Final scientific report: State-to-State Molecular Reactions in the Ultracold Regime

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Executive Summary

We have achieved the proposed goal to experimentally probe the AB + CD and AB + C types of reactions with state-to-state resolution, which we also compared to advanced theoretical calculations to help elucidate the role of quantum mechanics in the processes of bond breakage and formation. Our approach uses reactants that are prepared at ultracold temperatures ($< 1\,\mu K$) such that the quantum effects of translational motion are an important factor. Specific example reactions, including the potassium-rubidium metathesis reaction KRb + KRb $\rightarrow$ K_2 + Rb_2 as well as the atom exchange reaction Rb + KRb $\rightarrow$ Rb_2 + K, are chosen because the technology of quantum internal and motional state control of these types of molecules is particularly advanced. The results for the entire funding period are fruitful. For the majority of this grant, we have constructed a one-of-the-kind quantum degenerate gas apparatus that integrates ion detection and velocity map imaging capabilities, allowing us to explore the KRb + KRb $\rightarrow$ K_2 + Rb_2 bimolecular reaction in detail. Specifically, we first verified such a reaction indeed proceed at ultracold temperatures by direct detection of reaction products. We then mapped out the *complete* product state distribution, which was compared to a state-counting model based on statistical theory. Our results show an overall agreement with the statistical state counting model, but also reveal several deviating state-pairs. An exact quantum calculation for molecule-molecule collisions, that is needed to understand these deviations, is however beyond the current state-of-the-art. Beside scrutinizing the reaction products, we also directly observe the reaction intermediate complex, which was quite a surprise to us. The intermediate complexes are long-lived and can interact with the inferred light that we use to trap the ultracold gas. After molecule-molecule collisions, we then explored the more theoretically tractable Rb + KRb reaction, which is endothermic. Surprisingly, we observed an exceedingly long-lived KRb_2^* collisional complexes, with our experimentally measured complex lifetime deviating from conventional theoretical calculations by five orders of magnitude. This discrepancy has motivated many explorations of possible underlying causes, though no model yet captures this phenomenon completely. In the final year and the work that continues today, we extend upon these atom-molecule collision experiments to explore the origin of the long-lived KRb_2^* complex lifetime and develop means to control the outcome of the reaction complex. The 5-year funded work advanced our understanding of chemical reactions at the lowest possible temperatures and at the same time opened up many new questions that are beyond our initial imaginations.

Report Narrative

The beginnings of ultracold chemistry are intimately tied to the production of ultracold diatomic alkali (bialkali) molecules – the first molecules to be prepared under these conditions.[1] While such bialkali molecules are unconventional chemical species, their atomic alkali precursors are particularly amenable to laser cooling, and they can be readily produced with exquisite control - from their rovibronic level down to their nuclear hyperfine state.[2] As such, they represent an ideal model to explore chemistry with complete control of the internal states of the reactant. It should then be unsurprising that the first hints of cold chemistry were realized in early work using KRb in 2010, the first molecule to be prepared at these temperatures, though this could only be inferred through the observation of molecule loss which was attributed to chemical reactions.[3,4]

In the years since this work, my lab has developed an experimental apparatus that is capable not only of producing KRb species at temperatures near 500 nK but also detecting their intermediates and reaction products with state-to-state resolution using ion imaging.[5] Such capabilities are unprecedented in the ultracold community, allowing for the exploration of chemistry at these temperatures for the first time and answering many open questions. The work supported by this funding is described below.

Observing and steering sub-micro-Kelvin chemical reaction in slow-motion:
At first glance, studying reactions at ultra-low temperatures may seem counter-intuitive. However, this represents a previously unexplored regime to understand the role of quantum mechanics in reactions. My group made surprising discoveries of fundamental aspects of chemical reactions at such "ultracold" temperatures. First, we directly observed a chemical reaction ($2KRb \rightarrow K_2 + Rb_2$) at 500 nK,[6] which is among the lowest temperature of any reaction that has been recorded. We saw that such an "ultracold" reaction proceeds through a long-lived (several orders of magnitude longer than typical) intermediate, K_2Rb_2*. This came about because by preparing the reactants in the lowest ro-vibrational quantum state at 500 nK in a small exothermicity (10 cm^{-1}) reaction, we had tightly restricted the number of energetically allowed exit channels, prolonging the intermediate lifetime to several hundred nanosecond for direct observation. Furthermore, we demonstrated that the long-lived nature of the intermediate provides a handle to steer with light the reaction pathway away from its natural course.[7] *This work opens a way to catch a glimpse at this critical stage of chemical transformation.*

