AB-INITIO QUANTUM MECHANICAL CALCULATIONS OF WATER-ROCK INTERACTIONS: ADSORPTION AND HYDROLYSIS REACTIONS

ANTONIO C. LASAGA* and G. V. GIBBS**

ABSTRACT. The methodology of non-empirical ab-initio quantum mechanical calculations is used to elucidate the atomic processes occurring during water-rock interactions. The ability to deal with transition state theory in a non-empirical way in geochemical reactions is described. Based on new ab-initio results, a mechanism for the dissolution of quartz is proposed and tested. This mechanism and the ab-initio results are in accord with the experimental determination of the activation energy for quartz dissolution. The transition state in the mechanism is fully investigated using the quantum mechanical potential surface. The new results predict a non-trivial isotope kinetic effect for the dissolution reaction, which can be tested in future experiments. The success of the approach taken here opens up a new and powerful method of investigating surface reactions, including the prediction of catalysis.

INTRODUCTION

It has become increasingly clear that any quantitative study of heterogeneous kinetics must be based on a thorough understanding of the structure and dynamics of mineral surfaces. Great advances in our understanding of surface processes have resulted from application of new high technologies, in particular spectroscopic methods. These advances, coupled with the more traditional approaches to surface chemistry, have forced us to take a serious look at the atomic nature of mineral surfaces and to try to model the atomic processes as inferred from the various experimental probes. The roles of adsorption and desorption in surface chemical kinetics have been discussed in numerous previous papers (Furrer and Stumm, 1986; Rimstidt and Dove, 1986; Stumm, Wehrli, and Weiland, 1987; Blum and Lasaga, 1988; Carroll-Webb and Walther, 1988). Kinetic mechanisms proposed to understand the effect of pH on dissolution rates, the effect of ionic strength on surface rates, the dependence of rates on supersaturation or undersaturation of solutions, and the catalytic or inhibitory effects of dissolved constituents require a good knowledge of the specific atomic species involved and of the chemical and physical nature of the mineral surface. A rigorous approach to the atomic nature of surface kinetics including the types of activated complexes relevant to adsorption, dissolution, and precipitation will clarify greatly the nature of these processes.

A first-principles investigation of the bonding and atomic dynamics of minerals and their interaction with both hydrated ions and water can

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answer significant questions such as the link between local defects or impurities and the bulk kinetic properties, or the nature of the bonds and forces involved in surface reactions, or the association of a local structure with a particular catalytic or inhibitory effect. The task at hand is one of evaluating the interatomic forces from the fundamental laws of physics and a handful of universal constants (such as Planck’s constant, the electron charge, the speed of light, the mass of nuclei and electrons)—hence the word *ab-initio*. No empirical data or semi-empirical constants are introduced into the calculations. *Ab-initio* methods have become as good as experiments for the accurate prediction of structures and vibrational frequencies of gas-phase molecules. Fortunately, current computational levels enable us to extend the applications to mineral surface reactions. As will be emphasized again, an essential component of successfully carrying out *ab-initio* calculations on silicates and their surface reactions is the **local** nature of the chemical forces shaping the structures and dynamics of silicates. Our earlier work (Gibbs, 1982; Lasaga and Gibbs, 1987, 1988, 1989) has shown that *ab-initio* calculations on molecular clusters, which account for interactions with nearest and next-nearest neighbors, are capable of reproducing the crystal structure and the equations of state of many silicates quite successfully.

In this paper we will first discuss briefly the basic theory behind *ab-initio* methods. Then a discussion of transition state theory, in light of the *ab-initio* capabilities, will be presented. This discussion will be followed by an analysis of the molecular mechanisms in water-silicate reactions and the *ab-initio* elucidation of the adsorption and kinetic barriers involved in the bulk chemical reactions occurring at mineral-water interfaces.

**AB-INITIO THEORY**

The basic problem in the quantum treatment of chemical bonds is obtaining solutions to Schrodinger’s non-relativistic time-independent equation for all the electrons in the system:

\[
\hat{H}\Psi_{\text{elec}} = E(\mathbf{R})\Psi_{\text{elec}}
\]

(1)

where \(\mathbf{R}\) refers to the **fixed** positions of all the atomic nuclei. The eigenvalue, \(E(\mathbf{R})\), is the Born-Oppenheimer energy of the atomic cluster. \(\Psi_{\text{elec}}\) is the electronic wavefunction and is a function of the coordinates of all electrons. The wavefunction also depends parametrically on the fixed nuclear coordinates, \(\mathbf{R}\). The \(\hat{H}\) in eq (1) is simply a differential operator which has the form

\[
\hat{H}_{\text{elec}} = \frac{\hbar^2}{8\pi^2m} \sum_{i}^{\text{electrons}} \left( \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \right) + V(x, \mathbf{R})
\]

where the last term, \(V(x, \mathbf{R})\), is the coulomb energy arising from all electron-electron, electron-nucleus, and nucleus-nucleus interactions
and depends on both the positions of the electrons, \( x \), and the fixed nuclear position, \( \mathbf{R} \).

The driving force for all the surface chemical reactions is the chemical interaction between the atoms in the system. If the variation in energy of the whole system, \( E(\mathbf{R}) \), is known as a function of the positions of the atoms in a cluster, \( \mathbf{R} \), the forces and thereby the motion of atoms can be readily computed. Such potential surfaces are now becoming available (see discussion in Lasaga and Gibbs, 1989).

To a good approximation, the wavefunction, \( \Psi^{\text{elec}} \), can be written as a product of functions of only one electron coordinates, \( \psi_i(x, y, z) \). In the molecular orbital parlance, this strategy is called the Hartree-Fock approximation. The one-electron functions, \( \psi_i \), are called molecular orbitals. These molecular orbitals form the basis for the conceptual treatment of bonding in molecules. In principle, we could solve eq (1) numerically for \( \psi_i \); however, in practice, it is much more efficient to expand the molecular orbitals as a sum over some set of prescribed atomic orbitals, \( \phi_\mu \),

\[
\psi_i = \sum_{\mu=1}^{N} c_{\mu i} \phi_\mu \tag{2}
\]

and then find the set of coefficients, \( c_{\mu i} \), that most closely make \( \psi_i \) satisfy the one-electron differential equation when their product is inserted into (1).

The set of atomic orbitals, \( \{\phi_\mu\} \), used to obtain the molecular orbitals in eq (2) is termed the basis set. The size of the atomic orbital set, \( N \), varies with the accuracy demanded of the calculation. A minimal basis set is one that merely contains the minimum atomic orbitals needed to accommodate all the electrons in the system up to the valence electrons. For example, a minimal basis set on oxygen would have one 1s function, one 2s function, and three 2p functions (see table 1). Bigger basis sets are labeled extended basis sets (see table 1). Mathematically, if the number of “different” atomic orbitals increases to infinity (that is, this set forms what is termed a “complete” set), then the orbitals, \( \psi_i \),

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obtained by the coefficients $c_{ni}$ will be the exact solutions to the one-electron differential equation. In turn, this limit would yield the best possible solution to the full Born-Oppenheimer Schrodinger equation within the Hartree-Fock approximation. Such a solution is termed the Hartree-Fock limit.

