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Metal Oxides in the Environment

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August 2002

Theory, Modeling and Simulation

MSCF

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Metal Oxides in the Environment

Abstract

Oxides are ubiquitous in much of environmental chemistry. Silica and related glasses are potential vehicles by which radioactive elements may be sequestered and stored. The migration of toxic waste in ground water is largely influenced by interactions at the liquid-solid interface, with several metal oxides making up the bulk of soil. In addition, metal oxides with Brönsted acid or Lewis base functionality are potential replacements for many traditional liquid catalysis that are hazardous to work with and difficult to dispose. In this proposal, we targeted two such areas of oxide chemistry. The long-term behavior of silicate materials slated for use in the entombment of high-level waste (HLW), and the use of solid acid metal oxides as replacements for toxic sulfuric and hydrofluoric acid used in industry (referred to as Green Chemistry). Thus, this project encompassed technology that can be used to both remediate and prevent pollution. These oxide systems were studied using density functional theory (DFT). The comparatively large size and complexity of the systems that will bweree studied made use of high-accuracy electronic structure studies intractable on conventional computers. The 512 node parallel processor housed in the Molecular Science Computing Facility (MSCF) provided the required capability.

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Number of Hours Allocated for the Past Three Years (Exclude Refund Deposits)
3rd 350,000 NH, 2nd 362,500 NH, 1st 250,000 NH; TOTAL 962,000 NH

Number of Hours Actually Used in the Past Three Years (Exclude Refunded Amounts)
3rd 322,449 NH , 2nd 155,207 NH, 1st 205,000 NH; TOTAL 682,656 NH

Appendix A — First Year Overview

Exciton Dynamics in Silicates

We have used density function theory in a plane wave code to calculate the effects of introducing electronic excitations (in the triplet state). The goal was to fully characterize the self-trapped exciton (STE) state in quartz, and to determine the mechanism and barrier for an oxygen vacancy migration in both the ground and excited states. Two significant discoveries were made during the first year of this project.

It has long been believed that the self-trapping mechanism in quartz involved only one state in which an oxygen distortion in the crystal led to the STE. In addition, the pathway to the STE from the initial excitation, that produces a free exciton, remains in debate. The transition has been speculated to be directly down hill or to occur via a curve crossing.

We have discovered that there exist other self-trapped states in addition to the oxygen-distorted state. One of these states is a silicon-distorted state that lies energetically very close to the oxygen-distorted state. We have characterized the structural relaxation and the relative luminescent energies. Our results reveal that these STE states are likely responsible for two distinct luminescent bands. We are currently verifying these results using ab initio calculations as well as applying new techniques within the DFT method (see next section on proposed work).

Secondly, we have calculated the migration barrier and pathway of both the E' (a singly charged oxygen vacancy) and neutral oxygen vacancy. To the best of our knowledge this is the first calculation of the oxygen vacancy migration barrier. In addition, we have determined the migration energy and pathway of the oxygen neutral vacancy by the presence of a (triplet) electronic excitation. This calculation shows that the barrier is shifted down by a factor of 1/4 from the ground state, implying that oxygen vacancy migration is significantly facilitated in the presence of electronic excitations. This can have significant impact for both nuclear waste materials and electronic devices.

Solid Metal Oxide Acids and Green Chemistry

We have completed a study of the activation of silica by SO_3. The reaction of SO_3 with silanol groups on silica results in the silyl ester of sulfuric acid grafted to the silica surface. This new catalyst is thermally stable and exhibits an acidity similar to that of the industrial zeolite ZSM-5. We believe that this new material has the potential to function as an alkylation catalyst and is currently being tested as such. We will patent the process by which the new catalyst is created.

We have completed an extensive study of hydrogen bonding in zeolite solid acids. Certain zeolite-adsorbate systems exhibit unusual ^1H chemical shifts as far downfield as 22 ppm. We have optimized 13 different adsorbates on ZSM-5 models to obtain detailed structural information on the hydrogen bonding, and have directly calculated the ^1H chemical shifts. The results are in excellent agreement with the experimental NMR, and provide the first detailed explanation of strong hydrogen bonds in zeolites.

