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Recent Computational Studies in Solid State Chemistry

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IN HONOR OF SIR JOHN MEURIG THOMAS ON HIS 60TH BIRTHDAY

We discuss the role of computational studies in solid state chemistry. The principle methodologies are first summarized. We then highlight some areas in which there has been rapid recent progress. These include the modeling of crystal structures, the behavior of defects and dopants in ceramic oxides, and the interaction of molecules with Brønsted acid sites in zeolites. We emphasize the increasingly predictive nature of simulation techniques in solid state chemistry.

Introduction

Computational methods are now a central technique in solid state science. The field has changed qualitatively in recent years with the focus moving from reproduction (and illumination) of experimental data to detailed *predictive* calculations on highly complex systems. Examples of recent achievements include the elegant *ab initio* electronic structure studies of the 7 × 7 reconstruction of the surface of silicon by Stich *et al.* (*1*), the elucidation of the details of the mechanism of activation of the microporous catalytic system Ni-zeolite Y (George *et al.* (*2*); Catlow and Thomas (*3*)), and the prediction (prior to observation) of the elastic constants and equation of state (EoS) of the high pressure, perovskite related polymorph of $MgSiO_3$ which comprises a major component of the lower part of the earth mantle (Cohen (*4*)). Accurate knowledge of the EoS is essential if seismic data are to be interpreted in terms of the temperature and composition of the mantle.

Several recent reviews of the field are available (see, e.g., Catlow and Price, (*5*); Harding, (*6*); Catlow, (*7*); Catlow *et al.* (*8*), and we shall not present a broad account of either the methodologies or achievements of computational solid state chemistry. Rather, we will discuss a number of recent developments in our own work which highlight the trend towards realistic and accurate predictions in complex systems. The themes we emphasise concern the development of high quality *interatomic potentials,* the refinement and prediction of the *structures,* of both *crystalline* and *amorphous solids,* the accurate and predictive modeling of the behavior of *impurities in ceramics,* and finally the elucidation of the mechanisms of *protonation* of molecules in *microporous acid catalysts.*

2. Methodologies

Computational solid state chemistry employs the full range of techniques available to the computational chemist and solid state physicist. It is useful to classify these into first, *simulations* which are based on an effective potential which subsumes knowledge of electronic structure into a numerical or analytical function describing the variation of the total energy of the system with

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the position of the nuclei. Such potentials may then be used in energy minimizations (EM) and in Monte Carlo (MC) and molecular dynamics (MD) simulations. The first of these allows an economical determination of minimum energy structures for crystals, defects, surfaces, and sorbed molecules, but is limited by the static lattice approximation; the second allows ensemble averages (and their variation with temperature) to be studied; the third yields full dynamical detail albeit for a limited time period (<1 ns with currently available computer resources). The simulation methodologies are now well developed and the crucial factor limiting progress concerns the accuracy of the interatomic potentials, a topic to which we return below.

Electronic structure techniques, in which the Schrödinger equation is solved to some level of approximation, are also used increasingly in solid state studies. Hartree–Fock methods have dominated in computational chemistry and the techniques employed range from semiempirical (in which matrix elements are approximated using empirical data or ignored) to *ab initio* in which all integrals (above a threshold) are evaluated analytically or numerically. The former may now be used to study systems with large numbers (>100) atoms; while the latter give more precise information on smaller systems and can be used to refine models developed via semiempirical techniques. Calculations may be performed on clusters (with embedding procedures, in which the cluster is surrounded by some approximate representation of the rest of system, being increasingly used), or on periodic arrays of atoms. In the latter category the periodic, Hartree–Fock code CRYSTAL developed by Dovesi, Pisani, Roetti, Saunders, and coworkers (see, e.g., Pisani *et al.* (9) deserves special notice, owing to the impact it is having on our understanding of the electronic structure and properties of insulating solids.

Local density approximation (LDA) techniques, which have been extensively used in the solid state physics community, are now increasingly recognized as an important technique in solid state chemistry. The essence of the local density approximation is the use in evaluating the total energy of the system of expressions for the exchange and correlation energy that are appropriate to the electron gas of uniform density. The method has the advantage that its computational requirements scale less severely with the size of the system investigated compared with Hartree–Fock methods. In addition correlation effects are included directly, whereas HF methods must be extended to include representation of configurational interaction (CI) (although correlation terms may be included via a density expression following an evaluation of a HF wave function). HF methods do, however, have the advantage that the approximations are more clearly defined and that there is considerable experience in establishing suitable basis sets, gained from molecular quantum chemistry. Both techniques have a valuable role to play as will be evident from the discussion below.

One of the most important roles of high quality quantum mechanical calculation is in deriving reliable *parameterizations for interatomic potentials*. Indeed for many problems it is more appropriate to use the electronic structure techniques to determine potentials rather than to undertake an electronic structure calculation directly. The use of *ab initio* methods in this way is, of course, not new; but recently it has become possible to achieve higher levels of accuracy than were hitherto possible. We illustrate these points by two recent studies: the first employing HF techniques and the second LDA methodologies.

