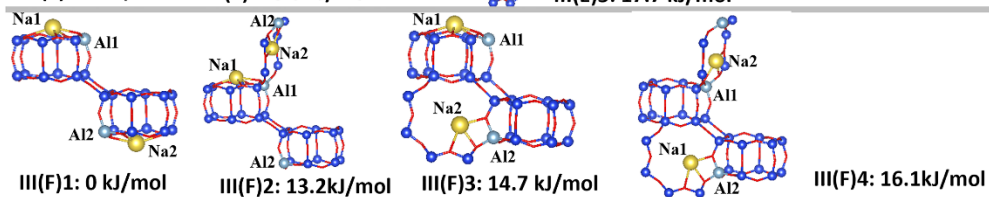
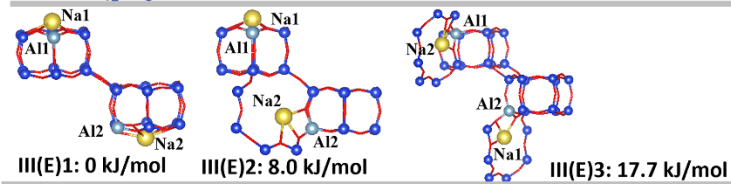
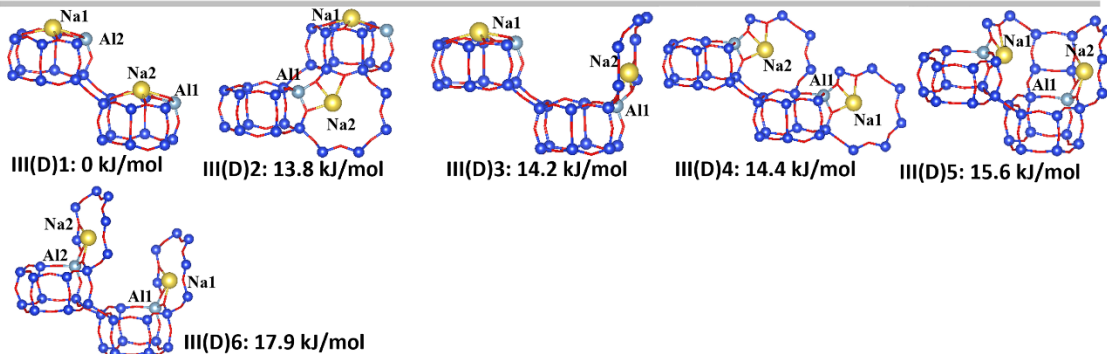
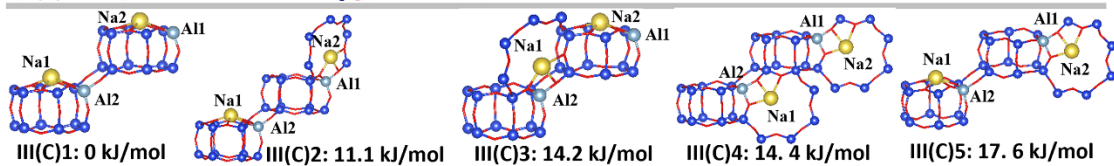
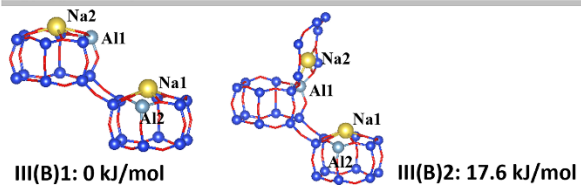
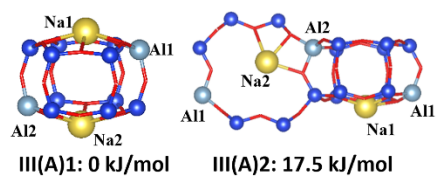
APPENDIX B

Appendix for Chapter 6









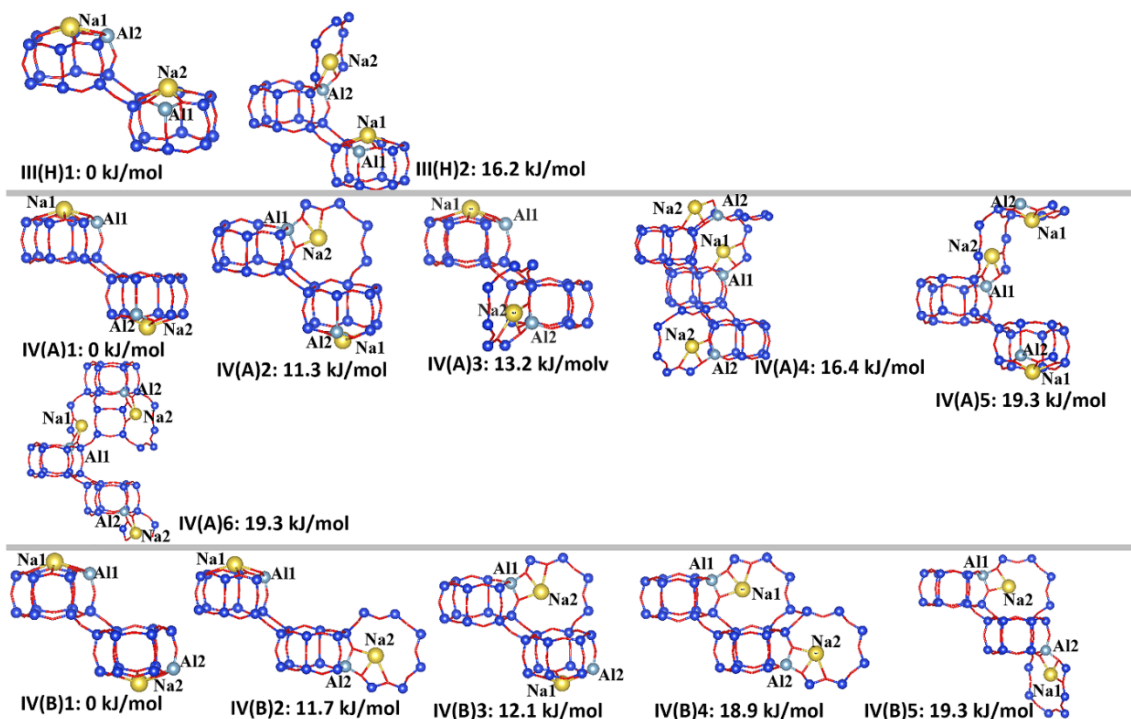


Figure B1 The local structures of all the CHA(17) models to do the NMR calculations. The cases with molecular dynamics calculations are: I(A)1, I(A)3, I(C)1, I(C)2, I(C)3, I(E)1, I(E)3, I(E)4, I(F)1, I(F)2, I(G)1, I(G)3, II(A)1, II(A)2, II(A)3, III(A)1, II(A)3, II(B)1, II(B)2, II(B)3, II(D)1, II(D)2, II(F)2, II(F)5, III(A)2, III(E)2, III(F)1, III(F)3, IV(A)1 and IV(A)3. The energy report here is from DFT static calculations. Reproduced from Ref.¹⁷⁹ with permission from the Royal Society of Chemistry.

