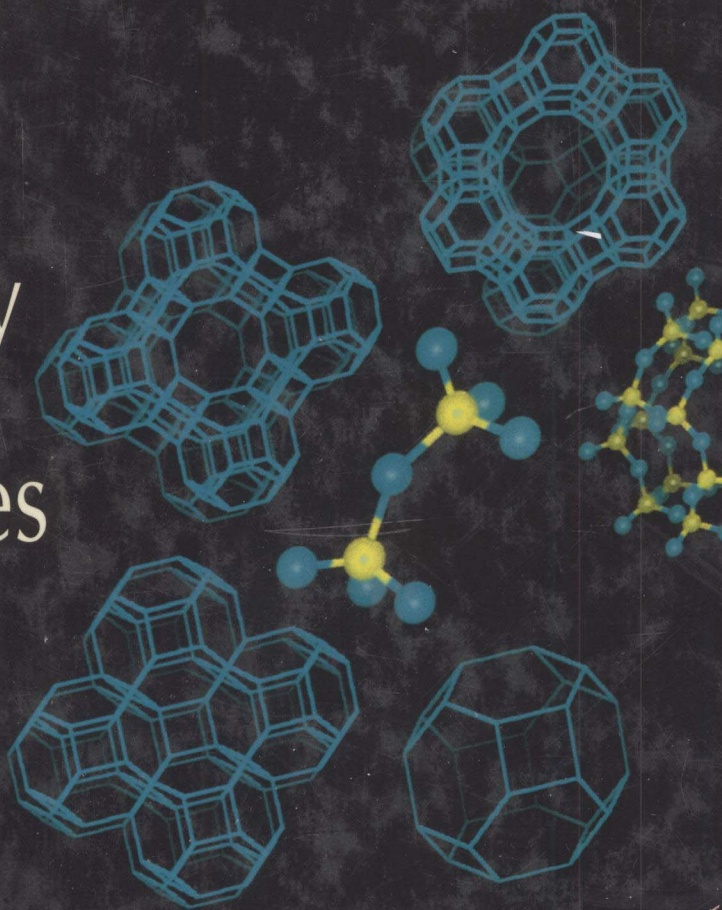


# Modelling of Structure and Reactivity in Zeolites



edited by C.R.A. Catlow

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*edited by*

**C.R.A. Catlow**

*The Royal Institution, London.*



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# **Modelling of Structure and Reactivity in Zeolites**

## Preface

Zeolites form an extraordinarily diverse and exciting class of advanced inorganic materials which are attracting increasing attention owing to their ion-exchange, molecular sieving but above all to their wide-ranging 'shape-selective' catalytic properties. These in turn arise from their acidity, from their ability to accommodate a wide range of metallic species and from their microporous crystal structures. One of the most significant developments in zeolite science in recent years has been the use in their study of the techniques of computational chemistry. Simulation methods are having a substantial impact on our understanding of the diffusion and docking of molecules within the pores of microporous materials; they are also helping us to understand (and hopefully in the future to predict) the complex crystal structures adopted by this class of solids. Moreover, the phenomenon of nucleation and growth of these crystals is also amenable to theoretical study. Perhaps the greatest challenge comes in the application of quantum mechanical techniques to the study of reaction mechanisms and pathways of sorbed organic molecules. Moreover, all areas of the field are illuminated and assisted by the availability of high-quality molecular graphics.

This book aims to illustrate and discuss these themes and to show the current capabilities and future potential of theoretical and computational methods in zeolite science.

Many of the authors of this volume met at the 8th International Zeolite Conference organised by R.A. van Santen and P.A. Jacobs held in Amsterdam in July, 1989. The editor is grateful to Professor van Santen for his support for and many contributions to the application of theoretical techniques to the study of zeolites. Similar thanks are due to Professor Sir John Meurig Thomas to whom the field discussed in this book also owes many debts of gratitude.