2.1 *Periodic Boundary Conditions Hartree–Fock Studies of Interatomic Potentials in* α-Al_2O_3

α-Al_2O_3 is a widely investigated and important ceramic material; moreover, interatomic potentials derived for this oxide may form the basis of models used for aluminosilicate and other Al containing oxide phases. Earlier empirically derived potentials of Catlow *et al.*(*10*), while unquestionably useful, showed clear deficiencies; the calculated elastic constants do not adequately reproduce experimentally, and the potential fails to predict the "α," (corundum structured) phase as the most stable polymorph.

Recently, therefore, Gale *et al.* (*11*) have reported a detailed *ab initio* study of the material, with the primary aim of determining improved interatomic potential parameters. The work employed the CRYSTAL code referred to above, which is designed to treat periodic systems. Using a good quality basis set comprising a 6-21G contraction for aluminium and 8-51G for oxygen, it was first shown that the crystal structure of α-Al_2O_3 could be accurately reproduced. Next the geometry optimized structure was varied systematically by perturbing in turn the unique cell parameters, *c*/*a* ratio and internal coordinates by up to 10% and the resulting energy hypersurface was fitted to a Born model potential. Interestingly, a fully satisfactory fit could be obtained only when the charges of the Al (and of the O) were allowed to be less than their formal values of +3 and −2. The optimized value, together with the other fitted parameters, is reported in Table Ia. We note that the fitted charge is close to that obtained from a Mulliken population analysis.

TABLE Ia

BUCKINGHAM POTENTIAL PARAMETERS DERIVED FOR CORUNDUM BY FITTING TO THE *ab Initio* ENERGY HYPERSURFACE

Charge Al (*e*)	2.08425
Charge O (*e*)	−1.38950
Al–O	
A (eV)	101111.71
ρ (Å)	0.1515
O-O	
A (eV)	723.54
ρ (Å)	0.3385
C (eV Å^6)	3.38
Al–Al	
A (eV)	31113.32
ρ (Å)	0.2063

Note. Short range potentials are of the form $V(r) = Ae^{-r/\rho} - Cr^{-6}$ with C = O for Al–Al and Al–O interactions.

TABLE Ib

CALCULATED STRUCTURE AND PROPERTIES FOR α-ALUMINA FROM THE *ab Initio* DERIVED INTERATOMIC POTENTIALS

Potential	Experimental	Calculated
a (Å)	4.7602	4.7688
c (Å)	12.9933	12.9869
Al *z* coordinate	0.3522	0.3531
O *x* coordinate	0.3062	0.3025
C_{11}	49.69	59.69
C_{12}	16.36	24.61
C_{13}	11.09	19.56
C_{14}	−2.35	−3.86
C_{33}	49.80	54.78
C_{44}	14.74	14.29
C_{66}	16.67	17.54
ε^0_{11}	9.34	3.82
ε^0_{33}	11.54	5.08

Note. See Ref. (*11*) for details, including reference to experimental data. Elastic constants in units of dyne cm^{-2} × 10^{11}.

Table Ib compares the experimental structural, dielectric, and elastic constants with those calculated using the potential parameters reported in Table Ia. We note that as this is a rigid-ion model, (i.e., no treatment of electronic polarizability is included) it is not possible to obtain a satisfactory reproduction of the dielectric constants. Otherwise the model performs well, yielding good structural parameters and elastic constants that are in acceptable agreement with experiment. The slight overestimation of the latter constants is to be expected in view of the omission of the correlation term from Hartree–Fock energies, as this term would serve to "soften" the potentials. Overall the potentials are satisfactory, especially when we recall that *no* empirical information was used in their derivation, and the results indicate the considerable potential of the

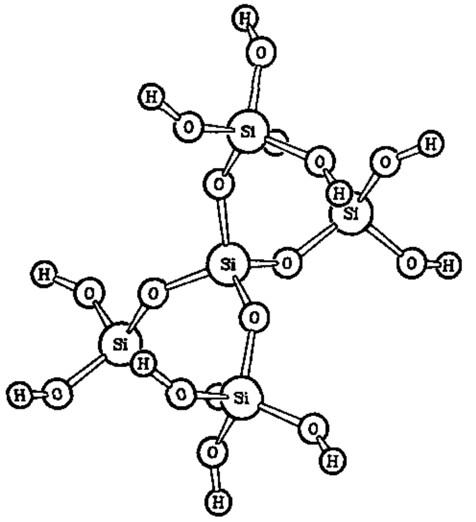

FIG. 1. $S_{15}O_{16}$ cluster used in LDA cluster calculations of Purton *et al.* (*12*).

CRYSTAL technique in leading to high quality interatomic potentials for solids.

2.2 *LDA Investigations of Interatomic Potentials for SiO_2*

This study (*12*) adopted a related but different approach to the problem of deriving potentials for solids using *ab initio* techniques. A large cluster was employed, which as illustrated in Fig. 1 comprises a central SiO_4 tetrahedron linked to four other SiO_4 tetrahedra, with the valencies of the terminal oxygens being saturated by H atoms. The energy was calculated using LDA techniques employing a Gaussian basis set. The second derivatives of the total energy with respect to atomic displacements were calculated for the central nine atoms by a numerical procedure involving displacing the atoms by a small distance. These derivatives were then fitted to a Born model potential. It was found in this case that a formal charge model could adequately fit the *ab initio* data. The resulting parameters are reported in Table IIa, while Table IIb gives a comparison of the calculated and experimental properties. We note that in this case empirical polarization parameters have been included for the oxygen atom; these are based on the shell model formalism of Dick and Overhauser (*13*) and are close to the early parameterization of Sanders *et al.* (*14*).