To go beyond the Hartree-Fock limit and obtain the full solution to the Schrodinger equation (in the non-relativistic and Born-Oppenheimer limit), one would have to combine various solutions each consisting of products of one-electron wavefunctions. In general, for the ground state of a $2n$ electron system, only the $n$ molecular orbitals with the lowest molecular orbital energies are included in the Hartree-Fock solution. The rest of the molecular orbitals obtained will be excited molecular orbitals. Other possible wavefunctions of the product type can be formed by using excited molecular orbitals in the product. The set of all possible products can now be introduced as a basis set to solve the full Schrodinger equation. Such a calculation corrects the energy for what is termed electron correlation (that is, it corrects for the assumption of average motion used in the one-electron differential equation for the molecular orbital, $\psi_i$). This method is termed configuration interaction, because the sum is one over many electronic configurations involving excited electronic states (that is, the new molecular orbitals added to the list). For most chemical systems, the solutions obtained by extensive application of configuration interaction (high $N$) become equivalent to the exact solution of the potential energy surface discussed earlier.

The form of the one-electron functions employed in the expansion of the molecular orbital, eq (2), is obviously important for an accurate solution. We expect that the better the one-electron functions mimic the atomic orbitals of the atoms involved, the better our solution will be for $\psi$, even with a small number, $N$, of atomic orbitals. We have a fairly good idea of what the atomic orbitals look like from the exact solution of the hydrogen atom. The most salient feature of the hydrogenic atomic orbitals is their exponential dependence on the distance from the nucleus. These atomic orbitals form a very good set in which to expand the molecular orbitals in (2). However, in computing the average electrostatic potential a huge number of electron repulsion integrals involving the atomic orbitals on different atoms are needed. In the calculations to be discussed later, we typically carry out over one to ten million electron integrals per energy point. Therefore, the method requires that the integrals be calculated efficiently. Efficient integral evaluation is not possible with hydrogenic-like orbitals, also termed Slater-type orbitals or STO for short. Instead, the next new trick (introduced by Boys, 1950) is to write the STO themselves as a sum of gaussian functions. Gaussian functions are very convenient because any many-electron and many-atom integral can be computed immediately with analytic formulae. Hence the huge savings in time more than
offsets the need to expand each atomic orbital, $\phi_{\mu}$, in terms of a number $M$ of gaussian functions:

$$
\phi_{\mu} = \sum_{\nu=1}^{M} d_{\mu\nu} g_{\nu}
$$

(3)

The gaussian functions, $g_{\nu}$, in eq (3) have the form

$$
\phi_{\mu} \propto \exp (-\alpha r^2)
$$

where the exponent $\alpha$, controls how close to the nucleus the gaussian is, that is, how “diffuse” the atomic orbital will be. The size of the $M$ used in expanding each atomic orbital in terms of gaussians (eq 3) is usually included in the basis set description. Thus a STO-3G set is a minimal basis set with each atomic orbital (that is, each STO) expanded by three gaussian functions in eq (3) ($M = 3$). For extended sets, one normally utilizes more gaussians to describe the inner (core) atomic orbitals; therefore, more numbers are given in the label. For example, a 3-21G basis set is an extended basis set with three gaussians used to expand the core atomic orbitals, two gaussians used to expand one set of valence atomic orbitals and one gaussian used to expand a more “diffuse” set of atomic orbitals. (This is a split-valence basis set.) If, in addition, orbitals of higher angular momentum than required by the electrons in a given atom are employed (termed polarization functions), an asterisk is added. For example, the 3-21G* basis would add 3d orbitals on all second row atoms.

As an illustration, a Gaussian 3-21G* basis set for silicon will consist of the following atomic orbitals:

1s, 2s, 2p_x, 2p_y, 2p_z— all described with 3 Gaussians in eq (3)
3s, 3p_x, 3p_y, 3p_z, inner orbitals—2 Gaussians
3s, 3p_x, 3p_y, 3p_z, outer orbitals—1 Gaussian
3d_x^2, 3d_y^2, 3d_z^2, 3d_{xy}, 3d_{xz}, 3d_{yz},—1 Gaussian (polarization)

Altogether, 19 atomic orbitals will be inputed into the ab-initio calculations per Si atom, requiring 33 gaussian functions to describe them. For a calculation on H_3SiOH, there would be 36 atomic orbitals (19 on Si, 9 on O, and 2 on each H) input to obtain the molecular orbitals. The 36 atomic orbitals would be expanded by 60 gaussians.

Once an accurate wavefunction has been obtained in ab-initio calculations, the forces on all the atoms in a cluster can be computed exactly and analytically using well-developed quantum mechanical techniques. This ability enables us to carry out a full ab-initio minimization of the cluster geometry and extract the optimal equilibrium geometry. In general, the optimization algorithm searches for a stationary point, that
is, a molecular structure such that for all atomic coordinates the force is zero. Mathematically, this means that

$$\frac{\partial E}{\partial x_i} = 0 \quad i = 1, \ldots, 3N$$

(4)

for a cluster of N atoms, where E is the potential energy as a function of the atomic nuclear positions that is, the Born-Oppenheimer energy, E(R), in eq (1) and x_i refer to the x, y, z coordinates of the N atoms. Having reached a stationary point, it is important to ascertain whether the structure is a **true minimum**. This test is achieved by analyzing the eigenvalues of the second derivative or **Hessian matrix**:

$$H_{ij} = \frac{\partial^2 E}{\partial x_i \partial x_j}$$

(5)

For a true minimum, the eigenvalues of H must be all positive except for the six zeroes corresponding to three translations and three rotations of the cluster (which don’t change the energy in our case). This test is essential not only because it can enable us to explore postulated atomic structures and verify their stability but also because it empowers us to distinguish minima from saddle points and other more complex stationary points to be discussed in the next section. On the other hand, the eigenvalues do not permit us to determine whether the minimum is the minimum of lowest energy—a global minimum.

The kind of accuracy possible in solving the Schrodinger equation today can be clearly seen by the impressive agreement of many **ab-initio** results with experimental data (Gibbs, 1982; Sauer, 1989). As an example, figure 1 gives a number of results comparing **ab-initio** calculated interatomic bond lengths with experimental values. There is no question that with the present capabilities we can tap into the actual potential surfaces that account for the chemical behavior of a wide range of systems. Our next task is to extend this capability to understand the dynamics of geochemical reactions.

**TRANSITION STATE THEORY AND MINERAL KINETICS**

The ability to predict accurate potential surfaces means that we are in a position to investigate the nature of the kinetic barriers, including the activated complexes, of key surface processes. In fact, Born-Oppenheimer potential surfaces can be used not only with the transition state approach to kinetics but also with the much more general and exact collision theory (scattering S-matrix theory). While methods based on collision and scattering theory have pointed out deficiencies in the traditional transition state theory (TST), they have also served to uphold many of TST’s simple claims. In turn, new generalized transition state theories have been born. For complex systems, the transition state approach, while admittedly approximate, has been well established.
In coming to grips with adsorption, dissolution, precipitation, catalysis, and inhibition, geochemists have come to rely on the tools of transition state theory (Aagaard and Helgeson, 1982; Chou and Wollast, 1984; Dibble and Tiller, 1981; Helgeson, Murphy, and Aagaard, 1984; Knauss and Wolery, 1986; Lasaga, 1984; Murphy and Helgeson, 1987; Rimstidt and Barnes, 1980; Wood and Walther, 1983). Much has been written about the "activated complexes" on the surfaces of minerals. Numerous recent papers have invoked transition state theory in developing the mechanisms of low temperature water-rock reactions (see Lasaga, 1981; Aagaard and Helgeson, 1982). It is clear that one of the central themes in our understanding of heterogeneous kinetics is the elucidation of the important activated complexes and their modification by both surface properties and the composition of the solution near the surface as well as by temperature and pressure. One of the great
advantages of the *ab-initio* methods discussed in this paper is the remarkable ability to predict quantitatively reaction pathways and transition states for geochemically interesting reactions. At the same time, the rigorous molecular theory proposed here also paves the way to a solid foundation of the treatment of transition state theory in water-rock kinetics.

