

The Fracturing of Glass

Only recently have the atomic interactions underlying glass fracture been defined. The work suggests ways to slow or even stop the growth of cracks in glass and other brittle materials

by Terry A. Michalske and Bruce C. Bunker

Glass is one of the oldest and most widespread of commodities: it has been produced since 7000 B.C. and currently accounts for a \$20-billion-a-year industry in the U.S. alone. Yet in spite of its impressive history of meeting a remarkable range of consumer needs, glass has always been limited in its applications by its tendency to fracture. This inherent weakness poses an increasing challenge to engineers. Young and promising technologies that require fiber-optic networks, ceramic bone replacements or novel optical and electronic components have placed a high premium on glasses and ceramics that will prove particularly resistant to cracking. A transoceanic fiber-optic cable, for example, must have a long service life to make laying the cable on the ocean floor a viable enterprise.

Until recently very little was understood about the mechanism by which glass cracks. In the mid-1960's, for instance, when investigators reported precise measurements showing that the stress needed to crack glass decreases with increasing exposure to water, they helped to explain why water aids glass cutters but did little to illuminate precisely how it does. An answer to the question of how glass cracks started to emerge in 1979. In that year the two of us, together with our colleagues at the Sandia National Laboratories and, independently, Stephen W. Freiman of the National Bureau of Standards, began to develop mathematical and chemical models to describe the fracture of glass at the atomic level. We are still developing and refining the models, but our efforts have already been rewarded. The physical and chemical interactions that control the rupture of interatomic bonds at the tip of a crack provide a fascinating link between the atomic structure

of materials and the real-world concerns of product reliability. Moreover, the fundamental knowledge evolving from atomistic studies of crack propagation enhance the ability to utilize glass and other oxide materials in many of the demanding applications now being planned.

Most of us are introduced to the topic of glass fracture at an early age. The lesson may involve a shattered milk glass or the crash of a window struck by an errant baseball. When glass shatters, cracks seem to appear instantaneously. High-speed photography reveals that cracks can spread through glass at speeds of hundreds of meters per second, or roughly half the speed of sound in glass.

Even though the fracture of glass can be a dramatic event, many failures are preceded by the slow extension of preexisting cracks. A good example of a slowly spreading crack is often found in the windshield of an automobile. The extension of a small crack, which may have started from the impact of a stone, can be followed day by day as the crack gradually propagates across the entire windshield. In other cases small, unnoticed surface cracks can grow during an incubation period and cause a catastrophic failure when they reach a critical size. Cracks in glass can grow at speeds of less than one-trillionth of an inch per hour, and under these conditions the incubation period can span several years before the catastrophic failure is observed. On an atomic scale the slow growth of cracks corresponds to the sequential rupturing of interatomic bonds at rates as low as one bond rupture per hour. The wide range of rates over which glass can fracture—varying by 12 orders of magnitude (factors of 10) from the fastest shatter to the slowest

creep—makes the investigation of crack growth a particularly engaging enterprise.

Surprisingly, glass is intrinsically one of the strongest materials known. Under high-vacuum conditions flaw-free glass can withstand tensile loads greater than two million pounds per square inch, which is 10 times the strength of most commercial metal alloys. In normal service, however, glass surfaces are exposed to abrasives and chemicals that create small surface cracks and promote their growth, ultimately reducing the strength of the glass. The effects of chemicals on the growth rate of cracks pose the greatest challenge to the design engineer, since these effects not only reduce the immediate strength of the glass but also can result in the failure of a structure that has supported a stress load for several years.

One of the most potent chemical agents is water, which presents a particularly severe threat because it is always in the atmosphere. Water can accelerate the rate of crack growth more than a million times by attacking the structure of the glass at the very root of the crack. Much of our work has centered on understanding from an atomistic point of view how water and other chemicals accelerate crack growth and how the acceleration can be slowed, stopped and even reversed.