We note that the agreement between theory and experiment is very good. Moreover, the potential performs well in more stringent tests including the calculation of phonon dispersion curves (Fig. 2) and the pressure dependence of the crystal structure (Fig. 3).

Overall these two studies encourage confidence in the role which *ab initio* techniques can play in deriving high quality potential parameters for use in solid state simulations.

TABLE IIa

FITTED POTENTIAL PARAMETERS FOR SiO_2

	Short-range potentials	
	Si–O	O–O
A (eV)	1459.6749	5811.0347
p (Å)	0.31118	0.20477
C (eV $Å^{-6}$)	10.63	28.76
Short range cutoff 11.0 Å		

Note. Three body force constant O–Si–O k_b = 1.5683 eV/rad^2. O shell charge −2.8482. O shell spring constant, K_s = 80.0 eV/Å^2.

TABLE IIb

ELASTIC AND DIELECTRIC CONSTANTS FOR SiO_2 CALCULATED USING *ab Initio* POTENTIALS

C_{11}	8.688	9.02
C_{33}	10.598	10.10
C_{44}	5.826	4.50
C_{66}	3.987	4.20
C_{14}	−1.806	−1.78
C_{13}	1.193	1.36
C_{12}	0.700	0.61
ε_0		
ε_{11}	4.540	4.048
ε_{33}	4.640	4.357
ε_{00}	2.40	1.92

Note. See Ref. 12 for details and reference to experimental data. Elastic constants in units of 10^{11} dyne cm^{-2}.

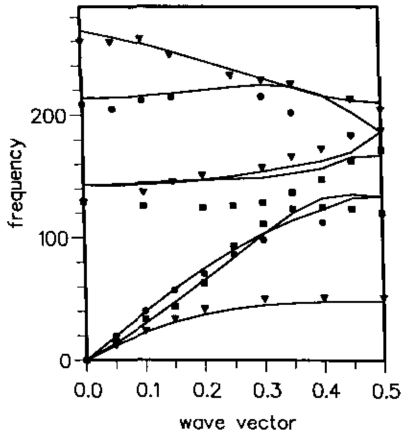

FIG. 2. Phonon dispersion curve in the $\xi 00$ direction calculated using *ab initio* potential. Squares and triangles indicate experimental data. See reference (*12*) for details.

We consider that both HF and LDA techniques have important complementary contributions to make to this field, as have both periodic boundary and cluster calculations. The use of these methods offers the possibility of a major extension in the predictive capacity of computational methods in solid state chemistry.

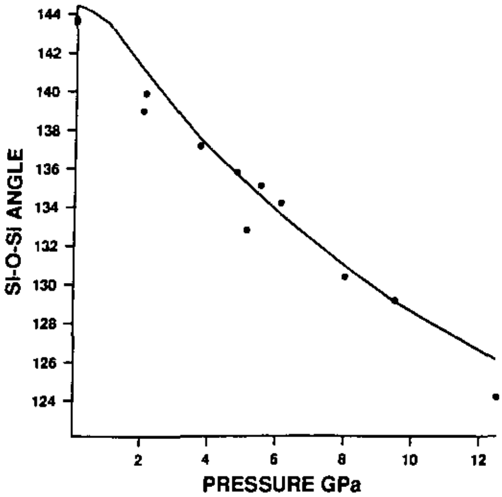

FIG. 3. Calculated pressure dependence of the crystal structure of SiO_2 using *ab initio* potential. Dors are experimental data.

3. Applications

As noted we will highlight three areas where recent studies have shown the trend towards increasingly predictive calculations. They include studies of crystal structure modeling, simulations in ceramic science, and molecule-active site interactions.

3.1. *Crystal Structure Simulation*

The ability to model accurately the structures of inorganic crystals, given accurate interatomic potentials has been known for many years. In the field of inorganic structural studies lattice energy minimization techniques were successfully used by Catlow *et al.* (*15*) and Parker *et al.* (*16*), especially in modeling silicate structures as reviewed by Catlow and Cormack (*17*). Moreover, the ability to model highly complex structures such as zeolites was clearly demonstrated by Jackson and Catlow (*18*), while recent studies of Bell *et al.* (*19*) and Tomlinson *et al.* (*20*) showed clearly how subtle, complex features of zeolite structural chemistry, e.g., the monoclinic distortion in silicalite and the polymorphism in zeolite β, could be successfully simulated. An important recent development has been the extension of the range of such simulations by including vibrational entropy terms calculated by standard lattice dynamical techniques, which permit free energy rather than simple energy minimizations to be performed. Such calculations allow the investigation of lattice expansions and phase transformation, and have been used with great success by Parker and Price (*21*).

Despite their success all the above studies are limited in their scope. Essentially they have reproduced known crystallographic properties, and as such have provided valuable insight into the factors controlling structural properties, (although the phase transition studies of Mg_2SiO_4 by Parker and Price (*21*) have a more genuinely predictive character). Recently, however, the emphasis of the field has changed markedly with simulations being used to *refine* approximately known structures and with the development of an increasing capability for generating structures from a minimum amount of experimental information.