We have also completed a study of zeolite-catalyzed H-D exchange in substituted benzenes. This study builds on our previous work that showed the H-D exchange in benzene involved a novel mechanism that avoided the carbenium-ion transition state assumed in liquid acid catalyzed reaction. This new study improves on the accuracy of the initial report, and demonstrates the effect electron withdrawing and releasing substituents have on activation energies.

We are finishing a study of the deprotonation energy of the zeolite chabazite using plane wave DFT methods. In order to calculate deprotonation energies, we need the difference in total energy between a neutral and anionic system. In order to calculate the energy of an anion using periodic boundary conditions, a neutralizing background charge must be used. Unfortunately, this approximation does no provide volume independent results. Thus, the value of the deprotonation energy depends on the size of the unit cell. We have demonstrated for the first time the difficulties this poses for the determination of the deprotonation energy of a zeolite.

We are preparing for publication a study of MTG chemistry in ZSM-5. The MTG (methanol to gasoline) process is very important to industry. Any improvements in this process could have great impact in cost and energy saving. We have found that MTG chemistry involves a "carbon-pool" mechanism, in which a particular intermediate is formed during an induction period, after which the synthesis of gasoline precursors, (i.e. ethylene) are rapidly formed. We have experimental and theoretically determined the intermediate, and the probable pathway for hydrocarbon synthesis.

Finally, we are close to completion of a study of alkoxy formation on zeolite solid acids. It is now well established the when propene is adsorbed on zeolites a "surface alkoxy" or "surface ester" is formed. It has been common belief that many other alkenes also form such surface alkoxy species. Our research shows that for many alkenes this reaction is thermodynamically unfavorable, and thus is much less likely than commonly assumed.

Publications Resulting from MSCF Usage

K. Tsemekhman and H. Jónsson, `Dipole moment and long-range interaction between self-trapped excitons in alpha-quartz', (to be submitted to Phys. Rev. B, 2001).

R. M. Van Ginhoven, J. Song, K. Tsemekhman, L. R. Corrales, and H. Jonsson, `Theoretical calculations of self-trapped excitons in quartz', (to be submitted to Phys. Rev. Lett., 2001).

B. Park and L. R. Corrales, 'Total energy dependence on the distribution of boroxol rings in vitreous B_2O_3', (to be submitted to J. Non-Cryst. Solids, 2001).

R. M. Van Ginhoven, B. Park, H. Jónsson and L. R. Corrales, "Cleavage and recovery of molecular water in silica" (to be submitted to J. Chem. Phys., 2001).

R. M. Van Ginhoven, L. R. Corrales, and H. Jonsson, 'Self-trapped excitons in fused silica" (to be submitted to Phys. Rev. B, 2001).

R. M. Van Ginhoven, L. R. Corrales, K. Peterson, M. Dupuis, and H. Jonsson, “A computational study of excitons in quartz-like clusters”, (to be submitted to J. Chem. Phys., 2001).

J. Song, L. R. Corrales, G. Kresse, and H. Jónsson, `Migration of O-vacancies in alpha-quartz: The effect of excitons and electron holes’, Physical Review B (in press, 2001).

J. Song, R. M. Van Ginhoven, L. R. Corrales, and H. Jonsson,`Self-trapped Excitons at the Quartz(0001) Surface’, Faraday Disc. 117, 303 (2000).

L. R. Corrales, J. Song, R. M. Van Ginhoven, and H. Jónsson, “Computational Studies Of Self-Trapped Excitons In Silica”, in *Defects in SiO_2 and Related Dielectrics: Science and Technology*, Eds: G. Paccioni et al., pages 329-337 (Kluwer Academic Publishers, Dordrecht, 2000).

J. Song, H. Jónsson, and L. R. Corrales, “Self-trapped Excitons in Quartz “, *Nuclear Instruments and Methods in Physics Research B* **166-167**, 453-460 (2000).

