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# Silica fracture

## Part II *A ring opening model via hydrolysis*

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A quantitative model of environmentally sensitive crack growth of amorphous silica (a-silica) is based upon semiempirical molecular orbital (MO) calculations (AM-1 method) of a water molecule interacting with strained three- and four-fold silica rings and a five-fold ring-chain structure. The energy barrier for hydrolysis of strained 3-fold rings is only 7 kcal mol$^{-1}$, the energy barrier for hydrolysis of strained four-fold rings is 29 kcal mol$^{-1}$; for a five-fold ring-chain it is 39 kcal mol$^{-1}$. Thus, the MO model predicts that the energetics of Region 1 slow crack growth is controlled primarily by the distribution and hydrolysis of three-membered silica rings in the a-silica structure, and Region III is controlled by the distribution and energy of contraction of four and four+membered rings.

## 1. Introduction

In Part 1, the fracture of a Si–O–Si bond without the interaction of water was modelled using AM1 molecular orbital (MO) theory. A ring contraction model was presented as the preferred path of crack propagation through vitreous silica. The effects of environment on the fracture of vitreous silica (v-silica) and other glasses has been of interest for many years, because it is well known that water and other polar liquids with lone pair electrons greatly enhance the rate of crack growth. Several phenomenological stress corrosion models have been produced to describe the mechanism by which water interacts with a crack tip with varying degrees of success in predicting fracture mechanics results. One of the most successful, the Michalske–Freiman (MF) model of slow fracture [1], involves an atomistic three-part reaction sequence for water attack at the strained Si–O–Si bond bridging the crack tip (Fig. 1a). In this part, AM1 MO theory will again be used to study the details of fracture in the presence of water or hydrolysis of silicate rings.

### 1.1. Michalske–Freiman model

Step I. A water molecule is adsorbed at the strained crack tip. The oxygen lone pair on the water interacts with a silicon atom. A hydrogen bond is formed between the water molecule and the bridging oxygen.

Step II. Two silanol groups are formed by cleavage of the Si–O bond and the O–H bond in the adsorbed water.

Step III. The remaining weak hydrogen bond breaks to form two fracture surfaces which are covered with silanols.

The MF model shows how various molecules, such as water, ammonia, hydrazine, and formamide, can chemically lower the energy required to break siloxane bonds in silica and give rise to linear stress intensity, $K_1$, versus log crack velocity, $V_c$, relationships. However, as discussed by Michalske and Bunker (MB) [2], the MF model "does not address the effect of strain on the chemical reactivity of the solid". This deficiency is addressed in the MB model which is based upon the development of strained bond angles in v-silica.

Five steps are proposed in MB model (Fig. 1b) leading to formation of a chemically active kink site followed by bond rupture. A kink site is defined as "a bond which is strained enough to drastically increase its reaction rate". Kink motion is "the reaction of an active bond with an environmental molecule to produce a broken bond". Thus, in the MB model, "the stress corrosion rate is controlled by the number of active sites along the crack front (kinks) and their rate of reaction with the environment". The kinks in v-silica thus serve a similar function to dislocations in crystalline solids.

### 1.2. Michalske–Bunker model

The five step MB model is shown in Fig. 1b.

Step I. Apply stress to a ring in the v-silica lattice.

Step II. Conformation change occurs (the ring puckers).

Step III. The siloxane (Si–O–Si) bond angles are extended.

Step IV. The O–Si–O bond angle is pinched to form a kink, plus adsorption of a reactive molecule of the kink site.

Step V. Bond rupture occurs.

The local environment encountered at the crack tip in either the MF or MB models is a strained Si–O

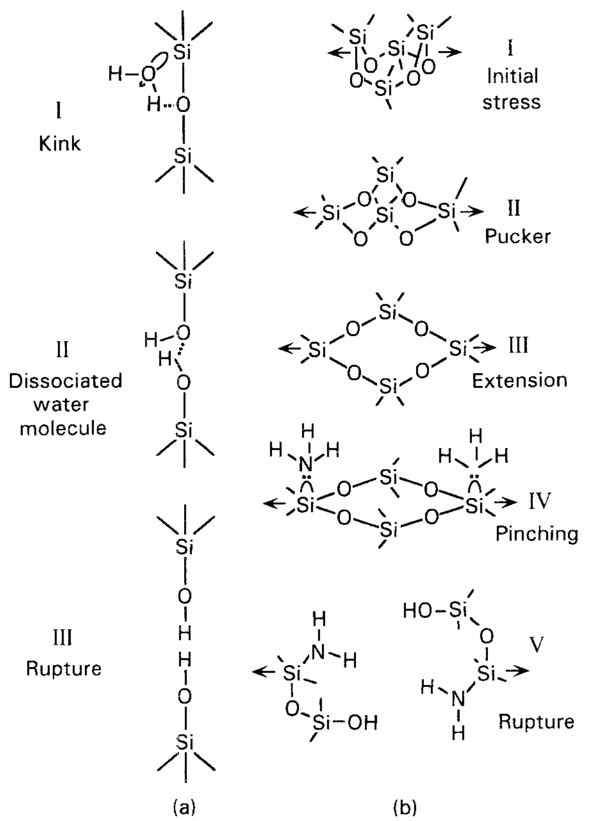


*Figure 1* Reaction steps in environmentally enhanced fracture of vitreous silica in (a) the Michalske–Freiman model [1] and (b) the Michalske–Bunker model [2].

bond. However, any specific Si–O bond must be part of a ring structure within the bulk vitreous silica. Various models of vitreous silica describe the structure in terms of distributions of three-, four-, five- and six-fold or greater rings [3]. The bond angles and bond distances and relative ring energy vary as a function of the number of tetrahedra in the ring, with planar four-fold rings having the lowest energy and two-fold rings having the highest energy [4]. The effect of ring geometry and energy must be accounted for in an accurate model of bond fracture. The objective of this paper is to examine the effects of silica ring size and structure on fracture of siloxane bonds with and without the presence of water. The structural changes that occur during fracture, in terms of changes in bond angles and bond distances, are related to the kinks proposed in the MB model.