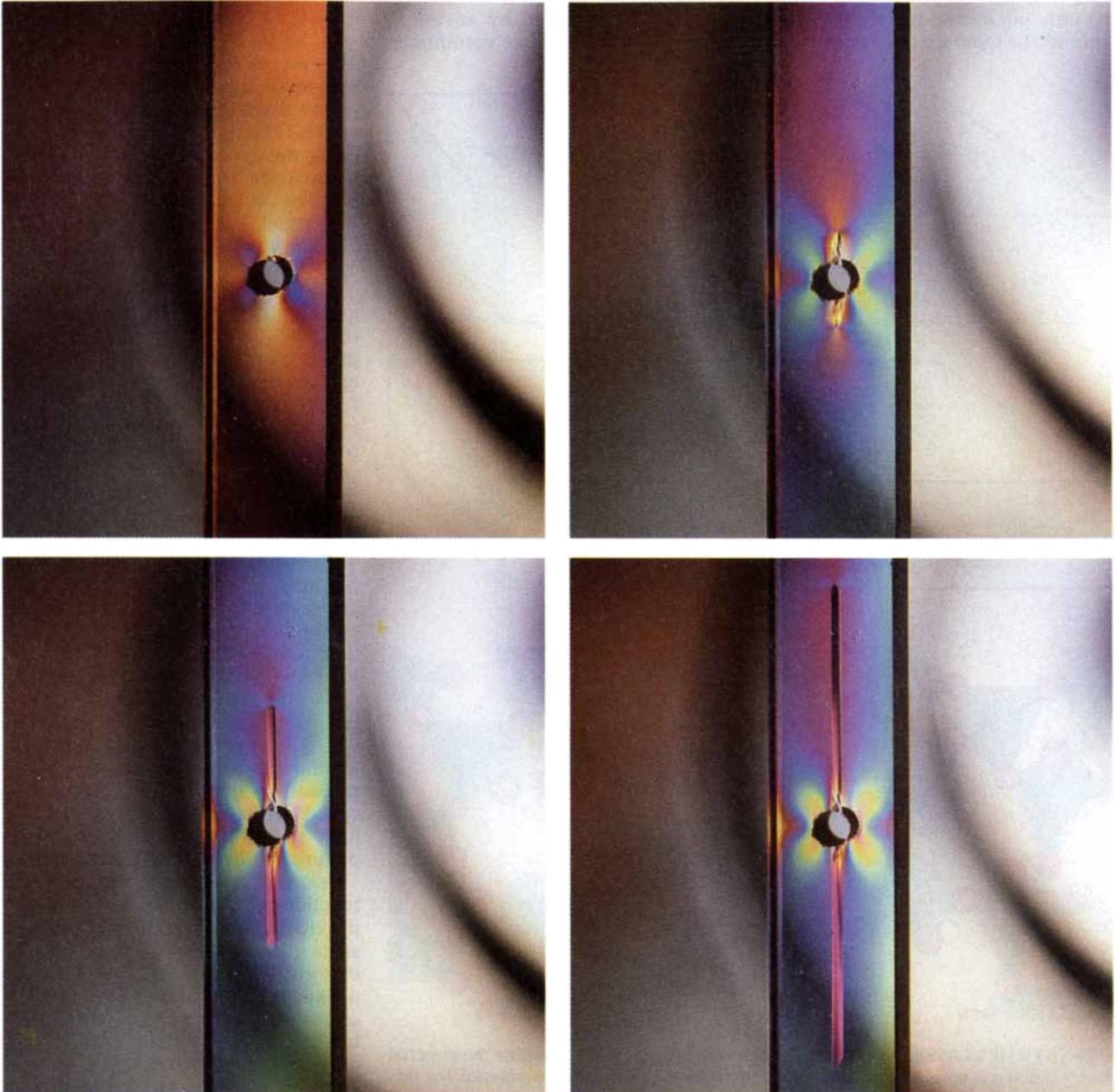
Artisans, of course, have long recognized and utilized the ability of water to cause glass to crack more easily. Evidence suggests that early American Indians exploited the effect of water in making arrowheads from flint, a form of silica (silicon dioxide) related to glass, sand and quartz. Indians in the Catahoula Lake area of Louisiana, for instance, performed a ceremony in which they

steamed flints before knapping (fracturing) them. Recent experiments on similar materials confirm that knapping is made easier by soaking flint in water. Today glaziers often apply water, usually in the form of saliva, to the shallow crack produced by their scribing tool. The water decreases the stress required to propagate the initial crack and causes the glass to break more smoothly.

A scientific basis for determining

the conditions necessary for crack growth and fracture began to evolve 60 years ago with the pioneering work of A. A. Griffith of the Royal Aircraft Establishment. Griffith sought to calculate the minimum energy necessary to make a crack grow. He started with the well-known observation that atoms at the surface of a solid do not mesh with their neighboring atoms in the same way as atoms in the interior do: the atoms sit rather

uncomfortably on the surface of the solid, and so their energy is higher than the energy of the interior atoms. As a consequence, anytime a new surface is created, energy must be supplied. Griffith reasoned that a crack can grow in glass only when the applied mechanical energy, or stress, is greater than the energy of the new surfaces created by the fracture. (Until the applied stress exceeds the minimum, the energy is stored in



GROWTH OF CRACKS in a glass bar with a hole drilled in its center has been monitored in a series of experiments done by the authors and their colleagues at the Sandia National Laboratories. Compressive load applied along the long direction of the bar creates tensile stress that propagates two cracks, one above the hole and one below it. The rate at which the cracks is meas-

ured with a microscope that sits on top of the apparatus. The entire assembly is enclosed in a high-vacuum chamber so that the chemical environment can be carefully controlled. Here a large amount of water vapor is present, which speeds the growth of the cracks. The photographs, made using polarized light, show that stresses are concentrated at the tip of each advancing crack.

the glass as it would be in a spring.) By applying his knowledge of the surface energy of glass and using existing calculations for the stresses around surface cracks, Griffith determined the breaking load for cracked plates. He triumphantly confirmed his prediction in actual experiments with glass tubes.

Griffith also determined that the smaller the initial crack in a piece of glass is, the greater the applied stress must be to extend it. This explains why pristine fibers of glass having only minuscule surface flaws are from 100 to 1,000 times stronger than

ordinary window glass, which has usually acquired relatively large surface flaws in the course of handling. Griffith's energy-balance approach to strength and fracture also suggested the importance of surface chemistry in the mechanical behavior of brittle materials. Chemicals, such as water, that lower the surface energy of a solid ultimately will reduce the strength of the material.