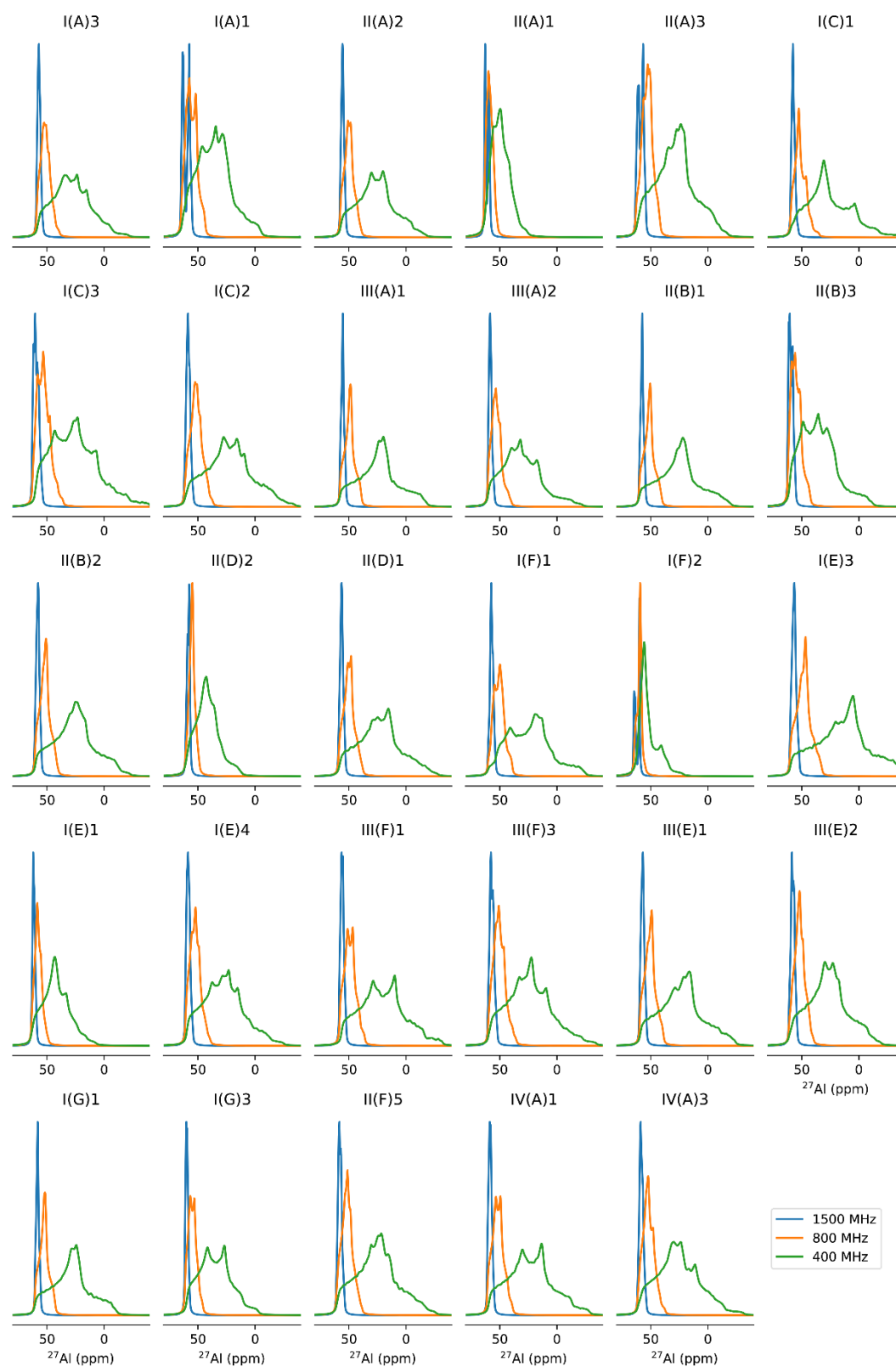


Figure B2 The ^{27}Al NMR spectra of static CHA(17) models at different magnetic fields, ranging from 400 to 1500 MHz ^1H Larmor frequency. Reproduced from Ref.¹⁷⁹ with permission from the Royal Society of Chemistry.

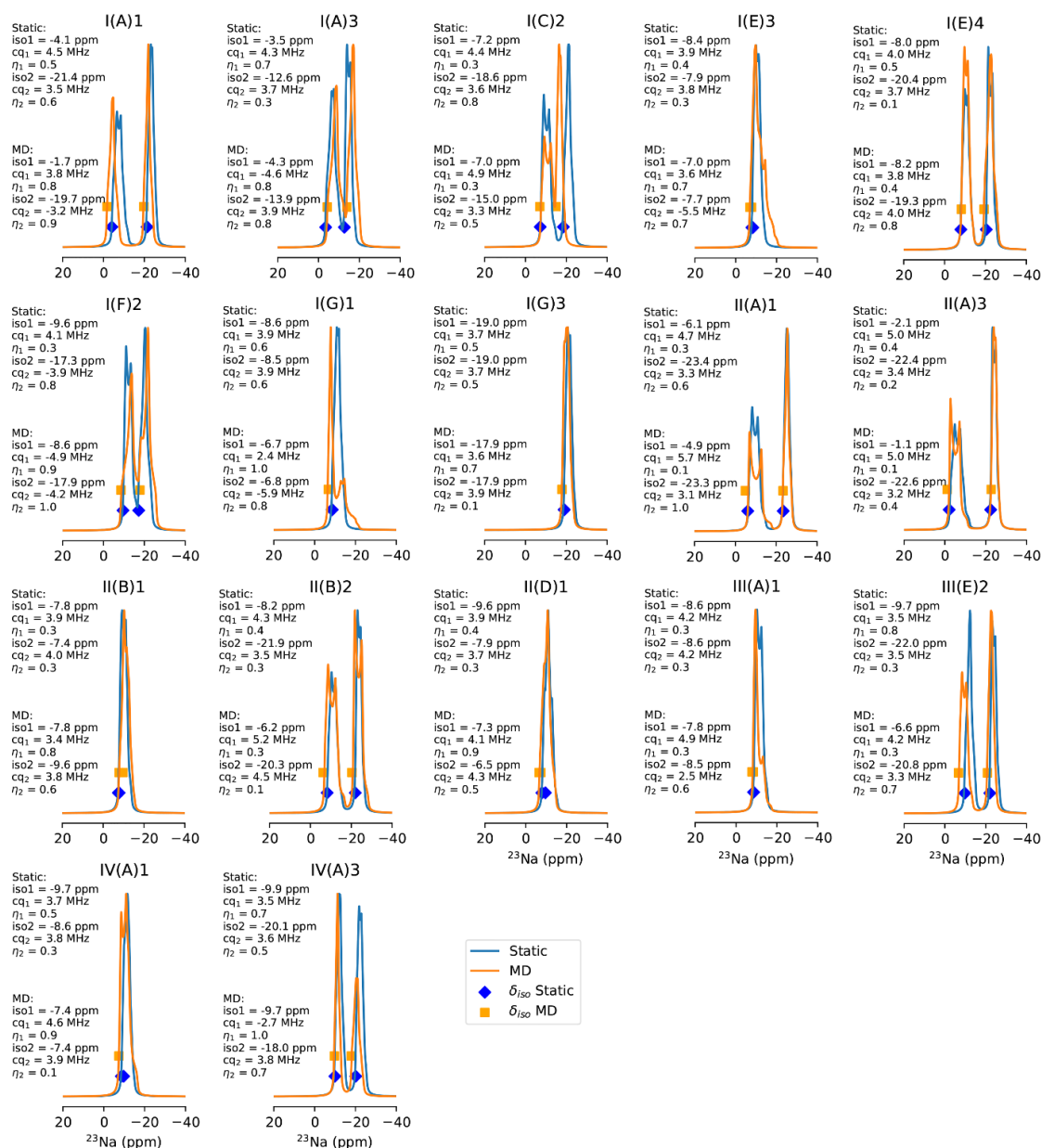


Figure B3 Simulated ^{23}Na NMR spectra of static and time-averaged CHA(17) models with distinct Na/Al configurations, which combined with those presented in Figure 6.11 in the main text, make up the full set of calculated CHA(17) spectra. Reproduced from Ref.¹⁷⁹ with permission from the Royal Society of Chemistry.



Figure B4 ^{23}Na - ^{23}Na dipolar couplings calculated from static (blue) and MD trajectory (orange). Reproduced from Ref.¹⁷⁹ with permission from the Royal Society of Chemistry.