L. R. Corrales, J. Song, R. M. Van Ginhoven, and H. Jónsson, “A comparative study of oxygen vacancy migration pathways in crystalline polymorphs of silica”, in Environmental Issues and Waste Management Technologies in the Ceramic and Nuclear Industries V, *(Ceramics Transactions, Volume 107)*, G. L. Smith, G. T. Chandler and B. Mobasher, eds. (The American Ceramics Society, Westerville, Ohio 2000, p. 139.

J. Song, L. R. Corrales, and H. Jónsson, “Exploring the excited states of vacancy defects in silica” Mat. Res. Soc. Symp. Proc. **540** (1999).

L. R. Corrales, R. M. Van Ginhoven, J. Song and H. Jónsson, “Vacancy migration barrier energetics and pathways in silica,” Mat. Res. Soc. Symp. Proc. **538** (1999).

D. H. Barich, J. B. Nicholas, and J. F. Haw, “GIAO Proton Chemical Shifts of Strong Hydrogen Bonds: the Importance of Electron Correlation,” submitted to *J. Am. Chem. Soc.*

J. Zhang, J. B. Nicholas, and J. F. Haw, “Solid Acids Formed by the Reaction of SO_3 with Oxide Surfaces,” submitted to *J. Am. Chem. Soc.* (1999).

J. B. Nicholas, “A Theoretical Explanation of Solvent Effects in Zeolite Catalysis,” invited, in press *Topics in Catalysis* (1999).

J. F. Haw, J. B. Nicholas, F. Deng, W. Song, Z. Wang, and T. Xu, “Cyclopentenyl Cations and the Mechanism of Hydrocarbon Synthesis in Zeolites,” to be submitted to *J. Am. Chem. Soc.*

J. B. Nicholas, T. Xu, and J. F. Haw, “Hydrogen Bonding in Solid Acids, a Theoretical and NMR Investigation,” to be submitted to *Nature.*

Oral Presentations Resulting from MSCF Usage

Renée M. VanGinhoven, Dissertation defense, University of Washington, Seattle, WA, January 2002.

Hannes Jónsson, APS March Meeting, Seattle, WA, Mar. 2001.

Hannes Jónsson, Technical University of Denmark, Center for Materials Physics, Copenhagen, Denmark, Dec. 2000. (invited)

Hannes Jónsson, Materials Science Institute, Princeton University, Nov. 1999. (invited)

Hannes Jónsson, APS National Meeting, Minneapolis, MI, Mar. 2000.

Hannes Jónsson, Faraday Discussion on "Excited States at Surfaces", Nottingham, UK. Sept. 2000.

H. Jónsson, J. Song and L. R. Corrales, "Oxygen vacancy migration: Ground and Excited State Energy Barriers and Pathways", Kohn symposium, Goteborg, Sweeden, June 3-4. (invited)

L. R. Corrales, "Computer simulation of radiation effects in oxides", June 2000, Sandia National Laboratory and Kirtland Air Force Research Laboratory, Albuquerque, NM. (invited)

L. R. Corrales, J. Song, R. M. Van Ginhoven, and H. Jónsson, "Computational study of self-trapped excitons in silica", April 2000, NATO Advanced Studies Institute on Defects in Silica and Related Dielectrics, Erice, Sicily, Italy. (invited)

L. R. Corrales, "Structural evolution of silica under irradiation", October 1999, International Conference on the Physics of Non-Crystalline Solids, Tucson, AZ. (invited)

L. R. Corrales, "Structure, luminescence, diffusion and phase separation in silica and silicates", September 1999, Department of Material Science and Engineering, University of Arizona, Tucson, AZ. (invited)

L. R. Corrales, J. Song, R. M. VanGinhoven and H. Jónsson, "Migration of oxygen vacancy radical defects and self-trapped excitons in silica" March 1999, American Chemical Society, National Meeting Anaheim, CA. (invited)

J. Song, H. Jónsson and L. R. Corrales, "Excitons and defects in silica", July 1999, Radiation Effects in Insulators – 10, Jena, Germany.

