High-Velocity Impact Dissociation of Molecular Species in Spacecraft-Based Mass Spectrometers

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High-Velocity Impact Dissociation of Molecular Species in
Spacecraft-Based Mass Spectrometers

Brandon M Turner

A dissertation submitted to the faculty of
Brigham Young University
in partial fulfillment of the requirements for the degree of
Doctor of Philosophy

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ABSTRACT

High-Velocity Impact Dissociation of Molecular Species in Spacecraft-Based Mass Spectrometers

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Mass spectrometers have proven to be vital to understanding the Solar System and the planets within it. Spacecraft containing mass spectrometers have been sent to numerous remote places and have determined important information about the atmospheric composition of Venus, Earth, Mars, Jupiter, and Saturn, along with other celestial bodies. Such results have shown a variety of small neutral molecules, such as CH₄, NH₃, H₂O, CO₂, and CO, neutral radicals such as atomic O, H, and N, and a host of small ions, such as H⁺, N⁺, and NH₄⁺. Closed ion source inlets, which allow for the detection of these small neutral molecules, contain a spherical antechamber that allows the neutrals to thermalize with the walls of the chamber through many successive collisions before they are introduced into the ionization region of the spacecraft mass spectrometer. These collisions, however, energetically excite neutral molecules and lead to many chemical changes, such as racemization, ionization, or even dissociation. When these changes occur, smaller neutrals can be produced, even if they were not in the original sample from the atmosphere or surface. As a result, the determination of the true composition of an atmosphere or a surface is cast into doubt.

Herein is given a brief description of mass spectrometry in space research and how the closed ion source has greatly assisted this process. Dissociation and other chemical changes caused by the high velocity impacts that occur in closed source antechambers is also addressed. A theoretical approach to understanding such dissociative processes that occur after high energy collisions in closed source antechambers is described and undertaken. Chapter 2 describes a proof-of-concept study using hexane as a representative molecule and determines the velocity at which widespread dissociation of hexane molecules is likely to occur in closed source antechambers. This same theoretical process is then utilized in Chapter 3 with many more members of the n-alkane family to probe what effect molecular weight has on the amount of dissociation. Alkanes of both higher and lower molecular weight than hexane (C₆H₁₄) are used to show the effect as a function of molecular weight. In all cases, it was found that the velocity at which half of the incoming neutral n-alkane molecules dissociate is roughly the same for all molecular weights studied. This result is then applied to current and future space research through a proposed hardware solution, which will reduce the amount of dissociation and a discussion of how this effect may be seen in the results obtained from future mission instruments. Lastly, future work with different molecular weights and with successive collisions (the second, third, fourth, etc.) is described. This future work will further expand the present study to show how different functional groups, which may be partly responsible for higher-than-expected levels of NH₃ and CO₂, are affected after a high velocity, high energy impact.

Keywords: homolytic bond cleavage, radical formation, high-velocity impacts, closed ion source inlets, spacecraft mass spectrometers
ACKNOWLEDGEMENTS

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1 Mass Spectrometry in Space: The Evolution of the Closed Ion Source Inlet

1.1 Abstract

Mass spectrometry has been used for decades to probe the composition of the atmospheres and surfaces of planetary bodies in the Solar System. The inlets on the first spacecraft mass spectrometers used a leak system to introduce molecules into the instrument for analysis. As technology has improved, these leak systems were replaced with a dual inlet, which contained an open source and a closed source. This closed source has since been used to determine, more accurately than ground-based methods, the composition of the atmospheres of Venus, Earth, Mars, Jupiter, and Saturn, and other minor bodies, including asteroids, comets, and moons. Sometimes, this meant reinterpreting the older data acquired using ground-based techniques; in other situations, the data found during previous missions or using other methods were confirmed. Closed sources have been used to analyze many planetary systems of the Solar System, including the Venusian system, the Jovian system, the Saturnian system, and, more recently and extensively, the Martian system. Missions to gather compositional data from other planetary systems are currently being planned and developed, but inherent problems, both known and unknown, with the high velocity impacts that occur in closed ion sources may cloud the accuracy of the results of these missions. Due to such high velocities, thermalizing impacts, and other surface chemistry that occurs in the antechambers of closed sources, the molecules that enter the inlet may not be the same as those that enter the ionization region of the spacecraft mass spectrometer. This is due to such processes as unimolecular dissociation, recombination, and adsorption and desorption.