As an example of the former developments we take first the work of Shannon *et al.* (*22*) who refined the structure of the zeolite Nu87, using lattice energy minimization techniques. Their starting point was a model proposed on the basis of electron diffraction data, but which could not satisfactorily refine high resolution powder diffraction data (obtained using the instrumentation available on the Synchrotron Radiation Source at the SERC Daresbury Laboratory). The minimizations led to a lower symmetry structure which accurately refined the latter data. Indeed the simulated structure is in excellent agreement with all available experimental data on this material. A further illustration is provided by the very recent work of Wright *et al.* (*23*) who have used energy minimization techniques in direct conjunction with crystallographic refinements in order to solve the structure of a novel metal containing microporous aluminophosphate (MAPO-36). These studies clearly establish energy minimization techniques as a valuable adjunct to experimental crystallographic studies of complex inorganic materials.

A simple example of the move towards increasingly predictive calculations is provided by the recent work of George *et al.* (*24*) who simulated the structures of zeolitic forms of GeO_2. Their results are illustrated diagrammatically in Fig. 4. They show that the energies of microporous structures (relative to that of the stable quartz polymorph) are broadly similar for both GeO_2 and SiO_2 based materials. Synthetic work on microporous Ge containing structures would clearly be of considerable interest.

The greatest ambition of this field is of course to predict crystal structures with a minimum (ultimately a zero) input of experimental data. Notable progress has been made by Pannetier *et al.* (*25*) and Deem and Newsam (*26*) who employed simulated annealing techniques to predict the structures of complex inorganic structures including zeolites. The potential of a combination of such approaches with more traditional energy minimization techniques has recently been demonstrated by Freeman and Catlow (*27, 28*). In "demonstration" studies on TiO_2, structures were generated by a simple simulated annealing approach subject only to the constraints of the observed cell dimensions of the different polymorphs. The models thus generated were refined by EM methods, generating accurate models for the rutile, anatase, and brookite structures. Having demonstrated the potential of this technique it will be applied in future studies to unknown systems.

This field is now developing rapidly and we can expect in the near future predictive procedures based on the type of methodology developed by Freeman, and integrated crystallographic/simulation refinement packages incorporating EM techniques and possibly MD methods (as has been achieved in protein crystallographic studies).

3.2. Ceramics

The behavior of defects in ceramics lies at the very heart of the implementation of computational techniques both from developmental and historical perspectives. Indeed, it was the desire to address problems concerning radiation damage in nuclear materials that led to the development of the first important static lattice code, HADES (*29*) which is based on the Mott–Littleton approximation.

Nuclear materials still pose important questions and recently a comprehensive study (*30*) has been made concerning the stability of 13 fission products in uranium dioxide. One of the objectives of this work was to predict the changes in stability exhibited by the fision products as a function of nonstoichiometry. Its importance arises from accident and high burn-up scenarios in which the fuel will become either hypo-

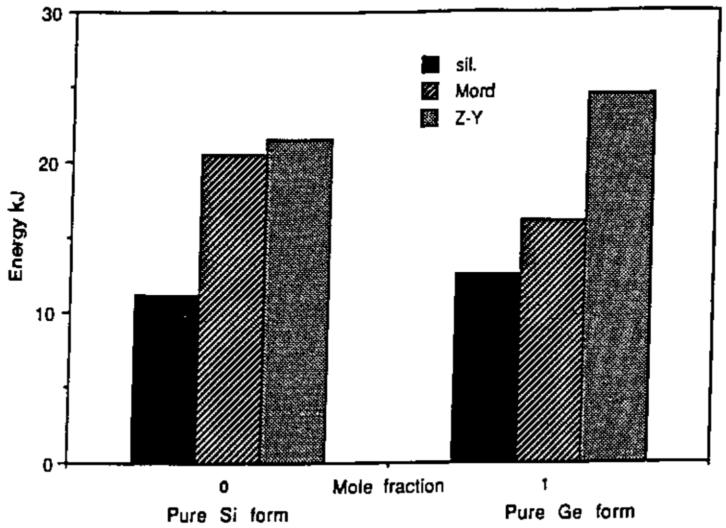

FIG. 4. Lattice energies (per mole of TO_2) for microporous SiO_2 and GeO_2 polymorphs relative to the energy of the quartz structure.

UO_{2-x} or hyper-UO_{2+x} stoichiometric. The solution energy of the fission products was calculated in a variety of trap sites, including not only simple cation and anion vacancies but also more complex sites composed of a number of vacant lattice sites. The results suggested that volatile species such as Xe, Cs and I would change their lowest energy trap site as a function of the stoichiometry. Furthermore, I, Br, and Te, most commonly stable as anions were predicted to be stabilized as cations in response to the oxidation of UO_2 to UO_{2+x} effectively buffering the redox process. Clearly such information is of great value in the design of advanced fuels which will be required to sustain much greater levels of actinide burnup. In this regard, other lattice hosts are being considered as possible candidates for advanced fuels and static simulation techniques are being employed to investigate their suitability. For example, predictions of the behavior of noble gases in α-U_3O_8 have been made (*31*). These suggested that Kr and Xe were less soluble in α-U_3O_8 than in UO_2 and, in addition, a particularly low activation energy for radiation assisted migration was identified. Consequently, the α-U_3O_8 lattice would vent any trapped fission gas more easily than conventional UO_2, clearly an undesirable characteristic.