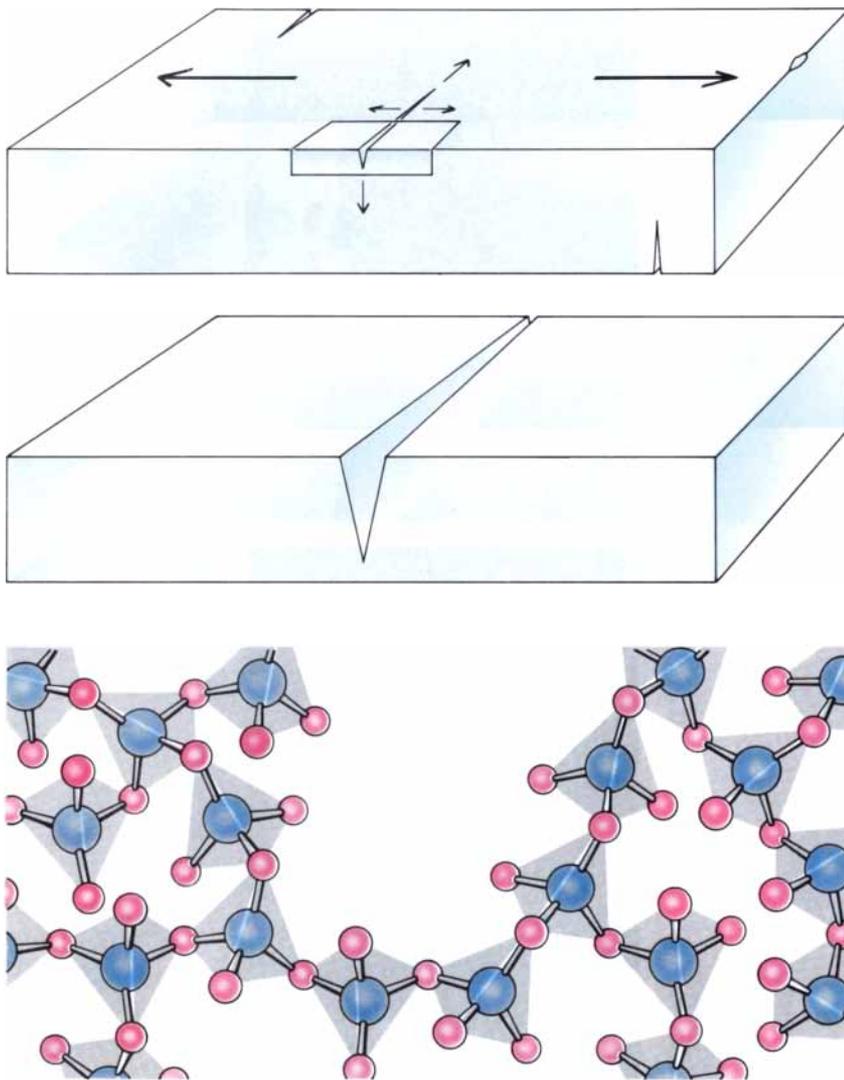
The 1950's and 1960's saw a flurry of activity in the experimental study of glass strength. Much of the new enthusiasm was spurred by advances in the ability to produce continuous

filaments of glass (fiber glass) that could serve to reinforce plastics. Various workers confirmed that water reduces the strength of glass and showed that the breaking load also depends on how long a stressed fiber is exposed to water. They found that load durations of only two weeks reduce the strength of glass three-fold. Moreover, it appeared that given enough time under a load the strength of the glass would actually approach zero. Obviously these observations were most disturbing to the glass-manufacturing community.

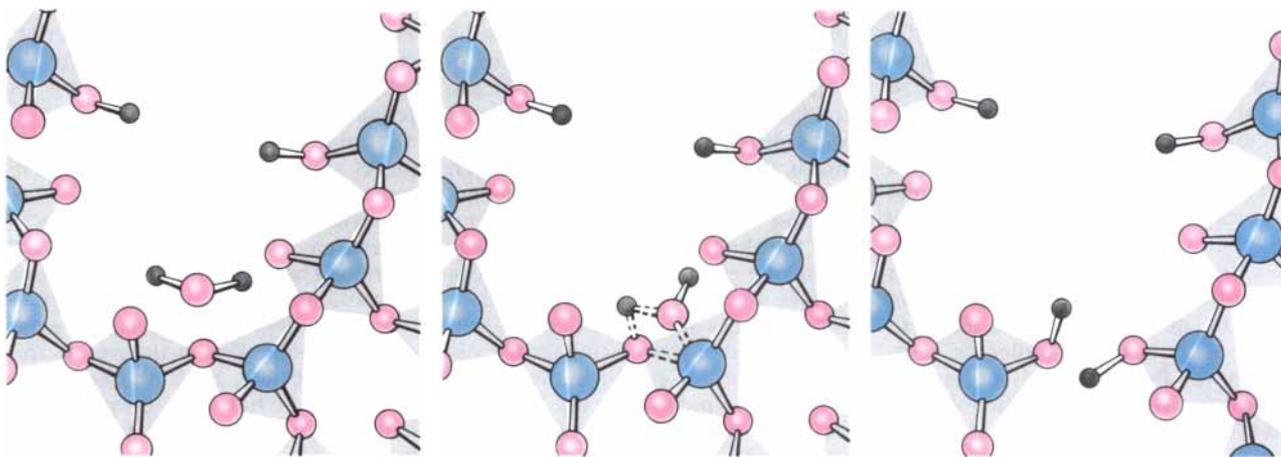
In the mid-1960's Sheldon M. Wiederhorn of the National Bureau of Standards and several other investigators studied just how the strength of glass changes with time. By measuring the growth of cracks under a microscope while carefully controlling the amount of stress and environmental conditions, they made several important discoveries. First, cracks in glass grow continuously at controlled rates; fracture is not simply an off-on phenomenon. Second, the rate of crack propagation depends on the applied stress and the amount of water in the environment. Finally, one can predict the time of failure by knowing how fast small surface flaws grow under stress; as small cracks in stressed glass slowly extend, more stress is concentrated, until rapid failure occurs.