Contrary to some usage in the literature, a significant point to make about transition state complexes is that they are not true minima and hence are not normal chemical species in the thermodynamic sense. For example, the attack by \( H^+ \) on the surface of feldspars will lead to a surface that has exchanged alkalies for \( SiOH \) or \( SiOH_2^+ \) groups. While these latter species are surface complexes, **none** of these chemical moieties is an activated complex. Further attack by \( H^+ \) or by \( H_2O \) will hydrolyze the \( Si-O-Al \) and \( Si-O-Si \) bridging bonds as shown in the reaction:

\[
H_2O + \equiv Si - O - Si \equiv \Rightarrow 2 \equiv Si - O - H
\]  

Again, neither side of the reaction in (6) represents the activated complex. Both sides represent "stable" surface species.

While the activated complex is not a true minimum, its structure is *uniquely and precisely* determined by the Born-Oppenheimer potential surface. To ascertain the structure of the activated complex, we must appraise carefully the topography of the potential surface describing the reaction sketched in eq (6). One of the aims of this paper will be to show the applicability of *ab-initio* methods in unravelling the details of the activated complex for reactions such as (6).

Rimstidt and Barnes (1980) use the shorthand notation \((SiO_2\cdot2H_2O)^+\) for the "activated complex" in the dissolution and precipitation of silica. While this approach is satisfactory for the purposes in their paper, it is important to remember that it is only a heuristic label: we expect the reaction itself to proceed with several elementary reactions, as will be discussed in detail later in this paper. The last example raises another serious misuse of the theory (not to be blamed on Rimstidt and Barnes, 1980). Activated complexes are specific to a particular **elementary reaction**. One cannot discuss the activated complex without specifying the nature of the elementary reaction taking place, nor can one speak of the activated complex of an overall reaction.

The definition and the structure of an activated complex is fairly straightforward, if one has access to the *ab-initio* molecular results possible today. In the last section we introduced the Hessian matrix of a molecular cluster. We also pointed out that an essential test for a stable structure is the requirement that the Hessian matrix at the "equilibrium geometry" have all positive eigenvalues (the potential energy surface must be concave upward in "all" directions). The same Hessian matrix can define the classical activated complex (see fig. 2). An activated complex is a stationary point in the many-body potential surface of all
the atoms of the cluster such that the Hessian matrix has all positive eigenvalues except for one negative eigenvalue (ignoring the six zero eigenvalues for translations and rotations). In other words, the shape of the potential surface in the neighborhood of the activated complex would look like a "saddle point" (fig. 2), if the potential surface were to depend on only two degrees of freedom. The saddle point arises because the activated complex is a minimum in one direction and a maximum in the perpendicular direction.

Of course, for molecular clusters the potential surface typically contains tens of degrees of freedom, and so the saddle point cannot be portrayed on a 2-dimensional diagram. But in any of these cases, the requirement is that one and only one eigenvalue be negative. The positive eigenvalues would correspond to normal vibrations of the cluster around its minimum energy geometry. The single normal mode associated with the negative eigenvalue cannot be a vibration and becomes the motion associated with the reaction coordinate.

The full reaction coordinate can be obtained by initiating a motion away from the stationary point (activated complex) using the negative eigenvalue normal mode. Subsequent moves are done employing the method of steepest descent (that is, all the atomic coordinates are changed in the direction of $-\hat{\nabla}V$). Note that with the theoretical tools available today, we can compute $E(R)$, $\partial E/\partial x_i$, and $\partial^2 E/\partial x_i \partial x_j$ com-
pletely within a near-exact solution of the Schrodinger equation (in the Born-Oppenheimer scheme). As a result, not only can the minima of the potential surface be obtained systematically, but also any activated complexes can be obtained and verified from the *ab-initio* Hessian. Furthermore, the same near-exact solutions allow a detailed analysis of the reaction coordinate both from the normal mode analysis and from the subsequent steepest descent calculation.

Therefore two rigorous concepts arise from the previous paragraphs: (1) the activated complex is uniquely defined by the requirement of a stationary point with a Hessian that has a single negative eigenvalue, and (2) the normal mode of the negative eigenvalue uniquely defines (at least near the activated complex) the reaction coordinate. There is no need for qualitative or ad-hoc activated complexes, if the potential surfaces are available! Note also that for the complex many-variable potential surfaces of interest to us, it is very possible to find several "activated complexes" in different regions of the surface. The task, then, is to find the relevant elementary pathway through one (or more) of these activated complexes that controls the overall geochemical reaction being studied.

To illustrate the previous ideas, one could use a simple potential surface (fig. 2) such as given by the formula:

$$E(x, y) = \cos (x)(e^y + e^{-y})$$

In this case the first derivatives, $\partial E/\partial x$ and $\partial E/\partial y$ are both set to zero at the stationary points: $(n\pi, 0)$, where $n = 0, \pm 1, \pm 2, \ldots$. To find the nature of the stationary points, however, we need to look at the Hessian (eq 5):

$$\frac{\partial^2 E}{\partial x^2} = -\cos (x)(e^y + e^{-y}) \quad \frac{\partial^2 E}{\partial y^2} = \cos (x)(e^y + e^{-y})$$

$$\frac{\partial^2 E}{\partial x \partial y} = -\sin (x)(e^y - e^{-y})$$

Evaluating the Hessian at the stationary point $(n\pi, 0)$ gives:

$$\begin{pmatrix}
(-1)^{n+1}2 & 0 \\
0 & (-1)^n 2
\end{pmatrix}$$

Thus, all stationary points in this example are "activated complexes" with one positive and one negative eigenvalue. (The transition state theory extension to this case would be interesting.)