Keywords: mass spectrometry, closed ion source inlets, surface chemistry, high velocity impacts
Mass spectrometry is a powerful analytical tool that has aided space exploration for more than a half century. Mass spectrometers are versatile instruments that can be designed to work in numerous locations in even the harshest environments with a large dynamic signal range (up to $10^9$).\textsuperscript{1} Miniaturized mass spectrometers have been used in nearly all aspects of space research and exploration.\textsuperscript{2,3} They can be used to measure quantitatively the abundances of a variety of different gases, determine isotopic abundances and ratios, and have high scan speeds and sensitivities, which allows for single ion counting in many instances.\textsuperscript{1} Through targeted and specific mission parameters, mass spectrometers have not only broadened our understanding of the unique chemical processes and environments found throughout the Solar System, such as the subsurface ocean and ejecting plumes on Enceladus,\textsuperscript{4} the volcanic activity on Io,\textsuperscript{5} and the formation of liquid methane and ethane seas on Titan,\textsuperscript{6} but they have also been indispensable in putting humankind safely into space.\textsuperscript{2,3}

The use of mass spectrometry for space research has come a long way from its initial use on satellites in the 1950s and 1960s to look at the atmospheric conditions around Earth, through use on crewed space missions, such as Apollo 15, Apollo 16, and Apollo 17,\textsuperscript{7} to further probe atmospheric conditions, to now being used on uncrewed orbiters and surface probes to study many of the planetary systems throughout the Solar System. The initial instruments adapted for space flight used Bennett RF mass spectrometers.\textsuperscript{8} Then, in the seventies and eighties, the first mass spectrometers to be flown to an atmosphere and planetary system other than our own were onboard the Venera 9 and Venera 10 landers, which were sent to Venus.\textsuperscript{9} This was the period of space exploration when there were only a few deep space missions. The material cost and human effort required to build these instruments and operate them safely in space were high. These early
space missions used large-scale, fully instrumented and coordinated platforms that worked in harmony to perform analytical exploration. Examples of these missions are the Voyager 1 and Voyager 2 missions, which were initially sent to explore Jupiter and Saturn, but have since gone beyond the reaches of our Solar System; the Galileo mission, which was sent to the Jovian system to explore the gas giant and many of its moons; and the Viking 1 and Viking 2 missions, which were among the first missions to travel to and return scientific data from Mars, just to name a few.\textsuperscript{10}

Many of the early mass spectrometric analyses performed on these space missions used a variation of a leak system to introduce atmospheric gas samples into the mass spectrometer, and some, like the Viking missions, used a gas chromatograph coupled to a mass spectrometer.\textsuperscript{1} The initial instruments adapted to space flight were Bennett radio frequency mass spectrometers, which used a plane grid to extract ions from the surrounding atmosphere.\textsuperscript{8} The Venera 9 and Venera 10 landers employed 3 porous plugs in series as a gas inlet and introduction system.\textsuperscript{9,11} The Pioneer Venus Large probe mass spectrometer used two small microleaks.\textsuperscript{12,13} Venera 11 and Venera 12 both used an electromagnetically operated microvalve to allow gas to enter the mass spectrometer in short bursts.\textsuperscript{14} All of these missions were sent to Venus, which has a thick, dense lower atmosphere, which makes it hard to perform mass spectrometric analyses due to the higher pressure and the high number density of molecules.

1.3 \textit{The Closed Ion Source Inlet}

Over time, as technology improved, and the need arose for better inlets that could quickly and effectively collect neutral molecules at high velocities in environments of very low pressure, such as the interplanetary medium and in the atmospheres of minor planetary bodies, more
complex inlet systems were adopted. As a result, perhaps the most used gas inlet system on spacecraft to date has been a dual inlet system, which utilizes an open ion source and a closed ion source. The closed ion source began as a semi-open source.\textsuperscript{15} In theory, this means that there was some system of obtaining the neutral molecules, usually a small chamber or tube, but these neutrals would be introduced into the ionization region of the mass spectrometer directly, without interactions with the walls of the instrument, as seen in Figure 1-1.\textsuperscript{16} Over time, the most modern iteration of the closed source was designed. The current design of the closed source is

Figure 1-1: A schematic of an axial ion source, which has a relatively open construction. The molecules entering the formation area through the Wehnelt electrode aperture are ionized by electrons from the anode and then reach the mass filter through the extraction orifice. The use of the formation chamber causes minor errors in analysis due to desorption and surface reactions. Reprinted with permission from \textit{The Vacuum Technology Book, Volume II}. © 2013 Pfeiffer Vacuum.
similar in design to the inlets that were flown on the Orbiting Geothermal Observatory (OGO)-6 and San Marco-3 satellites\textsuperscript{2,3,17-19} in 1969 and 1971, and then on the Atmosphere Explorer-C, -D, and -E missions in the early- to mid-1970s, in addition to the Dynamics Explorer mission, Pioneer Venus mission, and the Galileo Probe. Instruments on board these uncrewed spacecraft, which were designed to investigate the thermosphere of Earth, Venus, and Jupiter, respectively, were equipped with a closed ion source inlet to accurately detect nonreactive neutral species.\textsuperscript{20} A nonreactive neutral species is one that does not interact with metal chamber walls, such as CH\textsubscript{4} or CO\textsubscript{2}, due to only containing paired electrons. Contrariwise, a reactive neutral, such as atomic oxygen or atomic hydrogen, tend to be radical species that have unpaired electrons that readily react with the metal walls of closed source antechambers. The ability of these reactive neutral species to react with the walls of the chamber allow them to easily adsorb to the surface, recombine with other radical, reactive species, and then desorb as completely different molecules. Such recombination creates errors in analysis of native neutral species found in planetary atmospheres.