One of the most exciting developments in ceramic science over the last few years has centered around the realization of high temperature superconductivity initially in La_2CuO_4 doped with divalent ions such as Sr and Ba and subsequently in a range of more complex ternary oxides. Simulation techniques have been at the forefront in trying to understand key aspects of the solid state chemistry of high T_c oxides. In particular, defects formed as a result of oxidation and the energetics of hole pairing (*32–34*) have been investigated. These results also suggested that La vacancy formation would be the lowest energy mode of accommodating oxidation in La_2CuO_4, although a variety of oxygen interstitial species (e.g., O^{2-}, O^-, O_2^{2-}, or O_2^-) may be metastable.

In the superconducting materials, it has been suggested that polaron pair (or bipolaron) formation is responsible for the onset of the superconductivity. However, from experiment it is not clear which real-space pair (i.e., Cu^{3+}–Cu^{3+}, O^-–O^-, or Cu^{3+}–O^-) on which sublattices are favorable to bipolaron formation. Simulation studies (*34*) suggested that only O^-–O^- are stable with the highest binding energy of 0.12 eV occurring when the O^- ions are situated in next-nearest neighbor sites. The driving force for pair formation is the covalent interaction between the O^- species which in nearest and next nearest configurations is greater than the Coulombic repulsion. A further important result is that for Cu^{3+}–O^- and Cu^{3+}–Cu^{3+} pairs interlayer pairing was much more energetically favorable than intralayer pairing.

Ultimately, it will be necessary to employ a quantum mechanically based method to calculate the stability and structure of electronic defects such as hole states in La_2CuO_4, as the hole must, to some extent, have both metal and oxygen characters. However, the computer time needed is currently prohibitive if more than a modest sized cluster is treated quantum mechanically. In modeling La_2CuO_4 and $YBa_2Cu_3O_7$ (*35*) we have used embedding techniques, referred to in the Introduction, which attempt to overcome such a limited description of a crystal lattice by using a combination of quantum mechanical and classical simulation techniques: the innermost 10 or so atoms are treated using a Hartree–Fock self-consistent quantum approach while the surrounding ions are modelled using pair potentials employing Mott–Littleton techniques (*36*). The results for the cuprate materials show that when a hole is added to the normal charge state of the quantum cluster, it occupies Cu–O hybrid orbitals in the Cu–O crystal plane. Localization of holes to single oxygen ions requires 0.2 or 1.4 eV in the case of La_2CuO_4 and $YBa_2Cu_3O_4$ respectively. Conversely, doping of La_2CuO_4 by Sr^{2+} results in localization of the hole to a single axial oxygen ion in agreement with experimental results (*37*). Further studies, using embedded quantum cluster methods, of the effect of dopant ions and other lattice defects on hole localization will be essential if a full understanding of the high T_c mechanism is to be achieved.

Embedded quantum cluster methods have also been used to study the behavior of self-trapped excitons in a variety of insulating materials including alkali halides (e.g., KCl and LiCl) and oxides (MgO, Li_2O, and SiO_2). These electronic defects are composed of localized electron-hole pairs and are normally formed as a result of optical excitations. It was found (*38*) that the hole component is mostly localized on one anion displaced from its lattice site while the exciton electron is localized around the vacant anion site which is adjacent to the hole. The extent of the ion displacements, which can be quite different, depends upon the system in question and influences the degree to which the electron component is localized. In general, the differences occur as a result of the changes in the character of the chemical bonding between the anions. In particular, in alkali halides, the degree to which the hole is localized to a single anion is less than in oxides as a result of a bond which forms with a second anion which also becomes displaced from its lattice site. Nevertheless, the essential electronic structure of the excitons are very similar. This contrasts sharply with the results for hole localization (*39*). In this case, in alkali halides, the hole is symmetrically shared between two anions to form a V_k center. However, during the migration of the V_k center, at the saddle point, the V_k density is polarized to the extent that the electronic structure resembles that of a hole localized to a single center. The converse is true in MgO so that as a self-trapped species, the hole is localized on one anion while the structure of the saddle point for hole migration resembles a V_k center in which the hole is delocalized over two nearest neighbor oxygen ions.

The above examples highlight the role of embedded cluster calculations, a theme which is continued in the next section which considers catalytic systems.

3.3 Brønsted Acid Sites and Molecular Binding

Zeolites are found to be effective catalysts for a miriad of reactions, including many of commercial importance, such as petroleum cracking and the methanol to gasoline (MTG) process (*40*). The majority of these reactions are promoted by the acidity of framework defects, which largely comprise protonated bridging oxygens adjacent to an aluminum that has been isomorphously substituted for silicon, or a terminal silanol group.

High selectivities may be obtained through diffusion control of the product distribution, for example xylene isomers undergo equilibration in ZSM-5 at the channel intersections; however, only the *para*-isomer is able to diffuse along the straight channels and escape (*41*). Specific interactions between the framework surface and reactant molecules could influence the transition state, although this is a more complex problem.

In this section we will address the application of quantum mechanical techniques to the characterisation of Brønsted acid sites and the binding of small molecules as a precursor to elucidating reaction mechanisms. Diffusion through zeolite pores and its consequences for product distributions is most effectively studied using molecular dynamics as recently reviewed by Demontis and Suffritti (*42*).