### 1.3. Am-1 molecular orbital method

Dewar *et al.* [5, 6] have shown that the modified neglect of diatomic overlap (MNDO) semi-empirical MO method can be used to model the reactions of silicon-containing molecules. However, there are two situations in which MNDO produces large errors. MNDO overestimates core–core repulsions between atoms when they are separated by approximately van der Waals distances. This means that MNDO cannot reproduce hydrogen-bonds or accurately calculate the heat of formation, $H_f$, for strained or crowded molecules, such as those involved in bond fracture. The MNDO method also overestimates transition state energies and distorts transition state geometries, again fatal flaws for calculating bond-fracture mechanisms. The Austin Method (AM1) [5–7], a semi-empirical method, reduces these problems by modifying the core-repulsion function used in MNDO with additional Gaussian terms and the calculated structures and heats of formation match quite well with experimental values.

In studying nucleophilic reactions, such as those involved in water-enhanced bond fracture, it is necessary to model two reactions that occur simultaneously. A model of simple Si–O bond breaking similar to Fig. 1a, followed by disassociation of the $H_2O$ molecule, would not yield realistic results due to the creation of unpaired electrons in the reaction. AM1, and other semi-empirical methods, does not include the wavefunctions for unpaired electrons. This limitation is overcome by using a simultaneous dissociative proton-transfer reaction path, during which no unpaired electrons are formed. This approach has been applied to modelling the hydrolysis of a three-fold silica ring (Raman $D_2$ trisiloxane ring) [8–10] and is extended in this study to strained four-fold silica rings and a five-fold silica ring-chain cluster with and without the presence of water.

The structures used to model the Si–O bond-fracture mechanisms were optimized within the parameters of MOPAC 6.1 using the AM-1 method. Some earlier calculations, used for comparison, were done using MOPAC 5.0. The heats of formation obtained for the silica reactions are similar for both MOPAC 5.0 and 6.1. However, important features were recalculated using the newer 6.1 versions.

## 2. Results of bond-hydrolysis models

### 2.1. Three-fold silica ring hydrolysis

Breaking of Si–O bonds in three-fold silica rings has been modelled by West and Wallace [8–10], using MOPAC 5.0, in a study of the hydrolysis of a three-membered trisiloxane ring, also known as the $D_2$ Raman defect. The activated complex for hydrolysis has a small barrier of only 2.8 kcal mol$^{-1}$ (Fig. 2). The

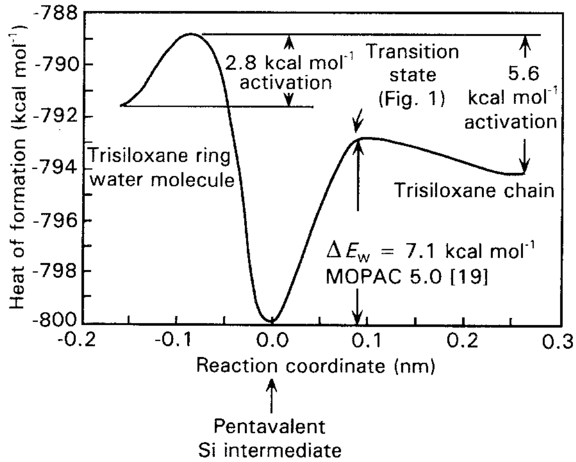


*Figure 2* Reaction path for the Si–O bond fracture during hydrolysis for a cyclotrisiloxane (three-fold) ring (modified from [10]).

barrier (saddle point) to Si–O pentacoordinate hydrolysis ($\Delta E_w$ is 7.1 kcal mol$^{-1}$ as also shown in Fig. 2. The overall activation energy for reforming a ring from the chain by condensation is 5.6 kcal mol$^{-1}$ (see [9, 10] for a description of the dissociative proton-transfer process involved in obtaining the complete reaction path). The low values of energy required for the bond-breaking reaction are due to formation of an intermediate transition state where the water molecule is pentacoordinately bonded to one silicon. A hypervalent silicon atom has been found consistently in AM1 calculations where water interactions are involved and has been observed experimentally in gas-phase reactions and in high-pressure Raman studies of silicon methoxide hydrolysis. The pentacoordinate silicon state occurs with low energy barriers because silicon can easily form sp$^3$d hybrid orbitals and assume five-fold coordination complexes [11, 12].

## 2.2. Four-fold silica ring hydrolysis

When water adsorbs on to the four-fold silica ring, a pentacoordinate silicon bond is formed with the structure shown in Fig. 3. Strain was imposed with 0.01 nm increments, thereby extending the bond length between Si(1) and Si(7). Only one transition state was found and the geometry of the saddle-point structure is shown in Fig. 4. Once again, a pentacoordinate silicon is involved. The structural evolution during hydrolysis creates an unstable two-membered ring that shares an edge with the four-membered ring. However, the energy barrier for hydrolysis of the four-fold ring is only 22 kcal mol$^{-1}$ (Fig. 5), nearly one-third less than the value associated with fracture without water as presented in Part I. The end point of the hydrolysis reaction is the conversion of the four-membered ring into a four-membered chain, as shown in Fig. 5.