Once the activated complex has been found, the familiar formulae of TST can be used to learn something about the thermodynamic parameters of the activated complex reaction, $\Delta S^\ddagger$, $\Delta H^\ddagger$ as well as about
the rate constant, \( k \). Classical TST gives the following formula for the rate constant, \( k \):

\[
k = \frac{kT}{h} \frac{q^\ddagger}{V} \frac{\gamma^{\text{react}}}{\gamma^\ddagger} \exp\left(-\frac{\Delta E^\ddagger}{RT}\right)
\]

(7)

where \( k \) is Boltzmann’s constant, and the partition functions, \( q/V \), can all be derived from the geometry of the species and the vibrational frequencies (see Lasaga, 1981). The term \( \Delta E^\ddagger \) represents the energy difference between the energy at the stationary point (activated complex) and the minimum potential energy of the reactants. The \( \gamma \) terms represent activity coefficients for the various species and are assumed to be near unity, if the proper standard state has been chosen. If we incorporate the zero-point energies of vibrations from the vibrational partition functions into the exponential, we have:

\[
\Delta H^\ddagger = \Delta E^\ddagger + \frac{1}{2} \sum_i \hbar \nu_i^\ddagger - \frac{1}{2} \sum_i \hbar \nu_i^{\text{react}}
\]

(8)

We can then rewrite eq (7) as

\[
k = \frac{kT}{h} \frac{\gamma^{\text{react}}}{\gamma^\ddagger} e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT}
\]

(9)

where

\[
\Delta S^\ddagger = R \ln \left( \frac{q^\ddagger/V}{q^{\text{react}}/V} \right)
\]

(10)

The usual Arrhenius parameters (\( k = A \exp (-E_a/RT) \)) can be extracted from eq (9) to yield:

\[
E_a = RT + \Delta H^\ddagger
\]

(11)

and

\[
A = e^{\frac{kT}{h} \frac{\gamma^{\text{react}}}{\gamma^\ddagger}} e^{\Delta S^\ddagger/R}
\]

(12)

Eqs (7) to (12) enable us to link the microscopic results of ab-initio methods to the macroscopic observables of kinetic studies.

**MOLECULAR MECHANISMS OF WATER-ROCK KINETICS**

With the vast increases in computational power, it is now feasible to calculate ab-initio potential surfaces that incorporate bond-breaking and bond-forming processes. This means that we are now in a position to obtain the robust potential surfaces needed to map out the terrain wherein the dynamics of the geochemical reactions take place and begin
to tackle the kinetic and structural questions that arise in the quantitative treatment of geochemical reactions. In particular, the reaction pathways and energetics of surface reactions involving oxides and silicates can be studied from the atomic point of view with these techniques.

One of the notable conclusions from recent work (Gibbs, 1982; Lasaga and Gibbs, 1987, 1988; Dovesi and other, 1988) is that a major part of the structure and energetics of silicates and oxides can be accounted for by short-range directional forces, that is, what would be labeled "covalent" bonding in the traditional sense. As a result, relatively large (but finite) clusters of atoms that mimic the local environment can provide very significant insights into the atomic forces and bonding of minerals and glasses. As a corollary, we extend this local concept to the study of surface reactions.

One of the most important potential energy surfaces to investigate from the point of view of geochemical kinetics, petrology, ceramics, and rock mechanics is the hydrolysis of the Si–O–Si structural unit at the surface of silicates, that is, the reaction

$$\text{H}_2\text{O} + \equiv \text{Si} - \text{O} - \text{Si} \Rightarrow 2\equiv \text{Si} - \text{O} - \text{H}$$

(13)

This reaction is a key step in the dissolution processes occurring at the surfaces of silicates. Reaction (13) is also one of the essential aspects of the widely studied hydrolytic weakening in the area of rock mechanics. One of the current areas of active research in that field involves determining the molecular details of water or hydrogen defects in minerals. The incorporation of water by reactions, such as (13), can affect the rates of diffusion or creep by many orders of magnitude. In addition, reaction (13) is the basic step by which water is initially incorporated into silicate melts, thereby significantly affecting both the phase diagrams and the transport properties such as viscosity and diffusion.

Figure 3 illustrates a four step model of the elementary reactions that govern the dissolution of silica and similar silicates. These steps depict the sequential hydrolysis by water molecules of the three to four Si–O–Si bridges anchoring a surface silicon atom. At the end of the four hydrolysis steps, the silicon is bonded to four OH groups and leaves the surface as an orthosilicic acid molecule. None of the steps illustrated in figure 3 depicts the activated complex. Figure 4 focuses on one of these hydrolysis steps. The attack of water molecules is decomposed into two molecular steps. The first step in figure 4 involves the adsorption of water near a Si–O–Si group. The second step involves the formation of a new Si–O bond by the oxygen of the adsorbed water and the cleavage of the Si–O–Si group. It is the activated complex associated with this step we believe accounts for the energetics of silica dissolution.

Ab-initio studies of adsorption.—Ab-initio studies of adsorption have been done in a number of earlier papers (Sauer 1987, 1989; Geerlings and others 1984; Hobza and others 1981; Mortier and others 1984;
Chakonmakos and Gibbs, 1986). As discussed by Hobza and others (1981), in studying the adsorption energetics of water on silica surfaces, the appropriate reaction to use is:

\[
\text{H}_2\text{O} \cdots \text{H}_2\text{O} + M \Rightarrow M \cdots \text{H}_2\text{O} + \text{H}_2\text{O}
\]

(14)

where M stands for the appropriate silica surface group. In other words, the energy gained in adsorbing the water must be weighed against the energy lost in breaking a hydrogen bond. In fact, a study of the
The hydrophilic or hydrophobic nature of a surface group can be done by comparing the $\Delta H_0$ for adsorption to the $\Delta H_0$ for the reaction

$$H_2O + H_2O \Rightarrow H_2O \ldots H_2O$$

the product being the water dimer (Hobza and others, 1981).

The first step in our ab-initio study, therefore, is to ascertain the nature of water adsorption at silica surfaces. Note that the adsorption step in figure 4 occurs close to the silicon atom. This type of adsorption, where a hydrogen bond is formed between the hydrogen of the incoming water and the oxygen of the silica surface, is termed “acceptor” adsorption. Normally the surface of silica is covered by numerous silanol (SiOH) groups reaching about six to seven OH groups per 100 Å² (Iler, 1979). By far the most favorable mode of adsorption of water on silica is by “donor” adsorption onto a silanol group that is, by the hydrogen bonding of the H in the silanol group to the oxygen of the incoming water molecule so that water “sits oxygen down on the SiOH groups” (Iler, p. 627). This is shown in figure 5. The major role of silanol groups in water adsorption is shown by the hydrophobic character of silica, once the silanol groups are eliminated during dehydroxylation (heating to several hundred degrees for several hours). The surface
Fig. 5(A) Typical hydrated silica surface. Note the waters prefer to adsorb at the silanol groups; (B) the dehydroxylated silica surface containing hydrophobic siloxane groups.

of the dehydroxylated silica is composed of essentially Si–O–Si siloxane bonds (see fig. 5B). We will discuss the adsorption onto silanol groups below.

The key step in the kinetics of silica dissolution, however, requires a special type of water adsorption, that is, the acceptor adsorption shown in figure 4. This type of adsorption is required by the need to form a new SiO bond between the oxygen of the water molecule and the surface silicon atom in step 2 of figure 4. Note that the kind of adsorption postulated in figure 4 (and exhibited below) leads to a surface silicon that is 5-fold coordinated. The existence of 5-fold coordinated silicon in glasses and melts has been postulated in several MD papers (Angell and others, 1988; Kubicki and Lasaga, 1988) and inferred from recent spectroscopic work (Stebbins and McMillan, 1989; Xue and others, 1989). Although there are no mineral structures known to us that contain 5-fold coordinated silicon, there is both theoretical and experimental evidence for its existence. In fact, 5-fold coordinated silicon seems to play a key role in the high pressure increase of diffusion in silica glass (Kubicki and Lasaga, 1988). Ab-initio studies have shown that the SiO$_5$ moiety is indeed a stable structure (Damrauer and others, 1988). For example, figure 6 shows the fully optimized structure of Si(OH)$_5$ at the 3-21G* level (all 27 independent degrees of freedom of the molecule were optimized). The geometry is that of a distorted trigonal bipyramid. As discussed earlier, the full Hessian is computed, and all the 27 non-zero eigenvalues (frequencies of vibration) are indeed positive for the structure in figure 6, verifying its stability. In fact, as the OH$^-$ approaches one of the faces of the silicon tetrahedron, the energy monotonically decreases toward the minimum. The stability of 5-fold Si in gas phase complexes has also been verified recently in some time-of-flight experiments (Damrauer and others, 1988).
The situation with silicon is in interesting contrast to the behavior of its cousin, carbon. Numerous ab-initio studies of the $S_n^2$ nucleophilic reaction at carbon centers, for example reactions such as:

$$F^- + CH_3Cl \rightarrow CH_3F + Cl^-$$

have shown that the reaction pathway is schematically that shown in figure 7 (Wolfe, Mitchell, and Schlegel, 1981). Note that in this case, the 5-fold coordinated carbon moiety is not a stable species but rather an activated complex.

