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Introduction:

Understanding the rate coefficients and branching of reactions in extraterrestrial atmospheres is of vital importance because it allows us to build a more complete picture of the overall chemical makeup and photochemical behavior in these alien environments. Gaining insight into these exotic reactions is crucial not only for understanding extraterrestrial environments, but also for providing a better understanding of reactions on Earth. The atmosphere of Titan, Saturn’s largest moon, is notably rich in nitrogen compounds and chemical reactions, which makes it an immensely important environment to study.[1] Titan’s reducing atmosphere resembles that of early Earth (the first one billion years of Earth’s existence). By analyzing the chemical composition of meteorites, which offer an appropriate approximation of the materials that were present on early Earth, we can conclude that early Earth also had a reducing atmosphere before developing the oxidizing atmosphere that is prevalent today. Investigating Titan’s atmospheric chemistry provides a more nuanced understanding of chemical processes that once occurred on our home planet, and possibly the origins of life.[2]

The extraterrestrial atmosphere of Titan is a low temperature environment. The region of Titan’s atmosphere that resembles Earth’s troposphere reaches temperatures as low as 71 K (**Figure 1**).[3] Rate coefficients at such low temperatures remain an under-studied area of astrochemical research. By understanding these coefficients, we can map both the production and the loss pathways of the chemical species found in Titan’s atmosphere. The production pathways are

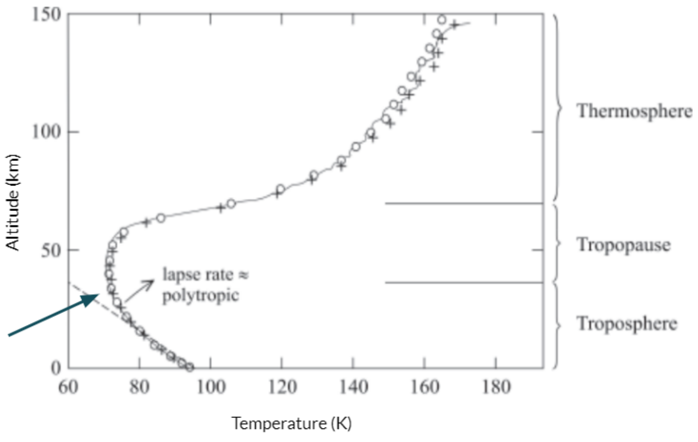

Figure 1. Titan’s temperature profile with low temperature indicated by blue arrow.[3]

important for understanding how the chemical species observed in Titan's atmosphere are formed. The loss pathways can lead to products that will react further in the atmosphere. Production and loss pathways have distinct effects on Titan's atmospheric photochemistry.[4] Small errors in rate constant values lead to inaccurate modeling, making it of utmost importance to correctly determine these low-temperature rate constants and associated branching ratios.

The 2004 Cassini mission of the Huygens probe, performed by the National Aeronautics and Space Administration (NASA), obtained observational data that provides the basis for our current understanding of Titan's atmospheric composition. The mission provided insight into Titan's surface, but most importantly for our investigation, it measured Titan's lower atmosphere for the first time. These measurements provided information as to what chemical species were confirmed to be present in Titan's atmosphere, which opened the door to ground-based studies into the potential formation and loss mechanisms of these observed species.[5] The observational data obtained by the mission offer a starting point for the modeling of Titan's atmospheric chemistry.

For our research, we aim to investigate the reaction between two prominent compounds confirmed to be in Titan's atmosphere, namely, electronically-excited nitrogen, $N\ (^2D)$ and ethene (C_2H_4). Notably, $N\ (^2D)$ is created via the absorption of solar radiation in Titan's atmosphere and is known for its long radiative lifetime, making it a compelling compound to study.[6] Numerous studies have reflected disagreements regarding the temperature dependence of the reaction rates associated with this reaction. Previous *ab initio* molecular orbital calculations showed that reaction rates varied with temperature as the rates were much lower at low temperatures.[7] On the other hand, other measured rate constants for the reaction over the temperature range of 50–296 K showed that rate constants did not vary with temperature.[8] These contradicting reports reflect the necessity of further experimental studies.