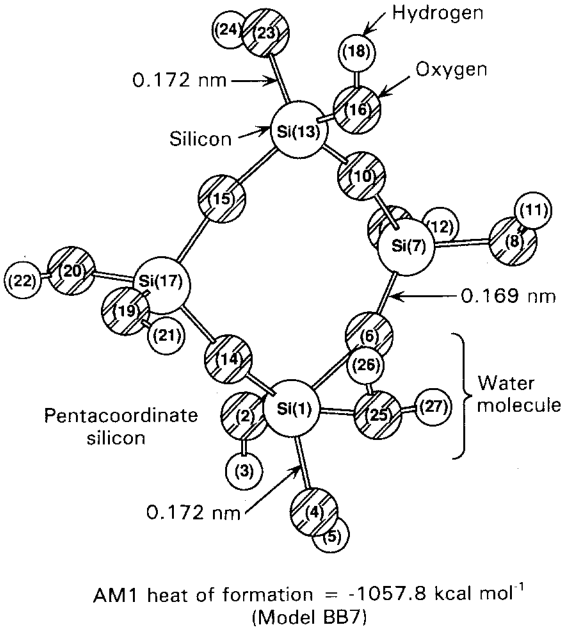


*Figure 3* A cyclotetrasiloxane (four-fold) ring with a pentacoordinately bonded water molecule.

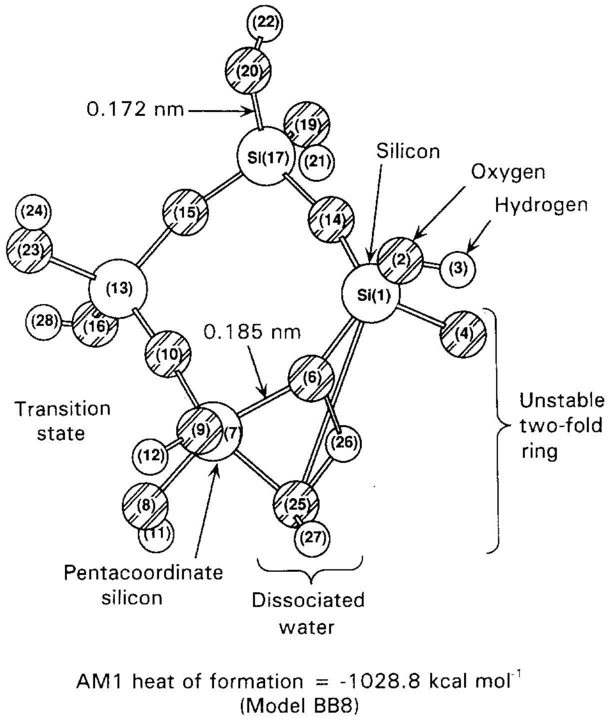


*Figure 4* The transition state for an Si–O bond fracture in a cyclotetrasiloxane (four-fold) ring with water interaction.

## 2.3. Five-fold ring-chain structure hydrolysis

The limitations of RHF, UHF, or Cl methods in studying bond breaking are due to creation of unpaired electrons. The problem of unpaired electrons was minimized in the water-free fracture calculations by using the unrestricted Hartree Fock (UHF) method. However, adsorption of water at the strained bonds avoids this concern because unpaired electrons are not produced during a hydrolysis reaction. Instead, the water molecule acts as a nucleophile by donating charge which prevents formation of unpaired electrons [10].

As in Part I, strain of a silica tetrahedron bonded to a four-membered tetrasiloxane ring was chosen to represent the effects of the vitreous silica (v-silica) matrix on the fracture process. This five-fold ring-chain structure is shown in Fig. 6.

In modelling the strain-enhanced hydrolysis of the five-fold silica ring-chain structure (Fig. 6) the RHF AM1 theory in MOPAC 6.1 was used. The complete series of models computed is shown in Figs 6–10. Fig. 6 shows the initial structural configuration prior to the interaction of the water molecule with the siloxane bond. The water molecule hydrogen bonds to the silica cluster (structure not shown) which decreases the Si(1)–O(2) bond distance from 0.173 nm to 0.169 nm. A transition state occurs as the water molecule interacts with the cluster (Fig. 7). This transition state precedes formation of a pentacoordinate silicon, Si(1), which is bonded to the lone pair electrons of the water molecule (Fig. 8).

The critical structural change occurs (Fig. 9) through the formation of two petacoordinate silicons, Si(1) and Si(3) and an unstable disiloxane ring. The water molecule dissociates from the silica cluster in this transition state (Fig. 9). The final step is the