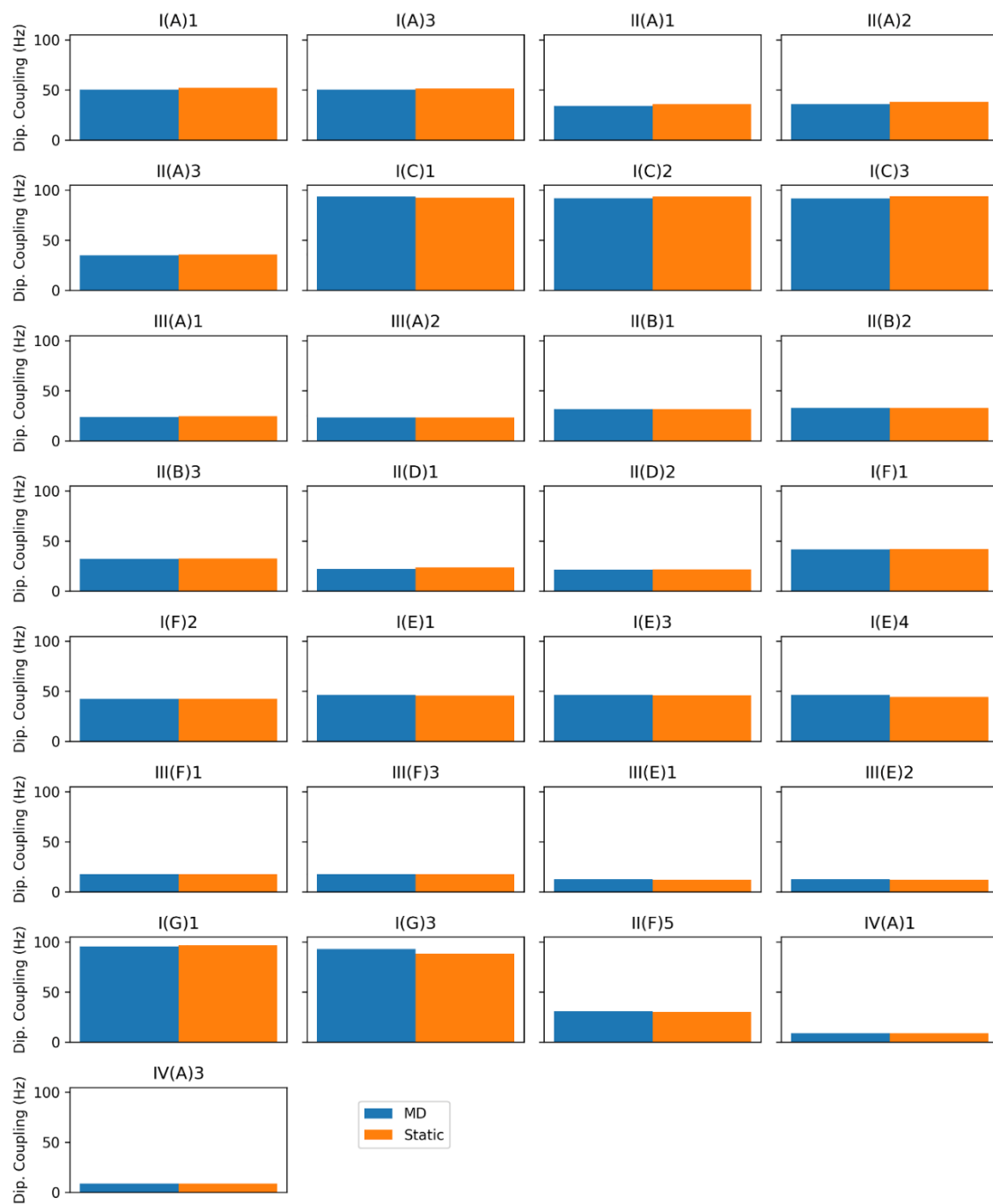


Figure B5 ^{27}Al - ^{27}Al dipolar couplings calculated from static (blue) and MD trajectory (orange), showing little difference. Reproduced from Ref.¹⁷⁹ with permission from the Royal Society of Chemistry.

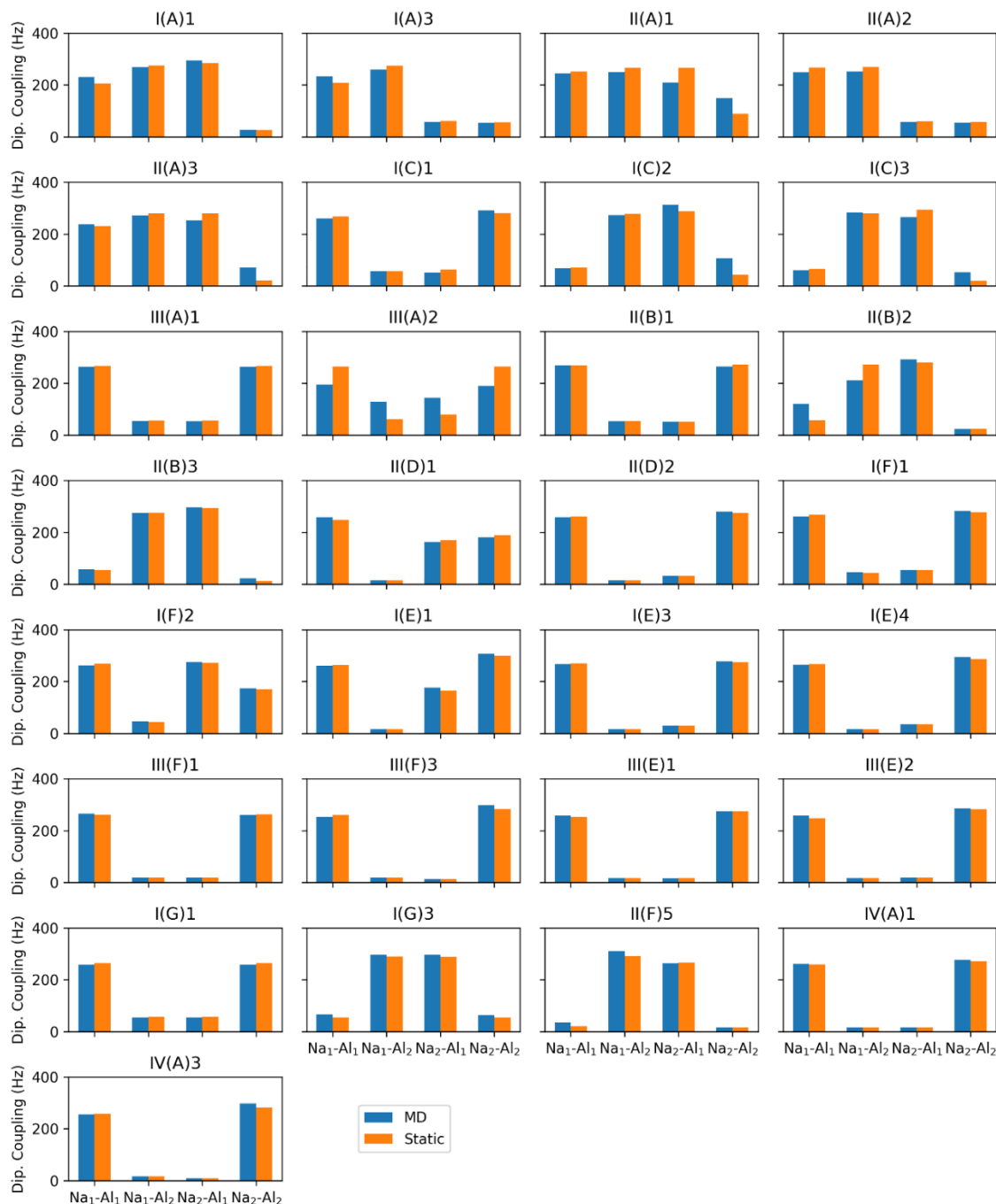


Figure B6 ^{23}Na - ^{27}Al dipolar couplings calculated from static (blue) and MD trajectory (orange). Reproduced from Ref.¹⁷⁹ with permission from the Royal Society of Chemistry.

Table B1 The ^{27}Al NMR parameters of CHA(17).