Past low-temperature kinetic studies have used supersonic flow reactors to investigate the $N\ (^2D)\ + C_2H_4$ reaction, such as the work performed by Hickson et. al. However, they have neglected an in-depth analysis of the branching ratio $N\ (^2D)\ + C_2H_4$ reaction towards the cyclic nitrogen tautomeric compound *c*-CH_2NCH, known as 2H-azirine (**Figure 2)**.[6] Creation and loss mechanisms of nitrogen-containing organic compounds in Titan's atmosphere are of vital importance due to their prebiotic availability. Hickson et. al identified the $N\ (^{2}D)\ + C_2H_4$ reaction as the only source of 2H-azirine in Titan's atmosphere. However, this study's analysis of the branching toward 2H-azirine was not well determined. Hickson et. al used a Laval nozzle as an introductory method with laser-induced fluorescence to detect this compound.[6] While highly sensitive, laser-induced fluorescence may not be widely applicable for other atmospheric studies due to its selectivity. Thus, it is important to explore alternative methods.

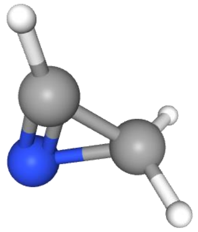

Figure 2. 3D conformer (ball and stick) of 2H-azirine.[9]

Although existing models have predicted sizable yields of 2H-azirine, the compound has not been detected by infrared spectroscopy in the lower atmosphere of Titan. This suggests the presence of an additional loss mechanism due to its potential reactivity with hydrogen atoms.[6] It is important to note that we will be focusing on the cyclic isomer of 2H-azirine, which has a higher energy barrier for the reaction with hydrogen in comparison to the linear isomer. This barrier minimizes the prevalence and speed of this loss mechanism, which would indicate that our desired product is present in moderate amounts.[6] Cyclic 2H-azirine is characterized by its strained ring, which enables its involvement in several photochemical reactions, including polymerization processes on Titan.[10] The compound's large dipole moment suggests it may be possible to detect 2H-azirine using Atacama Large Millimeter/submillimeter Array's (ALMA) rotational spectroscopy technology.[5] Thus, our proposed investigations into the true abundance of this molecule could determine whether ALMA studies would be merited in the future.

To improve upon existing studies of the branching ratios of $N\ (^{2}D)\ + C_2H_4$ towards 2H-azirine, we propose the usage of CRESUSOL outlined by Oliver Durif of the Lawrence Berkeley National Laboratory, and collaborators, which includes the physical chemist Mitchio Okumura from The California Institute of Technology. This instrumentation, established in 2021, offers an extension to the Cinétique de Réaction en Ecoulement Supersonique Uniforme (CRESU) technique by coupling it to synchrotron radiation at SOLEIL in France.[4] Specifically, this technique will allow for our study of the $N\ (^{2}D)\ + C_2H_4$ reaction towards the cyclic isomer of 2H-azirine. We propose additional improvements to CRESUSOL with the addition of the false-coincide suppression for photoelectron-photoion coincidence (PEPICO) spectroscopy outlined by Osborn et. al.[11] Overall, through our improvements to CRESUSOL and our focus on 2H-azirine, this proposal offers an alternative method to provide a more complete photochemical model of Titan's atmospheric chemistry.

Methods:

The work of Mitchio Okumura primarily entails the study of kinetics and reaction dynamics for applications in atmospheric chemistry. Durif and collaborators, including Okumura, introduced the CRESUSOL technique, which combines CRESU with synchrotron radiation at SOLEIL in France, to study low-temperature kinetics. For our study, we propose the usage of the CRESUSOL technique as outlined by Durif et. al with the addition of a false suppression scheme that was established by Osborn et al.[4,11] The goal of our research is to detect the rate of the formation of 2H-azirine from the reaction between $N\ (^2D)$ and C_2H_4.

