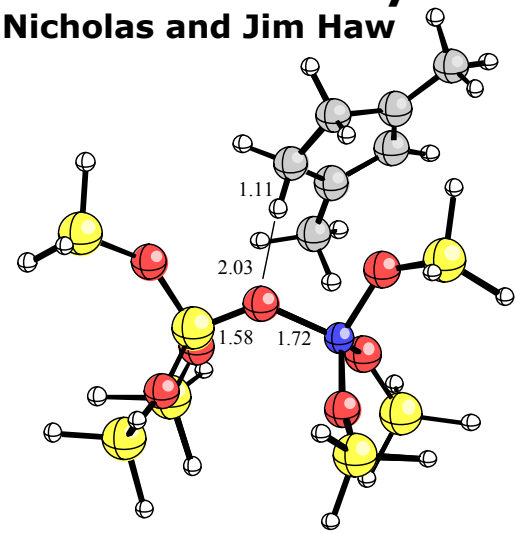
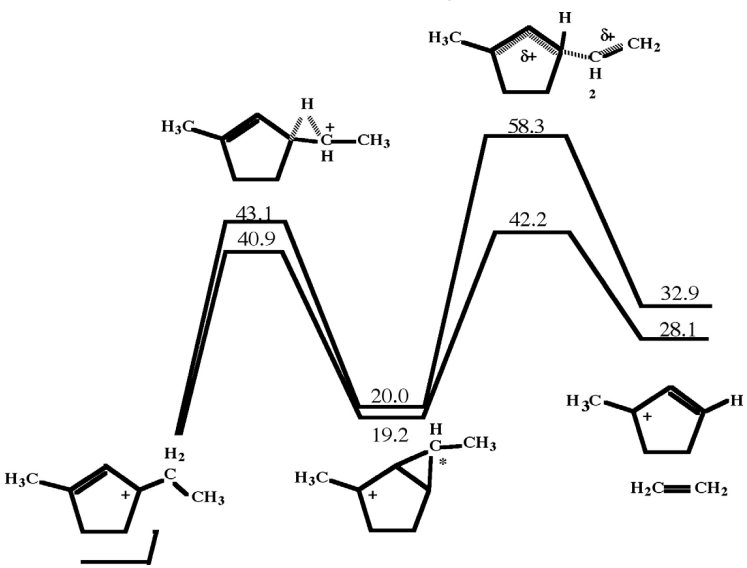
GC-6 Highlight

USC, EMSL, Genentech

Solid Metal Oxide Acids and Green Chemistry

John Nicholas and Jim Haw





The methanol-to-gasoline (MTG) process is widely used in industry. In this work, the MTG process was determined to proceed by a "carbon-pool" mechanism in which the formation of the reactive intermediate 1-3, dimethylcyclopentadiene (13CPD) proceeds by rapid production of gasoline precursors. The reactive intermediate 13CPD is known to be very stable in liquid acid. The proposed reaction mechanism involves first the synthesis of 13CPD, which is then repeatedly methylated to produce short-chain alkenes. The 13CPD cation was shown to be stable in the zeolite (top figure), and is only 5 kcal/mol lower in energy than the parent 13CPD, a key part of the reaction mechanism, which allows regeneration of the cation after it is "used" to produce alkenes. A very large number of possible reaction pathways that involve the 13CPD intermediate were tested. We have calculated numerous mechanisms by which 13CPD is alkylated, in thus developed a longer carbon chain that eventually leads to ethylene or propylene. We have also outlined the reaction mechanism by which 13CPD is converted to toluene, thus killing the reaction. In the bottom figure is shown the reaction mechanism for another key step in the reaction, the production of ethylene (and propene) following methylation of 13CPD. J. F. Haw, J. B. Nicholas, W. Song, F. Deng, Z. Wang, T. Xu, and C. S. Heneghan "Roles for Cyclopentenyl Cations in the Synthesis of Hydrocarbons from Methanol on Zeolite Catalyst HZSM-5," J. Am. Chem. Soc. **2000**, *122*. 4763.

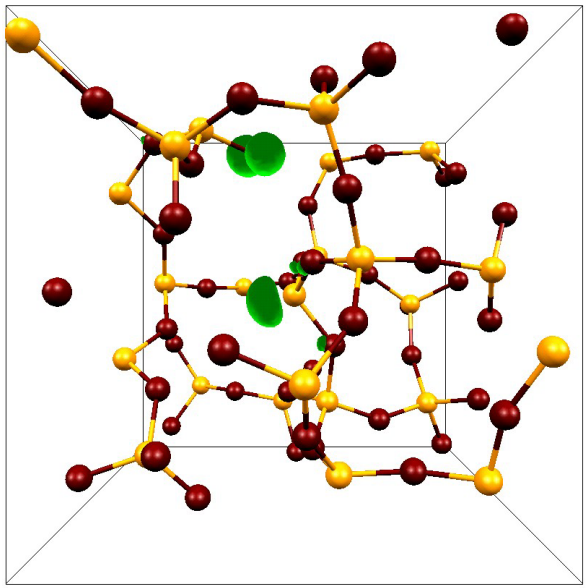
EMSL UP # 1799

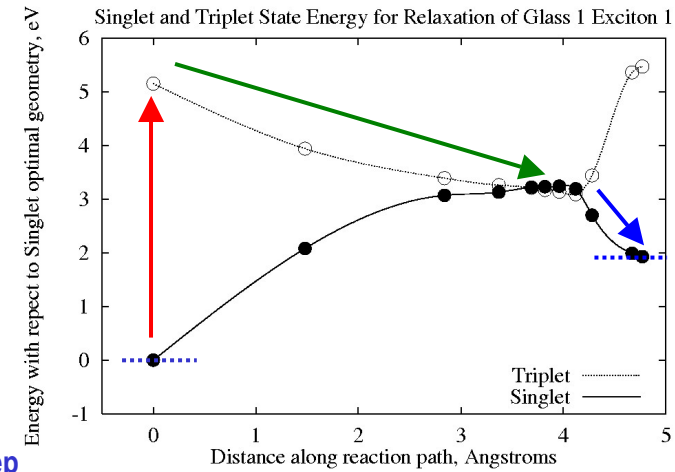
GC-6 Highlight

U. Washington, EMSL

Self-trapped excitons in fused silica

Renée M. Van Ginhoven, Hannes Jonsson, and L. René Corrales





Upon irradiation of silicate glasses , low-lying electronic excitations are induced that can lead to self-trapped excitons (STEs). The STEs can lead to bond breaking and the formation of interstitial oxygen as part of a degradation mechanism that can compromise the performance of glasses used in the containment of nuclear waste. The effects of STEs in fused silica were modeled to better understand the microscopic mechanism that leads to defect formation. The top figure shows the final structure and excess spin density for an exciton in a model glass. This structure has one broken Si-O bond, where these atoms moved apart from their initial distance of 1.7 Å to a distance of 3.7 Å. The surrounding silica network has relaxed significantly, with a lattice relaxation energy of 2.1 eV. The excess spin density shows that the exciton is localized across the broken bond. The lower figure shows the triplet (upper curve) and singlet (lower curve) state energy surfaces for the relaxation of the exciton in the model glass. The optimized exciton structure corresponds to the minimum energy point on the triplet state curve. The energy of this geometry is at or near a singlet-triplet crossing, so the transition back to the singlet ground state is expected to be non-radiative. A broken bond defect is retained when the system is de-excited to the singlet state and relaxed. The exciton has enabled the system to overcome a 3 eV activation barrier to a broken bond state.

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