Because of the extended 3D nature of zeolites it has until recently been necessary to select small model fragments to represent aluminosilicate materials, with cleaved Si–O–Si bonds being saturated with hydrogen to yield a charge neutral system. An effective alternative is to replace the terminal hydroxyl groups by hydride as this is of similar electronegativity while greatly reducing computational expense.

There is now an increasing trend towards embedding clusters in a representation of the long range electrostatic field, normally by surrounding the explicit fragment with point charges so as to reproduce the infinite Madelung potential. Vetrivel *et al.* (*43*) and more recently Gale and Catlow (44) have examined defects in silicalite using heterolytically terminated clusters with both formal (Si^{4+}, O^{2-}) and half formal charges (Si^{2+}, O^{-}), while Allavena *et al.* (*45*) chose a neutral species embedded in the electric field determined by Mortier's electronegativity equilization method (*46*).

Ultimately it will be possible to employ Greens function embedding techniques to perform cluster studies surrounded by the perfect lattice periodic wavefunction (*47*). Teunissen *et al.* (*48*) have made the first step towards this aim by examining the binding of ammonia to a Brønsted acid site in chabazite at high coverage using the periodic Hartree–Fock method. While it is currently not feasible to perform full geometry optimizations and to employ large flexible basis sets in such cases, valuable information is obtained against which less sophisticated embedding schemes may be assessed.

One of the most daunting aspects of the computational modeling of zeolitic defects is the large number of possibilities that must be considered. For example, to identify the most favorable acid site in ZSM-5, even assuming that there are no discontinuities in the framework and that each particular defect can be treated at infinite dilution, results in 12 possible tetrahedral sites for the incorporation of aluminum with a total of 48 distinct combinations of Al with a proton on an adjacent oxygen; it can be readily demonstrated that the energetic penalty for binding the proton further away from the aluminum is too great, even when dielectric effects are included in the model.

As can be seen the number of calculations to be performed to study this system is extremely large, and while there have been several studies of this problem, notably those of Derouane and Fripiat (*49*) and Alvarado-Swaisgood *et al.* (*50*), it is too prohibitive to examine all configurations using accurate *ab initio* methods with both reliable basis sets and large cluster models, let alone with inclusion of electron correlation. In this respect semiempirical quantum mechanical techniques can represent a useful starting point for more accurate calculations, both through the screening of possibilities to ob-

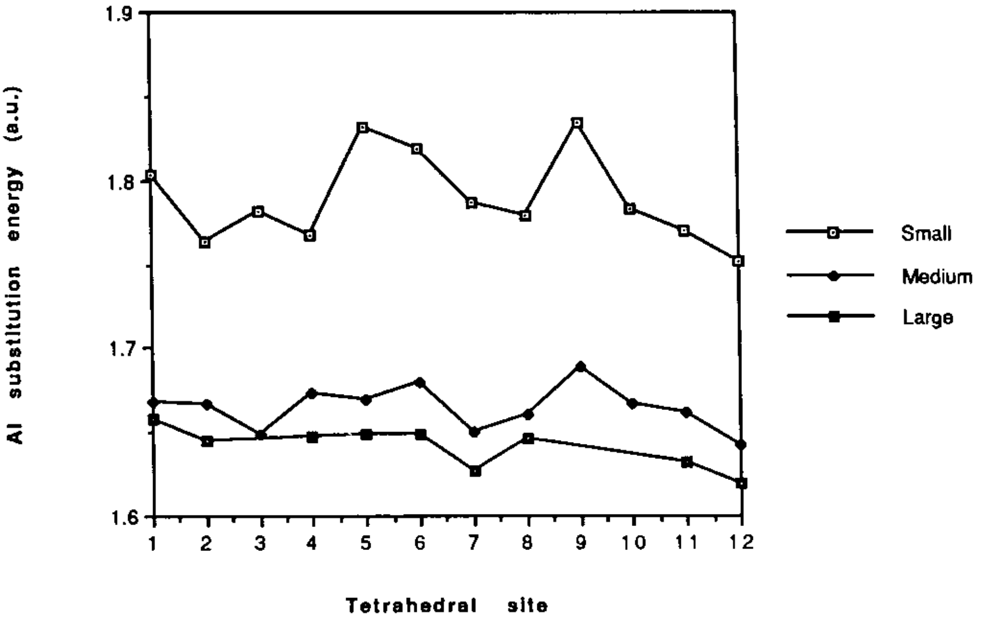

FIG. 5. Al substitution energies in silicalite for substitution at different tetrahedral sites for three sizes of the explicitly treated quantum mechanical region.

tain qualitative trends and through the prediction of geometries.

The problem of preferential aluminum siting in silicalite has also been examined by Gale (*51*) using the semiempirical technique CNDO/BW (*52*) (which is the Boyd–Whitehead modification of CNDO/1 which yields much improved geometries and energies relative to CNDO/2). Three sizes of cluster were considered: small, comprising just a single tetrahedral unit; medium, composed of a central T site surrounded by the first four neighbors; and large, which includes the second shell of adjacent tetrahedra resulting in a total of 17 explicitly considered T sites. Each of the clusters was generated for all 12 possible sites and embedded in the infinite electrostatic potential of the rest of the crystal as obtained through an Ewald summation (*53*). All atoms in the explicit cluster except for the outer surface of oxygens were allowed to optimize their geometry.

