

## Annual Report

- a. 56678-DN16
- b. Utilizing Gas-phase Fragmentation Chemistry for Ultra-complex Mixture Analysis: Towards Petroleum Structural Characterization by Tandem Mass Spectrometry
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### NARRATIVE

#### 1. Problem and Approach.

Petroleum crude oil represents one of the most challenging and complex natural mixtures to characterize<sup>1,2</sup>. Tandem mass spectrometry (MS/MS) potentially offers a means of identification of the elemental compositions ( $C_cH_hN_nO_oS_s$ ) of the components and their structures. In theory this approach involves isolation of a single component of the sample, which is then activated and fragmented into diagnostic charged pieces which are then detected. Based on these data the individual component chemical's structure is inferred. For petroleum, this approach is complicated by the large number of elemental compositions present in a typical isolation window and the isomeric complexity likely contained within each of these peaks. This problem can be reduced by temperature and/or chromatographic separation prior to MS/MS analysis. In the present approach we utilize series of standard compounds and theory to examine what the degree of resolvable spectral complexity is and how much an increased understanding of the fragmentation chemistries in play may mitigate this.

#### 2. Synthetic Work

We began by examining like  $C_cH_hN_n$  compounds as these are high abundance components of the positive mode electrospray and atmospheric pressure photoionization mass spectra. Our initial synthetic work centers on acridine and anthracene-derivatives and their isomers and isobars ( $C_{21}H_{21}N$ ,  $C_{21}H_{23}N$ ,  $C_{22}H_{18}N$ ,  $C_{20}H_{22}N$ ,  $C_{22}H_{24}N$ ,  $C_{23}H_{20}N$ , etc.). These model compounds have systematically varied location, size, number, and nature of substituent(s) to enable physical organic hypotheses of structural influence on fragmentation chemistry to be assessed. Substantially more varied sample types and sizes have subsequently been generated to target specific chemistries and functional relationships. Thus the carbon number range and double bond equivalents has been expanded systematically. Nitrogen-centered, secondary amine species have also been examined.

#### 3. Experimental Work

In addition to those already synthesized standards, a large suite of commercially available putative and known petroleum component molecules have been analyzed with energy-resolved tandem mass spectrometry. Both radical cation and protonated species have been investigated. Direct comparison between the two means of activation for those standards amenable to both ionization methods was also undertaken. A series of broad "rules" have been formulated based on these data ready for testing against the wider suite of synthesized chemicals. E.g., relative preponderance and nature of substituent loss(es); alkyl radical vs. alkene vs. other chemistries.

#### 4. Parallel Theoretical Work

Theoretical work characterizing the various potential energy surfaces of our analytes has been undertaken. Additional modeling of fragmentation reaction pathways, potential isomerization's and putative product ion and neutrals has also been undertaken. This work is ongoing and guided by the experimental findings. Density functional theory optimizations culminating at the M062X/6-311G(2d,2p) level of theory and supplementary single point *ab initio* calculations (MP2, with various, large basis sets) form the basis of these comparisons. Comparative rate calculations utilizing Rice–Ramsperger–Kassel–Marcus (RRKM) theory have and continue to be utilized to compare reaction progress as a function of time and degree of activation.

#### 5. Presentation and Publications

- 1) [Maha Abutokaikah](#), Joseph Frye, Curtis Stump, Giri Gnawali, Christopher D. Spilling, Benjamin J. Bythell, "Aromatic Core Formation and Side Chain Losses from Series of Isomeric Model Compounds of Petroleum: Energetics and Practical Applications". Invited talk, American Society of Mass Spectrometry Conference, San Diego, CA, 2018.
- 2) Abutokaikah, M.T.; Frye, J.W.; Stump, C.M.; Gnawali, G.R.; Spilling, C.D.; Bythell, B.J., Tandem Mass Spectrometry Characterization of Synthesized Anthracene Derivatives, Poster, Graduate Research Symposium, St. Louis, MO, 2018.

- 3) Abutokaikah, M., Stump, C., & Bythell, B.J., Investigating the Fragmentation Chemistry of Isomeric Polycyclic Aromatic Hydrocarbon Derivatives, Poster, American Society of Mass Spectrometry Conference, Indianapolis, IN, 2017.

6. What next?

We will continue the synthetic, experimental and theoretical work mentioned above. We will expand the experimental work to look at more complex mixtures of known solution content. This will probe the concomitant effects of ionization efficiency, compound abundance, and fragmentation chemistry. We are also in the process of combining our ongoing the experimental and theoretical data into a large database for broad statistical comparison. Manuscripts resulting from the fundamental physical chemistry examined are currently in the process of being written up currently. More general, broader practical applications manuscripts will follow over the next year.

7. Impact of the research on the PI and students involved during the reporting period.

The PRF funds have enabled me to train multiple students in mass spectrometry, analytical chemistry, and computational methods. Additionally, the award provided me with the ability to pay for these students to attend major conferences in the subject area and interact with scientists from around the world. The main graduate students supported by these funds have benefited substantially in terms of laboratory capabilities, confidence, and mentoring of the undergraduate and high school students over the course of the grant period. Undergraduate students have used the experience to help secure employment in the chemical industry locally, or to gain access to good graduate programs.

On a more personal note, I feel that the award itself and the application process, provided an excellent learning experience for me in terms of how to effectively communicate my ideas in written form to a very general audience. While, the peer review was occasionally chastening, it has been invaluable in subsequent endeavors (NSF, NIH, other funding agencies). Award of the grant also comes with the feeling of a certain level of credibility/acceptance from one's peers. I have learnt to manage students more effectively over the course of the grant and to effectively prioritize time and group resources over the course of the funding period. The PRF grant has contributed substantially to my (hopefully) being awarded tenure in the spring.

References:

- 1- Marshall, A.G., Rodgers, R.P.: *Petroleomics: Proc. Natl. Acad. Sci.* 105, 18090–18095 (2008).  
2- Marshall, A.G., Rodgers, R.P.: Marshall, A.G., Rodgers, R.P.: *Acc. Chem. Res.* 37, 53–59 (2004).