Structure	Static						MD					
	δ_{Al1}	C_{QAl1}	η_{QAl1}	δ_{Al2}	C_{QAl2}	η_{QAl2}	δ_{Al1}	C_{QAl1}	η_{QAl1}	δ_{Al2}	C_{QAl2}	η_{QAl2}
I(A)1	64.7	6.2	0.55	59.7	6.4	0.95	64.7	5.5	0.15	59.4	8.9	0.37
I(A)2	65.7	7.3	0.38	59.4	7.2	0.87						
I(A)3	58.9	7.5	0.55	59.3	6.8	0.62	59.9	10.5	0.92	58.8	9.2	0.89
I(B)1	64.0	4.5	0.58	59.7	7.8	0.43						
I(B)2	59.1	6.9	0.69	58.8	6.9	0.85						
I(B)3	64.2	7.6	0.86	60.3	7.7	0.50						
I(C)1	59.7	6.1	0.99	60.1	8.5	0.42	60.0	10.4	0.49	60.0	8.4	0.84
I(C)2	61.8	7.6	0.73	60.5	8.1	0.60	61.7	6.8	0.92	59.6	6.4	0.63
I(C)3	63.1	7.2	0.41	60.7	8.3	0.59	59.6	8.5	0.92	58.9	9.5	0.94
I(D)1	59.9	9.0	0.31	59.8	6.5	0.97						
I(D)2	62.9	5.3	0.98	59.7	6.0	0.99						
I(D)3	60.6	7.4	0.96	60.3	7.8	0.97						
I(D)4	60.6	8.5	0.41	60.8	7.8	0.75						
I(D)5	60.7	8.7	0.45	62.9	7.0	0.71						
I(E)1	62.5	6.1	0.66	63.3	5.1	0.93	62.5	5.3	0.92	63.4	6.4	0.94
I(E)2	62.8	6.7	0.92	62.0	7.5	0.76						
I(E)3	60.5	8.4	0.69	59.7	8.4	0.94	59.5	12.5	0.74	59.2	11.2	0.86
I(E)4	60.1	7.6	0.68	61.2	7.0	0.57	58.9	8.6	0.91	61.0	4.4	0.98
I(E)5	63.3	6.6	0.87	60.6	8.5	0.85						
I(E)6	61.5	6.9	0.72	65.1	5.8	0.36						
I(F)1	60.3	7.4	0.95	59.0	7.6	0.25	60.5	9.9	0.61	59.5	12.2	0.84
I(F)2	65.4	5.6	0.31	60.3	2.5	0.91	65.1	8.9	0.62	61.2	4.2	0.49
I(F)3	62.3	6.0	0.93	62.8	7.5	0.84						
I(G)1	60.4	6.8	0.87	60.3	6.8	0.87	60.2	7.1	0.15	60.2	9.7	0.92
I(G)2	61.9	5.3	0.82	61.8	5.3	0.84						
I(G)3	61.6	6.7	0.50	61.6	6.7	0.50	61.4	9.3	0.96	61.9	9.0	0.71
I(G)4	58.9	8.7	0.95	62.7	7.0	0.24						
I(G)5	62.3	5.4	0.86	60.9	7.1	0.45						
I(H)1	62.4	5.6	0.63	63.4	4.9	1.00						
I(H)2	65.8	5.5	0.05	63.3	4.5	0.67						
I(H)3	59.8	7.4	0.65	61.6	7.0	0.47						
I(H)4	62.5	6.6	0.99	61.6	7.1	0.90						
I(H)5	59.7	7.9	0.74	59.5	8.7	0.86						
I(H)6	62.4	7.2	0.78	64.9	5.9	0.20						
I(H)7	63.5	6.6	0.88	60.1	8.3	1.00						
I(I)1	58.3	7.8	0.18	59.9	6.9	0.96						
I(I)2	62.3	7.3	0.94	62.8	6.4	0.98						
II(A)1	63.5	4.4	0.45	60.5	5.0	0.46	62.7	6.7	0.73	61.3	9.2	0.80
II(A)2	57.8	6.9	0.73	57.5	7.2	0.62	58.9	10.5	0.70	58.2	10.2	0.27

II(A)3	63.4	7.4	0.62	59.0	6.7	0.88	63.3	6.3	0.48	59.7	8.8	0.82
II(B)1	60.2	7.1	0.95	59.8	6.9	0.86	59.4	9.8	0.29	59.2	9.4	0.22
II(B)2	60.9	7.5	0.66	59.8	6.8	0.94	62.1	11.0	0.42	58.3	12.4	0.31
II(B)3	62.3	5.9	0.42	60.3	6.9	0.87	61.7	9.4	0.86	59.0	4.8	0.49
II(C)1	59.7	7.7	0.56	59.5	7.3	0.68						
II(C)2	61.0	8.1	0.53	59.8	8.0	0.56						
II(C)3	63.9	5.2	0.19	59.2	7.1	0.67						
II(C)4	60.0	8.3	0.40	60.0	8.0	0.68						
II(D)1	59.2	7.6	0.74	58.5	7.4	0.64	58.0	6.9	0.77	58.9	6.1	0.49
II(D)2	60.7	5.6	0.86	58.5	4.5	0.86	60.3	5.7	0.62	59.7	4.6	0.65
II(D)3	61.0	6.9	0.74	60.0	7.1	0.90						
II(E)1	59.8	7.4	0.55	59.8	7.3	0.57						
II(F)1	59.5	7.7	0.61	59.5	7.2	0.91						
II(F)2	62.7	5.9	0.83	59.1	7.4	0.87						
II(F)3	58.6	7.6	0.80	62.5	6.0	0.72						
II(F)4	61.0	6.5	0.63	62.1	5.4	0.95						
II(F)5	59.6	7.5	0.78	61.0	7.1	0.76	59.8	6.5	0.52	62.1	4.6	0.98
II(F)6	62.7	5.9	0.83	59.1	7.4	0.87						
II(F)7	62.5	6.3	0.82	62.0	5.6	0.50						
II(G)1	60.9	7.4	0.72	59.4	7.4	0.73						
II(G)2	60.2	7.3	0.67	63.3	7.1	0.7						
II(G)3	60.1	8.6	0.55	63.3	5.7	0.72						
II(G)4	63.0	5.6	0.91	63.4	5.4	0.68						
II(H)1	59.4	8.0	0.8	59.0	7.4	0.89						
II(H)2	59.4	7.6	0.74	61.3	7.0	0.84						
II(H)3	65.3	5.9	0.63	62.0	5.4	0.43						
II(H)4	61.8	6.7	0.93	62.8	5.4	0.9						
II(H)5	60.9	7.3	0.7	61.6	7.6	0.84						
II(I)1	59.1	7.5	0.81	59.7	8.2	0.56						
II(I)2	58.8	7.2	0.98	62.4	5.7	0.89						
II(I)3	63.0	5.9	0.73	58.8	7.9	0.71						
II(I)4	62.4	5.2	0.97	60.9	6.4	0.44						
II(I)5	61.3	7.1	0.58	59.6	8.0	0.70						
II(I)6	61.0	6.7	0.67	61.5	6.6	0.59						
II(I)7	62.3	5.4	0.55	62.3	6.2	0.86						
II(J)1	59.2	7.7	0.73	60.5	6.9	0.77						
II(J)2	62.2	6.8	0.60	59.6	6.6	0.76						
II(J)3	62.6	5.5	0.83	59.8	8.1	0.63						
II(J)4	63.1	5.2	0.79	63.3	5.6	0.91						
II(J)5	59.7	7.9	0.84	64.4	6.0	0.71						
II(J)6	62.9	5.3	0.94	61.6	6.7	0.74						
II(J)7	61.3	7.1	0.52	62.4	7.8	0.70						
II(J)8	62.2	7.0	0.58	63.7	5.6	0.45						

II(K)1	58.2	7.5	0.55	59.0	7.5	0.80						
II(K)2	59.4	6.8	0.94	60.1	6.9	0.82						
II(K)3	59.3	6.8	0.93	60.0	7.0	0.82						
II(K)4	58.5	7.3	0.81	62.0	5.7	0.81						
II(K)5	58.2	7.3	0.83	61.9	5.7	0.81						
II(L)1	60.2	7.5	0.21	60.5	7.1	0.27						
III(A)1	57.8	7.0	0.88	57.8	7.0	0.88	57.7	7.1	0.58	58.0	7.7	0.58
III(A)2	60.4	6.0	0.69	60.4	7.4	0.76	59.6	7.3	0.03	59.0	5.5	0.95
III(B)1	60.7	7.2	0.96	59.6	7.5	0.60						
III(B)2	62.6	6.1	0.66	59.4	7.6	0.80						
III(C)1	61.5	7.8	0.55	60.7	7.8	0.49						
III(C)2	63.6	5.6	0.69	59.8	7.7	0.66						
III(C)3	60.8	8.6	0.60	63.4	5.7	0.78						
III(C)4	61.8	6.8	0.51	60.9	6.9	0.73						
III(C)5	61.9	7.3	0.62	58.7	8.5	0.59						
III(D)1	60.7	7.8	0.49	61.6	7.9	0.58						
III(D)2	62.7	7.3	0.65	60.7	7.9	0.71						
III(D)3	63.3	5.7	0.77	60.7	8.6	0.62						
III(D)4	60.8	6.9	0.73	61.8	6.8	0.52						
III(D)5	62.5	5.1	0.97	61.3	6.5	0.63						
III(D)6	62.9	5.4	0.68	63.0	5.6	0.92						
III(E)1	60.1	7.6	0.62	59.3	7.3	0.88	59.7	12.3	0.31	59.1	6.2	0.82
III(E)2	59.2	7.3	0.66	61.2	7.0	0.81	58.9	12.9	0.79	61.3	8.7	0.85
III(E)3	61.4	7.0	0.67	62.0	5.9	0.74						
III(F)1	58.5	7.9	0.56	58.5	7.9	0.56	59.0	8.4	0.66	58.3	6.9	0.64
III(F)2	59.4	7.4	0.89	61.4	5.8	0.94						
III(F)3	58.5	7.9	0.71	60.3	7.0	0.69	58.3	9.7	0.66	62.1	3.1	0.33
III(F)4	61.7	5.5	0.79	62.6	6.0	0.42						
III(G)1	59.2	7.5	0.70	59.3	7.1	0.60						
III(G)2	61.8	6.9	0.66	59.0	7.0	0.58						
III(G)3	59.2	7.7	0.70	62.3	7.3	0.59						
III(G)4	62.4	5.6	0.79	62.1	6.9	0.71						
III(G)5	61.4	6.9	0.65	62.9	5.6	0.53						
III(G)6	63.0	5.7	0.99	58.2	7.9	0.51						
III(G)7	62.3	5.8	0.97	62.9	5.7	0.94						
III(H)1	59.5	7.0	0.60	60.6	7.5	0.75						
III(H)2	59.4	7.1	0.75	63.1	5.8	0.68						
IV(A)1	60.9	7.9	0.58	61.3	7.8	0.61	60.0	10.7	0.69	60.0	9.7	0.8
IV(A)2	62.0	7.0	0.66	60.2	7.9	0.61						
IV(A)3	60.1	7.9	0.58	61.4	6.9	0.77						
IV(A)4	63.0	5.6	0.87	60.8	6.5	0.87						
IV(A)5	63.8	5.8	1.00	59.5	8.4	0.64						
IV(A)6	62.6	5.8	0.91	62.5	5.8	0.94						