Unfortunately many failures that may occur 10 years from now can result from small cracks that begin growing today at speeds of less than one-trillionth of an inch per hour—which, as we have mentioned, corresponds to the sequential rupturing of interatomic bonds at the rate of one bond per hour. Current experimental techniques are not capable of measuring these very slow crack speeds. It is for this reason that we have sought to develop an atomistic picture of the events at the crack tip.

In order to describe atomic-scale reactions at a crack tip we first must provide a picture of the structure of silica glass. The basic building block of most forms of silica is a close-packed tetrahedral unit that consists of a central silicon atom surrounded by four oxygen atoms. Each corner oxygen atom is shared by the silicon atoms of two adjacent tetrahedrons, so that each tetrahedron is connected to four neighbors to form a space-filling network. In crystalline forms of silica such as quartz the tetrahedrons occupy regular positions that are repeated throughout the crystal-



STRENGTH OF GLASS is controlled by the growth of cracks that penetrate the material (*top*). When the glass is stressed, the crack tip (*middle*) penetrates the material. For this reason the authors have sought to describe the growth of crack tips at the atomic level (*bottom*). The basic unit of silica glass is a close-packed tetrahedron consisting of a central silicon atom (*blue*) surrounded by four oxygen atoms (*red*). Each oxygen atom is shared by the silicon atoms of two adjacent tetrahedrons, so that each tetrahedron is connected to four neighbors. The tetrahedrons form a network of interconnected rings, each containing from five to seven tetrahedrons. For clarity the oxygen atoms are drawn smaller than the silicon atoms and not all bonds to tetrahedrons are shown.



WATER can react with glass and cause it to crack more easily. Here a water molecule enters a crack (*left*) and adsorbs onto the tip (*middle*). The molecule causes a concerted chemical reaction (*right*) in which a silicon-oxygen bond at the crack tip and an oxygen-hydrogen bond in the water molecule are both cleaved,

producing two silanol groups (hydroxyl groups attached to silicon). In the process the length of the crack increases by one bond rupture. The reaction with water lowers the energy needed to break the silicon-oxygen bonds by a factor of 20, and so the bond-rupture reaction allows cracks to grow faster.

line structure. In silica glass the tetrahedrons form a random network of interconnected rings, each of which usually contains from five to seven tetrahedrons [see *bottom of illustration on opposite page*]. As a crack grows, tetrahedral units are torn apart by the rupture of individual silicon-oxygen bonds. The crack tip reflects the dimensions of a single ring structure that has been pried open on one side, exposing the next silicon-oxygen bond to be broken. The smallest incremental distance the crack can move is the diameter of the silicate ring, which is from .4 to .5 nanometer (billionth of a meter). The precise value depends on the number of tetrahedrons in the ring.

Our results show that the amount of energy required to rupture the silicon-oxygen bond between two silicate tetrahedrons drops steeply—by a factor of nearly 20—in the presence of water. Specifically, if a piece of silica glass is kept in a near-perfect vacuum, the bonds between the silicate tetrahedrons are highly stable. They are so stable, in fact, that 1,300 calories of energy would have to be expended to destroy the silicon-oxygen bonds in one gram of the silica. (In comparison, 75 calories of energy are necessary to heat one gram of water from room temperature to boiling.) When water is present, however, a chemical reaction can take place between a water molecule and a silicon-oxygen bond, making the tetrahedral units much easier to separate.

A detailed picture of the interaction can be divided into three steps. First, a water molecule makes its way along the opening of the crack and

adsorbs to the crack tip. Spare electrons from the oxygen atom in the water molecule begin to form a bond with the unoccupied electron orbitals of a silicon atom. Meanwhile one of the hydrogen atoms in the water molecule is attracted to an oxygen atom in the silicon-oxygen chain. In the next step of the process the newly formed bonds strengthen while the original oxygen bond is weakened. Eventually the hydrogen from the water molecule is transferred to the oxygen in the chain and the silicon-oxygen chain ruptures. Finally, the water molecule and the original silicon-oxygen bond split apart and are replaced by two surface silanol groups (hydroxyl groups attached to silicon). The crack has advanced by one atomic step. The entire process is called dissociative chemisorption.

In short, the chemical reaction between the silica and the water reduces the amount of energy that must be supplied to make the crack extend. The highly stable silicon-oxygen bond has been replaced with two nearly equally stable reaction products, the surface silanol groups. Since the energy consumed by a chemical reaction is equal to the difference between the energies of the starting and ending complexes, it can be shown that the rupture of silicon-oxygen bonds by water requires only 78 calories per gram, as opposed to the 1,300 calories per gram required in a vacuum.

The model of dissociative chemisorption for crack-tip bond rupture has enabled us to predict which chemicals will make slow cracks grow in silica. Such chemicals must

be able to donate electrons to the formation of a bond with the silicon atom at the crack tip and also to donate a positively charged hydrogen atom to bind with the oxygen atom that was once attached to the silicon atom. In addition a single molecule of the chemical must be small enough to fit into the crack tip in such a way that the breaking and forming of the bonds can take place simultaneously. Ammonia and methanol, for example, satisfy both requirements, and we have found that both chemicals speed up the rate at which cracks grow in silica. In fact, the effect of ammonia, whose molecules are roughly the same size as water molecules, is nearly identical with that of water.