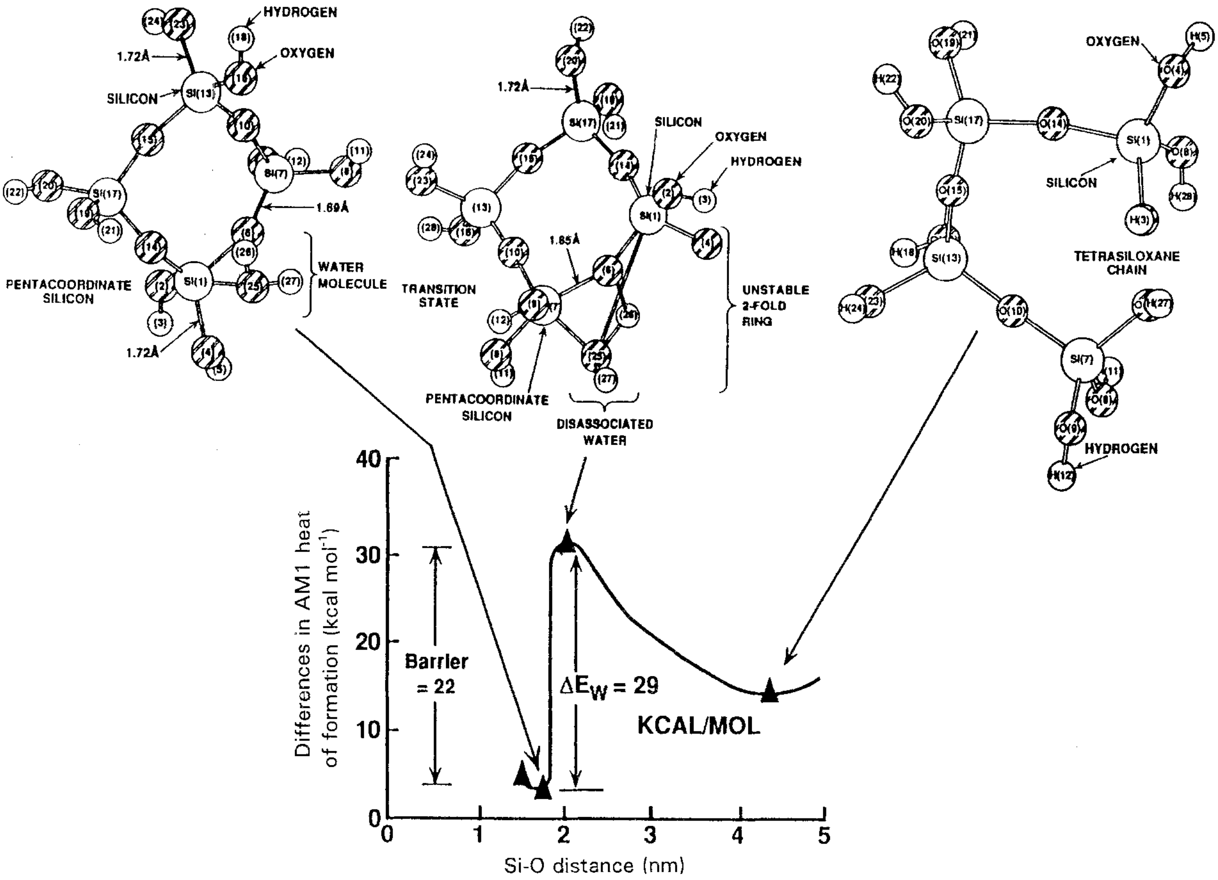


*Figure 5* Reaction path for the Si–O bond fracture with interaction of water for a cyclotetrasiloxane (four-fold) ring.

Si(1)–O(2) bond fracture with silicic acid cleaved from the four-membered ring (Fig. 10).

The formation of the unstable two-fold disiloxane ring shown in Fig. 9 is a critical step in the reaction pathway immediately before Si(1)–O(2) bond separation. Similar features were seen earlier in Part I for fracture of a four-fold ring without water and in Fig. 4, where a four-fold ring was fractured with water. The changes in structure are very similar in all three models. However, the energy barrier to create the disiloxane structure is very high without the presence of water.

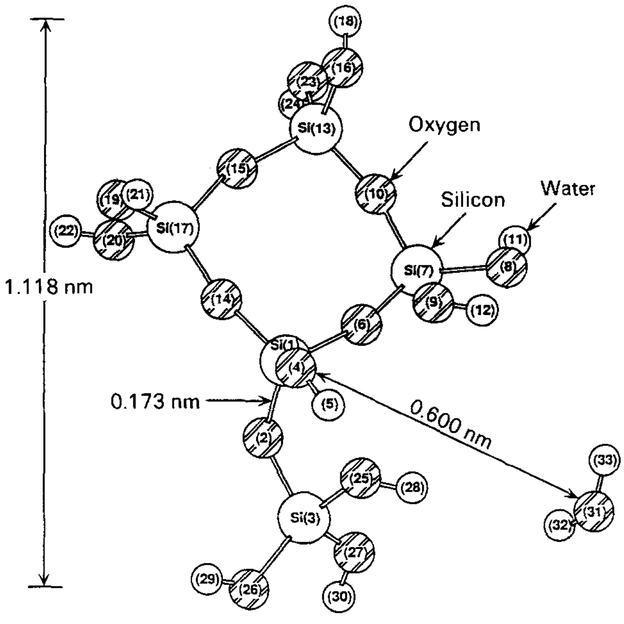
A summary of the energetics of the reaction pathway for water enhanced fracture of the siloxane bond, represented by Figs 6–10, is shown in Fig. 11. The energy barrier for the transition state that forms the unstable disiloxane bond is 22.6 kcal mol$^{-1}$. The formation of pentacoordinate silicon by the adsorbed water molecule is exothermic at $-17$ kcal mol$^{-1}$. Thus, the barrier to pentacoordinate hydrolysis of the bond is 39 kcal mol$^{-1}$, only 10 kcal mol$^{-1}$ higher than the value calculated for hydrolysis of a four-fold ring (Fig. 5).

