MPGMC Final Report

The aim of the originally proposed MPGMC project was to develop and carry out time-resolved spectroscopic experiments to link gas-phase and solution-phase chemistry, through a series of experiments designed to explore the effect of solvent on different classes of chemical and photochemical reactions. In the original proposal, we predicted the following 24 month timeline of **activities 1-9**, and are very pleased to report that all the proposed objectives have been addressed:

Months	3	6	9	12	15	18	21	24
1. Building the spectrometer / setting up data acquisition software	■	■						
2. Running test experiments: UV pump/UV-vis probe on thiophenol, UV pump, IR probe on CN reactions		■	■					
3. Photodissociation of phenols and pyrroles in solution/ Photochemistry of biologically relevant molecules			■	■				
4. Reactions of Cl/F/CN atoms with hydrocarbons in various solvents			■	■	■			
5. Ring-opening photochemistry				■	■	■		
6. Radical cyclization					■	■	■	
7. Development of theoretical models of solvent effects on reactions					■	■	■	■
8. Preparing data for publications				■	■	■	■	■
9. Primary supervision of younger researchers				■	■	■	■	■

1,2. Building the spectrometer/Running test experiments: The transient spectroscopy laboratory has been constructed and tested, and now enjoys daily use by the MC Fellow (Dr. Grubb), three graduate students, and three post docs. The lab has also been used by visiting scientists from Kyoto University, the University of Wisconsin, Oxford, and Kiel University.

3. Photochemistry of Biologically Relevant Molecules: The photostability of the DNA base adenine was investigated using transient spectroscopy, and the chemical bonds were found to be stable to much higher energy photons than in the gas phase.[1] An extension of this work to pairs of DNA bases, in collaboration with Kiel University, is currently underway. These studies may help elucidate some of the mechanisms by which biomolecules developed on the prebiotic Earth.

4. Reactions of CN atoms with Hydrocarbons in Various Solvents: An extensive longitudinal study has been performed observing CN reactions with hydrocarbons in many different solvent environments: chloroform, dichloromethane, methanol, acetonitrile, acetone, and tetrahydrofuran. Unique timescales for CN solvation, and subsequent reactions, are observable in each case. This is certainly one of the most comprehensive studies of the effect of solvent environment on the same reaction ever performed, and will be valuable for the development of theoretical models hoping to capture the properties of these common solvents. A manuscript describing this work is currently in preparation.

5. Ring-Opening Chemistry: The photolytic ring-opening dynamics of thiophenone and furanone were observed using transient spectroscopy.[2] Ring-opening is a pathway to which our previous time-of-flight gas phase experiments have been blind, but is easily observable via the transient infrared spectrum. With the aid of *ab initio* calculations, we proposed a mechanism involving internal conversion from the initially excited $n\pi^*$ state to a dark $n\sigma^*$ state and thence the ground state potential energy surface, which results in the observed ring-opening.

6. Radical Cyclization: The formation of oxetane rings via the Paternò−Büchi reaction, commonly used in molecular synthesis, was investigated using transient spectroscopy.[3] Specifically, we investigated the reaction between benzaldehyde and cyclohexene. We were able to identify the bi-radical intermediate structure of this reaction, and measure the relative rates of product oxetane formation and dissociation to reform the reactant molecules. Practically speaking, solvent or functional group modifications which alter these rates would therefore lead to more efficient oxetane synthesis.

7. Development of Theoretical Models of Solvation: Each experiment has contributed in its own way toward the development of theoretical models for solvation. The improved photostability of adenine in the liquid environment demonstrates the effect of the solvent on excited-state potentials **(activity 3)**, and the timescale of structural relaxation for the ring-opened molecules provide a good system for modeling vibrational cooling **(activity 5)**. The CN radicals generated in **activity 4** were observed to give rise to unique spectral features due to a charge transfer transition between the CN and solvent molecule. Ab initio calculations show that the optical frequency of this transition is highly dependent on the solvation geometry, and thus these charge transfer transitions provide direct insight into how these transient molecules interact with the surrounding solvent environment

8. Preparing Data for Publications: To date, the MC fellow has contributed to five publications stemming from the MPGMC project,[1-5] with three more publications currently in preparation. The research has also inspired a rich array of new experiments to be performed by future generations, investigating questions arising from the various experiments described in this report.

9. Primary Supervision of Younger Researchers: The MC fellow has been responsible for the primary mentorship of two masters students, and two PhD students. He has also provided guidance and assistance to other students in the group, and generated data analysis and data acquisition programs for other experiments in the laboratory.

Conclusion: In conclusion, MPGMC has been an immensely productive scientific undertaking. The transient spectroscopy laboratory constructed by the MC fellow is in continual use, and the project has already led to several high profile scientific publications.[1-5] The MC fellow has also developed, and publicly released, a data analysis program capable of decomposing the complicated and nonlinearly evolving spectra produced by transient spectroscopic experiments.[4] Since its release in July of 2014, it has been downloaded nearly 150 times and cited by five scientific publications. This software, the publications described above, and the future experiments performed in the new transient spectroscopy laboratory will ensure the legacy of MPGMC will live on well into the future.

References:

[1] G. M. Roberts, H. J. B. Marroux, M. P. Grubb, M. N. R. Ashfold and A. J. Orr-Ewing, *J Phys Chem A* **118,** 11211 (2014).

[2] D. Murdock, S. J. Harris, J. Luke, M. P. Grubb, A. J. Orr-Ewing and M. N. R. Ashfold, *Phys Chem Chem Phys* **16,** 21271 (2014).

[3] S. J. Harris, D. Murdock, M. P. Grubb, I. P. Clark, G. M. Greetharn, M. Towrie and M. N. R. Ashfold, *J Phys Chem A* **118,** 10240 (2014).

[4] M. P. Grubb, A. J. Orr-Ewing and M. N. R. Ashfold, *Rev Sci Instrum* **85,** 064104 (2014).

[5] S. J. Harris, D. Murdock, M. P. Grubb, G. M. Greetham, I. P. Clark, M. Towrie and M. N. R. Ashfold, *Chem Sci* **5,** 707 (2014).