The rate of crack growth depends not only on the chemical environment but also on the magnitude of the applied stress. The development of a complete model for the kinetics of fracture requires an understanding of how stress accelerates the bond-rupture reaction.

In the absence of stress, silica reacts very slowly with water. The dissociative reaction we have discussed causes the surface of silica glass to dissolve in water at a rate of 10^{-17} meter per second; stress-free silicon-oxygen surface bonds are so unreactive toward water that they will not even adsorb water vapor. Yet the application of stress can cause cracks to grow at speeds greater than one millimeter per second.

A crack tip focuses stress in much the same way as a needle point focuses an electric field. The closer one ap-

proaches the crack tip, the higher the stress becomes, until it reaches several million pounds per square inch within a few atomic dimensions of the tip. Exposed to these large stresses, the atomic structure of silica becomes distorted from its normal bonding configuration. Theoretical calculations show that if a silicate tetrahedron is distorted by pulling on the corner oxygen atoms, the silicon atom in the center is more likely to bond with a water molecule. Furthermore, the chemical interaction with water will decrease the force required to distort the silicon-oxygen bonds further.

With the results of the theoretical calculations to guide our selection of a model chemical system, we have experimentally explored how stress enhances reactivity. We have had to work with a simple model system because the experimental techniques

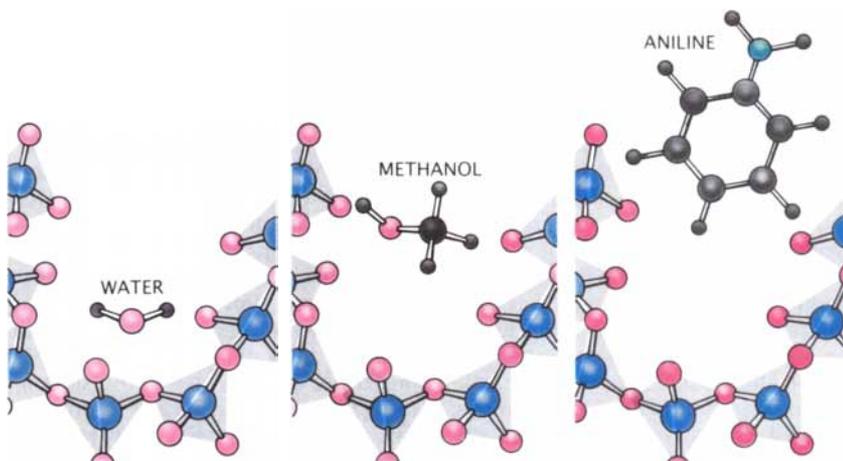
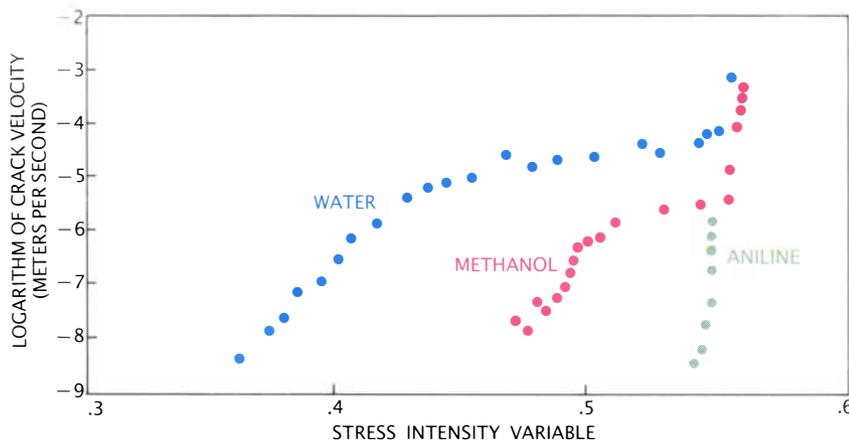
currently available do not enable us to observe directly chemical reactions along the line of atoms at the crack tip. Our model system consists of small rings of silicon and oxygen atoms (two silicon and two oxygen atoms per ring). Such so-called edge-sharing rings, which result when two tetrahedral units bond together along one edge, can be formed on the surface of silica powders heated to temperatures above 900 degrees Celsius. The edge-shared ring structures are practical for studying the effects of bond strain, because the bond angles and distances between atoms are greatly distorted from the distances and angles found in normal silica glass.

In order to examine the mechanism and kinetics of reactions between water (and other chemicals) and the edge-shared silicate rings, we have

employed a technique called Fourier-transform infrared spectroscopy. In infrared spectroscopy a sample is bathed in infrared radiation. The radiation transmitted through the sample is separated into individual frequencies, and the amount of radiation transmitted at each frequency is measured. At certain frequencies there will be a big drop in the amount of radiation received by the detector. The effect arises because each distinct molecular structure in the sample vibrates at a characteristic frequency. When that frequency is matched by the frequency of the infrared radiation, there is a "resonance" effect and most of the radiation is absorbed by the sample, leaving little to reach the detector. By noting both the frequency and the relative amount of absorbed radiation, one can determine what kinds of molecular structures make up the sample and what the relative concentration of each species is.

