Immobilization of Radionuclides in Oxides (GC2392)

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We use computer simulations to study structural changes that can take place over long time in oxide glasses as a result of electronic excitations, for example resulting from radioactive decay and as a result of hydrolysis.

At the most basic level, our project involves tests of methodology to establish what level of theory is needed in order to accurately reproduce electronic defects and chemical reactions in oxides, especially quartz and amorphous silica. We have recently reported [VanGinhoven et al. JCP 2003] an extensive study of excitons in silica clusters calculated by both wave function methods and density functional theory (DFT). It is clear from this and other studies we have performed that DFT calculations with functionals commonly used in condensed phase simulations are inadequate for the study of excitons and electron holes. We have found that the B3LYP functional is much superior, but it is too computationally demanding when extended systems are studied because of the necessity of evaluating exact exchange. Instead, we have developed an algorithm and implementation in the NWChem software package for self-interaction correction (SIC) to DFT. This is the first implementation that we know of which includes self-consistency and incorporates periodic boundary conditions to allow simulations of extended systems. Furthermore, our implementation includes atomic forces and therefore enables us to calculate minimum energy structures and transition states. The computational cost is in principle only a factor of 3 to 5 over regular DFT calculations, but more optimization of the code is needed before that theoretical limit is reached.

The DFT-SIC calculations have proven to solve many of the problems known to plague regular condensed phase DFT calculations and our code opens the possibility to address various questions that could not be addressed before computationally. Several test problems we have studied indicate that with some simple modifications the DFT-SIC approach can give similar accuracy for both stable structures and transition states as the much more expensive B3LYP functional. We have applied the DFT-SIC method to several problems in oxides. One is the spin density of a hole created by substituting an Al-atom for a Si-atom in quartz. Regular DFT, using LDA or GGA functionals, shows spin density that is delocalized over all four O-atom neighbors of the Al-atom. Experiments, however, show that the spin density is localized on one of the O-atoms, as manifested, for example, by lengthening of only one of the Al-O bonds. The DFT-SIC calculations indeed show localization on only one of the O-atoms. Another example comes from triplet state excitons in quartz. With DFT/GGA the the spin density of the lowest energy structure is smeared out over all 72 atoms in the simulation cell. Localized excitons can, however, be found and have been studied in this project previously, but they are metastable with respect to the delocalized state. With DFT-SIC the localized excitons become lower in energy in agreement with experiment. Finally, a similar reversal of the relative energy of localized and delocalized states is found for electron holes in amorphous silica. The DFT-SIC calculations show stable localized holes in agreement with experiment, while the holes delocalize at the DFT/GGA level of theory.

The relative energy and structure of different localized excitonic states in silica are still quite well described by DFT/GGA. We have used this level of theory to study the formation of defects in silica due to exciton formation. Ten different glass samples that are free of coordination defects have been generated (fig 1a shows a portion of one of the samples). The figure shows an unexpected damage process that was observed in one of the glasses. It is unexpected because no thermally activated process is required to form the

defect. First, the system is excited to the triplet state, representing a fast process of initial excitation to some very high energy singlet state and then intersystem crossing and trapping in the lowest triplet state. Since this is a long lived state, the system is then relaxed in the triplet state and a Si-O bond is found to break (see fig. 1b). When the system is then returned to the singlet state to represent radiative decay and then relaxed, the defect does not disappear, but rather develops into two coordination defects, a five-fold coordinated Si-atom and a small, strained right of just two Si-atoms and two O-atoms (see fig. 1c). The energy along this path evaluated both in the singlet and triplet state is shown in fig. 1d.

We then searched for various transition paths from this state. A transition to the original defect free structure involves a significant barrier of 0.76 eV. But, several other processes were found with similar activation energy that represent further migration of the defects. This could, therefore, be the first step in the formation of an interstitial O-atom defect. It is well known experimentally that radiation of glasses results in the formation of oxygen bubbles. Further simulation studies will address this and other defect formation mechanisms in glasses.

We have also studied the insertion of water molecules into coordination defect free glass samples and found, surprisingly, that there exist sites where the energy of the water molecule is comparable to the energy in liquid water. The barrier for dissociation of the molecule was found to be very small, on the order of 0.1 eV, and lead to a lower energy state with two hydroxyl groups. This represents an initial stage in hydrolysis of the glass. The importance of strain and anomalous Si-O rings has been studied to identify particularly reactive sites, and sites where electronic defects such as excitons and holes are likely to self-trap.