The CRESU method in isolation creates a uniform supersonic flow via isentropic expansion (the expansion with no heat or matter transfer) of a buffer gas to a low pressure reservoir through a converging-diverging Laval nozzle **(Figure 3)**.[12] The Laval nozzle is an antisymmetric channel that acts as a guide during the expansion of the gas, ultimately creating a supersonic flow of gas in a uniform direction.[13] The incorporation of this nozzle makes CRESU an effective method for low-temperature kinetic investigations of gas phase molecules because it can reach temperatures as low as 20 K, while maintaining the molecule in its gaseous phase.[4] However, due to the uniformity of the velocity, temperature, and pressure associated with supersonic flow, CRESU is unable to measure slow processes (rate coefficients less than $10^{-12} cm^3 \cdot s^{-1}$). In addition, this technique requires large pumping capacities to lower the temperature or pressure of the uniform flow, making CRESU heavy and expensive.[4]

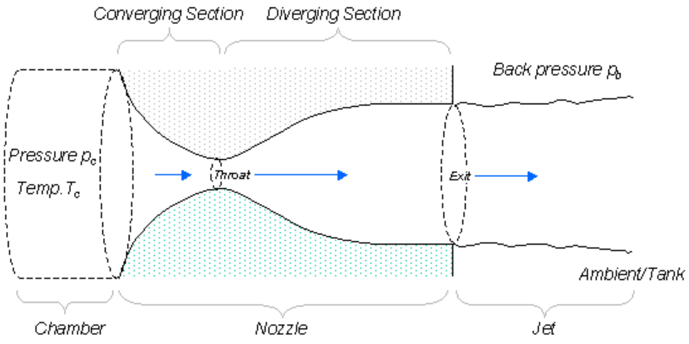

Figure 3. Converging-diverging Laval nozzle.[12]

By coupling the CRESU technique with the synchrotron radiation at SOLEIL, we can alleviate these limitations and enhance our capabilities for low-temperature kinetic investigation. Introduced by Durif et. al, this coupling of CRESU and SOLEIL radiation is achieved with a newly designed CRESUSOL instrument with a more compact apparatus. The CRESUSOL instrument allows for the creation of reactants with the photolysis laser and the isentropic expansion of our sample through a fine slit.[4] For our specific investigation, we will make the $N\ (^2D)$ component of the reaction through photolysis of the nitrogen gas (N_2) precursor. The C_2H_4 gas will be input directly from a gas cylinder into our reaction cell.[6]

For CRESUSOL, Durif et. al designed a 2.75-m long, 0.5-diameter chamber with two sections. The upper chamber (1.5 m in length) is known as the CRESU chamber. In this upper chamber, a Laval nozzle is used to create uniform supersonic flows for placement onto the reservoir (**Figure 4**). Durif et. al characterized the effectiveness of the Laval nozzles to create uniform temperature by scanning the uniformity of the flow through a variance of the distance between the Pitot tube (responsible for measuring flow velocity) and the Laval nozzle exit point. A uniform zone of 40 cm with an average temperature of 52 K was found.[4] This affirms the efficiency of this method in obtaining and maintaining desired temperature.

