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This theoretical proposal sought to characterize processes in systems in extreme disequilibrium with special reference to the role of electronically non adiabatic processes. The two major accomplishments are (i) The demonstration that real chemistry (i.e., bond formation, rearrangements etc). is possible under extreme conditions of temperature and pressure. In particular, it was proposed how air can be made to "burn". Private communication (December 1996) from two laboratories are that this process has now been seen. (ii) A new physically motivated quantum mechanical computationalscheme for treating multi electronic state dynamics has been developed and implemented. For systems of one or two nuclear degrees of freedom, the method has been validated against a numerical integration of the time dependent Shroedinger equation on a grid. The method allows for effective interface with quantum chemical methodology so that one can simultaneously solve for the electronic structure and the nuclear motion. This has already been demonstrated for several systems. Work is continuing on both aspects.

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PRINCIPAL INVESTIGATORS:	James L. Kinsey Raphael D. Levine Department of Chemistry William Marsh Rice University Houston, TX
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SENIOR RESEARCH PERSONNEL:	Todd J. Martinez
JUNIOR RESEARCH PERSONNEL:	Michal Ben Nun Tamar Raz

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This theoretical proposal sought to characterize processes in systems in extreme disequilibrium with special reference to the role of electronically non adiabatic processes. The two major accomplishments are (i) The demonstration that real chemistry (i.e., bond formation, rearrangements etc.) is possible under extreme conditions of temperature and pressure. In particular, it was proposed how air can be made to 'burn'. Private communication (December 1996) from two laboratories are that this process has now been seen. (ii) A new physically motivated quantum mechanical computational scheme for treating multi electronic state dynamics has been developed and implemented. For systems of one or two nuclear degrees of freedom, the method

has been validated against a numerical integration of the time dependent Shroedinger equation on a grid. The method allows for effective interface with quantum chemical methodology so that one can simultaneously solve for the electronic structure and the nuclear motion. This has already been demonstrated for several systems. Work is continuing on both aspects

Chemistry Under Extreme Conditions.

When a large supersonic cluster impacts a surface, the initially directed kinetic energy is randomized. For a very brief period (of the order of 100 fs) the cluster is very compressed and extremely hot, so hot that for impact velocities > 10 km/s electrons boil off. Our question was whether any chemistry can occur under such exceptional conditions. We have theoretically studied a number of reactions with special emphasis on reactions which need time, either because there is bond formation between constituents of the cluster or because activation by the cluster must precede reaction. Having demonstrated the theoretical feasibility, we turned to a number of diagnostic questions. These included:

- The development of a kinematic model which accounts for the conditions that we identify as conducive for reaction.
- Quantitative understanding of the role of the cluster; the mass of its constituents, the number of constituents (i.e., the size of the cluster), the intermolecular forces in the cluster, etc.
- Developing a physical understanding for the extremely rapid and facile thermalization of the impact energy. The lack of order in the cluster was shown to be a major factor.
- Examining the robustness of our conclusions in view of the large uncertainties that prevail regarding the intermolecular forces. This was addressed by developing and implementing an information theoretic methodology which does not require the intermolecular forces as input. This method not only validated the conclusions from the molecular dynamics simulations but also predicted a number of new phenomena.
- The onset of shattering. One unexpected prediction of the information theoretic approach was a new 'phase transition' made possible by the rapid heating which can be achieved by cluster impact. Specifically, it was predicted that at low velocities of impact the cluster recoils intact from the surface. Cooling of the cluster by evaporation begins much later. (Molecular dynamics simulation showed that this begins on the dozens of ps time scale). Beyond a threshold velocity the cluster very rapidly shatters into a very large number of small fragments. The phenomena itself and many details have by now been verified by experiment.

In particular, all these techniques were applied to the cluster induced $N_2 + O_2$ reaction. We are very pleased to report that two laboratories have just informed us that they have seen this reaction and are now working on its quantitative characterization.

Dynamics on multi electronic states.

A classically motivated, fully quantum mechanical method for the description and computation of dynamics involving several electronic states has been developed and implemented. The specification of method is governed by the need to have a clear physical interpretation of the results, by the recognition that the motion on a given electronic state can often (but not always) be well approximated by classical mechanics and by the need for a computational procedure that is simple enough that polyatomic systems can be handled. These desiderata are realized by the spawning technique which is discussed below. The method is derived from a variational principle and so can yield quantum mechanically numerically converged results. The parameter that governs the numerical accuracy of the method has a clear physical significance. One more feature of the method is that it allows for smooth interface with the methodologies of quantum chemistry so that the electronic structure problem can be solved simultaneously with the time propagation of the nuclear dynamics. In our studies it is found that the quantum chemistry part takes >95% of the computational effort.

The derivation of the method shows that in principle it scales with the number of nuclear degrees of freedom just like the method of classical trajectories. In other words, large systems should be amenable to the proposed approach. Not everybody agreed, but we have by now (December 1996) gone up to systems of nine degrees of freedom and so far, the expected scaling holds.

The key to the method is the concept of 'spawning'. This means that nuclear basis states are not used (i.e., they are 'virtual') until they are needed by the Schroedinger time propagation. The other point of these virtual states is that they are not standing still. Rather, they evolve, centered about classical trajectories on a given electronic states. What this means is that the method has only to handle deviations from classical behavior rather than the classical behavior itself. These deviations are of two kinds. (i) The inter electronic state transitions which are the issue of interest and (ii) The intra electronic state corrections to classical mechanics. The latter are expected to be small and a computationally much faster version of the method, which neglects the intrastate corrections, has been provided. We refer to the published literature for more details.