IV(B)1	60.1	7.4	0.65	59.9	7.2	0.71
IV(B)2	59.5	7.4	0.79	62.2	7.1	0.68
IV(B)3	61.9	7.1	0.72	59.2	7.2	0.83
IV(B)4	62.1	7.1	0.64	62.5	7.1	0.62
IV(B)5	61.6	7.0	0.65	62.7	5.9	0.70

Table B2 Static ^{27}Al and ^{23}Na NMR parameters of CHA(35). Note the Na positions are shown in Figure 6.2. Note the values in the brackets are the dynamic average results.

Na positio ns	^{23}Na			^{27}Al		
	δ_{Na} (ppm)	C_{QNa} (MHz)	η_{QNa}	δ_{Al} (ppm)	C_{QAl} (MHz)	η_{QAl}
SII	-8.5 (-8.0)	4.0	0.26	59.6 (59.5)	7.6	0.75
SIH	-21.1 (-19.6)	3.5	0.42	61.1 (61.9)	7.0	0.75
SIH'	-21.5	3.4	0.33	62.6	5.9	0.73

Table B3 ^{23}Na NMR parameters of CHA(17).

Structures	Static						MD					
	δ_{Na1}	C_{QNa1}	η_{QNa1}	δ_{Na2}	C_{QNa2}	η_{QNa2}	δ_{Na1}	C_{QNa1}	η_{QNa1}	δ_{Na2}	C_{QNa2}	η_{QNa2}
I(A)1	-4.1	4.5	0.49	-21.4	3.5	0.61	-1.7	3.8	0.76	-19.7	3.2	0.93
I(A)2	-2.8	4.8	0.49	-21.8	3.5	0.37						
I(A)3	-3.5	4.3	0.68	-12.6	3.7	0.30	-4.3	4.6	0.83	-13.9	3.9	0.80
I(B)1	-6.2	4.5	0.26	-23.5	3.3	0.31						
I(B)2	-5.5	4.2	0.51	-12.0	3.6	0.28						
I(B)3	-1.6	4.7	0.37	-22.4	3.3	0.10						
I(C)1	-9.1	4.0	0.60	-6.1	4.1	0.23	-8.9	4.0	0.89	-12.6	3.6	0.77
I(C)2	-7.2	4.4	0.27	-18.6	3.6	0.75	-7.0	4.9	0.30	-15.0	3.3	0.54
I(C)3	-5.2	4.4	0.26	-20.8	3.5	0.31	-7.3	4.6	0.84	-10.0	2.9	0.37
I(D)1	-7.6	3.9	0.33	-7.5	4.0	0.37						
I(D)2	-6.7	4.2	0.32	-21.1	3.5	0.41						
I(D)3	-6.4	4.3	0.31	-19.2	3.6	0.58						
I(D)4	-8.5	4.4	0.35	-19.4	3.6	0.55						
I(D)5	-7.2	4.2	0.35	-20.9	3.4	0.31						
I(E)1	-9.8	3.9	0.40	-16.1	3.8	0.98	-8.3	4.7	0.16	-15.1	3.8	0.79
I(E)2	-6.3	4.3	0.25	-17.7	4.1	0.33						
I(E)3	-8.4	3.9	0.37	-7.9	3.8	0.30	-7.0	3.6	0.75	-7.7	5.5	0.66
I(E)4	-8.0	4.0	0.47	-20.4	3.7	0.11	-8.2	3.8	0.36	-19.3	4.0	0.77
I(E)5	-8.9	3.8	0.39	-22.4	3.5	0.28						
I(E)6	-23.5	3.4	0.38	-22.5	3.5	0.32						
I(F)1	-7.6	3.7	0.31	-5.9	3.9	0.25	-6.8	3.1	0.71	-4.4	4.4	0.49
I(F)2	-9.6	4.1	0.27	-17.3	3.9	0.81	-8.6	4.9	0.88	-17.9	4.2	0.97

I(F)3	-4.6	4.4	0.32	-19.6	3.4	0.61						
I(G)1	-8.6	3.9	0.61	-8.5	3.9	0.60	-6.7	2.4	0.97	-6.8	5.9	0.77
I(G)2	-19.7	3.7	0.32	-19.8	3.7	0.31						
I(G)3	-19.0	3.7	0.47	-19.0	3.7	0.48	-17.9	3.6	0.71	-17.9	3.9	0.12
I(G)4	-8.7	3.7	0.47	-20.2	3.6	0.40						
I(G)5	-18.4	3.8	0.39	-19.0	3.8	0.34						
I(H)1	-10.0	4.0	0.55	-16.6	3.8	0.84						
I(H)2	-24.7	3.3	0.36	-15.8	3.7	0.92						
I(H)3	-8.9	4.1	0.58	-20.5	3.7	0.13						
I(H)4	-8.3	4.1	0.44	-18.4	4.0	0.24						
I(H)5	-8.8	3.6	0.59	-9.4	4.0	0.51						
I(H)6	-23.2	3.4	0.38	-22.4	3.5	0.27						
I(H)7	-9.7	3.6	0.66	-22.2	3.5	0.30						
I(I)1	-9.8	3.8	0.55	-8.7	4.1	0.62						
I(I)2	-6.8	4.3	0.32	-18.0	3.6	0.96						
II(A)1	-6.1	4.7	0.32	-23.4	3.3	0.61	-4.9	5.7	0.06	-23.3	3.1	0.95
II(A)2	-3.7	4.8	0.56	-11.9	3.7	0.20	-5.7	4.3	0.53	-13.3	3.8	0.68
II(A)3	-2.1	5.0	0.41	-22.4	3.4	0.18	-1.1	5.0	0.06	-22.6	3.2	0.42
II(B)1	-7.8	3.9	0.35	-7.4	4.0	0.29	-7.8	3.4	0.79	-9.6	3.8	0.56
II(B)2	-8.2	4.3	0.43	-21.9	3.5	0.29	-6.2	5.2	0.28	-20.3	4.5	0.12
II(B)3	-6.3	4.3	0.25	-21.3	3.4	0.33	-5.8	5.2	0.53	-17.8	3.4	0.64
II(C)1	-9.7	4.1	0.53	-8.2	4.2	0.22						
II(C)2	-6.7	4.4	0.24	-21.4	3.4	0.43						
II(C)3	-7.2	4.4	0.20	-21.1	3.5	0.17						
II(C)4	-8.0	4.3	0.23	-20.8	3.5	0.57						
II(D)1	-9.6	3.9	0.36	-7.9	3.7	0.28	-7.3	4.1	0.90	-6.5	4.3	0.52
II(D)2	-11.1	3.9	0.41	-20.5	4.0	0.74	-7.6	4.7	0.76	-19.8	5.4	0.51
II(D)3	-6.4	4.1	0.30	-21.7	3.6	0.41						
II(E)1	-8.3	3.9	0.27	-8.6	3.9	0.33						
II(F)1	-7.9	3.9	0.32	-9.4	3.9	0.35						
II(F)2	-8.3	3.9	0.32	-21.6	3.5	0.44						
II(F)3	-10.2	4.0	0.66	-19.9	3.4	0.46						
II(F)4	-19.8	3.6	0.53	-20.0	3.7	0.61						
II(F)5	-20.9	3.5	0.33	-8.7	4.0	0.54	-18.2	3.3	0.78	-7.6	2.6	0.27
II(F)6	-8.3	3.9	0.32	-21.6	3.5	0.44						
II(F)7	-21.5	3.4	0.22	-23.1	3.4	0.26						
II(G)1	-9.8	3.8	0.50	-10.2	3.8	0.72						
II(G)2	-8.8	4.0	0.64	-20.1	3.7	0.47						
II(G)3	-9.3	3.9	0.35	-18.8	3.6	0.64						
II(G)4	-19.0	3.7	0.58	-22.6	3.4	0.27						
II(H)1	-9.2	3.7	0.49	-10.0	3.9	0.46						
II(H)2	-9.1	3.7	0.47	-20.9	3.6	0.42						
II(H)3	-22.9	3.6	0.15	-23.6	3.3	0.36						