C.R.A. CATLOW  
July, 1991

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# **Zeolites: Structure, Synthesis and Properties—An Introduction**

**C.R.A. Catlow**

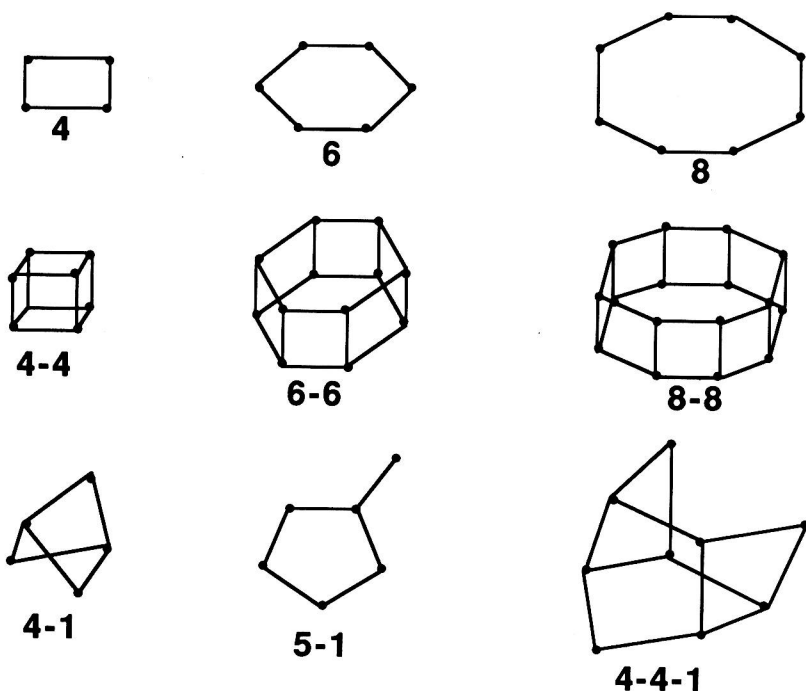
## **1 INTRODUCTION**

Zeolites are microporous inorganic compounds, that is their crystal structures contain large pores and voids; effective pore sizes in microporous solids range from  $\sim 3 \text{ \AA}$  to over  $10 \text{ \AA}$ , sufficient to permit the diffusion of organic molecules—a feature which gives rise to many of the most important applications of the materials. The strict definition of the term zeolite is restricted to aluminosilicates; but in practice, the field now encompasses microporous aluminophosphates, and even germanates.

Interest in zeolites has been fuelled by their widescale use, first as heterogeneous catalysts, where the ‘shape and selectivity’ conferred upon the materials by their microporous structure is vitally important. Older, but still very relevant, applications are in gas separation and ion exchange; aluminosilicates commonly contain relatively loosely bound cations in their pores which can be readily exchanged with other cations from solution. These applications will be discussed in greater detail below. The next section will summarize the crystal chemistry of zeolites, which we follow with a brief account of their hydrothermal synthesis. Later sections of the chapter will review the need for modelling and introduce the techniques currently in use.