Note that the reverse of the hydrolysis reaction summarized in Fig. 11 is a condensation reaction with the release of a water molecule as the silicic acid molecule is bonded to the four-fold tetrasiloxane ring. The barrier to the condensation reaction is only 22.6 kcal mol$^{-1}$.

## 3. Discussion

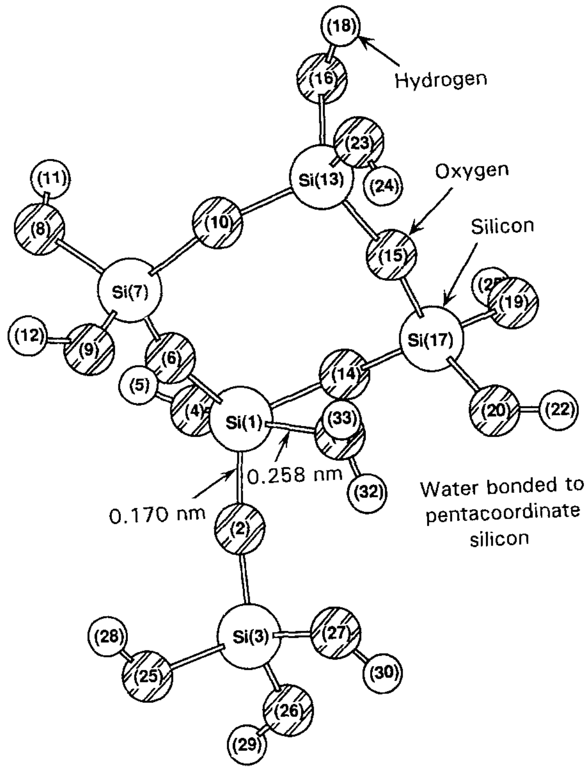
Results from these calculations show that fracture cannot be modelled by simply straining a single Si–O bond. Both "halves" of a molecular structure must be strained in a manner that permits adjustments in bond angles to occur. The angular changes produce minimal energy configurations, as summarized in Fig. 5, hydrolysis of a four-membered ring, and Fig. 11, hydrolysis of a ring-chain structure. The lower energy intermediate and transition state structures shown in Figs 5 and 11 all resulted from rotation of bond angles as stain was applied. Hybridization of silicon sp$^3$d orbitals into a pentacoordinate state occurs, thereby producing the transitional structures. The strain energy is stored as electronic excitations.

The importance of structural rearrangement in the fracture process is illustrated by the results of the ring-chain fracture. Fig. 11 shows the strain of only one dimension, the Si(1)–Si(3) bond distance as the ring-chain structure is fractured. The difference between Figs 8 and 9 is only 0.003 nm in Si(1)–Si(3) distance, but the optimized structures are extremely different in appearance and bond angles. The transition state structure rotated to form the lower energy pentacoordinate silica structure. The angular rotation occurred because it offered the most favourable energy pathway when a small increment of strain was applied. The transition state structure shown in Fig. 7 is akin conceptually to the "kink" step proposed in the MB



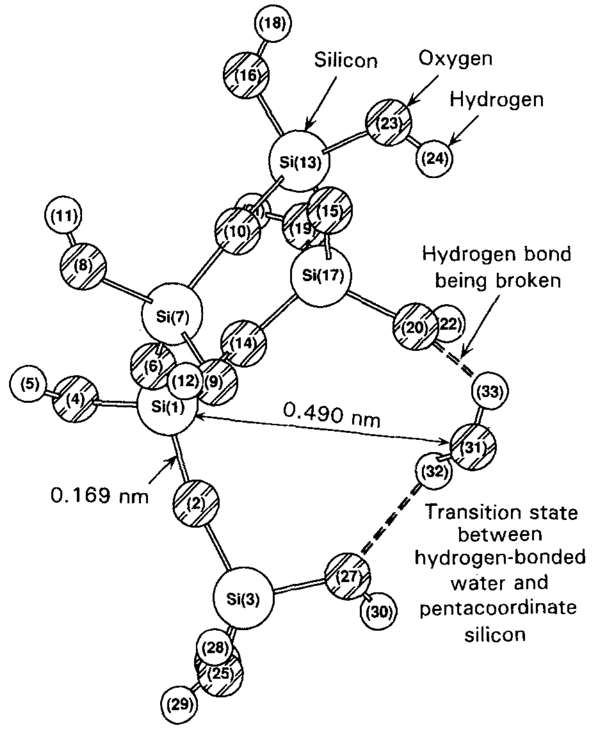
AM1 heat of formation = –1293.4 kcal $\mathrm{mol}^{-1}$
(Model BB1)

*Figure 6* The initial configuration of water starting to interact with the five-fold ring-chain structure.