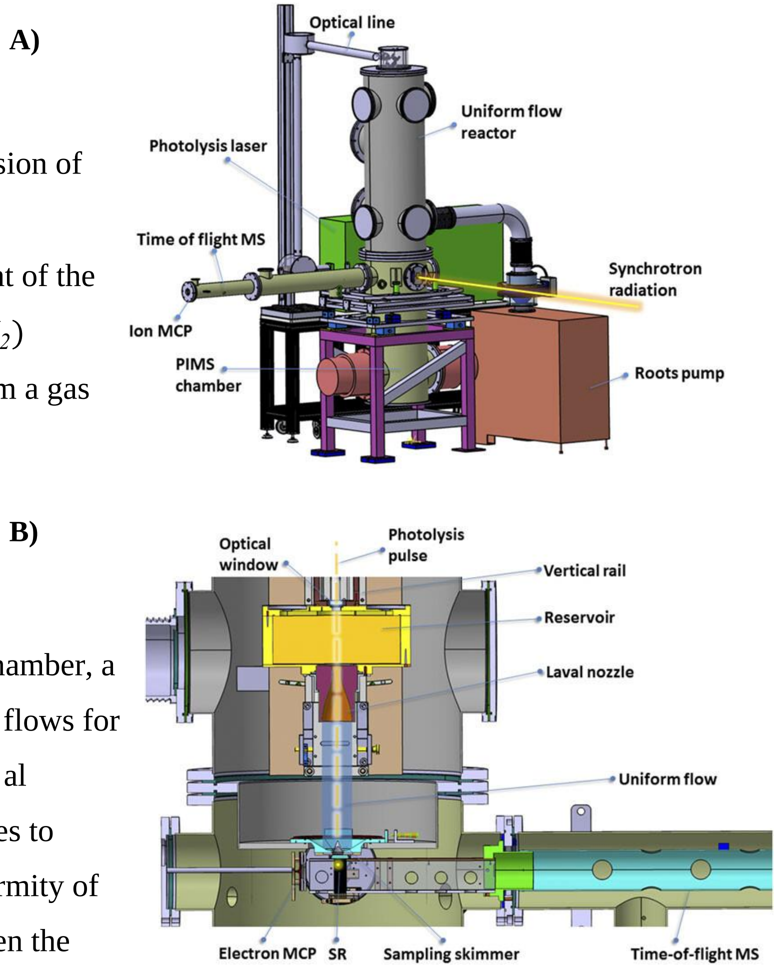

Figure 4. A) Outside view of CREUSOL setup B) Inside view of reaction and detection chamber.[4]

A 1.25-m long, 0.5 m diameter Photoionization/mass spectrometry (PIMS) detection chamber is located below the CRESU chamber. In this chamber the gasses introduced from the CRESU chamber are analyzed by a time-of-flight (TOF) mass spectrometer that is coupled to vacuum ultraviolet (VUV) synchrotron radiation to allow for photoionization. The detection chamber is placed onto a metal frame to allow for vertical movement, providing precise alignment to the synchrotron radiation beam. VUV radiation is advantageous due to its intensity and tunability, which lets us adjust the photoionization energy to a wavelength that ionizes the molecule of interest with reduced fragmentation.[4] As described by Nahon et. al, synchrotron radiation from the Dichroïsme Et Spectroscopie par Interaction Avec le Rayonnement

Synchrotron (DESIRS), which is an undulator-based beamline at SOLEIL that covers the VUV range of 100–200 nm, is a high-resolution photon source.[14] To combine CRESU and SOLEIL radiation, the apparatus described above is placed on the DESIRS VUV beamline. In order to fit the new instrument on the VUV DESIRS beamline, a smaller apparatus with reduced pumping capacities is necessary. Although this change is beneficial due its ease of transport, this reduction in pumping capacity can suppress the continuous supersonic flows necessary for temperatures lower than 50 K.[4] However, for our study of Titan's lower atmosphere, this temperature range is permissible because Titan's atmosphere does not reach temperatures lower than 71 K.[3]

To optimize counting efficiency (the ability to sense and count particle passage), Durif et. al implemented a photoion-photoelectron (PEPICO) coincidence detection scheme.[4] PEPICO combines photoelectron spectroscopy and mass spectrometry. This detection method examines electron and ion pairs that originate from a single ionization event.[11] If an electron and cation originate from a single ionization event, they are assigned as a coincidence. In PEPICO, electrons and cations are accelerated in opposite directions by a constant electric field where velocity map imaging is conducted for both the electrons and the cations. However, this method leads to a high number of false coincidences.[4] False coincidences occur when ions and electrons from different ionization events arrive within the same TOF range of interest, making it appear to be a coincidence despite not being one. This is because any electron-cation pair with an arrival time less than the predetermined tolerance (usually less than the TOF of the heaviest cation) is labeled a coincidence.[11]