L. R. Corrales, J. Song, R. M. VanGinhoven, and H. Jönsson, "Oxygen vacancy migration and formation from self-trapped excitons in silica", April 1999, American Ceramics Society, National Meeting, Indianapolis, IN. (invited)

J. B. Nicholas, III Congress of the International Society for Theoretical Chemical Physics, scheduled Nov. 1999, Mexico City. (plenary lecture)

J. B. Nicholas, International Symposium on Separation and Purification, scheduled Oct. 1999, Saskatoon, Saskatchewan. (keynote speaker)

J. B. Nicholas, University of Washington, May 1999, Seattle, WA. (invited)

J. B. Nicholas, ACS Spring Meeting, March 1999, Anaheim, CA. (invited)

J. B. Nicholas, DOE Laboratory Catalysis Research Symposium, Feb. 1999, Alburquerque, NM. (invited)

J. B. Nicholas, Computational Studies of Interfacial Phenomena, PNNL, Sept. 1998, Richland, WA (invited)

J. B. Nicholas, ACS Summer Meeting, August 1998, Boston, MA. (invited)

J. B. Nicholas, West Coast Theoretical Chemistry Conference, June 1998, Richland, WA

J. B. Nicholas, San Diego State University, San Diego, CA, May 1998. (invited)

Poster Presentations Resulting from MSCF Usage

R. Van Ginhoven, J. Song, L. R. Corrales, and H. Jonsson, `Self-trapped Excitons in alpha-Quartz', Chemical Physics Summer School, Gordon Research Conference, Rhode Island, June 2000.

J. Song, L. R. Corrales, and H. Jónsson, "Defects and Excitons in silica", Spring Meeting 1999, American Physical Society, Atlanta, GA.

L. R. Corrales, R. M. Van Ginhoven, J. Song, and H. Jónsson, "Vacancy migration barrier energetics and pathways in silica," Fall Meeting 1998, Materials Research Society, Boston, MA.

J. Song, L. R. Corrales, and H. Jónsson, "Exploring the excited states of vacancy defects", Fall Meeting 1998, Materials Research Society, Boston, MA.

J.B. Nicholas, 4th DOE Meeting on Homogeneous Catalysis and Organometallic Chemistry, June 1998, Baltimore, MD.

Significant Methods/Routines or Codes Developed

The dimer method, used for climbing up energy surfaces and finding saddle points, was implemented and tested for parallel computations using VASP on the SP. This method is similar in spirit to eigenvector following methods, but it does not require second derivatives and inversion of the Hessian matrix, and can therefore be used in conjunction with plane wave based

DFT calculations. This took a long time to implement because of a bug in the parallelization of the VASP code. The code is running properly now and is being used in long time scale simulations of the activated dynamics of excitons in SiO_2 glass where diffusion and bond breaking events are revealed without any preconceived bias about the dynamics in the system.

We have also implemented a new and more efficient version of the NEB method which is more stable and guarantees that one of the images of the system in the elastic band converges to a saddle point. This is done in parallel. These enhancements of the VASP code have been made available through the VASP user home page.

Appendix B — Second Year Overview

Self-Trapped Excitons in SiO_2

In the first year, our work focused on DFT/PW91 calculations and we found several triplet state self-trapped exciton (STE) states in quartz, two that mainly involve displacement of oxygen atoms (STE-Ob and STE-Oc) and one that mainly involves displacement of a single Si atom (STE-Si). We calculated the luminescence for these STEs and for excitons attached to various defects. In one case, the oxygen vacancy, we calculated the drop in diffusion activation energy barrier of the defect due to the presence of an exciton. In the second year, we have carried out calculations of STEs at the (0001) quartz surface. We also carried out preliminary calculation of STEs in amorphous SiO2. A central focus of our calculations has, however, been tests of the theoretical methodology. A procedure has been developed for improving the accuracy of our calculations and this has enabled us to achieve good agreement with experimental measurements. A clear microscopic picture of the triplet state energy landscape has emerged which is consistent with some of the conclusions reached earlier by experimentalists, and we have also proposed new interpretation of some of the experimental data.