The aluminum substitution energies for the three sizes of cluster are illustrated in Fig. 5. This demonstrates the importance of employing large clusters with extensive ionic relaxation in order to achieve reliable results, as was also noted in the interatomic potential calculations of Schröder *et al.* (*54*) If, as a first approximation, we assume the error with cluster size converges as a geometric progression the probable error in the substitution energy even for a 17 tetrahedron fragment is likely to be of the order of 16 kJ mole^{-1}.

More importantly it can be seen that even the relative order of site preferences changes as a function of cluster size, limiting the value of calculations on small fragments. The absolute magnitude of energy differences between sites also decreases with increasing cluster size leading to the conclusion that ionic relaxation tends to lead to an equalization of site energies; hence, the synthesis conditions and kinetics may play a more crucial role. Furthermore, if we do assume that aluminum siting is thermodynamically controlled then the order of preference is greatly altered by the presence of the charge compensating cation. In the case of ZSM-18, the first aluminosilicate containing three-rings to be characterized (*55*), aluminum substitution is energetically unfavorable in the three-ring (T4). However, when one of the oxygens in this ring is protonated then this transforms T4 into the preferred location for Al (*56*).

Of particular relevance to the understanding of acid catalysis in zeolites is the ability to determine the preferred binding arrangements of typical molecules with Brønsted acid sites. Ugliengo *et al.* (*57*) have examined the coordination chemistry of terminal silanol groups, while Sauer (*58*) have performed detailed investigations of the binding energies of H_2O, NH_3, and CH_3OH to framework protons. The work of Sauer *et al.* (*59*) has yielded systematic corrections for aspects such as basis set errors and zero point energies. Until recently these treatments have been restricted to clusters containing no more than three tetrahedral units. Again because of the large number of possibilities to be examined there is a need for both general principles for the prediction of binding geometries and for more economical computational techniques to perform preliminary evaluations. In studying this problem we must note that tetrahedra can adopt one of two configurations providing the Si–O–Si angles are nonlinear. These two arrangements can be described as either "edge" or "face" conformations. In the case of the former the tetrahedron exposes two pairs of oxygens to binding species, whereas the latter configuration also has a sterically unhindered triangle of oxygen ions. Using the reliable semiempirical method MNDO/PM3 (*60*) we can demonstrate the fundamental differences between these two environments. Two clusters containing five tetrahedra, $(Si(OSi(OH)_3)_4)$, representing both conformations, were completely geometry optimized for the purely siliceous case. Subsequently, aluminum was subsituted at the central tetrahedral site and one of the adjacent oxygens was protonated. While the geometries examined here represent extreme cases, rather than any one specific aluminosilicate, the conclusions may be interpolated to intermediate environments.

Here we examine the coordination chemistry of H_2O and H_3O^+ with the above cluster, following the work of Gale (*61*) who considered the analogous situation for ammonia. A wide variety of initial coordinates was selected in order to characterize the full range of local minimal. The stable structures are illustrated in Fig. 6.

For the edge cluster, water forms the expected doubly hydrogen-bonded complex with one H bond from the framework proton to the oxygen of water and one from a water hydrogen back to the framework with distances of 1.82 and 1.76 Å, respectively (see Fig. 6a). This resembles the binding arrangement found by Sauer *et al.* (*62*) from smaller scale *ab initio* calculations on smaller clusters. The face conformation also exhibits the expected complex analogous to that described above. However, there is a second binding geometry (Fig. 6b) that is 43 kJ $mole^{-1}$ more stable. In this structure both hydrogens of the water molecule coordinate to the two unprotonated face oxygens of the cluster at a distance of 1.8 Å, while there is a third weak interaction between the framework proton and the water oxygen at 2.5 Å. Because of the spatial distribution of the oxygen lone pairs it is not feasible to satisfy simultaneously the requirements for three strong hydrogen bonds.

A third, and less stable, binding arrangement (Fig. 6c) exists between H_2O and both the edge and face clusters in which the framework proton coordinates to the oxygen of water, but instead of the water hydrogens forming one strong H bond to the cluster it overlaps both hydrogens equally with the two lone pairs of one oxygen. The resulting H–O distances for this weak interaction are 2.6 Å. Although not favored energetically relative to the other possibilities, this configuration represents a minimum on the path for rotation of the bound water molecule.

Turning now to the hydroxonium ion, (H_3O^+), this species achieves its most sta-