In an attempt to help circumvent the issue of false coincidences, Durif et al. optimized skimmer conditions via Computational Fluid Dynamics (CFD) calculations and added a graphite coating on the time-of-flight (TOF) electrodes.[4] However, this improvement failed in eliminating false coincidences. The prevalence of false coincidences affirms the need for a more efficient method for determining ion origin for electrons. Therefore, we propose implementing a false suppression scheme that includes temporal-ion deflection coupled with a position sensitive detector (PSD) as outlined by Osborn et. al **(Figure 5)**.[11] In this false suppression scheme, the ions are deflected dynamically using triangle waveforms from a waveform generator. Using the timestamp of the sync pulse from the waveform generator, voltages at the time of deflection are obtained. This allows for the discernment of the coordinates and the deflection voltages by the static deflection of the ions. The cations are placed in a time-dependent electric deflection field located at a specific location that is a fraction of their TOF. For each test, the deflection of the cations with known TOFs establishes a region where the cations associated with the true coincidence event will hit the PSD. Coincidences that are false will arbitrarily hit locations outside this region and can thus be eliminated.[11]

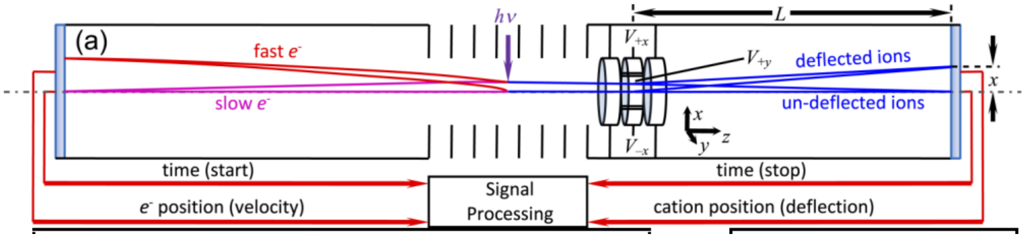

Figure 5. Set up of the false-coincidence suppression scheme for PEPICO experiment includes the propagation of the molecular beam along the y-axis, that ultimately crosses the photon beam (purple). A three-element ion deflector is located at the start of the cation flight tube on the right. With fast position-sensitive detectors, we can detect charged particles (blue rectangles). Observables measured are shown (red arrows), with the information pertaining to constituents found in parenthesis.[11]

The incorporation of this false coincidence suppression scheme for PEPICO spectroscopy will improve our dynamic range by normalizing the cations present in the incorrect spatial dimension. Osborn et. al outlines the following procedure to discern false coincidences[11]:

1. Calculate TOF using the following equation:

   $t_{ion} - t_{elec}$ ***(Equation 1.)***

   Here, t_{elec} and t_{ion} are indicative of the timestamps for electron and ion detection.

2. Using the TOF from step 1, calculate a deflection time (t_{defl}) using:

   $t_{defl} = t_{elec} + \text{TOF} \times n$ ***(Equation 2.)***

   In this case, n is a constant that is independent of the photoion's mass. When multiplied by the TOF, this constant represents the time needed for ion travel from its origin position to the center of the central deflector element.

3. Then, obtain the voltages of the deflector plates associated with the x and y-coordinates at the time of deflection and convert the voltages to predicted ion impact coordinates using the following linear transformation:

$$r_{calc} = r_0 + V \cdot \begin{pmatrix} P_1 & P_2 \\ P_3 & P_4 \end{pmatrix}$$ ***(Equation 3.)***

This calculation will be specific to each experiment. In this case, r_0 is the offset of image center and P_{1-4} corresponds to the matrix elements of the transformation.

4. Calculate the distance (Δr), which is the difference between the calculated and experimentally observed position.

   $$\Delta r = \sqrt{(x_{expt} - x_{calc})^2 + (y_{expt} - y_{calc})^2} \qquad \textbf{\textit{(Equation 4.)}}$$

5. If Δr is greater than the predefined tolerance (approximately the radius of a photoion spot on the detector), this can be labeled as a false coincidence and removed from the dataset.
   a. If Δr is within the tolerance, then it can be defined as a true coincidence and added as an event on the TOF spectrum.

Because this false coincidence suppression scheme has the potential to lessen the number of false coincidences previously encountered by Durif et al, we propose its implementation with the CRESUSOL technique for our investigation of the $N\ (^2D)\ + C_2H_4$ reaction.