The large, 72 atom system needed to represent STEs in quartz can only be handled at the approximate DFT/PW91 level of theory. Higher level calculations can only be applied to small clusters. For the reliable CCSD(T) method, a single SiO2 unit is already a large calculation. A theoretical study of STEs in quartz must, therefore, find some practical balance between the approximations in the methodology, and errors due to small system size. We have carried out extensive tests of DFT/PW91 and other higher level methods which can only be applied to small systems. As a result of these tests, we have developed a procedure where cluster calculations are used to improve on the triplet state energetics of the bulk configurations (which are subject to periodic boundary conditions to eliminate surface effects). DFT/PW91 calculations give good results for the ground, singlet state, but the PW91 functional is not as good for the triplet state. We have found that the error in the triplet state is large for delocalized states but small for localized states. The main problem is a large underestimate of the triplet state energy for the highly delocalized triplet state in perfect quartz. This is likely directly related to the well known underestimate of the band gap in DFT-PW91 calculations (a problem that is even worse in the local density approximation, DFT/LDA). We have found, however, that DFT/B3LYP calculations give quite good agreement with higher level wave-function based calculations, even for quartz-like clusters. The problem is that B3LYP can only be used for rather small clusters because of the inclusion of exact exchange (attempts to use the CRYSTAL code, which includes exact exchange and periodic boundary conditions have not been successful. Only very small systems can be handled by CRYSTAL).

The optimal way we have found to estimate the energy of the triplet state with respect to the singlet state (for a given geometry of the 72 atom cell with periodic boundary conditions) is to add a correction obtained from DFT/B3LYP and DFT/PW91 calculations of Si8O25 clusters snipped out of the full configuration. Broken bonds are capped with H-atoms to reduce surface effects. This procedure has given an energy landscape for the triplet state which appears to be in good agreement with experiments.

The most striking feature of the triplet state energy landscape is how flat it is. Large displacements of the atoms (on the order of 1 A) can result in insignificant changes in the energy of the system. This immediately suggests that there are several local minima on the triplet state surface, i.e. many STEs. This is consistent with the fact that luminescence from the triplet state is found to give broad and structured peaks. An extreme example of this is experimental data collected at low temperature (80 K) which shows two emission peaks, one at 2.8 eV and another at 4.0 eV. This coincides very nicely with the two O-displaced STEs we have found, where the calculated emission is 2.8 eV and 4.3 eV. The barrier from one to the other is on the order of 0.2 eV, so room temperature experiments would only detect the 2.8 V emission. The 4.0 eV peak had been assigned to a defect, but our calculations suggest that this is also due to a STE. Experiments on the temperature dependence of the luminescence (lifetime of the triplet state) have indicated that the system can get thermally activated from the most stable STE to a new state from where the system is quenched non-radiatively. The experimentally estimated activation barrier is 1 eV. This is quite consistent with our Si-displaced STE, which is estimated to be close to a crossing of the singlet and triplet state. The barrier to get to the Si-displaced STE is calculated to be 0.5 eV, going through the perfect crystal configuration. It is likely that the triplet state energy of the perfect crystal configuration is still somewhat underestimated in our calculations (as indicated by comparison with CCSD(T) calculations of small clusters). The agreement here with experiments is still quite good, and our calculations have succeeded in giving a microscopic interpretation to a qualitative picture that had emerged from experiments. With this success, the stage is set for studying STEs in amorphous SiO_2.

We have carried out preliminary studies of amorphous SiO_2 and STEs formed in amorphous SiO_2. We have managed to generate 72 atom configurations with no configurational defects, i.e. where all Si atoms are formally fourfold coordinated by O atoms, and all O atoms are twofold coordinated by Si atoms. The system is, however, still not well annealed, and we have found that formation of STEs (by exciting the system to the triplet state and relaxing) leads to significant annealing of the system. We need to carry out much more extensive annealing runs before we can carry out meaningful studies of the STEs in amorphous SiO_2. This is the main topic of next years research.

