

The group's main interest is in understanding the mechanisms of chemical reactions. This pursuit involves the development of methods for constructing potential energy surfaces for chemical reactions and the reaction dynamics on these surfaces.

Ab initio quantum chemistry provides accurate information about the energetics of chemical reactions. The potential energy surfaces (PESs) are constructed as an interpolation of this *ab initio* data evaluated at a relatively small number of relevant molecular geometries. Significant progress has now been achieved for moderate sized molecules, so that many different chemical reactions have been investigated. Most of these reactions involve competing mechanisms or reaction pathways and could not be treated using simpler approximate methods. The end result of this work should be a much clearer understanding of the mechanisms of reactions at the molecular level. We are currently pursuing a number of objectives, including improved accuracy of PES for larger molecular systems, highly accurate PES for quantum reaction dynamics studies of four and five atom systems, many-body expansions for the weak interactions involved in collisional energy transfer and molecular clusters, and coupled surfaces for nonadiabatic reactions.

The group's work has been enhanced through collaborations with overseas scientists including Dr Mark Brouard at the University of Oxford and the dynamics group of Professor Aoiz and Dr Jesus F. Castillo, Universidad Complutense de Madrid, Associate Professor Dong Hui Zhang at the National University of Singapore, Professor David Yarkony, Johns Hopkins University (nonadiabatic dynamics), and Dr C. Crespos and Professor G.-J. Kroes, University of Leiden (reaction at surfaces).



Reaction Dynamics for $\text{H}+\text{H}_2\text{O} \leftrightarrow \text{OH}+\text{H}_2$ and $\text{H}+\text{D}_2\text{O} \leftrightarrow \text{HOD}+\text{D}$

Recent experiments by Mark Brouard at Oxford have extended the available data on these seminal reactions to high translation energy in the reactants. We have completed a combined classical and quantum study of the reaction dynamics. (with M. Brouard [U. Oxford], J. Castillo [U. Complutense de Madrid], D.H. Zhang [National U. Singapore])

Reaction Dynamics for $\text{H}+\text{N}_2\text{O} \leftrightarrow \text{OH}+\text{N}_2$

We have completed a preliminary study of this reaction using classical dynamics on a PES constructed with density functional theory. The theoretical dynamics confirm the presence of two competing reaction mechanisms which was inferred from experimental observations by the Brouard group. A more accurate PES, evaluated with high level *ab initio* data, has also recently been completed. (with J. Castillo and colleagues [U. Complutense de Madrid])

Hydrogen Abstraction in $\text{H} + \text{CH}_4$

The abstraction reactions, $\text{H} + \text{RH} \rightarrow \text{H}_2 + \text{R}^*$, have been observed to yield an unusual distribution of rotation–vibration states in the H_2 product. To investigate the mechanism of this class of important combustion reactions, we have constructed accurate PESs for the simplest example, $\text{H} + \text{CH}_4$. To facilitate very high dimensional quantum scattering

calculations of this reaction, new algorithms for evaluating the PES at billions of molecular configurations has been developed. *(with D.H. Zhang [National U. Singapore])*

Nonadiabatic Chemical Reactions

Many reactions, particularly in combustion and atmospheric chemistry, take place in more than one electronic state. The PES for these electronic states can intersect, and new methods are being developed to describe all the energy surfaces involved and their “interactions”. Significant progress on code development for this very difficult and important project has been accomplished. Preliminary calculations on a model system have verified that it is possible to construct, by interpolation, the potential energy matrix which governs a nonadiabatic reaction. *(with C. Evenhuis, and D.H. Zhang [National U. Singapore], D. Yarkony [Johns Hopkins U., USA])*

Deuterium Exchange

Deuterium takes an active part in interstellar chemistry, leading to an enhancement of the abundances of deuterated molecules. In interstellar clouds, such processes are known as deuterium fractionation. The most relevant of them are thought to be gas phase ion-molecule reactions; specifically the reaction $\text{H}_3^+ + \text{HD} \rightarrow \text{HD}^+ + \text{H}_2$. An accurate molecular potential energy surface for this system has been evaluated, so that accurate theoretical rate coefficients can be evaluated for this reaction and isotopic analogues. *(with G. Moyano)*

<http://rsc.anu.edu.au/research/collins.php>