Table 2 gives our results for the adsorption of water on $H_3SiOH$. Note that the calculations that follow truncate the continuous surface silica lattice by using hydrogen atoms. It is essential to reiterate that the validity of this approach has been verified in the various previous studies.

---

Fig. 6. Ab-initio calculation of the geometry of the fully optimized fivefold coordinated silicon using a 3-21G* basis set.

Fig. 7. Sketch of the energy changes along the $S_n^2$ replacement reaction involving tetrahedral carbon atoms ($F^- + CH_3Cl \rightarrow CH_3F + Cl^-$).
on silicate crystal structures mentioned earlier (Gibbs 1982; Lasaga and Gibbs, 1987, 1988; Dovesi and others, 1988). The validity will also be shown by comparing the results obtained here with results of larger clusters. For each case in table 2, the structures and energies were obtained by optimizing all 21 degrees of freedom at the appropriate level of theory. This full minimization is important to verify whether the proposed structures are truly minima (see above), although the full minimization has not always been carried out in past work. Calculations employed both the 3-21G* extended basis set and the more robust 6-31G* basis with added electron correlation at the MP2 level (see Hehre and others, 1987). Figures 8 and 9 give the H₃SiOH and H₂O optimized geometries for the two basis sets. Note the generally very good agreement between the two calculations, showing the adequacy of the 3-21G* basis set. One important difference between the two sets is the narrowing of the SiOH angle in the higher level calculation. This narrowing predicts a SiOH angle of 116°, in very good agreement with the experimentally derived angle in silanol, 113° (Hair, 1967). The SiO bond is also slightly longer in the higher level calculation. The water results at the MP2/6-31G* level are in excellent agreement with the experimental data on the water molecule (r_OH = 0.958 Å, and HOH angle = 104.5°).

Fig. 8(A) Fully optimized 3-21G* geometry for the cluster H₃SiOH. (B) The fully optimized MP2/6-31G* geometry for H₃SiOH, including electron correlation.
Figure 10 gives the results for the water dimer. The optimized water dimer structure also compares well with recent gas-phase experimental data on the gas water dimer by Dyke (1984): $r_{\infty} = 2.98$ Å and tilt angle = $123^\circ$. The energy obtained in forming the hydrogen bond is given in table 2.

Figure 11 gives the geometry of the adsorbed water molecule in the case of donor adsorption onto the silanol group. Note the strong hydrogen bond formed. The oxygen-oxygen distance in figure 11 is 2.66 Å, which is actually shorter than the oxygen-oxygen distance (2.80 Å) calculated for the water dimer (fig. 10). Analysis of the Hessian matrix verifies that the adsorbed structure is a local minimum. In fact, table 2 indeed confirms that water adsorption onto the hydrogens of silanol groups on silica surfaces is energetically favorable; that is, the energy change for the reaction:

\[
\equiv \text{SiOH} + \text{H}_2\text{O} \rightarrow \equiv \text{SiOH} \cdot \cdot \cdot \text{OH}_2 + \text{H}_2\text{O}
\]

from table 2 is $\Delta E = -3.5$ kcal/mole.

Figure 12 gives the analogous adsorption for the more relevant (to us) acceptor adsorption. In agreement with the experiment, this adsorption is not as stable as the one onto the silanol group. However, an analysis of the Hessian matrix indeed shows that the geometry in figure
Fig. 11. Fully optimized 3-21G* geometry of the donor adsorption of water to the hydrogen of a silanol group.

12 corresponds to a full minimum in the Born-Oppenheimer surface. Note that for the 3-21G* calculation the distance from the silicon to the oxygen of the water molecule is 2.79 Å, which corresponds roughly to the OO distance in the water dimer. Furthermore, the distance between the hydrogen of the adsorbed water and the silanol oxygen is 1.91 Å, slightly larger than the OH distance (1.83 Å) in the water dimer. The MP2/6-31G* result for the acceptor adsorption (fig. 12B) has the water molecule even farther from the Si atom, although the hydrogen bonded OH distance is quite similar, 1.98 Å. In both cases, the OH bond length of the water molecule lengthens for the hydrogen atom involved in the H-bond. Likewise, the original SiO bond length increases upon adsorption of the water molecule, a precursor state to the ultimate rupture of the bond in the subsequent dynamics.

The energetics of reaction (21) for the case of the acceptor adsorption (see table 2) are not favorable (ΔE > 0). Because this adsorption is precisely the type of adsorption onto siloxane bonds (fig. 15), the unfavorable ΔE confirms the hydrophobic nature of the dehydroxylated disiloxane-rich surface of silica.

Fig. 12(A) Fully optimized 3-21G* geometry of the acceptor adsorption of water to the SiO bond in SiOH; (B) fully optimized MP2/6-31G* geometry of the acceptor adsorption of water to the SiO bond in SiOH.
Fig. 13. Potential energy variation as a function of the distance of the incoming water molecule from the Si atom in H₃SiOH. The calculation used a 3-21G* basis set and at each distance optimized all other degrees of freedom.

The energetics of the H₂O acceptor adsorption are of interest in monitoring the molecular dynamics of the adsorption process. We can obtain an interesting profile by fixing the bond distance between the silicon atom and the oxygen of the incoming water molecule and then optimizing all the remaining degrees of freedom. Figure 13 shows the results for several SiO bond distances. Note that the energy rise to the right of the minimum is quite gradual, so that the chemical interaction between a water molecule and the silica surface would extend out to nearly 7 Å away from the surface. This result has significant implications for the treatment of the adsorbed layer in silicates. The potential depicted in figure 13 would also be present in more complex scenarios and so would play a large role in the molecular dynamics of aqueous-silicate interfaces. Even though the full treatment must add the many-body effects of several water molecules and possibly other ions as well as temperature effects, the results in figure 13 suggest that the so-called Stern layer in silicates (the region of strong chemical adsorption) may be several water molecules thick, even in “pure” water.

Figures 14 and 15 show the analogous results for a 6-31G* **full** optimization calculation on disiloxane and the acceptor adsorption of water onto the disiloxane bridge. In agreement with our localization hypothesis, the SiO and OH bond distances in figure 15 agree closely with the corresponding distances in figure 12B.