II(H)4	-7.4	4.3	0.33	-24.4	3.5	0.43							
II(H)5	-20.7	3.6	0.45	-21.2	3.5	0.39							
II(I)1	-8.5	3.6	0.62	-8.8	3.9	0.34							
II(I)2	-9.6	3.6	0.69	-22.1	3.4	0.35							
II(I)3	-10.7	3.9	0.57	-19.8	3.5	0.41							
II(I)4	-19.6	3.7	0.50	-21.2	3.6	0.46							
II(I)5	-8.4	3.9	0.52	-20.5	3.5	0.34							
II(I)6	-20.9	3.6	0.23	-21.3	3.5	0.51							
II(I)7	-21.5	3.4	0.21	-23.2	3.4	0.24							
II(J)1	-9.4	3.4	0.70	-9.8	4.1	0.58							
II(J)2	-9.0	4.2	0.65	-21.0	3.6	0.28							
II(J)3	-9.3	4.1	0.37	-19.5	3.6	0.48							
II(J)4	-22.2	3.4	0.30	-19.6	3.6	0.47							
II(J)5	-10.0	3.5	0.67	-21.3	3.5	0.32							
II(J)6	-19.2	3.6	0.60	-19.3	3.6	0.70							
II(J)7	-20.9	3.6	0.21	-20.1	3.4	0.62							
II(J)8	-21.6	3.4	0.34	-19.1	3.6	0.41							
II(K)1	-9.0	3.4	0.59	-8.4	4.1	0.25							
II(K)2	-7.1	3.8	0.54	-22.4	3.6	0.38							
II(K)3	-7.2	3.8	0.54	-22.5	3.6	0.38							
II(K)4	-9.5	3.4	0.68	-20.6	3.5	0.44							
II(K)5	-9.9	3.4	0.70	-20.8	3.5	0.44							
II(L)1	-9.3	3.9	0.64	-8.5	4.2	0.56							
III(A)1	-8.6	4.2	0.31	-8.6	4.2	0.31	-7.8	4.9	0.28	-8.5	2.5	0.56	
III(A)2	-7.6	4.3	0.24	-25.5	3.2	0.18	-6.5	4.3	0.97	-23.5	2.3	0.61	
III(B)1	-9.1	3.6	0.53	-8.1	4.0	0.29							
III(B)2	-9.8	3.7	0.61	-22.2	3.4	0.27							
III(C)1	-9.3	3.4	0.59	-10.2	4.0	0.35							
III(C)2	-9.6	3.5	0.60	-20.0	3.6	0.49							
III(C)3	-9.2	4.0	0.28	-20.9	3.5	0.50							
III(C)4	-20.8	3.6	0.32	-21.2	3.4	0.52							
III(C)5	-7.6	3.9	0.49	-18.7	3.8	0.61							
III(D)1	-10.2	3.9	0.37	-9.0	3.4	0.58							
III(D)2	-9.0	4.0	0.50	-20.9	3.6	0.33							
III(D)3	-9.3	4.0	0.28	-21.0	3.5	0.50							
III(D)4	-20.8	3.6	0.32	-21.1	3.4	0.52							
III(D)5	-21.3	3.5	0.43	-21.4	3.5	0.35							
III(D)6	-21.7	3.4	0.35	-21.3	3.5	0.38							
III(E)1	-9.6	3.6	0.72	-9.5	4.0	0.32	-8.5	4.3	0.93	-7.1	4.2	0.60	
III(E)2	-9.7	3.5	0.83	-22.0	3.5	0.32	-6.6	4.2	0.34	-20.8	3.3	0.65	
III(E)3	-21.7	3.4	0.44	-22.5	3.4	0.29							
III(F)1	-9.7	3.7	0.45	-9.5	3.7	0.43	-7.7	4.4	0.55	-7.7	4.3	0.86	
III(F)2	-7.3	4.0	0.49	-22.2	3.5	0.42							

III(F)3	-9.4	3.7	0.54	-20.8	3.6	0.45	-8.9	4.8	0.21	-18.0	3.9	0.07
III(F)4	-22.8	3.4	0.34	-22.9	3.4	0.32						
III(G)1	-9.7	3.6	0.68	-10.4	3.8	0.79						
III(G)2	-10.7	3.7	0.89	-22.0	3.5	0.32						
III(G)3	-10.1	3.5	0.68	-20.7	3.6	0.41						
III(G)4	-21.9	3.5	0.34	-21.4	3.5	0.45						
III(G)5	-20.7	3.4	0.47	-22.4	3.5	0.36						
III(G)6	-8.2	4.2	0.78	-19.4	3.7	0.52						
III(G)7	-20.4	3.6	0.47	-21.0	3.5	0.50						
III(H)1	-9.6	3.7	0.35	-9.8	3.7	0.35						
III(H)2	-10.2	3.7	0.79	-21.8	3.4	0.28						
IV(A)1	-9.7	3.7	0.47	-8.6	3.8	0.26	-7.4	4.6	0.93	-7.4	3.9	0.13
IV(A)2	-8.9	3.7	0.35	-20.2	3.6	0.43						
IV(A)3	-9.9	3.5	0.67	-20.1	3.6	0.48						
IV(A)4	-21.2	3.4	0.53	-21.2	3.5	0.40						
IV(A)5	-5.3	4.2	0.17	-18.9	3.7	0.60						
IV(A)6	-21.4	3.5	0.40	-21.0	3.5	0.45						
IV(B)1	-9.6	3.6	0.68	-10.6	3.6	0.81						
IV(B)2	-10.1	3.5	0.85	-22.0	3.5	0.31						
IV(B)3	-10.4	3.5	0.90	-21.8	3.5	0.30						
IV(B)4	-21.7	3.5	0.21	-21.9	3.5	0.22						
IV(B)5	-20.1	3.5	0.47	-22.0	3.5	0.32						

Table B4 The geometric descriptors and their contribution to the ^{23}Na NMR σ parameters for static NMR calculation in CHA(17).