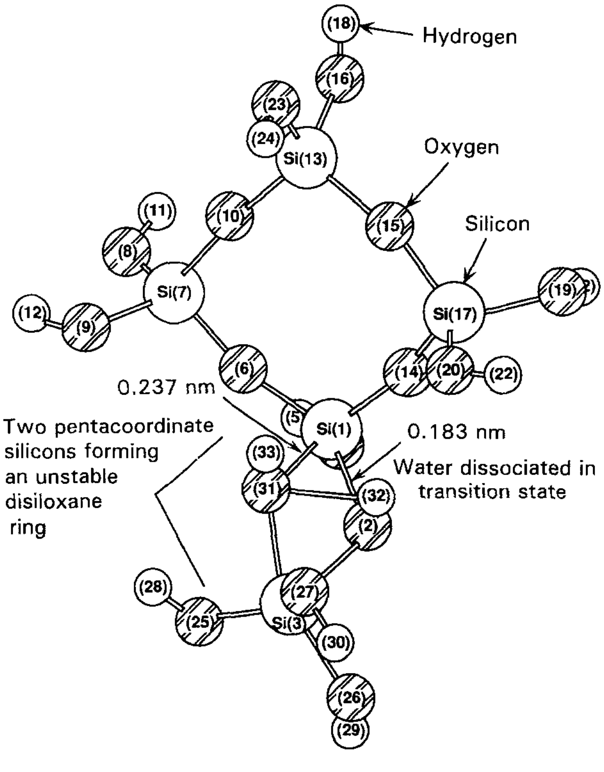
AM1 heat of formation = -1308.7 kcal $\mathrm{mol}^{-1}$
(Model BB2)

*Figure 8* The intermediate five-fold ring-chain structure during Si–O bond fracture wherein the water is pentacoordinately bonded to a silicon atom.



AM1 heat of formation = -1305.3 kcal $\mathrm{mol}^{-1}$
(Model BB5)

*Figure 7* The transition state between the hydrogen-bonded water molecule and the pentacoordinate silicon state.



AM1 heat of formation = -1271.5 kcal $\mathrm{mol}^{-1}$
(Model BB3)

*Figure 9* The transition state during Si–O bond fracture wherein the water is dissociated and forms a disiloxane ring.

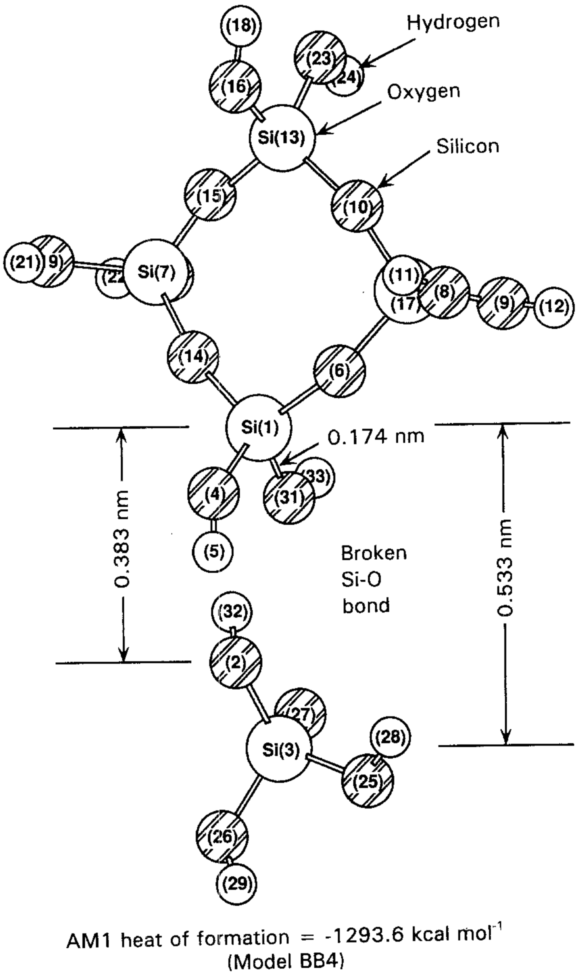


*Figure 10* The final model of five-fold ring-chain Si–O bond fracture with the interaction of water.

model [2]. However, Fig. 11 shows that the sequence of structural alterations involved in hydrolysis is much more complex than that proposed in the MF or MB models of Fig. 1.

An important feature of the AM1 MO method is that the energy pathway for fracture can be calculated.

The relative heats of formation of the various bond fracture and hydrolysis models described above are summarized in Fig. 12. Water-free bond fracture appears to be relatively constant except for the four-fold $D_1$ ring. The four-fold ring is slightly easier to fracture; i.e. by 12 kcal mol$^{-1}$. The three-fold ring, $D_2$ defect, is more difficult to break. This can be understood by examining the transition states in the fracture of the $D_1$ ring. Both of the transition states (see Part I), have formed, or nearly formed, a trisiloxane ring which itself is not broken.

In the case of fracture of the Si–O bond in a single $D_2$ ring there are no ring-like structures possible in the transition state. Formation of a two-fold disiloxane ring is very energetically unfavourable in vitreous silica based on work by Galeener [4] and Revesz and Gibbs [13]. Therefore, the UHF AM1 fracture barrier for the three-fold ring of 96 kcal mol$^{-1}$ is higher than either the four-fold ring or the five-fold ring-chain structure which can undergo intermediate transition states, even without water present.

Fig. 12 shows that when water is present, the rings open more easily the smaller the ring size. This effect of water-enhanced ring-hydrolysis interchanges the relative energy required for breaking of $D_1$ and $D_2$ rings. A four-fold ring is more stable than a three-fold ring with respect to hydrolysis but is less stable with respect to water-free dilational fracture. Thus, as water interacts with Si–O–Si bonds at the tip of a fracture, the interactions favoured will be the lowest energy path for hydrolysis. The crack front will tend to follow a path that optimizes the number of $D_2$ rings encountered. Only if there is a local region where the pathway between three-fold rings is too long will the crack front be arrested by the higher energy of hydrolysis of four-fold rings. Applying increments in stress (increasing $K_1$) will enlarge the strain field and increase the probability that a water molecule in the crack tip will encounter a $D_2$ ring. Thus, a dependence of crack velocity on stress intensity will occur in a humid environment. In vacuum the crack tip will tend to follow the $D_1$ rings in a quantitized, step-like manner to pursue the lowest energy path through the structure.