Complete characterization of a reaction process involving 4 atoms:
Complementary to making a movie of chemical transformations at the reaction intermediate, we can gain complete characterization of reactions by controlling the reactants and fully map the products with quantum state resolution. While vast theoretical and experimental efforts produced an accurate quantum description of the simplest reaction, the type $AB + C \rightarrow A + BC$ for light atoms,[8] reactions involving 4 atoms, for example of the kind $2KRb \rightarrow K_2 + Rb_2$ that we investigate, are a new frontier that challenges our understanding.[9] We achieved "coincident detection" of K_2 and Rb_2 reaction product pairs from the same event, including their quantum states. This allowed us to fully characterize the entire (57 pairs or channels) reaction product state distribution to probe underlying reaction dynamics. While the complete quantum dynamics calculation is beyond the current state-of-the-art, the existence of the long-lived intermediate is expected to yield a statistical distribution of reaction outcomes where each exit quantum channel is equally likely to be populated. We compared our data to the statistical theory and revealed 7 channels of deviation.[10] *Our work provide a rigorous test of current theoretical models and motivate new theoretical advances. This complete dataset will serve to benchmarking future calculations when available computational power is advanced by many orders of magnitude.*

Manipulating the quantum state of reaction outcomes:
While the molecular rotation and vibration phase space are fully explored by the dynamics of the ultracold reaction process, we found that the the nuclear spin degrees of freedom remains a spectator. We leveraged nuclear spin conservation to manipulate the parity (even or odd) of the reaction product rotations.[11] *Building on this result, a new research direction is underway to detect quantum coherence and entanglement in chemical reactions and utilize reactions as a new mechanism to generate quantum entanglement resources.*

Surprising long-lived atom-molecule intermediate complexes:
Given the rich chemistry displayed at these temperatures, we then sought to explore the more theoretically tractable endothermic KRb + Rb reaction. Though this reaction does not proceed to products, rapid loss of both atomic and molecular species has been observed when co-trapped, suggesting a similar loss mechanism to that of the reactive KRb + KRb case. By modulating the intensity of our trapping light, we observed the formation of a long-lived KRb_2 complex (0.39(6) ms), living for 10^5 times longer than predicted by RRKM theory and remains an open question. *An on-going work exploring possible explanations is underway. This includes making measurements studying spin-rotation changing collisions and comparing to theoretical observations.*

List of Publications

1. Y. Liu, K.-K. Ni. Bimolecular chemistry in the ultracold regime. *Annu. Rev. Phys. Chem.*, 73:73-96, 2022.
2. M. A. Nichols, Y.-X. Liu, L. Zhu, M.-G. Hu, Y. Liu, and K.-K. Ni. Detection of long-lived complexes in ultracold atom-molecule collisions. *Phys. Rev. X*, 12, 011029, 2022.
3. G. Quéméner, M.-G. Hu, Y. Liu, M. A. Nichols, L. Zhu, and K.-K. Ni. Model for nuclear spin product-state distributions of ultracold chemical reactions in magnetic fields. *Phys. Rev. A*, 201, 052817, 2021.
4. Y. Liu, M.-G. Hu, M. A. Nichols, D. Yang, D. Xie, H. Guo, and K.-K. Ni. Precision test of statistical dynamics with state-to-state ultracold chemistry. *Nature*, 593, 379-384, 2021.
5. M.-G. Hu, Y. Liu, M. A. Nichols, L. Zhu, Goulven Quemener, O. Dulieu, and K.-K. Ni. Nuclear spin conservation enables state-to-state control of ultracold molecular reactions. *Nat. Chem*, 13, 435-440, 2021.
6. Y. Liu, M.-G. Hu, M. A. Nichols, D. D. Grimes, T. Karman, H. Gua, and K.-K. Ni. Photo-excitation of long-lived transient intermediates in ultracold reactions. *Nat. Physics*, 16, 1132–1136, 2020.
7. Y. Liu, D. D. Grimes, M.-G. Hu, and K.-K. Ni. Probing Ultracold Chemistry using Ion Spectrometry. *Phys. Chem. Chem. Phys.*, 22, 4861-4874, 2020.
8. M.-G. Hu, Y. Liu, D. D. Grimes, Y.-W. Lin, A. H. Gheorghe, R. Vexiau, N. Bouloufa-Maafa, O. Dulieu, T. Rosenband, and K.-K. Ni. Direct Observation of Bimolecular Reactions of Ultracold KRb Molecules. *Science*, 366. 1111, 2019.