In Fourier-transform infrared spectroscopy, instead of detecting each individual frequency optical interference techniques are used to scan the entire frequency range rapidly. A single scan contains all frequencies of infrared radiation, and so the time necessary to gather the pertinent data is only a fraction of a second, whereas conventional infrared spectroscopy typically requires half an hour or so to produce a complete spectrum. The individual frequencies are then separated by the mathematical technique of Fourier analysis. The advantage gained by Fourier-transform infrared spectroscopy is obvious: when one is studying rapid chemical reactions, one needs swift and accurate measurements of how the amounts of reactants, reaction intermediates and products are changing over time.

Fourier-transform infrared spectroscopy enables us to follow the kinetics of reactions among chemicals that play an important part in the fracture of glass. We can distinguish among the edge-shared rings (the reactants), the water molecules adsorbed to the rings (the reaction intermediates) and the silicon hydroxide groups (the products). Our work has led to three interesting findings. First, a silicon atom in a strained ring is much more likely to accept electrons than a silicon atom in stress-free glass. Consequently the silicon atom in the strained ring is more likely to adsorb electron-donating molecules such as water, ammonia and methanol. Second, all the chemical



MOLECULAR SIZE of a chemical substance affects its ability to speed the growth of cracks in glass. Water, which has a molecular size of only .26 nanometer (billionth of a meter), causes cracks to grow much faster than methanol (.36 nanometer) does, and aniline (.42 nanometer) has hardly any effect (*top*). In essence, water can readily enter a crack opening (which has a diameter of .4 to .5 nanometer), methanol has difficulty getting in and aniline is so big that it never arrives at the sites of bond rupture (*bottom*).

species that make cracks grow more rapidly in silica glass also dissociatively chemisorb on the strained ring: they cleave one of the distorted silicon-oxygen bonds in the ring. Conversely, chemicals that do not react with the edge-shared rings have no effect on crack growth in silica.

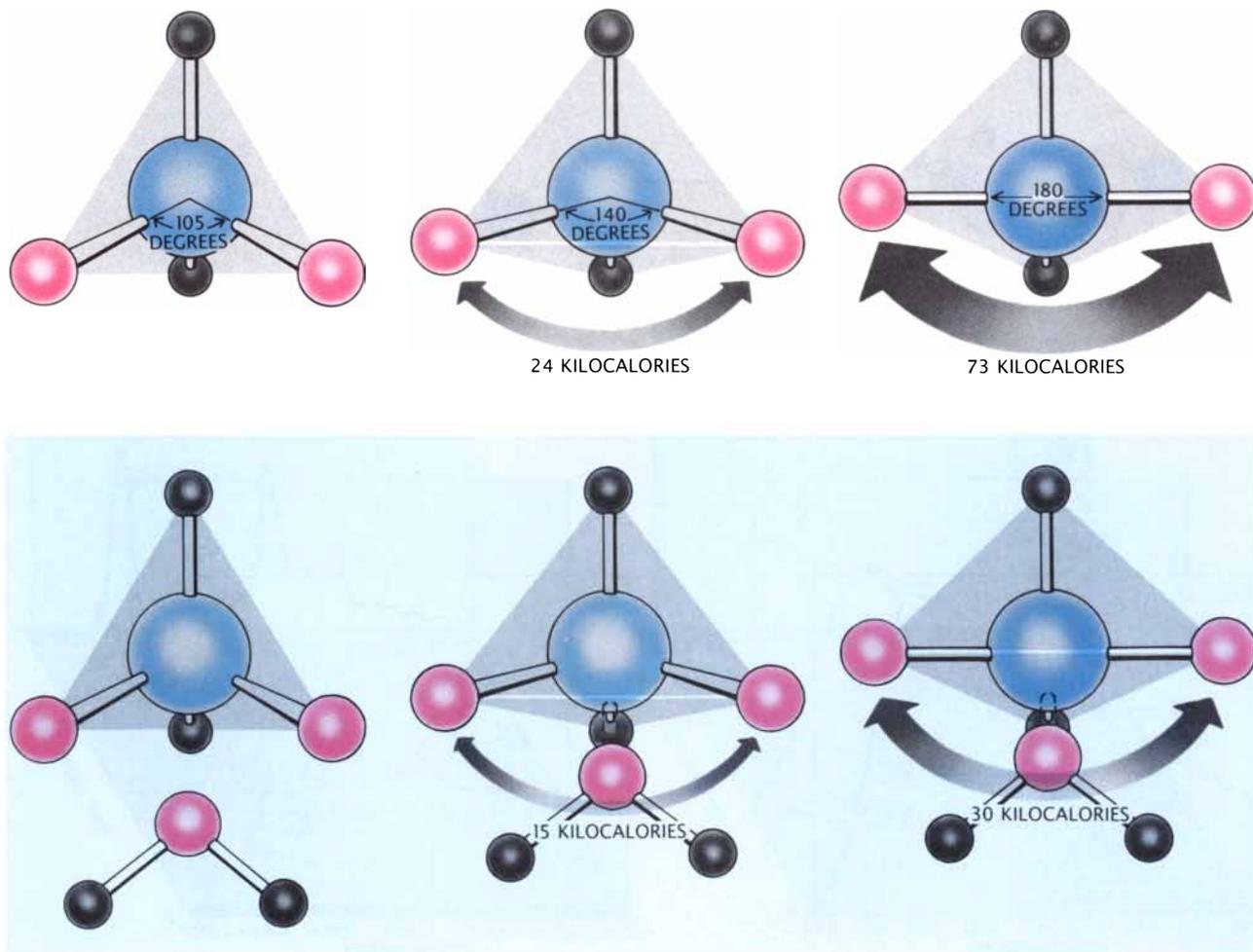
Finally, the rate of ring cleavage when we expose our simple model system to water vapor is more than 100,000 times higher than the rate at which a flat, unstressed surface of silica will react with water. The results provide direct experimental evidence that silicon-oxygen bonds can be broken rapidly by a stress-enhanced reaction with water and other chemicals.