## **2 CRYSTAL CHEMISTRY**

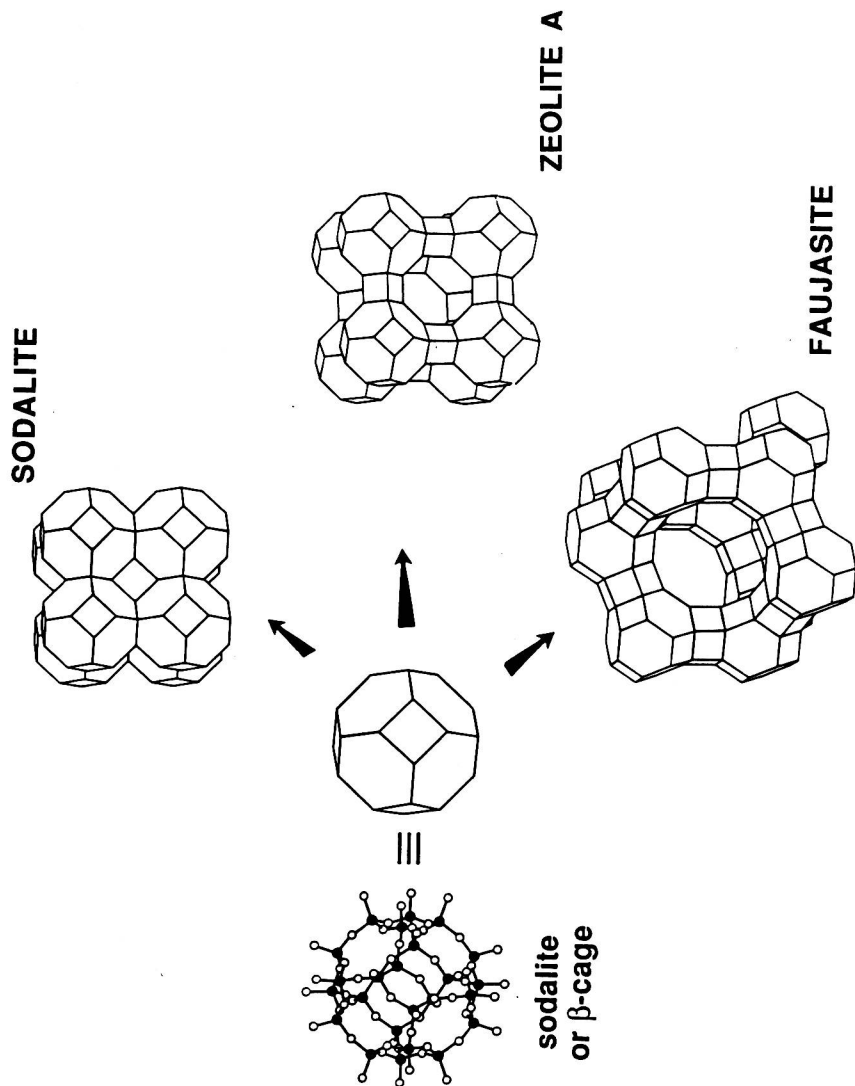
In common with the vast majority of silicate systems, zeolites have structures based on  $\text{TO}_4$  tetrahedra, where T is a silicon or aluminium atom (or phosphorus in the related aluminophosphates). The tetrahedra share all



**Figure 1.1** Secondary building units (SBU) in zeolites. The corner of the polyhedra represent tetrahedral (Y) atoms.

corners, thus generating a three-dimensional network. As noted, the resulting networks have low densities with large pores and voids. The structures are commonly discussed in terms of levels of organization above the basic tetrahedral units known as secondary building units (SBU), comprising single- or double-ring structures as illustrated in Fig. 1.1, which in turn are linked together to generate the structure of the zeolite. Higher subsidiary levels of structural organization can be identified in polyhedral building blocks, for example the 'sodalite unit' (or  $\beta$  cage) shown in Fig. 1.2 which comprises both four- and six-rings linked together to form a cubo-octahedron; each of the 'vertices' of this truncated octahedron has a four-ring of T atoms, while the eight faces are six-rings as shown in the figure. The cage has an internal free diameter of  $\sim 6 \text{ \AA}$  assuming a conventional van der Waals radius for oxygen—sufficient to encapsulate small molecules.