Results and Discussions:

Previous low-temperature kinetic studies that have implemented CRESU have been limited due to crossflow detection. This is because the boundary layer and gas of interest are both in the expansion chamber, making it difficult to extract the contributions of the boundary layer under supersonic flow. As a result, spectral analysis is complicated and associated gradients in temperature and pressure pose challenges to the extraction of necessary information. Similarly, CRESU in isolation makes the study of spectroscopic molecular clustering processes difficult.[13] However, the new CRESUSOL instrument addresses these concerns.

The first results of the CRESUSOL instrument demonstrate its capabilities for the study of low-temperature gas phase reactions, including previously excluded clustering processes. The tunable synchrotron radiation enables soft ionization of clusters and reveals isomeric structures of products from photoionization spectra. Durif et. al demonstrates the effectiveness of CRESUSOL through the acquisition of the photoionization spectrum of *n*-butane. After introduction in the Laval nozzle at a temperature of 132 K, the ion signal as a function of photon energy was collected over an hour period, as shown in **Figure 6.** The signal was normalized for the DESIRS beamline at SOLEIL. As noted by Durif and colleagues, the collected data were in alignment with existing studies. The CRESUSOL instrument was also successful in detecting formic acid dimer and diacetylene molecule formation.[4] These initial results affirm the efficiency and proof-of-concept of this innovative instrumentation.

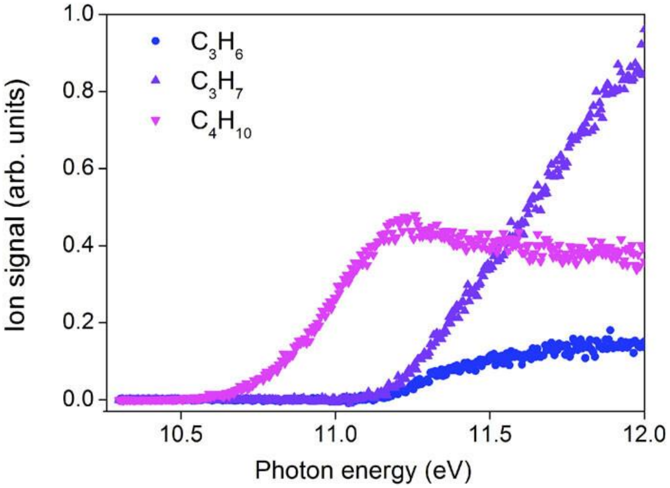

Figure 6. Photoionization spectrum of butane (m/z = 58.12) in supersonic flow functioning at 132 K with a buffer gas of Ar.[4]

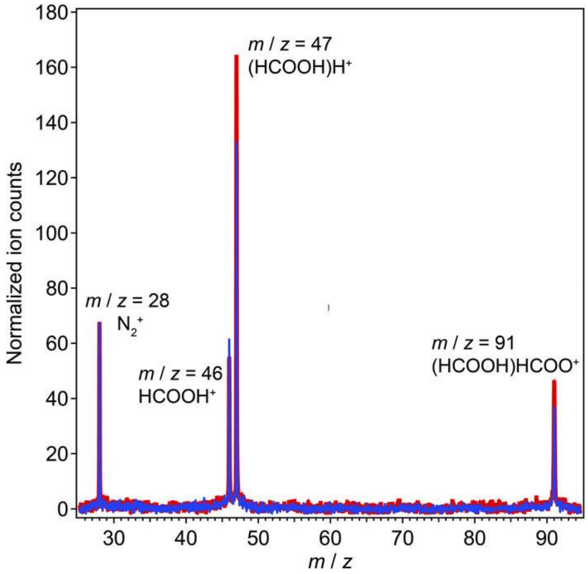

Figure 7. PEPICO mass spectrum of N2/HCOOH flow at 74.6 K recorded at 11.28 eV for 200 seconds. Blue spectrum recorded from the end of Laval nozzle to reach the skimmer of 2.5 cm, while red spectrum was recorded at 25 cm from the end.[4]

As previously noted, the CRESUSOL technique suffered from a prevalence of false coincidences due to the implementation of the PEPICO detection scheme. To address this, Durif et. al sampled the flow through a skimmer that separated the reaction chamber. **Figure 7** displays the results obtained from the PEPICO mass spectrum of the $N_2/HCOH$ flow at 74.6 K. While this affirms the capabilities of the CRESUSOL instrument, Durif et. al describes the persistent presence of false coincidences in the results despite sample skimmering.