The crack velocity, $V$, versus stress intensity, $K_1$, relationship for silicate glasses, established by Weiderhorn [14], is shown in Fig. 13. These curves can be classically reproduced by a rate equation of the form

$$V = V_0 \exp\left[(-E_a + bK_1)/RT\right] \tag{1}$$

where $E_a$ is the activation energy, $b$ is a constant, $R$ the gas constant, $T$ the temperature, $V_0$ some initial crack velocity. The term $(-E_a + bK_1)$ is the energy term that characterizes the energy of fracture. Taking the natural log of both sides

$$\ln V = \left[(-E_a + \beta K_1)/RT\right] + \ln V_0 \tag{2}$$

$$\ln V = \left[(-E_a/RT) + (\beta/RT)K_1 + \ln V_0\right. \tag{3}$$

$$\ln V = (\beta/RT)K_1 + (\ln V_0 - E_a/RT) \tag{4}$$

$$\ln V = mx + b \tag{5}$$

Therefore, the slope $= \beta/RT$, should remain constant for different kinds of barriers, $E_a$. However, if the concentration of the different kind of barriers is different, then $\beta$ should be directly proportional to the concentration of the ring structures that make up these various barriers

$$\beta \propto \text{ring structures} \tag{6}$$

If the crack tip follows three-membered rings, $D_2$, in hydrolysis with a much lower barrier, $E_a$ (hydrolysis), then the slope of log $V$ versus $K_1$ is less steep (Region 1) and predicts higher crack velocities at higher concentrations of water.

In vitreous-silica

$$[D_2] \ll [D_1] \tag{7}$$

by a factor of at least 4 [4] and the AM1 MO models predict that

$$E_a\,(\text{hydrolysis}) < E_a\,(\text{ring contraction}) \tag{8}$$

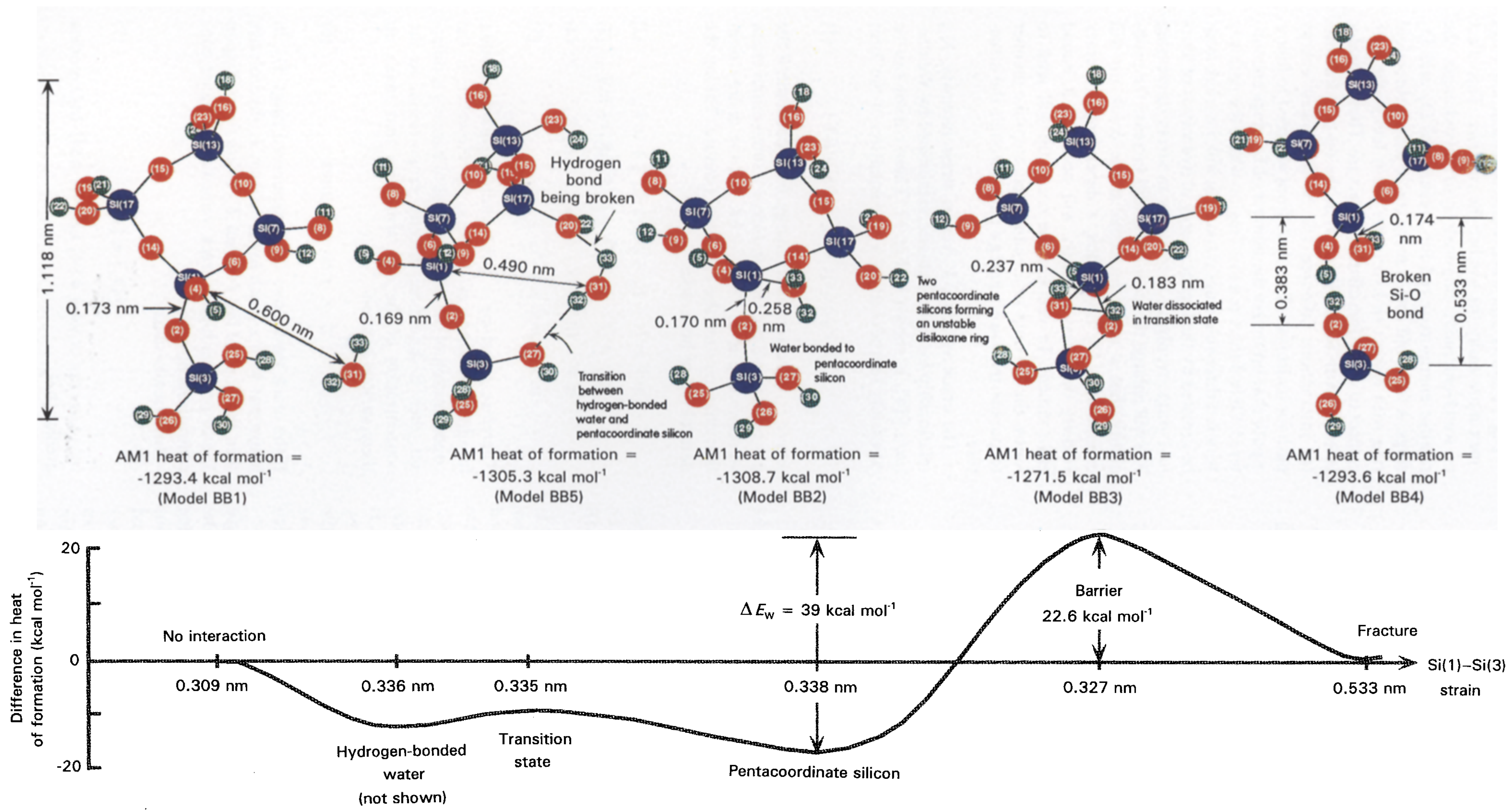


*Figure 11* The reaction path for the Si–O bond fracture with the interaction of water for a five-fold ring-chain structure.