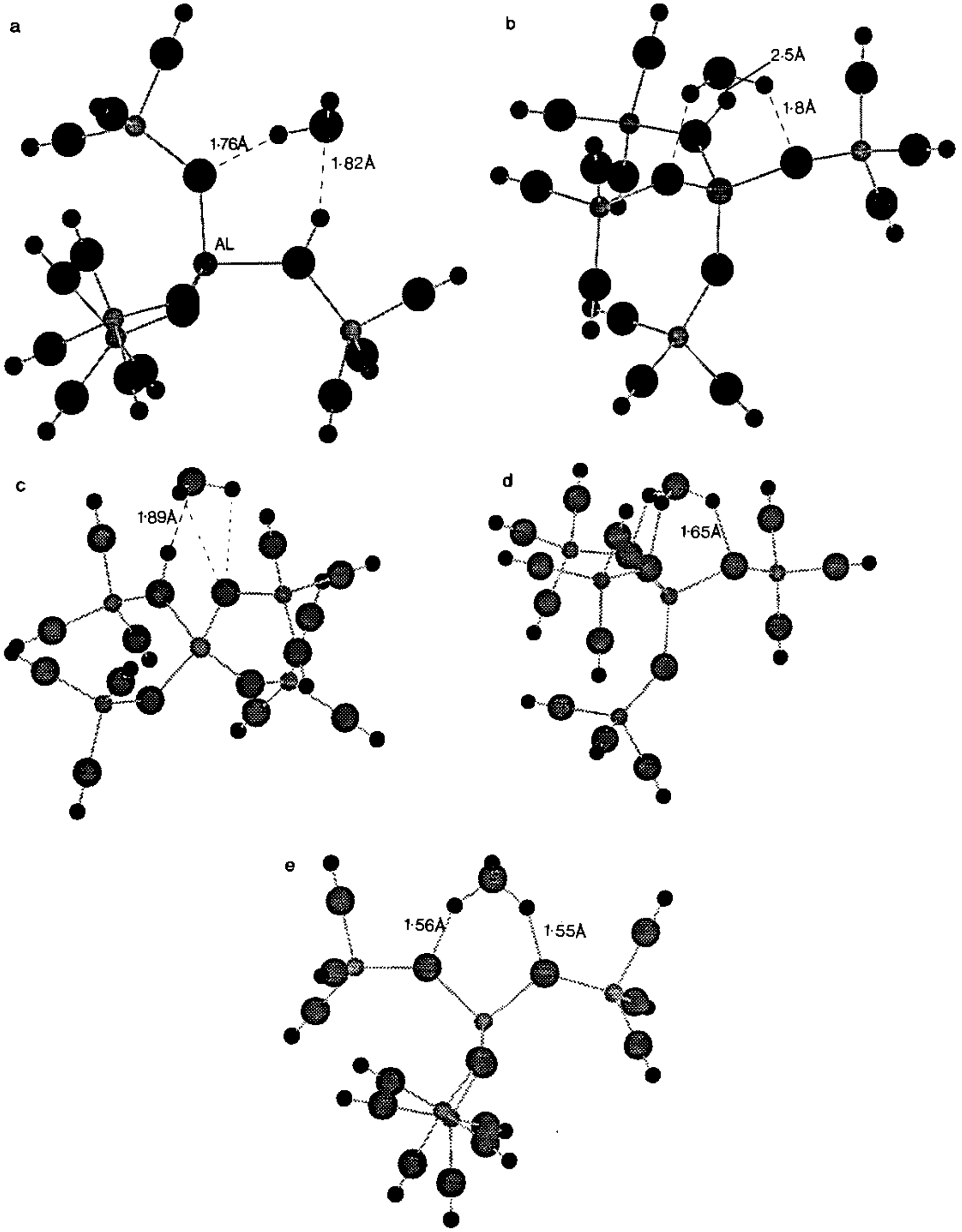

FIG. 6. Calculated MNDO/PM3 geometries for water and the hydroxonium ion bound to the zeolite cluster $HAl(OSi(OH)_3)_4$. (a) H_2O doubly H-bonded to the edge conformation. (b) H_2O with two strong H bonds and one weak one to the face cluster. (c) Single H-bonded configuration for H_2O. (d) H_3O^+ coordinated to the face cluster. (e) H_3O^+ coordinated to the edge cluster.

ble complex with the face conformer by forming three equal hydrogen bonds to the triangle of oxygens with a shortened distance of 1.65 Å (Fig. 6d). However, in the absence of a long range electrostatic potential this is not sufficient to stabilize it relative to the physisorbed system, the energy difference being approximately 84 kJ mole^{-1}. The situation is even more unfavorable for the edge configuration (Fig. 6e) as only two strong hydrogen bonds can be attained to compensate for the proton transfer energy, resulting in a further destabilization of 105 kJ mole^{-1}.

An important feature of all the binding geometries is the sp^3 hybridization of the oxygens and more particularly the spatial direction of the lone pairs. The optimum hydrogen bonding arrangement is obtained when the O–H. . . O angle approaches linearity and thus these two factors can be used to explain the coordination chemistry. Earlier *ab initio* calculations necessitated the use of high symmetry geometries due to computational cost. However, this requirement often leads to oxygen lone pairs being force into sp^2 hybridized orbitals consequently lowering the apparent basicity of the zeolite model. In fact the optimized geometries of symmetry constrained calculations often represent transition states, rather than minima.

Although semiempirical methods cannot be relied upon for quantitative accuracy, their use in calculations on larger framework models than are currently possible with *ab initio* techniques allows us to gain valuable insight into the properties of complex materials such as zeolites. This allows qualitative trends to be derived and assists understanding of the correlation of structural features with the chemical properties of materials.

4. Summary and Conclusion

Computational methods are now advancing rapidly in the complexity of the systems examined and the accuracy of the calculations. The future emphasis will be on prediction rather than reproduction of experimental results. In addition, the ability of simulations to provide insight into processes and reactions in solids and surfaces will make a growing contribution to future studies in solid state chemistry.

Acknowledgments

Yr ydym yn ddiolchgar i'r Athro Syr John Meurig Thomas am yr holl drafodaethau buddiol a'i gyfraniad i'r gwaith a gyflwynir yma.

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