1. Scope of the Program

I am developing a new program to use microwave and millimeter-wave rotational spectroscopy to probe stable and reactive species relevant to combustion chemistry, and to use this capability to study reaction dynamics and kinetics. Rotational spectroscopy is known for its unsurpassed resolution and precision in determining molecular structure. The program will be based on chirped-pulse Fourier transform millimeter-wave (CP-FTmmW) spectroscopy, which is rapidly revolutionizing the field of molecular spectroscopy. The CP-FTmmW spectroscopy is capable of acquiring ~10 GHz wide rotational spectra with sub-MHz resolution in several microseconds with meaningful relative intensities of the transitions of multiple reaction products. The technique is nearly universal (applicable to all polar species) chemical tool that is conformer- and state-specific, quantitative and non-destructive, and suitable for studies of stable and transient species. The versatility of the CP-FTmmW technique is sufficient to allow its application to a wide range of experiments in reaction dynamics and kinetics.

2. Previous Work

a. Argonne chirped-pulse Fourier transform millimeter-wave spectrometer

The chirped-pulse Fourier transform millimeter-wave spectrometer for W-band (75–100 GHz spectral region) from BrightSpec Company that has a number of unique capabilities was installed and tested at Argonne. The combination of the Argonne BrightSpec spectrometer and the fast oscilloscope is capable of acquiring, in 5 microseconds, 11 GHz of spectral range within the W-band. This broadband mode of operation is similar to that of the original CP millimeter-wave spectrometer developed by the PI and coworkers. The broadband mode will be instrumental in recording rotational spectra of rapid processes, such as fast reactions in the flow tube reactor, or passage of photoproducts in a supersonic jet expansion. The rotational transitions of multiple reaction products can be detected with meaningful relative intensities, which can be converted to the relative abundance of the species given that the rotational temperature \( T_r \) can be determined. With the exception of small linear or diatomic molecules, the number of detected transitions is usually sufficient to infer the \( T_r \) from the spectrum.

When slower processes are under investigation, high duty cycles with long averaging times are available. Under these conditions the CP technique can, in principle, reach staggering ~10^5 dynamic ranges (signal-to-noise ratio, S/N) while acquiring up to 10^5 resolution elements (detection channels). However, the broadband mode of operation described above will face the limitations related to the speed with which the data can be digitized and processed by even fastest
oscilloscopes. Furthermore, the onset of spurious lines of different nature can be observed in the spectrum. To overcome these obstacles, the segmented chirped-pulse spectroscopy was developed\(^5\) and implemented in our spectrometer as the High Dynamic Range (HDR) mode. In the HDR regime the narrow-band chirps polarize the molecular rotational transitions in small 30 MHz segments of the 75–110 GHz band and the fast digitizer acquires the free induction decays (FIDs) from those segments, one after another. The spurious lines caused by mixing of the molecular lines with the local oscillator frequencies and with each other are, for the most part, left out of the narrow 30 MHz detection windows.

In the case of periodic processes with intermediate duty cycles, yet another approach is required. BrightSpec in collaboration with the PI has developed a new regime of the spectrometer termed synchronized (or sync-) HDR, in which the consecutive acquisition of 30 MHz segments is time-gated. With the shortest 133 microsecond acquisition on-time, the sync-HDR mode is applicable to relatively fast periodic processes while retaining the advantages of the HDR mode.

b. Pyrolysis of acetone

One of the proposed directions of this program is utilizing the pulsed flash pyrolysis reactor\(^6\) to study combustion-related chemistry in complex mixtures. The preliminary results of the first flash pyrolysis measurement using the sync-HDR mode of the Argonne chirped-pulse spectrometer are shown in Figure 1. Acetone molecules containing 50% normal acetone, CH\(_3\)COCH\(_3\) and 50% fully deuterated acetone, CD\(_3\)COCD\(_3\), entrained in argon carrier gas, are introduced to the pulsed flash pyrolysis reactor with a backing pressure of about 1 bar.

![Figure 1](image)

Figure 1. Pyrolysis of acetone (50% CH\(_3\)COCH\(_3\) and 50% CD\(_3\)COCD\(_3\)) studied by chirped-pulse Fourier transform millimeter-wave spectroscopy. Acetaldehyde CH\(_3\)CHO, CH\(_3\)CDO and CD\(_3\)CHO are observed as the pyrolysis products.
The acetone precursor is observed at S/N ~ 4000 after approximately 3 hours of averaging (upper panel of Fig. 1). When heating the nozzle to 1800 K the transitions of acetaldehyde are observed (lower panels of Fig. 1). One of the explanations for the appearance of acetaldehyde in the pyrolysis of acetone may be H-atom addition/elimination reactions that are discussed in the next section. Other products observed are ketene and propyne. We are working on building a model that will describe the chemistry leading to the observed pyrolysis products.