The calculations of STEs at the surface have revealed a gradual drop in the STE as it approaches the surface of quartz. At the hydroxylated surface, the STE leads to the formation of an OH radical (which could initiate surface chemistry). It is reasonable to expect this drop in energy since the energetic cost of displacements of lattice atoms becomes smaller near the free surface. This means that STEs formed in bulk quartz will tend to migrate out to the surface. Since the lifetime of STEs in quartz is on the order of 1 ms, and the diffusion barrier is estimated from our calculations to be on the order of 0.5 eV (which is likely an underestimate, it may be closer to 1 eV), the STEs could diffuse over a large distance at temperatures slightly above room temperature. The non-radiative decay from the Si-displaced STE will be a competing process, however, and in the end only a small region near the surface may feed STEs into the SiO_2 surface. In the coming year, we will study similar things in TiO_2 which is frequently used as a photocatalyst.

Solid Metal Oxide Acids and Green Chemistry

We have done extensive computations of the mechanism of the MTG (methanol to gasoline) reaction. This process is very important to the petroleum industry. Considering the huge use of gasoline in the U.S., and the recent increases in oil prices, any improvements in this process could have great impact in cost and energy saving. We have found that MTG chemistry involves a "carbon-pool" mechanism, in which a particular intermediate is formed during an induction period, after which the synthesis of gasoline precursors, (olefins) are rapidly formed. We have experimentally and theoretically determined the intermediate, and the probable pathway for hydrocarbon synthesis. We are extending out study of MTG chemistry on conventional zeolites to the modified silico-alumino-phosphate (SAPO) materials, which also catalyze the MTG reaction. As very closely related reaction, the conversion of Methane to Olefins (MTO) is also being studied.

Based on our previously developed predictions of stable carbenium ions on zeolites, we completed a study of the reaction of a stable carbenium species (an acid) with coadsorbed probe molecules (bases). The equilibria established between the acids and bases were entirely predicted by our theoretical calculations, and is fully consistent with the energetic criteria we developed earlier for stable carbenium ions.

We completed a study of the deprotonation energy of the zeolite chabazite using plane wave DFT methods. In order to calculate deprotonation energies, we need the difference in total energy between a neutral and anionic system. In order to calculate the energy of an anion using periodic boundary conditions, a neutralizing background charge must be used. Unfortunately, this approximation does no provide volume independent results. Thus, the value of the deprotonation energy depends on the size of the unit cell. We have demonstrated for the first time the difficulties this poses for the determination of the deprotonation energy of a zeolite.

We have completed an important study of the acidity of sulfated zirconia (SZ). SZ has often been assumed to be a solid super acid, having an acidity greater than 100% sulfuric acid. We have used theoretical prediction and experimental NMR to identify previously unassigned peaks in the NMR spectra of adsorbates (trimethylphosphate and pyridine) on SZ. These data help explain the reactivity of SZ and quantify its acidity.

We finished a study of alkoxy formation on zeolite solid acids. It is now well established the when propene is adsorbed on zeolites a "surface alkoxy" or "surface ester" is formed. It has been common belief that many other alkenes also form such surface alkoxy species. Our research shows that for many alkenes this reaction is thermodynamically unfavorable, and thus is much less likely than commonly assumed.

Appendix C — Overview of the Past Three Year's Accomplishments and Activities Third Year Overview

STEs in SiO2

Studies of excitons in fused SiO_2 were carried out to understand the effect of self-trapped excitons (STEs) in waste containment glasses. This project required a large amount of the CPU allocation because the first task was to create several amorphous SiO_2 structures. The amorphous structures were created by using high temperature annealing with DFT calculations combined with classical dynamics. Recently developed algorithms to enable the system to explore configuration space much more efficiently were attempted, however a major bug in the code prevented this from being implemented. Instead, annealing simulations were carried out that were more costly, nonetheless a series of configurations were obtained that were then used to carry out studies of STE and of water reaction and diffusion in bulk amorphous silica.