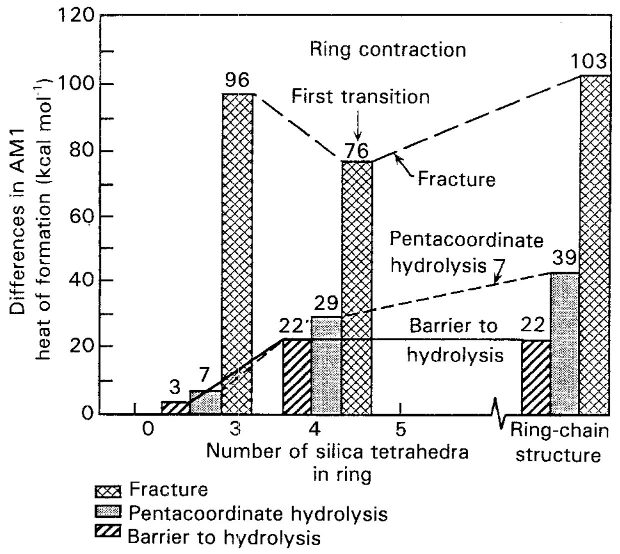


*Figure 12* The differences in AM1 barriers to fracture and hydrolysis for different size silicate structures.

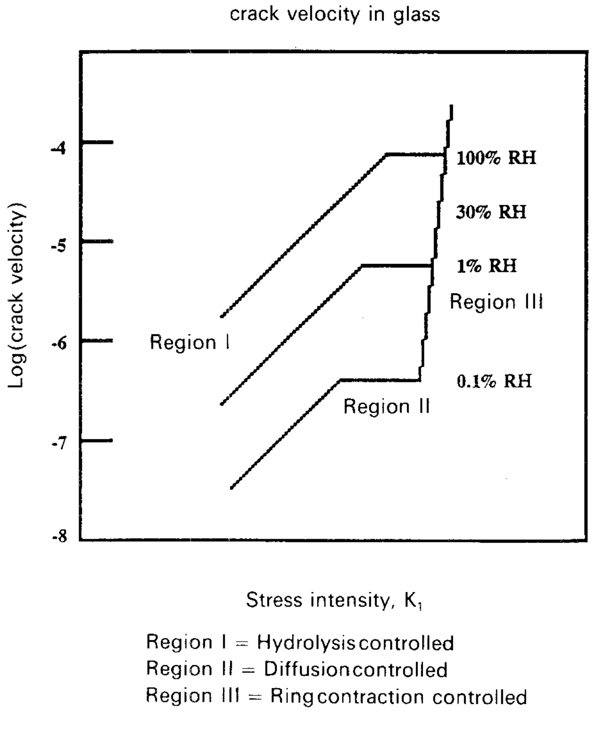


*Figure 13* The crack velocity versus stress intensity for v-silicates, based upon Weiderhorn [14].

With the increase in the concentration of four-membered rings, [$D_1$] in v-silica along with the increase in $E_a$ (ring contraction), Region III [14] should be steeper and occur at higher stress intensities, as is observed. This explains why the slope of Region III crack growth is three to four times steeper than Region I.

Another interesting feature is that slow crack growth occurs below the ultimate fracture strength of v-silica [14]. This is classically explained by the existence of stress concentrations. However, it may be that a significant component of stress concentration involves ring contraction at energies below those required to break an Si–O bond.

## 4. Conclusions

Ring hydrolysis is the critical step in the environmentally sensitive crack growth of vitreous silica. The AM1 molecular orbital models indicate that crack tips will move along lowest energy pathways; the crack will follow a path of four-fold $D_1$ rings in vacuum and a path of three-fold $D_2$ rings in the presence of water. The energy barrier for pentacoordinate hydrolysis of $D_2$ rings is only 7 kcal mol$^{-1}$, the barrier for $D_1$ rings is 29 kcal mol$^{-1}$ and for a five-fold ring-chain it is 39 kcal mol$^{-1}$. Fracture by water-free dilation has an energy barrier of 77 kcal mol$^{-1}$ for four-fold rings, whereas the barrier is 96 kcal mol$^{-1}$ for a three-fold ring and 103 kcal mol$^{-1}$ for a ring-chain fracture.

The lower energy values for water-free fracture of the larger structures are due to formation of transition states during fracture which result in trisiloxane-like rings. The transition states give rise to a two-step fracture process, which is lower in energy but still two to three times higher than water-enhanced fracture. These findings predict that the fractal nature [15] of a water-enhanced fracture surface is different from a dry fracture surface and is related to different ring structures in the material. This model also confirms at an atomic scale the characteristics of slow crack growth where Region I is controlled by hydrolysis of three-membered rings and Region III is controlled by the energy of contraction of four and four + membered rings. The fracture process is quantified by the transition state structural rearrangements. The strain energy in the transition states is in the form of excited electronic states and will be released as a characteristic photon and phonon spectrum.

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