CHA(17)	Geometrical descriptors							Contribution to the ^{23}Na σ (ppm)						
	CN _{Na-O}	d _{Na-O} (Å)	CN _{Na-Si}	$\alpha_{\text{O-Na-O}}$ (°)	d _{minNa-O} (Å)	d _{minNa-Si} (Å)	CN _{Na-O(Al)}	CN _{Na-O}	d _{Na-O} (Å)	CN _{Na-Si}	$\alpha_{\text{O-Na-O}}$ (°)	d _{minNa-O} (Å)	d _{minNa-Si} (Å)	CN _{Na-O(Al)}
I(A)1	6.00	2.66	5.00	99.05	2.27	3.15	4.00	-35.7	106.9	-3.9	-19.4	104.1	36.4	-8.3
	3.00	2.43	6.00	85.45	2.35	3.10	2.00	-17.9	97.7	-4.7	-16.7	107.5	35.8	-4.1
I(A)3	6.00	2.68	4.00	97.26	2.28	3.16	4.00	-35.7	107.5	-3.2	-19.0	104.4	36.5	-8.3
	6.00	2.61	6.00	98.06	2.37	3.20	0.00	-35.7	104.9	-4.7	-19.2	108.4	37.0	0.0
I(C)1	6.00	2.64	5.00	98.10	2.25	3.18	2.00	-35.7	106.0	-3.9	-19.2	102.8	36.8	-4.1
	6.00	2.66	5.00	97.15	2.29	3.08	2.00	-35.7	106.7	-3.9	-19.0	104.9	35.6	-4.1
I(C)3	6.00	2.65	5.00	98.04	2.28	3.08	2.00	-35.7	106.3	-3.9	-19.2	104.4	35.6	-4.1
	3.00	2.47	7.00	85.05	2.32	3.19	2.00	-17.9	99.0	-5.5	-16.6	106.0	36.9	-4.1
I(E)1	6.00	2.64	5.00	98.74	2.31	3.13	2.00	-35.7	105.9	-3.9	-19.3	105.6	36.2	-4.1
	3.00	2.39	4.00	87.08	2.37	3.01	3.00	-17.9	96.0	-3.2	-17.0	108.7	34.8	-6.2
I(E)3	6.00	2.65	5.00	97.98	2.29	3.11	2.00	-35.7	106.2	-3.9	-19.2	104.7	35.9	-4.1
	6.00	2.67	5.00	96.29	2.27	3.11	2.00	-35.7	107.0	-3.9	-18.8	104.1	35.9	-4.1
I(E)4	6.00	2.65	5.00	97.57	2.27	3.12	2.00	-35.7	106.4	-3.9	-19.1	104.0	36.1	-4.1
	3.00	2.44	7.00	85.60	2.30	3.13	2.00	-17.9	97.9	-5.5	-16.7	105.2	36.1	-4.1
I(F)1	6.00	2.65	5.00	96.99	2.29	3.14	2.00	-35.7	106.2	-3.9	-19.0	104.8	36.3	-4.1
	6.00	2.66	5.00	95.96	2.28	3.07	2.00	-35.7	107.0	-3.9	-18.8	104.5	35.5	-4.1
I(F)2	6.00	2.63	6.00	99.38	2.35	3.14	2.00	-35.7	105.4	-4.7	-19.4	107.7	36.3	-4.1
	3.00	2.41	5.00	85.40	2.32	2.98	3.00	-17.9	96.7	-3.9	-16.7	106.4	34.4	-6.2
I(G)1	6.00	2.65	5.00	97.49	2.27	3.14	2.00	-35.7	106.3	-3.9	-19.1	103.8	36.3	-4.1
	6.00	2.65	5.00	97.59	2.27	3.14	2.00	-35.7	106.2	-3.9	-19.1	103.8	36.3	-4.1
II(A)1	6.00	2.64	7.00	100.44	2.35	3.15	4.00	-35.7	106.1	-5.5	-19.6	107.7	36.4	-8.3
	3.00	2.45	4.00	84.91	2.44	3.08	2.00	-17.9	98.4	-3.2	-16.6	111.5	35.6	-4.1

II(A)2	5.00	2.48	4.00	99.64	2.32	3.24	4.00	-29.8	99.7	-3.2	-19.5	106.3	37.5	-8.3
	6.00	2.63	6.00	97.61	2.36	3.21	0.00	-35.7	105.4	-4.7	-19.1	108.2	37.1	0.0
II(B)1	6.00	2.64	5.00	97.58	2.31	3.13	2.00	-35.7	106.2	-3.9	-19.1	105.9	36.2	-4.1
	6.00	2.65	5.00	97.24	2.28	3.15	2.00	-35.7	106.4	-3.9	-19.0	104.5	36.3	-4.1
II(B)2	6.00	2.63	6.00	99.47	2.28	3.16	2.00	-35.7	105.6	-4.7	-19.5	104.3	36.5	-4.1
	3.00	2.45	7.00	85.63	2.35	3.12	2.00	-17.9	98.3	-5.5	-16.7	107.6	36.0	-4.1
II(B)3	6.00	2.64	5.00	98.09	2.28	3.13	2.00	-35.7	106.2	-3.9	-19.2	104.2	36.1	-4.1
	3.00	2.45	7.00	85.29	2.35	3.16	2.00	-17.9	98.3	-5.5	-16.7	107.4	36.6	-4.1
II(D)1	6.00	2.64	5.00	98.49	2.30	3.12	2.00	-35.7	105.9	-3.9	-19.3	105.1	36.1	-4.1
	6.00	2.67	5.00	96.04	2.29	3.10	2.00	-35.7	107.2	-3.9	-18.8	104.8	35.8	-4.1
II(D)2	6.00	2.63	7.00	99.44	2.33	3.17	2.00	-35.7	105.7	-5.5	-19.5	106.5	36.7	-4.1
	4.00	2.75	6.00	90.87	2.30	3.20	3.00	-23.8	110.5	-4.7	-17.8	105.3	37.0	-6.2
II(F)5	3.00	2.45	7.00	85.74	2.34	3.12	2.00	-17.9	98.3	-5.5	-16.8	107.3	36.0	-4.1
	6.00	2.65	5.00	97.65	2.26	3.14	2.00	-35.7	106.5	-3.9	-19.1	103.4	36.3	-4.1
III(A)1	6.00	2.64	5.00	97.68	2.30	3.15	2.00	-35.7	106.1	-3.9	-19.1	105.5	36.4	-4.1
	6.00	2.64	5.00	97.68	2.30	3.15	2.00	-35.7	106.1	-3.9	-19.1	105.5	36.4	-4.1
III(A)2	6.00	2.61	7.00	100.89	2.31	3.12	2.00	-35.7	104.8	-5.5	-19.7	105.7	36.0	-4.1
	3.00	2.49	6.00	84.31	2.39	3.14	2.00	-17.9	99.9	-4.7	-16.5	109.5	36.3	-4.1
III(E)1	6.00	2.67	5.00	96.58	2.27	3.14	2.00	-35.7	107.0	-3.9	-18.9	103.9	36.3	-4.1
	6.00	2.66	5.00	97.11	2.28	3.15	2.00	-35.7	106.8	-3.9	-19.0	104.6	36.3	-4.1
III(E)2	6.00	2.67	5.00	95.95	2.26	3.17	2.00	-35.7	107.4	-3.9	-18.8	103.6	36.6	-4.1
	3.00	2.46	7.00	84.90	2.34	3.15	2.00	-17.9	98.8	-5.5	-16.6	107.4	36.4	-4.1
III(F)1	6.00	2.67	5.00	96.79	2.30	3.10	2.00	-35.7	107.0	-3.9	-18.9	105.1	35.9	-4.1
	6.00	2.67	5.00	96.69	2.30	3.10	2.00	-35.7	107.0	-3.9	-18.9	105.1	35.8	-4.1
III(F)3	6.00	2.67	5.00	96.36	2.28	3.11	2.00	-35.7	107.2	-3.9	-18.8	104.5	36.0	-4.1
	3.00	2.45	6.00	85.47	2.32	3.13	2.00	-17.9	98.5	-4.7	-16.7	106.4	36.2	-4.1

Table B5 The geometric descriptors and their contribution to the ^{23}Na NMR σ parameters for MD NMR calculation in CHA(17).