3. Future Work

Some previous results by the PI and other members of the Argonne Chemical Dynamics group suggest importance of the H-atom addition/elimination reactions in combustion-related and other reactions in the gas phase.\(^7\)\(^8\)

We propose investigation of the pyrolysis of aldehydes and ketones using the chirped-pulse rotational spectroscopy aimed at understanding the properties, and quantifying the contribution of the H-atom addition/elimination reactions. The first two systems that we are planning to study are acetone and acetaldehyde. The initial pyrolysis results that were recently obtained by the PI in the newly built laboratory at Argonne, described in the previous section, suggest that applying chirped-pulse rotational spectroscopy to these studies is a promising direction. An important aspect of our investigation will be the effort to characterize\(^9\) the thermodynamic conditions in the miniature SiC tube that we are using as our flash pyrolysis reactor. The branching between the reaction pathways and the final products that we detect with the CP spectrometer are expected to be affected by the temperature and pressure distributions inside the reactor. Once the conditions of the reactor are characterized and can be controlled, we expect a better agreement between the experimentally measured product branching ratios and kinetic modeling for known reactions and a greater predictive power of the method for new chemical dynamical effects.

Expanding our initial studies of the pyrolysis of acetone, pyrolysis of acetaldehyde, CH\(_3\)CHO, will be investigated. It can involve the following reactions:

\[
\begin{align*}
\text{CH}_3\text{CHO} & \rightarrow \text{CH}_3 + \text{CHO} \\
\text{CHO} & \rightarrow \text{CO} + \text{H} \\
\text{CH}_3\text{CHO} + \text{H} & \rightarrow \text{CH}_3\text{CH}_2\text{O} \quad \text{(H-atom addition)} \\
\text{CH}_3\text{CH}_2\text{O} & \rightarrow \text{CH}_3 + \text{CH}_2\text{O} \quad \text{(H-atom elimination)}
\end{align*}
\]

The CHO, CH\(_3\)CH\(_2\)O, and CH\(_2\)O products and reactive intermediates can be detected and quantified with CP spectroscopy. Investigation of formaldehyde, CH\(_2\)O, product would require expanding the spectrometer to the E-band (60 – 90 GHz) spectral region. We are going to investigate what role does keto-enol isomerization play in the pyrolysis of acetaldehyde. Similar classes of reactions can be investigated for acrolein, CH\(_2\)CHCHO, and propanal. Preliminary results in acetone, CH\(_3\)CH\(_3\)CHO, are described in the previous section.

Recently, the PI has demonstrated that a combination of the CP spectroscopic measurement of products’ branching ratios with accurate kinetic modeling is a powerful approach to studying dynamical effects in chemical reactions.\(^6\)\(^10\) A signature of roaming dynamics in the thermal decomposition of ethyl nitrite in a flash pyrolysis reactor was observed and rationalized.\(^10\) We propose investigation of the importance of roaming reactions at the conditions that are relevant to combustion. One of the questions that remains open and can be addressed in our experimental program is the pressure dependence of branching into roaming reaction channels. We plan to devise a version of the reactor in which the pressure in the reactor can be varied, in a controlled way, by an order of magnitude or more, approximately from 0.2 to 2 bar.
Expanding beyond the studies of roaming dynamics, we propose investigating other chemical dynamics phenomena using the CP spectroscopy. As noted by Al Wagner and Stephen Klippenstein, a potentially important for creating reliable predictive models effect that is not presently well-understood is energy redistribution from the energized molecules proceeding through their transition states into the reaction products. Vibrational energy partitioning into various products may either initiate consecutive reactions or relax into the bath molecules depending on the gas pressure and properties of the reactions’ transition states. In the Argonne chirped-pulse spectrometer coupled with flash pyrolysis reactor the aforementioned dynamical effects will be reflected in the measured reaction products branching ratios. Accurate kinetic modeling that will be performed in collaboration with Raghu Sivaramakrishnan, Stephen Klippenstein and other members of the Argonne Chemical Dynamics group will guide our intuition in understanding the chemical dynamics beyond the experimental results.

References