LOW ENERGY ION-MOLECULE INTERACTIONS

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Final Project Report

for Grant DE-FG02-88ER13849 and predecessor grants

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Project Summary

This project has been dedicated to elucidating the dynamics of elementary ion-molecule reactions at collision energies between 0.1 and 5 eV under single collision conditions in crossed beams. The long-standing objective of this project has been to probe the potential energy surfaces for elementary gas phase reactions. The studies we have conducted throughout a sustained period of Department of Energy support have been directed at testing theory in benchmark systems, with the long term goal of extracting useful dynamical insights that can be transferred to the complex environment of hydrocarbon combustion, where energy disposal in polyatomic systems plays a critical role.

To support these objectives, crossed ion beam-neutral beam reactive scattering experiments have been being performed with the goal of using product quantum state distributions, energy disposal measurements, and state-resolved angular distributions to extract dynamical information on collision mechanics and features of the potential energy surfaces mediating ion-molecule reactions. These studies allow us to test and validate dynamical models describing chemical reactivity. Measurements of energy and angular distributions of the reaction products with vibrational state resolution provide the key data for these studies. The studies have been designed to foster interactions between theory and experiment, in which benchmark systems are probed experimentally with the most sophisticated techniques available and which

are also amenable to computations of structural and dynamical features at a high level. In addition to studying these benchmark systems, we have also studied more complex systems in which one can still apply the underlying "small system" concepts, gaining important insights into reactivity by probing critical subspaces of the full potential surface that governs the dynamics.

The bulk of the chemical reactions that occur in hydrocarbon combustion are between uncharged species. Ionic systems have generally not been regarded as primary players in gas phase combustion chemistry, although ions have been postulated at various times to be implicated in soot formation, and the role of ion-molecule reactions in creating flame ions is well-established. Because of the presence of a significantly longer range force in ionic systems, these species provide special opportunities for understanding reaction dynamics and extending concepts relevant to energy consumption and utilization. In isolated binary collisions, ionic systems can be probed over a much wider range of translational energies than is typically the case for neutrals, because the translational energy of the colliding reagents can be varied so readily. The concepts of chemical reactivity that emerge from these studies are not restricted to ionic systems alone. Many neutral systems, as well as ionic systems, have multiple minima surfaces, as interconverting reaction intermediates are separated by small barriers, and these features can control reaction rates and energy disposal. Finally, ion chemistry in hydrocarbon flames occurs essentially independently of neutral chemistry. Since proton and hydrogen atom transfer (in addition to charge transfer) are major ion reaction channels, evidence for the role of transient *neutral* intermediates M can be assessed through the formation of ion of the form M^+ and MH^+ .

Summary of Key Results

The work we have accomplished during the tenure of this research breaks down into the following areas:

- Proton transfer reactions: in H_2^+ (Publications 1-6, 8), we examined the competitive roles of vibration and translation in effecting proton transfer reactions. Proton transfer reactions of the flame ions HCO^+ and H_3O^+ were also studied in detail (Publications 9, 10, 13-15).
- Reactions of carbon-containing cations were studied to understand the dynamics of C-C bond formation, a process important in soot formation (Publications 16, 17, 19-22, 25, 31-33)
- Reactive scattering from double minimum potentials was probed to elucidate the role of entropic bottlenecks in controlling rates and product state distributions in ion-molecule reactions (Publications 18, 23, 27, 28)
- More recent work has focused attention on hydrogen atom transfer reactions the oxygen atomic anion, O^- , undergoes with small molecules in the collision energy regime from 0.1 to 5 eV. Molecular collision partners studied to date include HF, H_2O , NH_3 , and CH_4 (Publications 34-38, 44, 47)
- The $\text{O}^- + \text{D}_2$ system has been particularly rich, with vibrationally-resolved product differential cross sections measured over the collision energy range from 0.25 eV to 1.80 eV. Manipulation of the expansion conditions for production of D_2 via supersonic beams has allowed the D_2 reagent rotational temperature to be varied from 40 K to 400 K. Owing to the strong role that non-collinear collisions play in controlling the branching ratio between electron detachment and particle transfer in the $\text{O}^- + \text{D}_2$ system, the rotational temperature

has been shown to modify product angular distributions significantly. (Publications 39, 42, 43, 45, 46)

- Our most recent studies have focused on reactions of OH^+ , H_2O^+ , and H_3O^+ and isotopomers with NH_3 , C_2H_4 , and C_3H_6 . Studies of charge transfer in these systems have revealed both long range electron transfer controlled by Franck-Condon factors and energy resonance, as well as electron transfer with isotope scrambling, occurring in much shorter range collision processes. (Publications 51-55)
- As one of a vanishingly small number of practitioners who have used crossed beam methods to probe such reactions, we have been asked to contribute a number of reviews, encyclopedia chapters, and perspectives to the literature. (Publications 29, 30, 37, 40,41, 48-50)

Ph.D. Students supported by this grant with current places of employment listed:

Robert M. Bilotta, 1980. Mitre Corporation

Frederick N. Preuninger, 1981. AT&T Technologies.

Robert A. Curtis, 1984. Eastman Kodak Company.

Joseph E. Moryl, 1985. Unknown.

William R. Creasy, 1985. EAI Corporation.

David M. Sonnenfroh, 1985. Physical Sciences Inc.

Meihua Shen, 1990. Applied Materials.

David F. Varley, 1993. Coherent Lasers.

Michael A. Carpenter, 1996. School of Nanotechnology, SUNY Albany.

David C. Sperry, 1999. Pfizer Research Labs

Susan Troutman Lee, 1999. Thermo-Finnigan Corporation

Elizabeth Richards O'Grady, 2003. Agilent Corporation

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