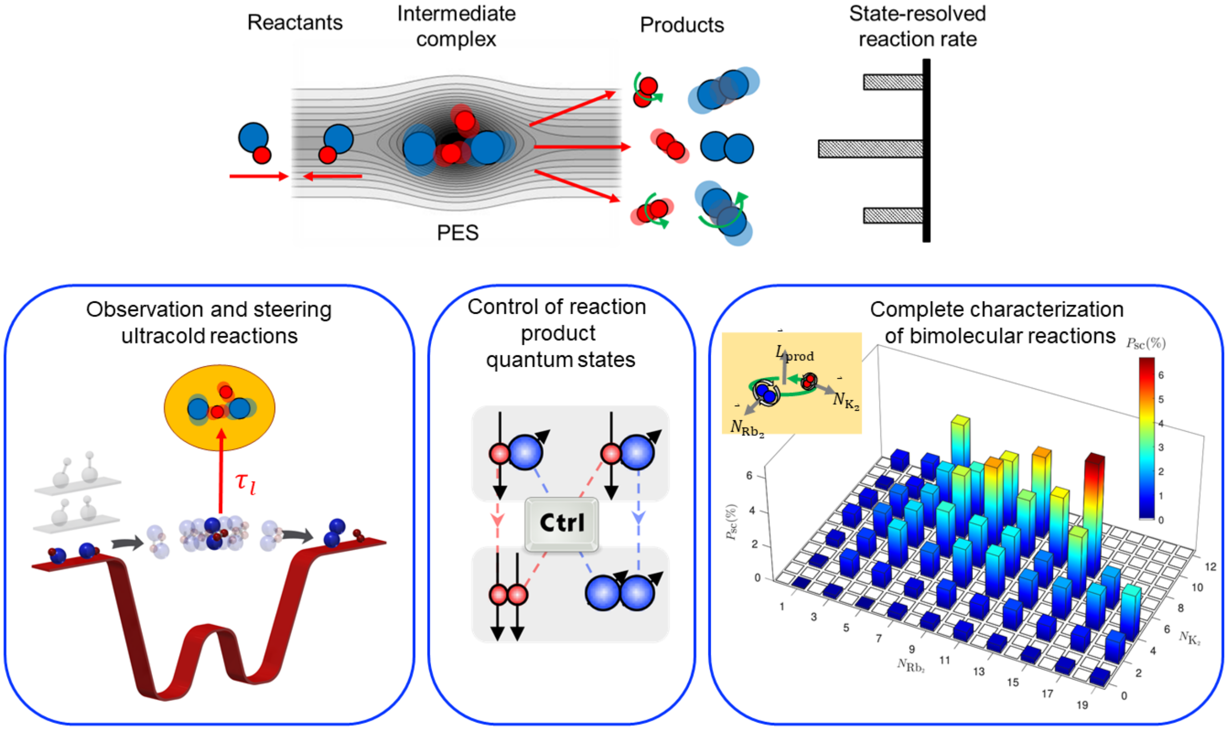

Figure 1: Summary of results from the DOE funding, facilitated by our unique ability to probe the intermediates and products of ultracold chemical reactions. Bottom left: by using ion imaging, we were able to determine the lifetime of the intermediate complex in the KRb + KRb reaction as well as its photoexcitation rate by light used to trap these cold molecules. Bottom middle: by exploiting spin-conservation in this system, we were able to control the distribution of products from this reaction. Bottom right: by mapping the population of all energetically-allowed products formed from this reaction, we were able to determine the state-resolved branching ratio and test of statistical theory, providing a benchmark for quantum dynamics calculations beyond the current state of the art.

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