The energetics given in table 2 must be corrected for zero-point energy of vibration to convert the energies to enthalpies, that is,

$$\Delta H_{0K} = \Delta E + \sum_i \frac{1}{2} \hbar \nu_i^p - \sum_i \frac{1}{2} \hbar \nu_i^R$$  \hspace{1cm} (17)
where P and R stand for product and reactant respectively, that is, the adsorbed complex and the infinitely separated water + surface in one case or the water dimer and the adsorbed water complex in the other. To calculate this correction, a full normal mode analysis of each stable configuration is carried out. The frequencies are obtained in a fully ab-initio manner by using the analytically derived Hessian matrix from the electronic wavefunctions. The corrected $\Delta H$ are given in table 2. Note that part of the correction to the $\Delta E$ for the case with the infinitely separated reactants arises from the conversion of a translational degree of freedom into a vibrational degree of freedom. The more relevant corrections are the corrections to the $\Delta E$ for reaction (14) or (16) shown in table 2 (which don’t have this loss of degree of freedom). The donor adsorption is stabilized (lower $\Delta H$, $-3.96$) by the zero-point correction while the acceptor adsorption is destabilized by the correction ($\Delta H$ increases to 0.22 kcal/mole).

*Transition state of the hydrolysis reaction.*—Having obtained the adsorption data, the next step is to ascertain the kinetics of the hydrolysis reaction, which requires computation of the activated complex.
Returning to figure 2, it is clear that the hydrolysis reaction proceeds in such a manner that the original SiO bond is broken and new Si–OH and OH bonds are formed. Figure 16 illustrates this reaction path. In the parlance of reaction dynamics, we term the initial configuration the entrance channel and the final (product) configuration, the exit channel. Both endmembers in figure 16 are stable species (true minima); the transition state complex must lie somewhere in between.

![Diagram of hydrolysis reaction](image)

Fig. 16. Reactant (entrance channel) and product (exit channel) structures in the hydrolysis reaction (3-21G* basis).

To find the activated complex, a convenient method is the so-called linear synchronous transit (LST) method (Halgren and Lipscomb, 1977). In this method, the two stable endmember geometries are interpolated to produce a simple reaction coordinate. In the LST scheme the reaction coordinate, \( f(0 \leq f \leq 1) \), is essentially an interpolation parameter between the interatomic distances, \( r_{ij} \), of the two minima (the reactants and products). Thus for a given parameter, \( f \), the corresponding inter-atomic distances between any pair of atoms \( i \) and \( j \) is given by:

\[
r_{ij} = (1 - f)r_{ij}^R + fr_{ij}^P
\]

where \( r_{ij}^R \) and \( r_{ij}^P \) are the interatomic distances for the reactant and product geometries respectively. For a system with \( N \) atoms, there are \( N(N - 1)/2 \) interatomic distances and only \( 3N - 6 \) independent degrees of freedom (the \( x, y, z \) of atoms). Therefore eq (18) is an overdetermined systems of equations. In the LST approach eq (18) is solved in the least squares sense for each value of \( f \) (see Halgren and Lipscomb, 1977).

We can apply the LST scheme to the two minima shown in figure 16. The results of applying the LST scheme to the hydrolysis reaction are shown in figure 17. Note the very large energy barrier between the entrance and exit channels. If figure 17 represented the true energetics of the hydrolysis reaction, then our mechanism would be quite at odds
Fig. 17. LST calculation of the variation in energy along the LST "reaction coordinate" for the 3-21G* hydrolysis reaction illustrated in figure 16.

with experimental data on the activation energies of silicate-water reaction kinetics. However, the structure at the maximum in figure 17 is not a stationary point, as required for a true activated complex (\(\partial E/\partial x_i\) is not zero for all \(x_i\) in fig. 17). The next step, therefore, is to optimize further the LST structure. Because the complex involves the transfer of a hydrogen atom from the incoming water to the departing water (see fig. 16), we expect (by symmetry) that the two OH bonds would be nearly equal in the activated complex. Similarly, the two SiO bonds (the one being formed and the one being broken) should be of similar length at the activated complex. Taking this into account, we optimized the \(f = 0.5\) LST structure with respect to all degrees of freedom except with the constraint that the two SiO bond lengths and the two particular OH bond lengths be equal. The resulting optimized geometry is shown in figure 18. Note that the SiO bond lengths are both now lengthened to 1.84 Å (from the minimum geometry). The OH bond distances are 1.20 Å.

The most interesting result of the new optimization is the dramatic drop in the energy difference, \(\Delta E\), to the value 21.87 kcal/mole (see table 3). This new value should be close to the final \(ab initio\) activation energy barrier for the reaction, \(\Delta E^\ddagger\). This \(\Delta E\) value is also remarkably close to the activation energy for silicate dissolution and in particular for quartz dissolution (Lasaga, 1984).

Again to compare the \(\Delta E\)'s to experimental quantities we must include the zero-point vibrational energies.

\[
\Delta H^\ddagger = \Delta E^\ddagger + \sum_{i=1}^{3N-7} \frac{1}{2} \nu_i^{\ddagger} - \sum_{i=1}^{3N-6} \frac{1}{2} \nu_i^{ads}
\]  

(19)
Fig. 18. Approximate transition state for the hydrolysis reaction discussed in the text, using 3-21G* basis.

This correction is quite non-trivial in this case and reduces the barrier by 1.22 kcal/mole (see table 3). Note that part of the loss in the barrier is due to the fact that the activated complex is "loose" compared to the adsorption complex. Structures with many elongated bonds tend to have lower frequencies of vibration and hence smaller \( \frac{1}{2}h\nu \) corrections. Therefore, the increase in zero-point energy of vibration is bigger for the stable adsorption complex than for the activated complex. This correction has important consequences for the isotope effect in the dissolution and precipitation of quartz, which will be discussed later.

The approximate activated complex in figure 18 was obtained by a reasonable constraint on the bond lengths. When a calculation of all the forces on the atoms is performed, one indeed obtains near zero values for all the forces (a near stationary point). Furthermore, the full frequency calculation on the structure in figure 18 yields all positive eigenvalues (normal frequencies) except for one negative eigenvalue (imaginary frequency), as required for an activated complex. Therefore, this structure is very close to the true activated complex. In fact, the

<table>
<thead>
<tr>
<th></th>
<th>( \Delta E^* )</th>
<th>( \Delta E^{**} )</th>
<th>( \Delta E^{***} )</th>
<th>( \Delta E^{****} )</th>
<th>( \Delta E^{**'} )</th>
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<td>( E_2 )</td>
<td>21.87</td>
<td>22.74</td>
<td>16.70</td>
<td>~30.05</td>
<td></td>
</tr>
<tr>
<td>Vibrational Zero-Point</td>
<td>-1.22</td>
<td>-1.30</td>
<td>-1.30</td>
<td>~1.25</td>
<td></td>
</tr>
<tr>
<td>( \Delta H_0 )</td>
<td>20.65</td>
<td>21.44</td>
<td>15.40</td>
<td>~28.80</td>
<td>18.0'</td>
</tr>
</tbody>
</table>

*Approx 3-21G* results.  
**Full 3-21G* transition state.  
***MP2/3-21G* results.  
****Approx MP2/6-31G* results.  
'Quartz dissolution data.
structure in figure 18 can be input into a full search for a stationary point, and the result, the true activated complex, is given in figure 19. That this is a true activated complex follows from the exact satisfaction of the two key requirements: (1) the structure in figure 19 is a stationary point for all degrees of freedom (eq 2) and (2) the eigenvalues of the second derivative matrix (Hessian) are all positive except for one negative and the usual 6 zeroes. Interestingly enough, the symmetry of the two SiO bonds is closely maintained in the full transition state complex. However, the two OH distances (1.104 and 1.310 Å) are not symmetrical. This assymetry arises from the symmetry breaking induced by the other groups in the activated complex and also manifests the malleable nature of the lengthened OH bonds.