A single configuration with 72 atoms can support a large number of different STEs. Several configurations were generated for different STEs by relaxing the system in the triplet state from different initial displacements of the atoms. An attempt was made to find the lowest energy STEs and then calculate the mechanism for the STE to diffuse from one configuration to another (using the same methodology we used earlier for calculating migration of defects, such as the oxygen vacancy). Some of the most interesting calculation were on the evolution of the system after the STE emitted a photon and the system returned to the ground state. The key question was how do STEs lead to bond breaking and the formation of interstitial oxygen, as has been observed in experiments where glasses are exposed to radiation or electron bombardment. This is an important degradation mechanism in waste containment glasses and, therefore, it is important to know the microscopic mechanism. Our studies indicate that a small change in the local environment can tip the balance between regeneration of the broken Si-O bond once the system returns to the singlet state, and permanent rupturing of the bond. It is possible that rather small distortions of the local environment in amorphous SiO_2 as compared with quartz is enough to give the experimentally observed enhancement in the rate of bond rupture. Our simulations give a microscopic picture of how this process takes place and what determines the rate.

Dipole Moment and Long-Range Interaction Between Self-Trapped Excitons in α-Quartz

We have carried out extensive calculations of the interactions of the excitons with their periodic images to test their effect on our exciton and defect calculations. A procedure was devised to evaluate both the elastic and electronic component of the interaction and the interaction was quantified within a dipole approximation. While the dipole moments are large (1 to 2 D) the screening is very effective and the singlet-triplet splitting is affected by less than 0.1 eV. This result was verified by doing DFT calculations on systems with double the box length.

Energy Landscape of Triplet State

Other calculations included the completion of an energy landscape for the triplet state that provides a direct comparison to experiments. An optimal way to estimate the energy of the triplet state with respect to the singlet state (for a given geometry of the 72 atom cell with periodic boundary conditions) is to add a correction obtained from DFT/B3LYP and DFT/PW91 calculations of Si_8O_{25} clusters snipped out of the full configuration. Additional calculations were carried out to estimate the lifetime of the different STEs in quartz, and their spin resonance signature, to enable detailed comparison with experiments.

Water in Silica

The reactivity of water with the silica network in the bulk has not been previously studied in a periodic system where the response of the network structure to the formation of SiOH bonds can be determined. As expected, a wide variation in the degree of reactivity, as determined by reaction barriers, is obtained. The most striking result is that the height of the reaction barrier is intimately coupled with the energy difference between the product and reactant states. When the reaction state is downhill from the product state, the barrier is low. As this energy difference becomes more positive the reaction barrier increases. The extent to which the network structure can anneal after hydrolysis determines the degree to which the reactant state is stabilized or destabilized. Molecular dynamics simulations at high temperature and high pressures were carried out to study the lifetimes for reaction and the extent to which the network relaxation upon reaction anneals reaction sites of the system. In addition, calculations were carried out to study to mechanisms of proton transfer. It is found that for small distances, the formation of free protons is unfavorable without first applying a field. A proton diffusion barrier is estimated in the presence and absence of unreacted water molecules that are in relatively good agreement with experiment.

Boroxyl Rings in Vitreous Borates

Borates are an important component in nuclear waste and other glasses, and boroxol rings are an important constituent in borates. However, the structural and energy distributions of boroxol rings are not well characterized. Boroxol rings consist of three borons in a ring bridged by oxygen atoms and are an important component that mediate the intermediate range structure in vitreous borate. These rings may play a key structural role in more complex glasses. In this work, the total energy of vitreous borate as a function of the number fraction of boroxol rings present in the system was calculated by density functional theory (DFT). The initial structures, where the number of boroxol rings was held fixed, were first generated by classical molecular dynamics (MD) simulations and then relaxed using DFT MD and optimization methods. From the pair distribution functions, it is found that the intermediate-range structure is strongly influenced by the existence of the boroxol rings. The total energy of vitreous B_2O_3 as a function the fraction of boroxol rings show two minima, one at about 0.15 and the other at about 0.75 with an energy maximum at 0.40. It is interesting that computer simulations give an energy minimum at a number fraction less than 0.40, whereas NMR and Raman experiment give a number fraction in the range of 0.6 to 0.85.