

Title: Nanoconfined Chemistry and Spectroscopy
PI's: Stephen Gray and Stuart A. Rice

Project 1: Rovibrational states of a Lithium atom/ion inside a C₆₀ cage.

Ab initio potential surfaces for C₆₀ atoms have been fit to a functional form based on atom-atom interactions. A Li atom is then inserted into the rigid C₆₀ cage, and the energy eigenvalues and eigenstates calculated using the Lanczos algorithm. The low energy spectrum of this system has gaps that are not yet well understood. The calculations performed to date reveal an unusual extreme sensitivity of the ground state of the system to the locations of the carbon atoms of C₆₀; random shifts in the C atom positions as small as 0.0001 nm from the I_h symmetry of the ground state cause the Li atom wavefunction to localize in various potential minima. Future work will include examination of tunneling between these potential wells to characterize the localization. A refined potential energy surface has just become available from Larry Harding and will be used to refine the calculations, and possible analogies with Anderson localization in a solid will be explored.

Project 2: Infrared multi-photon induced isomerization and dissociation of XCN (X=F, Cl, Br) in liquid Ar

This study was undertaken to determine if the successful infrared multi-photon induced isomerization of HCN to CNH in liquid Ar is generic in character or specific to the HCN system. The scheme is based on the notion that collisions destroy phase coherence rapidly on the time scale of the induced isomerization so that a classical mechanical analysis can be used to describe the reaction and its control. However, it is necessary to include all degrees of freedom of the reactant molecule and the solvent.

Classical molecular dynamics simulations of the field induced isomerization and dissociation of XCN (X=F, Cl, Br) in liquid were carried out on quantum mechanically computed molecular potential energy and molecular dipole surfaces. The interaction between XCN and the Ar host fluid was modeled with Lennard-Jones interactions between the individual X, C, N atoms and the Argon atoms. To compare the results with those obtained in the study of the HCN isomerization, similar field strengths, pulse duration, and liquid states were chosen. In each case and the frequency of the driving field was slightly blue-detuned from the bending frequency of the XCN molecule.

The results obtained show that the control scheme introduced by Gong, Ma and Rice for HCN isomerization is not generally applicable to the XCN systems. The difference in behavior between HCN and XCN field driven isomerization is traceable to the different dissipation rates for the several molecules in liquid Ar; the rate of dissipation of energy from a vibrationally excited XCN molecules is generally higher for XCN than for CNX, but the reverse is the case for HCN and CNH. The consequence of this difference is that when X = F, Cl or Br the reactant is trapped instead of the isomerization product. Other factors that contribute to the breakdown of the control scheme are:

- (1) More rapid intramolecular energy transfer in XCN (X = F, Cl, Br) than in HCN that is implied by the lower order nonlinear bending-stretching resonance spectrum of the former.
- (2) The absence of monodromy in the mechanics of HCN and the possible presence of monodromy in XCN (X = F, Cl, Br), implied by the shapes of the potential surfaces of these molecules. The existence of monodromy implies there are no global action variables and that the motion is essentially chaotic.
- (3) The masses of the halogen atoms are large compared to that of CN, so that the picture of "X rotating around CN", that is essential to the proposed mechanism for control of the isomerization of HCN, is not valid.

A paper reporting the results of this research is in the final stage of preparation.