Different modes of linking of sodalite units generate some of the commonest zeolite structures. By fusing the units together via their four-rings we generate the structure of sodalite itself, which is both a naturally occurring



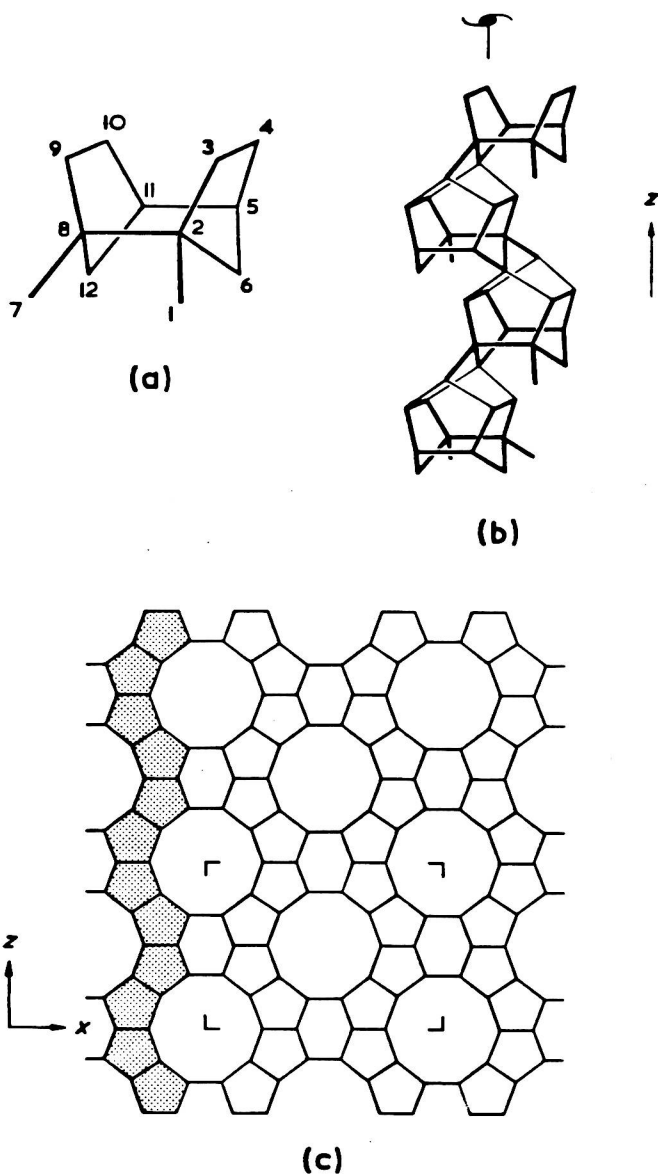
**Figure 1.2** The sodalite or  $\beta$  cage, linked to create the structures of sodalite, zeolite A and faujasite (zeolite X/Y).

mineral and a widely synthesized industrial material. One of the most celebrated variants based on the sodalite structure is the beautiful blue dye ultramarine in which  $S_3^-$  radicals (which adsorb in the red region of the visible spectrum) are trapped within the sodalite cage.

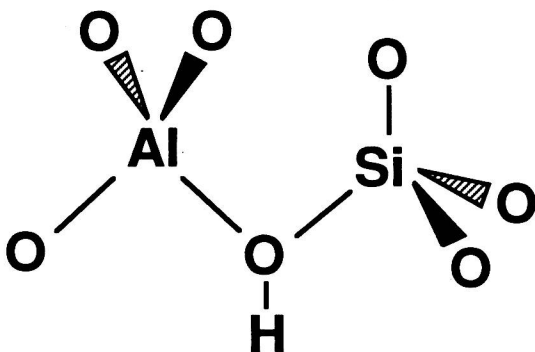
Bridging (rather than fusing) of sodalite units via four-rings generates the structure of zeolite A also shown in Fig. 1.2. The structure, which does not occur naturally, is very extensively synthesized owing to its use in ion exchange, gas separation and drying. An alternative mode of bridging, via six-rings, generates what is probably the single most important zeolite structure, illustrated in Fig. 1.2, and referred to as zeolite X or Y depending on the Si/Al ratio, as discussed below. The structure is also adopted by the rare mineral faujasite. The most intriguing feature of this framework is that the mode of linkage of the sodalite units generates very large voids, known as 'supercages', also shown in Fig. 1.2. Access to these voids is via large 'windows', also evident in the figure, whose molecular diameter is  $\sim 7.4$  Å. This allows organic molecules to diffuse both in and out of the supercages, and the zeolite is indeed one of the most important catalytic systems, being widely used in the cracking of long to shorter chain molecules in the gasoline range.

