

HIRSCHFELDER LECTURES IN THEORETICAL CHEMISTRY 2010-11

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Homochirality: Did Life Grind to a Start?

Monday, October 4 2:00 p.m. Room 1315 Chemistry

Recent experiments have uncovered an unexpected effect: a racemic slurry of crystallites, upon stirring or grinding with glass beads, can be converted essentially completely to a single enantiomer. We propose an underlying mechanism that involves an oriented aggregation of crystallites of the same chirality. A consequence of this picture is that, during the purification process, there must be an inverse relationship between the concentrations of molecules in solution and their populations in the solid phase; i.e., if left-handed crystallites are dominant, then in solution the concentration of right-handed molecules must exceed that of left-handed molecules. This counterintuitive prediction has just been verified in the laboratory for crystals of a derivative of the amino acid phenylglycine.

Mixed Quantum-Classical Dynamics

Tuesday, October 5 11:00 a.m. Room 1315 Chemistry

Molecular Dynamics (MD) simulation, the numerical integration of the classical mechanical equations of motion for interacting atoms, while very powerful, is based on two fundamental approximations, the Born-Oppenheimer Approximation and classical mechanical nuclear motion. These limitations can be overcome, in principle, by employing a fully quantum mechanical treatment of both the electronic and nuclear dynamics. This is impractical, of course, except for very simple cases. More generally, it is both desirable and necessary to retain a classical mechanical MD framework, augmented by only the most essential quantum effects; i.e., to employ a mixed quantum-classical dynamics (MQCD). This talk will develop the underlying assumptions of two general MQCD methods and analyze their strengths and weaknesses, focusing on their applicability to photochemical processes that involve multiple potential energy surfaces.

Dynamics at Metal Surfaces: The Role of Electronic Excitations

Wednesday, October 6 2:00 p.m. Room 1315 Chemistry

For chemical reactions at metal surfaces, the Born-Oppenheimer approximation is rarely valid; nonadiabatic behavior is the rule rather than the exception. Electron-hole pair transitions, charge transfer and hot-electron-induced motion can be dominant pathways for energy flow and can drastically alter reaction pathways. Recent experiments have demonstrated that molecular vibrational energy and reaction exothermicity can produce highly excited electrons, even resulting in electron emission. This talk will present progress toward a unified picture of nonadiabatic dynamics at metal surfaces, with application to multi-quantum vibrational-to-electronic energy transfer in the scattering of nitric oxide from a gold surface.