We next sought to determine if the dissociative-chemisorption reaction between water molecules and strained silicon-oxygen bonds is the factor that limits the rate of crack

growth. We made direct comparisons between the kinetics of the ring-cleavage reactions in our model compound and the speed of crack growth measured under identical environmental conditions. We found that ammonia is slightly more aggressive than water in rupturing strained silicon-oxygen bonds and also causes cracks in silica glass to grow somewhat faster than water does. Methanol is also more aggressive than water in rupturing strained silicon-oxygen bonds, but it is five orders of magnitude less effective in increasing the rate of crack growth than either water or ammonia. The comparison between reactions of our model compound in methanol and crack-growth measurements clearly indicates that the kinetics of fracture cannot be predicted solely on the basis of the kinetics of the underlying bond-rupture reactions.

What accounts for the unusual

behavior of methanol? As we mentioned above, the size of the attacking molecule also determines the ability of the molecule to promote crack growth. Water and ammonia have nearly identical molecular sizes (.26 nanometer), but methanol is a much larger molecule (.36 nanometer). Smaller molecules such as water or ammonia can readily enter a crack opening (which has a diameter of from .4 to .5 nanometer) and cause reactions that rupture bonds, but larger molecules such as methanol have difficulty getting in. Indeed, we have found that molecules larger than about .4 nanometer have no measurable effect on crack growth; they have an extremely small probability of ever making it to the sites where bond-rupture reactions take place. The size of the reactive molecule can influence crack speeds even when the molecule is smaller than the opening of the crack tip. In effect, the



THEORETICAL CALCULATIONS show that water lowers the energy necessary to stress, or distort, the basic tetrahedral unit of silica glass. In the absence of water a total of 73 kilocalories of energy must be expended to bend the angle between two oxygen

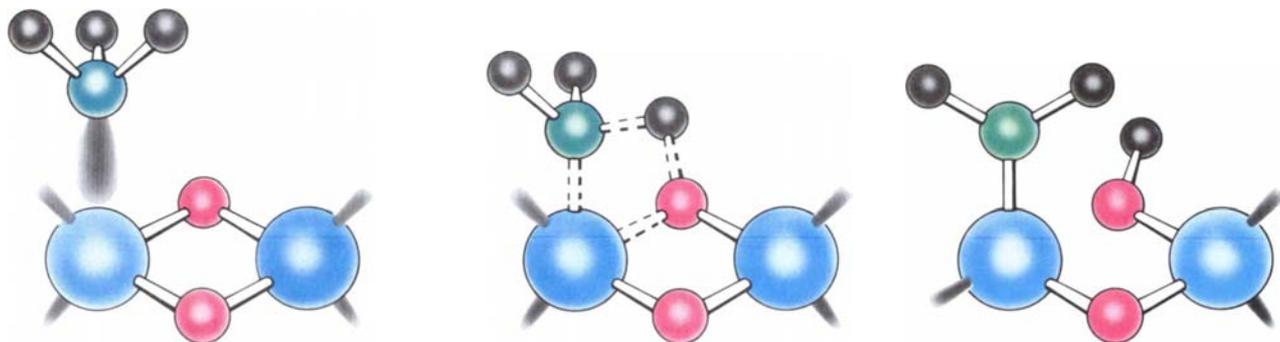
atoms from 105 to 180 degrees (*top*). In the presence of water the energy is only 30 kilocalories (*bottom*). To reduce the number of electrons that enter into the calculations, two of the oxygen atoms in the tetrahedron were replaced with hydrogen atoms.

region just behind the crack tip acts as a sieve that admits molecules to the tip at a rate determined by the size of the molecule.

A similar effect is observed in zeolite molecular sieves. Zeolites are aluminosilicate crystals containing well-