Fig. 19. Exact transition state for the hydrolysis reaction using the 3-21G* basis set.

The new values for $\Delta E^\ddagger$, $\Delta(\frac{1}{2}h\nu)$, and $\Delta H^\ddagger$ are in table 3. These values confirm the close approximation represented by the results from figure 18. This close agreement is important for other calculations, because it is usually non-trivial to converge on the exact activated complex. The activation energy predicted from our exact activated complex is in excellent agreement with experimental values. One should add that the correct comparison, given the kinetic mechanism in figures 2 and 4, should add the true enthalpy of adsorption for the water molecule, $\Delta H_{H_2O}^{ads}$ (Lasaga, 1981, p. 37), and RT correction in eq (11)

$$E_a^{exp} = RT + \Delta H^\ddagger + \Delta H_{H_2O}^{ads}$$

However, we expect $\Delta H^{ads}$ to be either close to zero or a small negative number (several kcal/mole—see table 2). The net effect of the corrections in (27) would most likely be to increase slightly the agreement.

Table 4 gives the frequency spectrum of the activated complex. Note that all frequencies are positive (real) except for one imaginary frequency. In particular, we want to look at the normal mode with the negative eigenvalue (an imaginary frequency because $(2\pi\nu)^2 = \lambda$; for our
Table 4

Transition state vibrational frequencies

<table>
<thead>
<tr>
<th>3-21G* H₅SiOH – H₂O Transition state</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frequencies (cm⁻¹)</td>
</tr>
<tr>
<td>---------------------</td>
</tr>
<tr>
<td>884.3 i</td>
</tr>
<tr>
<td>4011.1</td>
</tr>
<tr>
<td>3984.0</td>
</tr>
<tr>
<td>2496.6</td>
</tr>
<tr>
<td>2388.8</td>
</tr>
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<td>2296.7</td>
</tr>
<tr>
<td>2157.8</td>
</tr>
<tr>
<td>1300.1</td>
</tr>
<tr>
<td>1274.6</td>
</tr>
</tbody>
</table>

case, \( \nu^i = 884 \text{ cm}^{-1} \). As mentioned earlier, this normal mode is, in fact, the **reaction coordinate** for the hydrolysis reaction. Any normal mode gives the deviation of the atoms from the stationary point (in this case, the transition state). Therefore, to analyze the reaction coordinate normal mode, we perturb the transition state geometry by the normal mode vector corresponding to the 884 i frequency. Note that the amplitude of the perturbation is arbitrary, we are simply interested in the relative changes of the internal coordinates. Thus, we want to compare the internal coordinates of the transition state (see fig. 19) to the internal coordinates of the perturbed geometry. The changes along the reaction coordinate are compared in table 5. The asterisks in table 5 denote internal coordinates that have changed significantly. It is clear that the motion along the reaction coordinate involves predominantly the transfer of the H-atom, that is, the “vibration” has one OH distance increasing (1.31 Å \( \rightarrow \) 1.47 Å) and the other OH distance decreasing.

Table 5

Transition state reaction coordinate

<table>
<thead>
<tr>
<th>Internal coordinate</th>
<th>Stationary point</th>
<th>Normal mode value*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si O BOND</td>
<td>1.835</td>
<td>1.836</td>
</tr>
<tr>
<td>Si O BOND</td>
<td>1.831</td>
<td>1.835</td>
</tr>
<tr>
<td>Si H BOND</td>
<td>1.509</td>
<td>1.515</td>
</tr>
<tr>
<td>Si H BOND</td>
<td>1.490</td>
<td>1.484</td>
</tr>
<tr>
<td>Si H BOND</td>
<td>1.474</td>
<td>1.491</td>
</tr>
<tr>
<td>O H BOND*</td>
<td>1.104</td>
<td>1.044</td>
</tr>
<tr>
<td>O H BOND</td>
<td>0.960</td>
<td>0.966</td>
</tr>
<tr>
<td>O H BOND*</td>
<td>1.310</td>
<td>1.474</td>
</tr>
<tr>
<td>O H BOND</td>
<td>0.958</td>
<td>0.979</td>
</tr>
<tr>
<td>Si O H ANGLE</td>
<td>124.5</td>
<td>123.0</td>
</tr>
<tr>
<td>Si O H ANGLE*</td>
<td>87.6</td>
<td>95.2</td>
</tr>
<tr>
<td>O Si O ANGLE</td>
<td>69.9</td>
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<td>O H O ANGLE*</td>
<td>120.7</td>
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<td>128.5</td>
</tr>
<tr>
<td>H O H ANGLE*</td>
<td>136.6</td>
<td>141.9</td>
</tr>
</tbody>
</table>

*Changed internal coordinate along reaction coordinate (see text).
(1.10 Å → 1.04 Å). Interestingly, the two long SiO bonds (which ultimately must also get involved in the reaction) are not very active in the reacton coordinate normal mode. This result states that the H transfer dominates the hydrolysis reaction!

The dynamics of the activated complex can be nicely studied by an “ab-initio movie.” Part of the movie can be created by altering slightly the structure in figure 19 along the negative eigenvalue normal mode (along the reaction coordinate). The subsequent changes in geometry are derived from following the energy drop along the steepest descent direction. This scheme will display, in movie fashion, the entire reaction coordinate (in an ab-initio manner) as the activated complex slides right into one of the two minima in figure 16 (depending on which way the complex was “tilted”). Indeed, if the OH bond in figure 19 is slightly increased from 1.104 Å to 1.109 Å, the structure proceeds to move on to the exit channel depicted in figure 16. On the other hand, if the process is started right at the structure in figure 19, nothing will happen, which simply reiterates the stationary nature of the activated complex. Figure 20 gives a summary of such a movie by freezing the motion at different times. The initial frame in figure 20 has the water molecule at a distance beyond the adsorption minimum. The approach of the water molecule to the adsorption minimum (fig. 16) is calculated using ab-initio minimization of all other degrees of freedom except the Si-O distance to the water molecule, which is fixed. Once the minimum is reached, the “movie” follows the reverse of the steepest descent “movie” generated from the transition state to the minimum by the path discussed above. The total movie summarized in figure 20 depicts the arrival of a water molecule, its adsorption at the silica surface, the formation of a transition state complex, reaction, and the hydrolysis of the SiO bond yielding the products at the other minimum. It is interesting to note that initially the water molecule (see fig. 20A) is “harpooned” by a hydrogen bond with the O of the SiOH group. Therefore, the water molecule comes in with one of its hydrogen atoms pointing first. As the water molecule gets nearer, it begins to turn so as to be able to form the long Si-O bond of the adsorption minimum (fig. 20D). Figure 20D to G shows the uphill path to the transition state, and figure 20G to I the formation of the products (going “down-hill”).

