

# Theory in Materials Chemistry

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Computational studies based on electronic structure theory are being carried out to provide insight into properties of materials being studied in the molecular materials, nanospace architecture, and nanostructured thin film programs. Some examples are given below.

## Theoretical Studies of Reaction Mechanisms in Zeolites (with L. Iton)

### Protolytic Cracking of Hydrocarbons in Zeolites

#### Ethane cracking:

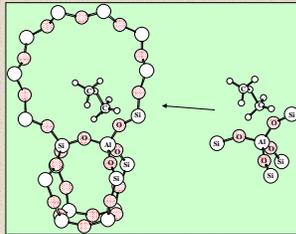
proton transfer:  $ZOH + C_2H_6 \rightarrow ZO \dots C_2H_7^+$  cracking  
cracking:  $ZO \dots C_2H_7^+ \rightarrow ZOCH_3 + CH_4$

#### Propane cracking:

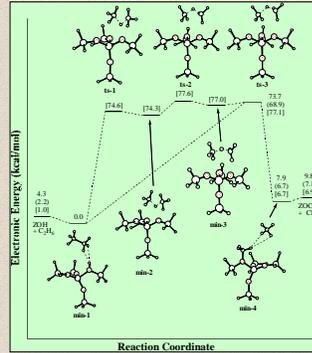
proton transfer:  $ZH + C_3H_8 \rightarrow ZO \dots C_3H_9^+$  cracking  
cracking:  $ZO \dots C_3H_9^+ \rightarrow ZOCH_2CH_3 + CH_4$   
regeneration:  $ZOC_2H_5^+ \rightarrow ZOH + C_2H_4$

Z = zeolite  
ZOH = OH is the acid site

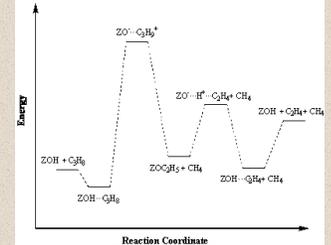
Illustration of the embedding procedure used to estimate long-range effects of the zeolite lattice.



### Reaction pathway and transition states for ethane cracking



### Reaction pathway and transition states for propane cracking



Our work on propane, as well as our previous study of ethane have been the first to show that the long-range electrostatic interaction from the zeolite framework significantly lowers the energy of the transition state relative to the reactants. This result is obtained from a new technique in which the potential energy surface is fully investigated with small clusters; which are then embedded into large clusters that better represent the environment of the zeolite pore.

Zeolite ZSM-5

## Theoretical Studies of the ET Donor Molecule (with J. Schlueter, U. Geiser, A. Kini, H. Wang)

### Theoretical Methods

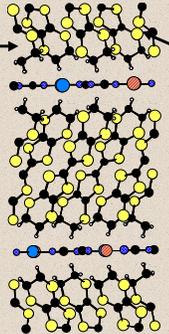
Density functional theory with the 6-31G\* basis set was used. The ET<sup>+</sup> dimer was constrained to have C<sub>2</sub> symmetry as in the crystal. The ET<sup>+</sup> dimer transition state was approximated by freezing the SCCS dihedral angle involving the terminal ethylene group at 0°.

### Crystal structure of the κ-(ET)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Br organic super conductor

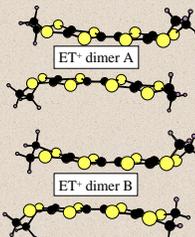
A volume anomaly has been observed around the glass transition, possibly due to freezing of the ET conformation (which would cause thermal expansion).

On the basis of resistivity relaxation measurements on quenched samples, a structural transition around 80 K with an activation energy of ca. 5 kcal/mol has been proposed in which the two terminal ethylene end groups of ET go from a disordered arrangement with both eclipsed and staggered conformations to an ordered state with only the eclipsed conformation.

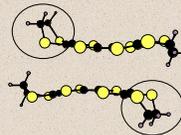
Computational studies have been carried out to determine the intrinsic energy barrier for the conformational change of ET.



ET = bis(ethylenedithio)tetrathiafulvalene



In the A conformation both terminal ethylene groups of an ET<sup>+</sup> molecule are eclipsed and in the B conformation they are staggered.



Transition state with chair type conformation on two ends

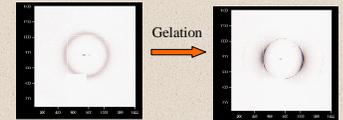
### Energy barriers

	ΔE kcal/mol	
Conformer	Inner	Outer
AA	0	0
TS	4.07	2.22
BB	-0.29	-0.23

### Conclusions

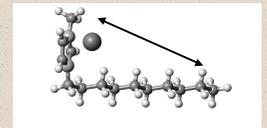
Theory shows that the conformational change in the ET<sup>+</sup> dimer involves an unexpected chair type structure in the transition state. The energy barrier is in reasonable agreement with experimental energy barriers for structural transitions which are in the range of 4 to 5.2 kcal/mol. The ordering effect has a profound effect on the Tc of these materials.

## Theoretical Studies of Complex Fluids (with M. Firestone)

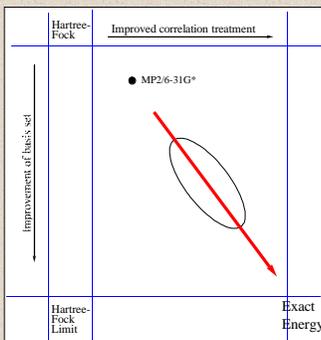


Ionic liquids, have recently attracted considerable attention as environmentally benign alternatives to conventional organic solvents in a range of synthetic, catalytic, and electrochemical applications. We are exploring means by which to enhance structural ordering in room temperature ionic liquids (RTILs) by various gelation mechanisms.

This work involves synthesis of RTILs and structural characterization by small-angle X-ray scattering coupled with electronic structure calculations. Structural ordering of such solvents may play a role in determining the course of chemical reactions or separation processes carried out in them.

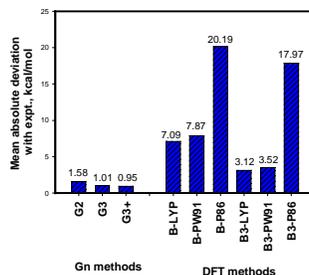


## Methods Development (with J. Pople, K. Raghavachari)



The Gaussian-n (G2, G3, etc) methods have been developed with improved correlation treatment and larger basis sets to approach the exact solution of the Schrodinger equation

### Comparison of performance of different methods on the new 148 molecule G2/97 neutral test set of enthalpies of formation at 298 K



### Major Accomplishments

The reaction pathway for cracking of propane on the surface of a zeolite pore has been elucidated and good agreement is found with experiment for the first time.

Computations show how nitrogen impurities reduce nucleation sites in the growth of nanocrystalline diamond thin films and may increase conductivity.

The development of Gaussian-3 model chemistry has provided a new level of accuracy for quantum chemical energy calculations.

Several papers have been on top ten list of "hot" chemistry papers for citations in *ScienceWatch* in last three years.

### Future Plans

Increased emphasis of theory in molecular materials including complex fluids, molecular magnets, and nanoparticles. Continued applications in UNCD and nanoporous materials areas.

Methods development will focus on extending our accurate quantum chemical methodologies to transition metals.