Detailed discussions of zeolite structures are available in refs 1 and 2 and in later chapters in this book (see especially Chapter 6 for illustrations of several structures). Here we draw attention only to one of several other classes of structure, namely the pentasil zeolites, so called as they are constructed of five rings. The most important of these is ZSM-5, shown in Fig. 1.3(c), which is used in a variety of catalytic applications, including both isomerization reactions and synthesis of hydrocarbons in the gasoline range from methanol. The SBU on which the pentasil class of structures is based is shown in Fig. 1.3(a). Their linkage to form chains is shown in Fig. 1.3(b), and Fig. 1.3(c) illustrates the joining of the resulting chains to give layers. In ZSM-5 the neighbouring layers are connected so that they are related by an inversion (*i*) operator; in a closely related structure (ZSM-11) a reflection operator ( $\sigma$ ) relates the neighbouring layers. The channel structure differs in the two zeolites: ZSM-5 comprises both straight and sinusoidal channels, whereas in ZSM-11 the interconnecting channels are both straight. Intergrowth of the two structural types is possible.<sup>3</sup> Moreover, several other pentasils have been synthesized in recent years. There are many other useful approaches to zeolite structural chemistry. An especially fruitful approach is based on the topological properties of two-dimensional three-connected nets which can generate three-dimensional nets by alternating up and down linkages. A detailed discussion of such models is given in Chapter 2.

One of the most interesting, but difficult, problems in zeolite structural



**Figure 1.3** (a) SBU in pentasil zeolites. (b) Linkage of SBUs to form chains. (c) Linkage of chains to generate layers in ZSM-5 structure.