There is another interesting prediction we can make based on the ab-initio activated complex. After establishing both stationary points, that is, the adsorbed complex (fig. 16) and the activated complex (fig. 19), the wavefunction can be used to extract analytically the full second derivative Hessian matrix (eq 5). All the vibrational frequencies can then be obtained from diagonalizing the vibrational matrix defined by (Wilson, Decius, and Cross, 1955):

\[ V_{ij}^{\text{vib}} = \frac{1}{\sqrt{m_i} \sqrt{m_j}} \frac{\partial^2 E}{\partial x_i \partial x_j} \]  

(21)
Fig. 20. *Ab-initio* "movie" of the approach, adsorption, and reaction of a water molecule leading to hydrolysis of the SiO bond. Calculations used 3-21G* basis sets.

where $m_i$ and $m_j$ are the atomic masses of the nuclei corresponding to coordinates $x_i$ and $x_j$, and $\partial^2 E/\partial x_i \partial x_j$ is the usual Hessian matrix. Hence, once the Hessian is obtained, not only can the frequencies used in table 3 be derived from the usual atomic masses, but also any *isotope effects* can be investigated by introducing the appropriate mass changes in eq (21) for $V^{\text{vib}}$.

A very interesting calculation would be to replace the incoming water in figures 16 and 19 by $D_2O$. Changing the masses of the atoms does not change the electronic energies and hence would not change $\Delta E^3$ at all; however, it will change the zero-point vibrational correction. Because $D_2O$ has heavier masses, the frequencies will be lower (recall $\nu = \frac{1}{2\pi} \sqrt{k/m}$ in simple vibrations) and decrease the zero-point correction. In fact, when the mass change is introduced, the zero-point correction for the activation energy of the $D_2O$ activated complex is only $-0.70$ kcal/mole. As a result the activation energy for quartz dissolution in $D_2O$ should be $0.6$ kcal/mole higher than that in $H_2O$. 
Careful experiments (Bill Casey, personal commun.) may be able to test this predicted shift in the activation energy.

We can carry this analysis further by using the transition state formulae for the reaction rate constant given earlier. Using eq (7) we can write:

\[
\frac{k(D_2O)}{k(H_2O)} = \frac{q^+(D_2O)q^{adH}(H_2O)}{q^+(H_2O)q^{adH}(D_2O)} \exp \left( -\frac{\Delta H^+(D_2O) - \Delta H^+(H_2O)}{RT} \right)
\]  

(22)

The partition function of any moiety can be broken down into a translational, rotational, and vibrational component:

\[
q = q_{\text{trans}} q_{\text{rot}} q_{\text{vib}}
\]

(23)

Because the translational partition function depends only on the total mass of the species, the translational partition functions all cancel in (22). The other partition functions (see Lasaga, 1981) reduce (22) to:

\[
\frac{k(D_2O)}{k(H_2O)} = \sqrt{\frac{I_2^+(D_2O)I^{adH}(H_2O) \Pi_i(1 - \exp (-\hbar \nu_{j}^{adH}/RT))_{D_2O}}{I_2^+(H_2O)I^{adH}(D_2O) \Pi_i(1 - \exp (-\hbar \nu_{j}^{adH}/RT))_{H_2O}}} \exp \left( -\frac{\Delta H^+(D_2O) - \Delta H^+(H_2O)}{RT} \right)
\]

(24)

where the Is stand for the product of the three principal moments of inertia for each of the moieties, and the product is taken over all positive vibrational frequencies (we exclude the imaginary frequency in the case of the transition state). The first product term on the right of eq (23) represents the rotational contribution to the rate constant ratio, the next two terms are the vibrational contribution, and the last term represents the contribution from the activation enthalpy difference discussed above. We can use the structural and vibrational data from the adsorption minimum (fig. 12A) and the transition state (fig. 19) to compute the effect of each term on the predicted rate constant ratio as a function of temperature. The results are given in table 6. The numbers in table 6 suggest that the rate of quartz dissolution in pure D_2O should be about a factor of three slower than the same rate for quartz dissolution in pure H_2O. Obviously a non-trivial isotope effect is predicted, which should be observed experimentally. Current experimental work (Casey, personal commun.) is being carried out to test the predictions.

The energetics of the reaction can be improved by carrying out a calculation adding electron correlation. If we carry out calculations at the MP2 level (see table 3), the activation energy changes to \( \Delta E^+ = 16.7 \) Kcal/mole. These results strongly indicate that we are indeed obtaining for the first time a look at the key chemical moieties driving the dissolution of quartz and related minerals.
Table 6

<table>
<thead>
<tr>
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<th>Temperature (°C)</th>
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<td>25</td>
</tr>
<tr>
<td>Rotn ratio</td>
<td>1.015</td>
</tr>
<tr>
<td>Vib ratio</td>
<td>0.837</td>
</tr>
<tr>
<td>$E_a$ ratio</td>
<td>0.361</td>
</tr>
<tr>
<td>$k(D_2O)/k(H_2O)$</td>
<td>0.307</td>
</tr>
</tbody>
</table>

Even more extensive calculations were done optimizing both the adsorption and the activated complex structures at the MP2/6-31G* level. The results are given in table 3. The approximate activated complex is given in figure 21. Note that in this case a full optimization of the transitions state complex has not yet been done, and hence the values are expected to be on the high side. Nonetheless the value of $\Delta H^\ddagger$ is in the vicinity of the observed energetics of silicate reactions.

![Diagram of MP2/6-31G* transition state](image)

Fig. 21. Approximate transition state optimized using the MP2/6-31G* basis set and electron correlation.

Future calculations will not only finish the optimization of the MP2/6-31G* transition state above but also carry out similar studies for the next higher cluster, disiloxane + water (fig. 15), that is, the hydrolysis reaction:

$$\text{H}_2\text{O} + \text{H}_3\text{Si} - \text{O} - \text{SiH}_3 \Rightarrow \text{H}_4\text{SiO} + \text{H}_4\text{SiO}$$

(25)

Another set of investigations will explore the effects of adsorbed cations on the hydrolysis reaction. Recent experiments (Dove and Crerar, 1989) have shown that hydrothermal dissolution of quartz can be significantly catalyzed by Na$^+$ and K$^+$ cations and to a lesser extent by Li$^+$ cations in the solution. The explanation of the catalytic effect should
be related to the effects of these cations on the molecular reaction by water discussed in this paper (see Dove and Crerar, 1989, for discussion).

While the applications in this paper have focused on quartz, there are several sets of experimental data that suggest that the hydrolysis of Si–O–Si groups by water molecules may very well be the most important reaction step in mineral dissolution. Therefore, the application of these results to other silicates may be fairly direct.

One problem that will have to be addressed at some point is the transference of the potential surface data to complex situations such as water in contact with a silicate surface. While it is true that there are many water molecules present during the dissolution of quartz, it is clear that the close chemical interaction of one water molecule with a Si–O–Si bridge at the surface will be dominated by the energetics that have been presented in this study. Therefore, while we cannot ignore the further complexities of liquid structure in the problem, the major features of the water reaction with Si-O bonds will emerge from the ab-initio calculations that we are capable of carrying out at this stage. The close agreement of calculated and observed activation energies indicates that indeed these molecular moieties are the ones relevant to surface reactions. To be able to probe actual molecular mechanisms, the details of activated complexes and even obtain a first principles “movie” of the adsorption and dissolution processes on surfaces is an exciting prospect. In turn, this result truly opens a new era for the study of surface reactions.

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