For our investigation, a false suppression scheme will be implemented with the CRESUSOL instrument to reduce the false coincidence barrier. The work of Osborn et. al demonstrates that PEPICO spectroscopy false suppression scheme can minimize the presence of inaccurate coincidence event classification. In addition, the scheme improved the dynamic range by approximately two orders of magnitude.[4,11] After performing argon molecular beam experiments, Osborn et. al implemented this false suppression method, as outlined in our methods. Osborn et. al acquired a TOF mass spectra of argon that demonstrates the efficiency of this technique **(Figure 8).** This scheme was able to successfully reduce the background by 3 orders of magnitude and eliminate the periodic false coincidences observed in the original mass spectrum.[11] The inclusion of this scheme in our research will lead to greater sensitivity and offer improvements to the CRESUSOL instrumentation.

The results of Osborn et. al and Durif et. al inform the direction of our investigation of the branching of $N(^2D) + C_2H_4$ toward 2H-azirine. Hickson et. al investigated the $N(^2D) + C_2H_4$ reaction at temperatures between 50 K and 296 K using a supersonic flow reactor combined with laser-induced fluorescence detections in the VUV range of 100–200 nm. It is important to note that this technique implemented by Hickson et. al may not be widely applicable for other low-temperature kinetic studies. This study obtained rate constants that were independent of temperature and larger than previously predicted.[6] These unexpected results warrant further study to prove its replicability and thus, verify its results. Hickson and collaborators encouraged further investigation of the branching towards cyclic 2H-azirine and its reaction with hydrogen as a loss mechanism.[6] For our research, we aim to use an enhanced CRESUSOL model to provide a more accurate representation of the branching toward our cyclic nitrogen, 2H-azirine. As previously discussed, disagreements in the literature pertaining to the temperature dependence of the reaction rates associated with $N\ (^2D) + C_2H_4$ encourage further study.[7,8] Our research will help to clarify this discrepancy. In our case, we will investigate the rate constants within the temperature range of 51 K to 120 K due to its applicability to conditions in Titan's lower atmosphere, which can reach as low as 71 K.[3]

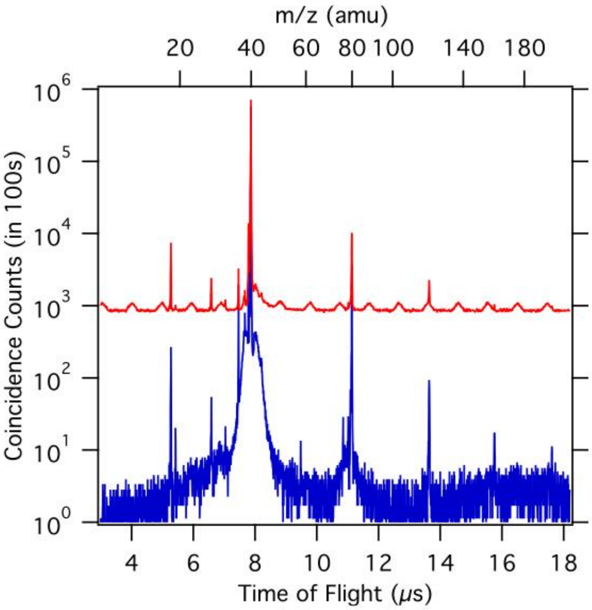

Figure 8. TOF coincidence spectrum of Ar molecule. Red trace is without the false suppression scheme, blue trace is with the false suppression scheme.[13]

When comparing the results of the new CRESUSOL apparatus to other low-temperature kinetic studies, CRESUSOL sets itself apart as the most efficient. Prior to the pairing of CRESU with synchrotron radiation, CRESU has been coupled to several optical techniques that have not been advantageous. Case in point, one method combines pulsed supersonic uniform flow with the optical technique of cavity ring-down spectroscopy. Cavity ring-down spectroscopy relies on measuring samples that absorb and scatter light. This combination produces results with a noticeably higher resolution than CRESU in isolation. However, this technique is ultimately less sensitive than CRESUSOL, and proves to only be useful for studying radicals, which is not the focus of our research.[4]