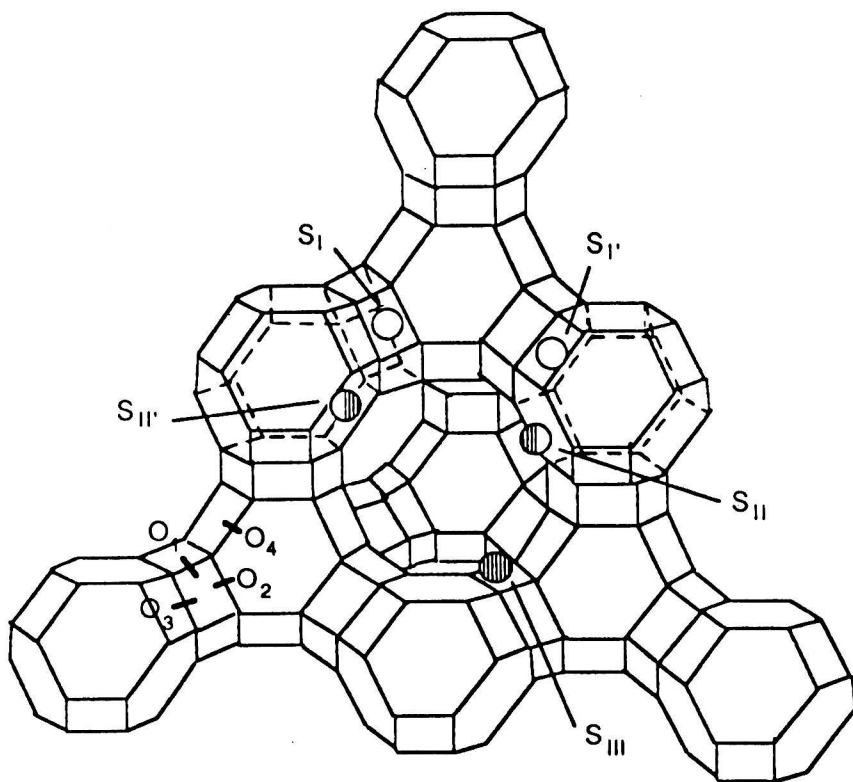


**Figure 1.4** Bridging hydroxyl group in aluminium substituted zeolites.

chemistry concerns the distribution of silicon and aluminium atoms over the T sites. The problem has been extensively investigated by a variety of theoretical and experimental techniques, as discussed in later chapters in this book. One of the guiding principles in this area has been Lowenstein's rule<sup>4</sup> which forbids Al-O-Al bridges. Despite controversy some years ago, it is now clear that in general zeolite structures accord with Lowenstein's rule (for which there is detailed crystallographic evidence for the case of zeolite A<sup>5</sup>) although a recent intriguing study of Barnes and coworkers<sup>6</sup> found evidence for non-Lowensteinian distributions in sodalite materials that had been synthesized at high temperatures.

The range of Si/Al ratios varies a great deal between different zeolites. ZSM-5 can only tolerate low levels of aluminium substitution; and an almost purely siliceous version of this structure (silicalite) can be synthesized. Zeolite X/Y can be prepared with Si/Al ratios varying from close to infinity (i.e. a nearly pure siliceous material) to  $\sim 1$ ; the lower ratios correspond to 'X' and the higher to 'Y'. Zeolite A is normally obtained with a Si/Al ratio of close to unity and a fully ordered Si-Al distribution over the tetrahedral sites, in accordance with Lowenstein's rule.

The incorporation of aluminium into the structure has two other major consequences. First the replacement of silicon by aluminium results in a net negative charge for the framework. This can be neutralized by protons which, it is generally accepted, are firmly bonded to the lone pairs of the bridging oxygen species—see Fig. 1.4. These acidic hydroxyl groups play a vital role in the catalytic activity of zeolites. Other acid sites present at defect or surface sites may also play an additional role. Alternatively, extra-framework cations, either monovalent (e.g.  $\text{Na}^+$ ,  $\text{K}^+$ ), divalent (e.g.  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ) or trivalent (e.g.  $\text{La}^{3+}$ ), may be incorporated into extra-framework sites.



**Figure 1.5** Extra-framework cation sites in zeolite X/Y.

Generally these are in some well-defined location with respect to the framework. For example, Fig. 1.5 shows cation sites occupied in zeolites X/Y. Thus the sites  $S_I$  are within the hexagonal prisms created on linking six-rings of the neighbouring sodalite cages; the  $S_{II'}$  are adjacent to the same six-rings but project into the sodalite cages. The  $S_{II}$  sites are next to non-linking six-rings and project out into the supercage; the  $S_{II'}$  sites are next to the same ring and again project into the sodalite unit. Other, less frequently occupied, sites ( $S_{III}$ ) are adjacent to four-rings. We shall see in later chapters how theory and modelling can play a major part in providing an understanding of the factors controlling cation distribution in zeolites.

The second consequence of the inclusion of aluminium in the zeolite framework is that the materials become hydrophilic. Indeed, as normally prepared the materials are extensively hydrated. Some of this water can be ascribed to hydration of the extra-framework cations. But additional mole-

cules may be loosely bonded to the framework. There is little detailed structural information on hydrated zeolites, with most structural studies being reported on samples that have been dehydrated (typically by heating to  $\sim 300$ – $400^\circ\text{C}$  for several hours).

Many other types of atom can be substituted into zeolite frameworks. A wide range of gallo silicates have been synthesized; but transition metal atoms such as titanium and iron have also been successfully introduced at tetrahedral sites, often with interesting and important consequences for the catalytic behaviour of the materials. In addition, as noted in the Introduction, a whole class of microporous aluminophosphates are now being extensively studied.

