

Final Report for AOARD Grant FA2386-10-1-4034 (or AOARD 104034)
“Unraveling the Nature of Chemical Reactivity of Complex Systems III”

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Abstract:

The most exciting result is the one published in *Science* this February. In that work (publication list # 6), strong effects of a pre-aligned CH stretching bond of methane on the $\text{Cl} + \text{CHD}_3(\nu_1=1)$ reaction are demonstrated in a crossed-beam imaging experiment. In comparison with our previous findings in the two analogous reactions of unpolarized $\text{CHD}_3(\nu_1=1)$ with F and $\text{O}(^3\text{P})$ atoms, a conceptual framework is proposed. Within the framework, two ways of steric control of a chemical reactions can be envisioned: For a reaction with weak, long-range anisotropic interactions in the entrance channel, such as $\text{Cl} + \text{CHD}_3(\nu_1=1)$, one can actively control the reaction outcome by pre-aligning the reactant; otherwise, the reactive outcome will be governed by the strong anisotropic interactions, as in the case of F or $\text{O}(^3\text{P}) + \text{CHD}_3(\nu_1=1)$ reaction, i.e., a “passive” control. In other words, what governs the reaction outcome is the tug-of-war between the externally controllable factors such as the pre-alignment (or orientation) of the reactant and the anisotropic interactions of the colliding reactants, which could re-orient (or scramble) the pre-aligned reactants during the course of the reaction.

Introduction:

The aim of this project is to understand and ultimately to control the reactive outcome of complex systems by vibrational excitations of a reactant. Reactions of methane with F, Cl, and $\text{O}(^3\text{P})$ are of prototypical H-atom abstraction mechanism, yet with vastly different energetics and barrier properties. Hence, their contrasting behaviors upon vibrational and translational excitations can serve as benchmark for deeper insights into polyatomic reaction dynamics. Exploiting the product pair-correlation measurement enables us to elucidate the energy flow in the transition-state region, and to shed new light onto the mode- and bond-selective chemistry.

Experiment:

The crossed-beam experiment was performed using the rotating source machine at IAMS, which is equipped with a uniquely designed ion-velocity-map imaging detector capable of measuring the product pair correlation. The ultrafast femtosecond laser facility is housed in a newly constructed clean room. The installation and tests of the entire laser system is now complete, and some preliminary diagnostic experiments have just begun.

Results and Discussion:

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14. ABSTRACT This is the final report of a project that attempts to understand and ultimately control the reactive outcome of complex systems. It was determined that what governs the reaction outcome is the tug-of-war between the externally controllable factors such as the pre-alignment (or orientation) of the reactant and the anisotropic interactions of the colliding reactants, which could re-orient (or scramble) the pre-aligned reactants during the course of the reaction.					
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In a paper published in *Science* **325**, 303 (2009), we reported a surprising result that CH stretching excitation in the early barrier $F + CHD_3$ reaction actually inhibits CH bond cleavage. In that report we conjectured the unexpected result arising from the anisotropic interaction between the F-atom and the stretch-excited, unpolarized $CHD_3(v_1=1)$, which effectively acts as a “negative” lens thereby deflecting the trajectories away from the transition-state that serves the bottleneck to reaction. Our conjecture was later confirmed by a theoretical quasi-classical trajectory study by Bowman and co-workers at Emory University (*J. Am. Chem. Soc.* **131**, 17534 (2009)).

A year later, in a related study on the central-barrier reaction of $O(^3P) + CHD_3(v_1=1)$ we discovered an exactly opposite steric-effect: CH stretching excitation in $O(^3P) +$ unpolarized- $CHD_3(v_1=1)$ significantly enhances the chemical reactivity by enlarging the cone of acceptance to reaction. We ascribed it being, again, the result of anisotropic interactions as the two reactants approach each other. But, now the interaction potential acts as a “positive” lens, thereby focusing the trajectories toward the transition state. We further asserted the origin of the above two counter examples being the location of the barriers. This work (publication list # 2) was published in the first issue of *Chemical Science* **1**, 126 (2010), a new flagship general chemistry journal of Royal Society of Chemistry, UK.

Following the line of reasoning for reactions with an early barrier, to a central barrier, and further to a late barrier, we then postulated that the late-barrier reaction might exhibit comparably weak anisotropic interaction potential in the entrance channel, thus could present a case for external control of stereochemistry. With this mind, we decided to revisit the $Cl + CHD_3(v_1=1)$ reaction that we reported in *Science* **316**, 1723 (2007) several years ago. This time our goal is to explore the “active” steric control of reactivity by pre-aligning the stretch-excited $CHD_3(v_1=1)$ reactants, rather than an unpolarized reactant in our previous investigations. The result of this exploration leads to another exciting breakthrough as evidenced by the newest addition, *Science* **331**, 900 (2011). More significantly, a conceptual framework is established from this series of studies, which can be related to the reaction barrier location such that the “rule” derived from it may very well be more general.

List of Publications:

SCI publications

1. *Deciphering the Nature of the Reactive Resonance in $F + CHD_3$: Correlated Differential Cross Sections of the Two Isotopic Channels*
J. Zhou, J. J. Lin, and K. Liu, *Mol. Phys.* (**R. N. Zare Issue**) **108**, 957-968 (2010).
2. *Enlarging the Reactive Cone of Acceptance by Exciting the C-H Bond in the $O(^3P) + CHD_3$ Reaction*
F. Wang and K. Liu, *Chem. Sci.* **1**, 126-133 (2010).
3. *Experimental and Theoretical Investigations of the Effects of the Reactant Bending Excitations in the $F + CHD_3$ Reaction (Commun.)*
G. Czako, Q. Shuai, K. Liu, and J. M. Bowman, *J. Chem. Phys.* **133**, 131101 (2010)
4. *Imaging the Nature of the Mode-Specific Chemistry in the Reaction of Cl Atom with Antisymmetric Stretch-Excited CH_4*
H. Kawamata and K. Liu, *J. Chem. Phys.* **133**, 124304 (2010).
5. *Reactive Scattering: Reactions in Three Dimensions*
P. Casavecchia, K. Liu, and X. Yang, in "Tutorials in Molecular Reaction Dynamics ", Chapter 6, pp 167-213, Edited by M. Brouard and C. Vallance (Royal Soc. Chem. 2010).
6. *Steric Control of the Reaction of CH Stretch-Excited CHD_3 with Chlorine Atom*
F. Wang, J.-S. Lin, and K. Liu, *Science* **331**, 900-903 (2011).

Invited talks at Conferences (* denoting plenary lectures)

- *1. *"The 14th East Asian Workshop on Chemical Reactions (EAWCR-14)"*, Nara, Japan, May 10-14, 2010.
- 2. *"Air Force Office of Scientific Research (AFOSR) Molecular Dynamics & Theoretical Chemistry Contractor's Meeting"*, Chantilly VA, May 24-26, 2010. (poster)
- *3. *"International Symposium on Advancing the Chemical Sciences II (ISACS-II)"*, Budapest, Hungary, July 14-16, 2010.
- *4. *"The 18th European Conference on Molecular Dynamics, MOLEC XVIII"*, Curia, Portugal, Sept. 5-10, 2010.
- 5. *"Frontiers in State-to-State Dynamics"*, in PACIFICHEM 2010, Honolulu, Hawaii, USA, Dec. 15-20, 2010.
- *6. *"Workshop on Cold and Controlled Collisions"*, Ringberg Castle, Tegernsee, Germany, Feb. 2-5, 2011.
- *7. *"Cross-Strait Workshop on Chemical Dynamics"*, Hsinchu, Taiwan, Feb. 18-21, 2011.