The aim of this project is to understand and ultimately to stereo-control the reactive outcome of complex systems by vibrational excitations of reactants. The most exciting result during this period is the paper published in Nature Chemistry 4, 636-641 (2012). In that work, we reported the complete three-dimensional characterization of the steric of a benchmark polyatomic reaction by measuring the dependence of the product state-resolved angular distributions on the spatial alignment of the reactive bond in a crossed molecular beam experiment. This is for the first time that a true three-dimensional view of the steric effects has been realized experimentally for any chemical reaction in the half century history of chemical dynamics. The results prove the existence of two distinct microscopic reaction mechanisms in the reaction of Cl + CHD3(v1=1) &#8594; HCl(v=0, 1) + CD3(00). Detailed analysis further reveals the origin of the stereodynamics in the HCl(v=0) + CD3(00) product channel can be captured by a textbook line-of-centres model. In contrast, a time-delay pathway, most likely mediated by reactive resonances, appears to be operative in forming the excited HCl(v=1) + CD3(00) product pair. The work received immediate attention upon publication, as highlighted by Science Editors' Choice under the title ?Angle of Attack?, in Science 337, 779 (2012).
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Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18
Final Report for AOARD Grant FA2386-12-1-4020
“Steric Control of Complex Chemical Reactions - II”

Date: Dec. 06, 2012

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Period of Performance: 01/12/2011 – 30/11/2012

Abstract:
The most exciting result during this period is the paper published in Nature Chemistry 4, 636-641 (2012). In that work, we reported the complete three-dimensional characterization of the sterics of a benchmark polyatomic reaction by measuring the dependence of the product state-resolved angular distributions on the spatial alignment of the reactive bond in a crossed molecular beam experiment. This is for the first time that a true three-dimensional view of the steric effects has been realized experimentally for any chemical reaction in the half century history of chemical dynamics. The results prove the existence of two distinct microscopic reaction mechanisms in the reaction of Cl + CHD\(_3\)(\(v_1=1\)) → HCl(\(v=0, 1\)) + CD\(_3\)(0\(0\)). Detailed analysis further reveals the origin of the stereodynamics in the HCl(\(v=0\)) + CD\(_3\)(0\(0\)) product channel can be captured by a textbook line-of-centres model. In contrast, a time-delay pathway, most likely mediated by reactive resonances, appears to be operative in forming the excited HCl(\(v=1\)) + CD\(_3\)(0\(0\)) product pair. The work received immediate attention upon publication, as highlighted by Science Editors’ Choice under the title “Angle of Attack”, in Science 337, 779 (2012).

Introduction:
The aim of this three-year project is to understand and ultimately to stereo-control the reactive outcome of complex systems by vibrational excitations of reactants. Reactions of methane with F, Cl, and O(\(^3\)P) are of prototypical H-atom abstraction mechanism, yet with vastly different energetic and barrier properties. Hence, their contrasting behaviors upon vibrational and translational excitations can serve as benchmark for gaining deeper insights into polyatomic reaction dynamics. Exploiting the product pair-correlation measurement enables us to elucidate the energy flow in the transition-state region of a chemical reaction, and to shed new light onto the mode- and bond-selective chemistry. By pre-aligning the reactant adds an entire new dimension in the field of chemical kinetics and dynamics.

Experiment:
The crossed-beam experiment was performed using the rotating source machine at IAMS, which is equipped with a uniquely designed time-sliced velocity-map imaging detector capable of measuring the product pair correlation. The combination of the capabilities of freely rotating the two molecular beams at will and the time-sliced imaging detection enables us to uniquely perform the stereodynamics study in full, as demonstrated in our recent Nature Chemistry paper.

The ultrafast femtosecond laser facility is housed in a newly constructed clean room. The installation and tests of the entire laser system is now completed, and some preliminary diagnostic experiments for solvation dynamics are in progress.

Results and Discussion:
The publications and the conference lectures listed below describe some of the works under the
support of this AFOSR/AOARD grant. In addition, I had the honour to receive the Switzerland CUSO Lecturer Award in April 2012. Needless to say, it will not be possible without the continuing supports from AFOSR/AOARD since 2008.

We now extend the stereodynamics investigation along two complementary directions. First, we will continue exploring the experiment with a laser pre-aligned CH₄(v₃=1) reagent. The reaction of Cl + CH₄ is of great importance in atmosphere chemistry as being a primary competing process to the ozone-hole catalytic reaction of Cl + O₃ as well as a regulating process of the potent and the second most important greenhouse gas CH₄ in the earth atmosphere. Unlike the CHD₃(v₁=1) reaction where the IR laser polarization aligns the unique C-H bond, all four C-H bonds will be excited in the antisymmetric-stretching mode of CH₄(v₃=1). Preliminary test results are extremely exciting, which shows an even stronger steric effect than the Cl + CHD₃ (v₁=1) reaction. This is quite intriguing and counter-intuitive in that apparently the four stretching-excited C-H bonds are not completely equivalent in this chemical reaction! We would like to gain deeper insights into this intriguing phenomenon. The other direction is to investigate the reactivity effects by initial rotational state selection. We believe the information thus obtained will complement the above alignment measurement. Together, they may shape up our thinking and help us to formulate a conceptual framework for polyatomic reactivity in general.

List of Publications:

SCI publications

1. "Quantum Dynamical Resonance in Chemical Reactions: From A + BC to Polyatomic Systems”
2. “Translational Energy Dependence of the Cl + CH₄(v₃=0,1) Reactions: A Joint Crossed-Beam and Quasiclassical Trajectory Study”
3. "Imaging the Effects of the Antisymmetric Stretch Excitation of CH₄ in the Reaction with F Atom”
5. "Revealing the Stereo-Specific Chemistry in the Reaction of Cl with Aligned CHD₃(v₁=1)”

Invited talks at Conferences (* denoting keynote or plenary lecture)