## 2.1 Structural investigations

The same structure techniques are used in investigating zeolites as are employed in the study of other complex inorganic materials. *X-ray diffraction* plays a major role. However, the limited availability of single crystals has required extensive use of high resolution powder methods. The ability to recover high-quality structural information from powder data was first established in the field of neutron diffraction where the technique of Rietveld or 'profile' refinement was developed in the early 1970s. The loss of information in a powder pattern due to peak overlap is at least partially overcome by analysing the whole profile expressed as a sum of component Bragg reflections with well-defined line shapes. The latter point is crucial; and, indeed, the technique was first developed in the field of neutron diffraction, as when using conventional instrumentation with reactor sources the Bragg peaks in neutron studies are accurately Gaussian. Several *powder neutron studies* of zeolites (e.g. refs 7–11) have therefore been reported during the last ten years. A further major advantage of neutron methods is that, unlike X-rays, there is a significant difference between the scattering lengths for neutrons of silicon and aluminium, allowing Si–Al distributions over the T sites to be studied. Moreover, the substantial scattering power of hydrogen for neutrons means that proton positions can be studied (although in practice deuterated samples are normally used to remove the large incoherent background observed when protonated materials are investigated).

Increasing use is, however, being made of powder X-ray methods. High-quality profile refinements are possible when synchrotron radiation is employed as the X-ray source, as the resulting Bragg peaks are narrow and well defined. A recent elegant study was reported by McCusker,<sup>12</sup> who used *ab initio* crystallographic methods with synchrotron X-ray powder data in order to solve the structure of a complex zeolite, sigma-2. Further studies of



this type are to be expected in the future; and recently Kaszkur *et al.*<sup>13</sup> have successfully located halogenated hydrocarbons sorbed in zeolite Y using these techniques.

High resolution electron microscopy provides the exciting opportunity of directly imaging zeolite structures. The technique is most appropriate in studying extended faults such as intergrowths for which diffraction, which is essentially an averaging technique, is inappropriate. Illustrations are provided by the early work of Thomas and Millward<sup>3</sup> who, as discussed above, detected intergrowths of ZSM-5 and ZSM-11. Elegant studies have been reported by Newsam *et al.*,<sup>14</sup> who showed that the structure of zeolite  $\beta$  was an intergrowth of two polymorphs—a topic that has been investigated theoretically, as discussed in Chapter 3. An excellent recent review of the field is given by Thomas.<sup>15</sup>

During the last decade, *magic angle spinning (MAS) nuclear magnetic resonance (NMR)* has had a major impact on zeolite chemistry. The magic angle technique allows high resolution data to be obtained for solids, since spinning the sample at the magic angle of  $54^{\circ}.44'$  effectively removes most of the line broadening influences in the solid state NMR spectrum. The greatest amount of work has been reported for  $^{29}\text{Si}$ -NMR. The value of the technique is that the chemical shift depends upon the local environment of the nucleus; and, in particular, a different shift will be produced depending on whether a particular silicon atom has 0, 1, 2, 3, or 4 silicon atoms in the four surrounding tetrahedral sites. A good discussion is given in ref. 16. Such information assists the development of models for the short-range order of silicon and aluminium atoms over the tetrahedral sites.

An intriguing recent development is the use of '2D-NMR' methods (using both the COSY and analogues of the NOESY methods) which have been applied extensively in solution NMR studies and which allow detailed studies of the couplings between spins acting both through space and along bonds. Such techniques (a good discussion of which is given by Fyfe *et al.*<sup>17</sup>) allow the connectivity of the different sites (characterized by different chemical shifts) to be determined—thereby providing valuable additional information in building up a three-dimensional structure. Fyfe *et al.*<sup>17</sup> have demonstrated the value of the approach with a complex zeolite ZSM-39; they also show how 2D-NMR studies can be fruitfully combined with high resolution powder diffraction techniques.

An increasingly important role in zeolite studies is being played by the X-ray spectroscopic method EXAFS (Extended X-ray Absorption Fine Structure), which examines the oscillations in intensity which occur on the high-energy side of X-ray absorption edges caused by the excitation of electrons from core levels into continuum states. Fig. 1.6 shows a typical example: the Ni K edge spectrum from hydrated nickel zeolite Y. The oscil-