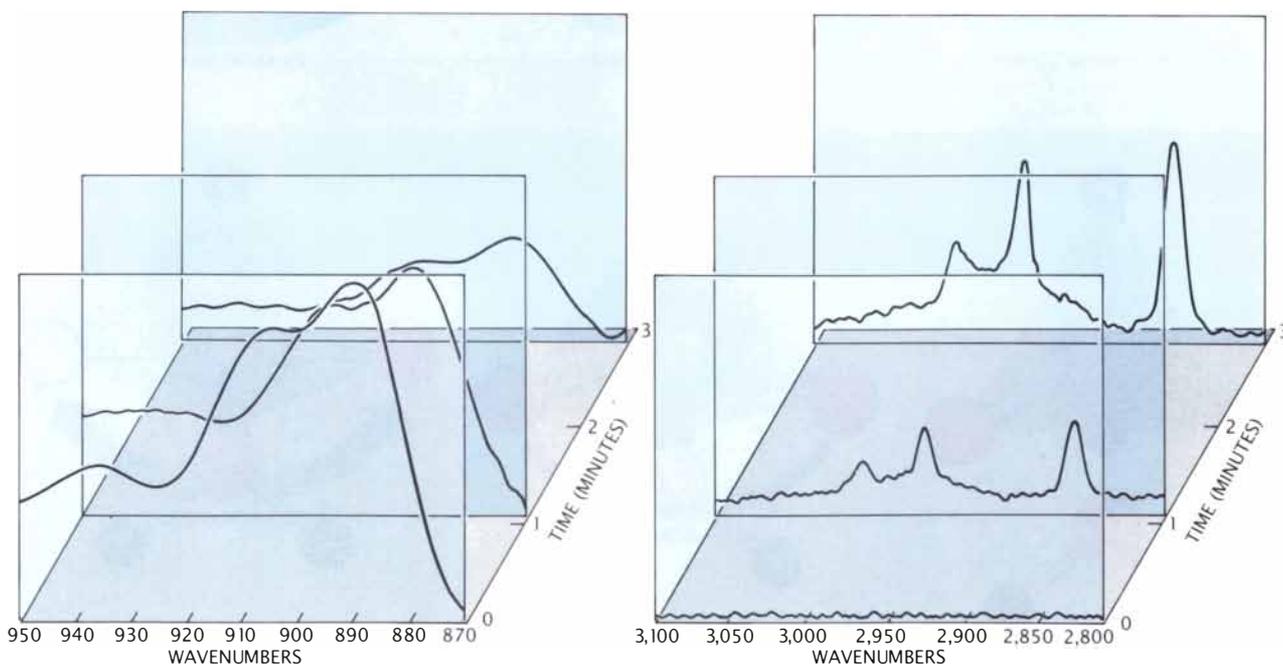
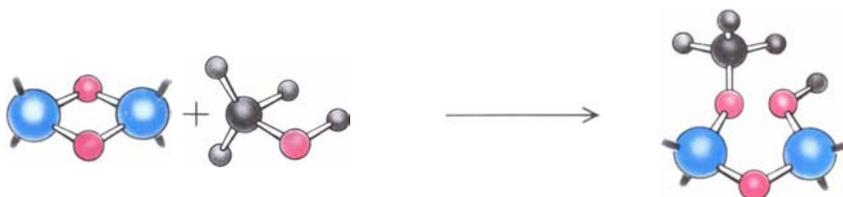
defined cage structures connected by openings of known size. Zeolites are employed to separate different chemicals by their size; the larger molecules are excluded, whereas the smaller ones pass through the openings and adsorb within the cage

structures. Using measured molecular diffusion rates in zeolites as our model for the crack-tip opening, we have shown that methanol should diffuse into a crack tip at a rate four orders of magnitude less than the rate of water. By taking into account



EXPERIMENTS confirm the importance of stress in promoting crack growth. The authors worked with small rings consisting of two oxygen and two silicon atoms. Such so-called edge-sharing rings are practical for studying the effects of bond strain, because the bond angles and distances between atoms are greatly

distorted from those of normal silica. Here the reaction between an ammonia molecule and an edge-sharing ring is shown. Ammonia is adsorbed on a strained silicon site; a dissociative-chemisorption reaction breaks the silicon-oxygen-silicon bonds. Such strained bonds react 100,000 times faster than unstrained ones.



FOURIER-TRANSFORM INFRARED SPECTROSCOPY is utilized to measure the rates at which various chemicals react with edge-shared silicate rings. Shown here is an example of a reaction involving methanol. The rates at which the rings (*left*) dis-

appear and the chemisorbed methanol (*right*) appear are monitored by bathing the samples in infrared radiation. When the frequency of the radiation matches a characteristic vibration of each molecule, a large absorption is recorded (*peaks in curves*).

the rate of molecular diffusion near the crack tip and the rate of dissociative chemical reactions on the strained silicon-oxygen bond, we can now predict to within an order of magnitude the relative rates of crack growth in silica glass exposed to different chemicals.

The results of our atomistic studies of fracture suggest several novel and interesting possibilities for predicting and controlling the strength of glass and other brittle materials. Our discovery of the importance of molecular diffusion near the crack tip indicates that surface coatings might be designed to block the opening of the crack and restrict the passage of small molecules, such as water, that can attack the bonds at the tip and chemically weaken glass. We are currently exploring this possibility by attaching large molecules to the crack walls and measuring their effect on the rate of subsequent crack growth when water is present. We find that we can decrease the crack-growth rate 1,000 times when we first apply such a molecular coating to the crack. If the coating can be applied commercially, it should greatly increase the structural lifetime of glass products.

The same thing should be true for ceramics. Our work on crack growth in other solids leads us to believe that the general conclusions developed for silica can explain the strength behavior of a wide range of brittle materials. The actual crack-tip reactions appear to vary from material to material, however, and the chemistry of each solid must be considered on a case-by-case basis. In complex silicate glasses, for example, the simple bond-rupture mechanism for crack extension can be complicated by the formation of reaction layers that are several micrometers (millionths of a meter) thick. Although the reaction layers do not affect the bond-rupture process directly, they can significantly alter the amount of stress concentrated at the crack tip.

Yet it is important to keep in mind that even though the interplay between surface chemical reactions and mechanical strength can be more complex than the interactions we have described in this article, a thorough understanding of how glass fractures does lay the groundwork for predicting how and when other materials will fracture. It may even provide clues for predicting that most overpowering of fracture events: an earthquake.

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