Next Research Direction:

Our overall objective is to examine low-temperature kinetics to understand Titan's atmospheric properties. Through an investigation of the kinetics of the $N\ (^2D)\ + C_2H_4$ reaction, we can discern branching toward 2H-azirine. We will use the improved CRESUSOL method to obtain the rate coefficients associated with the creation of cyclic 2H-azirine. These rate coefficients will be obtained by monitoring the photoionization signal intensity of the reactant and product channels to allow for kinetic data analysis. This procedure executed for the reaction rates associated with the temperature range of 50 and 120 K. To obtain these branching ratios, we will fit our rate into the overall model of $N\ (^2D)\ + C_2H_4$ reaction. Because the rates of formation of $N\ (^2D)\ + C_2H_4$ towards the reaction's other products have already been ascertained with relatively high accuracy, we will use these previously established rates to discern branching toward our desired product of cyclic 2H-azirine.

When studying low-temperature rate kinetics, it is crucial to utilize a method that is sensitive and can quantify and monitor multiple products simultaneously. Our usage of the coupled CRESUSOL will allow for efficient study.[4] Introduced by Osborn et. al and outlined in our methods, we also propose an enhancement to the CRESUSOL method with incorporation of a false coincidence suppression scheme for PEPICO spectroscopy. Reducing false coincidences will improve the sensitivity of our instrument and the accuracy of its results. Although PEPICO has proven to be an efficient method for the quantitative analysis of gaseous phase reactions in the application of atmospheric kinetics, the false coincidences encountered by Durif et. al emphasize the need for improvements.[11]

Our results will reveal the temperature dependence of the $N\ (^2D)\ + C_2H_4$ reaction of our measured range of 50 K to 120 K, quantify the rate constants associated with this reaction, and discern the branching ratio towards the closed-shell product of 2H-azirine.[6] Although past studies, including the work of Hickson et. al, focus on the range of 50- 296 K, our investigation will determine the temperature dependence from 50 K to 120 K. This range lies within the CRESUSOL capabilities and is reflective of Titan's troposphere.[3,4] Our selected temperature range will clarify the temperature dependence of this reaction, while maintaining its relevance to atmospheric conditions in Titan's troposphere.

Through our study of the branching ratio towards 2H-azirine, we will also be able to contribute to the current understanding of the mechanisms of elementary reactions in Titan's atmosphere. This understanding will provide explanations for the chemical networks of planetary models and strengthen our ability to accurately model these systems.[10] Our study is merited due to the lack of consistent data at low temperatures, which reflects the temperatures of extraterrestrial atmospheres, the neglect of specific reaction products and their further reactions, and the relevance of our species of focus.

Conclusion:

With this research, we aim to provide answers to Titan's atmospheric composition and properties through an investigation of the moon's nitrogen chemistry. The kinetics of Titan's atmosphere, known for its low temperatures, makes this a particularly mysterious mechanism that warrants further study. By studying Titan, we can obtain insight into a world beyond our own, which can provide a better understanding of early Earth's atmosphere. Specifically, we plan to elaborate on the mechanisms of branching towards 2H-azirine. Studying the cyclic nitrogen of 2H-azirine is pertinent to Titan due to its abundance as a product and its prebiotic value.[5,9] Our findings will outline an updated kinetic study that will illustrate more nuanced models of planetary systems, correcting for existing issues pertaining to sensitivity and size. The implementation of CRESUSOL provides an efficient means to examine low-temperature gas phase neutral–neutral reactions through its incorporation of synchrotron radiation. In addition, our proposal enhances CRESUSOL through our inclusion of the false-coincidence suppression scheme to improve PEPICO detection dynamic range. Our novel approach to the study of 2H-azirine improves upon existing methods and informs future astrochemical study of Titan and its lower atmosphere.

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