CHA(17)	Geometrical descriptors							Contribution to the ^{23}Na σ (ppm)						
	CN _{Na-O}	d _{Na-O} (Å)	CN _{Na-Si}	$\alpha_{\text{O-Na-O}}$ (°)	d _{minNa-O} (Å)	d _{minNa-Si} (Å)	CN _{Na-O(Al)}	CN _{Na-O}	d _{Na-O} (Å)	CN _{Na-Si}	$\alpha_{\text{O-Na-O}}$ (°)	d _{minNa-O} (Å)	d _{minNa-Si} (Å)	CN _{Na-O(Al)}
I(A)1	5.95	2.65	6.32	100.60	2.23	3.11	4.00	-35.4	106.2	-5.0	-19.7	102.3	36.0	-8.2
	3.63	2.61	5.81	91.27	2.29	3.10	2.00	-21.6	104.6	-4.6	-17.9	104.7	35.8	-4.1
I(A)3	5.79	2.66	4.89	97.83	2.24	3.14	4.00	-34.5	106.6	-3.9	-19.1	102.4	36.3	-8.3
	5.95	2.67	6.24	95.75	2.31	3.15	0.00	-35.4	107.1	-4.9	-18.7	105.5	36.4	0.0
I(C)1	5.89	2.67	5.66	96.58	2.23	3.15	2.00	-35.1	107.3	-4.5	-18.9	102.2	36.4	-4.1
	5.01	2.67	5.60	94.02	2.26	3.14	2.03	-29.8	107.2	-4.4	-18.4	103.6	36.3	-4.2
I(C)3	5.80	2.67	5.49	95.69	2.25	3.07	2.00	-34.5	107.3	-4.3	-18.7	102.9	35.5	-4.1
	5.75	2.67	5.58	95.94	2.23	3.16	2.02	-34.2	107.2	-4.4	-18.8	102.3	36.5	-4.2
I(E)1	5.98	2.66	6.38	97.91	2.26	3.11	2.00	-35.6	107.0	-5.0	-19.2	103.3	36.0	-4.1
	3.51	2.53	4.43	91.84	2.29	2.99	3.46	-20.9	101.5	-3.5	-18.0	105.0	34.5	-7.1
I(E)3	5.99	2.67	6.15	97.66	2.24	3.11	2.00	-35.7	107.0	-4.9	-19.1	102.4	36.0	-4.1
	5.87	2.67	5.76	96.77	2.25	3.11	2.00	-35.0	107.0	-4.5	-18.9	103.1	36.0	-4.1
I(E)4	5.94	2.67	5.85	97.12	2.23	3.13	2.00	-35.4	107.3	-4.6	-19.0	102.3	36.2	-4.1
	3.45	2.57	6.63	89.23	2.28	3.14	2.00	-20.5	103.3	-5.2	-17.5	104.2	36.3	-4.1
I(F)1	5.96	2.65	6.20	97.65	2.25	3.14	2.00	-35.5	106.5	-4.9	-19.1	102.8	36.2	-4.1
	5.91	2.65	6.05	97.03	2.24	3.06	2.00	-35.2	106.2	-4.8	-19.0	102.5	35.3	-4.1
I(F)2	5.95	2.65	6.54	97.97	2.27	3.12	1.99	-35.4	106.3	-5.2	-19.2	103.9	36.1	-4.1
	3.46	2.55	4.49	89.92	2.31	2.99	3.28	-20.6	102.2	-3.5	-17.6	105.7	34.6	-6.8
I(G)1	5.91	2.67	5.81	96.08	2.21	3.12	2.00	-35.2	107.0	-4.6	-18.8	101.3	36.0	-4.1
	5.90	2.66	5.90	96.55	2.21	3.12	2.00	-35.1	106.7	-4.7	-18.9	101.3	36.0	-4.1
II(A)1	5.90	2.64	6.08	100.60	2.28	3.14	4.00	-35.1	105.9	-4.8	-19.7	104.5	36.2	-8.3
	3.69	2.63	4.67	92.35	2.34	3.06	2.20	-21.9	105.6	-3.7	-18.1	107.1	35.3	-4.6
II(A)2	5.59	2.60	4.87	98.59	2.28	3.16	4.00	-33.3	104.4	-3.8	-19.3	104.6	36.5	-8.3

II(B)1	5.98	2.66	6.30	96.27	2.31	3.15	0.00	-35.6	106.7	-5.0	-18.8	105.6	36.4	0.0
	5.91	2.66	5.64	97.20	2.26	3.12	2.00	-35.2	106.7	-4.5	-19.0	103.5	36.1	-4.1
II(B)2	5.96	2.68	5.59	96.19	2.27	3.15	2.00	-35.5	107.6	-4.4	-18.8	103.7	36.4	-4.1
	6.00	2.64	6.75	99.61	2.26	3.13	2.02	-35.7	106.1	-5.3	-19.5	103.3	36.2	-4.2
II(B)3	3.36	2.57	6.37	88.89	2.29	3.12	1.99	-20.0	103.0	-5.0	-17.4	104.8	36.0	-4.1
	5.98	2.65	6.27	98.21	2.25	3.11	2.00	-35.6	106.6	-4.9	-19.2	103.1	36.0	-4.1
II(D)1	4.08	2.62	6.07	90.19	2.29	3.19	2.07	-24.3	105.1	-4.8	-17.6	105.0	36.8	-4.3
	5.95	2.66	6.19	98.04	2.25	3.10	2.00	-35.4	106.6	-4.9	-19.2	103.0	35.9	-4.1
II(D)2	5.85	2.66	6.02	97.12	2.24	3.10	2.00	-34.8	106.8	-4.7	-19.0	102.7	35.8	-4.1
	6.00	2.66	6.52	98.70	2.27	3.11	2.00	-35.7	106.6	-5.1	-19.3	103.8	36.0	-4.1
II(F)5	3.94	2.69	4.66	92.26	2.29	3.07	2.73	-23.5	108.1	-3.7	-18.0	104.9	35.5	-5.6
	3.79	2.62	6.22	89.16	2.27	3.12	2.15	-22.6	105.1	-4.9	-17.4	103.7	36.1	-4.4
III(A)1	5.95	2.67	6.03	97.13	2.24	3.13	2.00	-35.4	107.2	-4.8	-19.0	102.6	36.2	-4.1
	5.93	2.65	5.80	97.43	2.27	3.13	2.00	-35.3	106.5	-4.6	-19.1	103.8	36.1	-4.1
III(A)2	5.85	2.64	5.62	97.16	2.28	3.13	2.00	-34.8	106.1	-4.4	-19.0	104.4	36.2	-4.1
	5.97	2.64	6.99	100.19	2.27	3.11	2.00	-35.5	105.8	-5.5	-19.6	103.8	35.9	-4.1
III(E)1	3.48	2.62	5.79	88.86	2.33	3.12	1.93	-20.7	105.1	-4.6	-17.4	106.7	36.0	-4.0
	5.95	2.67	5.70	96.73	2.25	3.12	1.99	-35.4	107.2	-4.5	-18.9	102.9	36.1	-4.1
III(E)2	5.93	2.67	5.77	97.02	2.25	3.13	2.00	-35.3	107.1	-4.5	-19.0	103.1	36.1	-4.1
	5.94	2.66	5.84	97.48	2.24	3.10	2.00	-35.4	106.8	-4.6	-19.1	102.7	35.9	-4.1
III(F)1	3.48	2.59	6.40	90.42	2.29	3.14	1.99	-20.7	104.1	-5.0	-17.7	104.9	36.3	-4.1
	5.91	2.66	6.14	97.28	2.25	3.10	2.00	-35.2	106.7	-4.8	-19.0	102.9	35.9	-4.1
III(F)3	5.93	2.67	5.92	96.96	2.25	3.11	2.00	-35.3	107.0	-4.7	-19.0	102.9	35.9	-4.1
	5.96	2.68	5.68	96.79	2.25	3.14	2.00	-35.5	107.5	-4.5	-18.9	103.2	36.3	-4.1
	3.55	2.58	5.94	90.87	2.26	3.10	2.03	-21.2	103.5	-4.7	-17.8	103.6	35.8	-4.2

List of Publications

1. **Lei, C.**; Bornes, C.; Bengtsson, O.; Erlebach, A.; Slater, B.; Grajciar, L.; Heard, C. J., A machine learning approach for dynamical modelling of Al distributions in zeolites via $^{23}\text{Na}/^{27}\text{Al}$ solid-state NMR. *Faraday Discussions* **2024**.
2. **Lei, C.**; Erlebach, A.; Brivio, F.; Grajciar, L.; Tošner, Z.; Heard, C. J.; Nachtigall, P., The need for operando modelling of ^{27}Al NMR in zeolites: the effect of temperature, topology and water. *Chemical Science* **2023**, *14* (34), 9101-9113.
3. Jin, M.; Ravi, M.; **Lei, C.**; Heard, C. J.; Brivio, F.; Tošner, Z.; Grajciar, L.; van Bokhoven, J. A.; Nachtigall, P., Dynamical Equilibrium between Brønsted and Lewis Sites in Zeolites: Framework-Associated Octahedral Aluminum. *Angewandte Chemie International Edition* **2023**, *62* (31), e202306183.
4. H. Mohideen, M. I.; **Lei, C.**; Tuček, J.; Malina, O.; Brivio, F.; Kasneryk, V.; Huang, Z.; Mazur, M.; Zou, X.; Nachtigall, P.; Čejka, J.; Morris, R. E., Magneto-structural correlations of novel kagomé-type metal organic frameworks. *Journal of Materials Chemistry C* **2019**, *7* (22), 6692-6697.