A typical design for the dual inlet system, which includes a closed ion source and an open ion source, can be seen in Figure 1-2.\textsuperscript{17,21} For ionization of neutrals, the closed source contains a spherical antechamber with an entrance aperture for the incoming ambient gas to be collected and a cylindrical tube that connects this antechamber to the ionization region of the mass spectrometer. The inlet aperture is a knife-edge orifice,\textsuperscript{22} which minimizes contact between any potential neutrals coming out of the aperture with the gas stream coming into the hole, and is protected from contamination while the spacecraft travels to its destination through use of a ceramic annular closure, or break-off assembly.\textsuperscript{1,3,23} This closure is then removed after atmospheric insertion so the spacecraft instruments can perform their required function, which is
to allow the measurement of chemically inert species and non-surface reactive neutral species, such as N₂ and CH₄. This measurement is performed by relating the gas density in the chamber to the ambient density based on kinetic gas theory and knowledge of the vehicle trajectory and velocity.²,³

Figure 1-2: Schematic of the dual source inlet onboard the Cassini-Huygens spacecraft. The picture on the left shows the overall instrument design while the description of each part on the right provides the general layout of traditional dual ion source inlets, with the closed source at the top and the open source just below. Reprinted with permission from McSween et al., Proc. Natl. Acad. Sci. U. S. A. 2011, 108(48), 19177-19182. DOI: https://doi.org/10.1073/pnas.1013476108. Copyright © 2011 National Academy of Sciences.

Gases flowing into the antechamber then thermalize (energetically equilibrate) with the walls of the well-defined (and often gold plated) chamber¹⁸ through many collisions²⁴,²⁵. There are two major advantages to the thermalizing collisions that occur in the closed ion source. First, unlike in the open source, where a quadrupole bias voltage must be used to slow down the
incoming molecules before they reach the analyzer, the energy for all species coming from the closed source is similar because the gas has been thermalized. A higher energy into the analyzer results in wider mass peak widths in the associated mass spectrum.\textsuperscript{26} Also, a weak angle of attack dependence (a cosine function) makes the closed ion source useful for measurements at large angles.\textsuperscript{27} In fact, the closed source typically has around a $2\pi$ steradian field of view (which is a hemisphere) and an almost 50% measurement duty cycle on a spinning spacecraft.\textsuperscript{23,28} This allows instruments using a closed source to measure neutral composition in spite of the neutral winds found in many planetary atmospheres.

The second, and perhaps the more important, advantage to using a closed ion source antechamber is that a significant ram enhancement to sensitivity is achieved. For the ram enhancement to be realized, the conductance of molecules from inside the antechamber into either the ionization region or back through the knife-edge orifice into space must be much lower than the conductance of neutrals entering the antechamber. The conductance from space through the orifice into the instrument includes the molecules present in the volume per unit time that the spacecraft flies through as it travels through a planetary atmosphere. This conductance must be kept much higher than the combined conductances of exit through the transfer tube into the ionization region or back through the entrance aperture into space. The conductance of a tube of circular cross-section, such as the transfer tube from the antechamber into the ionization region of the mass spectrometer, is then given by equation 1-1,\textsuperscript{29}

\[
C\left(\text{in L/s}\right) = 2.6 \times 10^{-4} \times v \times \frac{D^3}{L}
\]  

(1-1)

where the diameter $D$ and the length $L$ are measured in centimeters and the average molecular velocity $v$ is in cm/s. In the molecular-flow regime, as would be the case in a closed source antechamber, conductance is independent of pressure. Additionally, this conductance into the
transfer tube is normally insignificant when compared with the conductance into or out through the main entrance aperture. In addition, the average molecular velocity of molecules leaving the antechamber, either back through the entrance aperture or into the transfer tube into the ionization region will be lower than the average molecular velocity of molecules entering the antechamber. As such, molecules will exit the antechamber much more slowly than they enter the chamber. The conductance of an aperture, or the conductance from the antechamber through the orifice back into space, for a gas of molecular weight $M$ in the molecular flow regime is found by using equation 1-2,29

$$C \ (in \ L/s) = 3.7 \times \sqrt{\left(\frac{T}{M}\right) \times A}$$

(1-2)

where $T$ is the temperature of the gas and $A$ is the area of the entrance aperture in cm$^2$. It should be noted here that the temperature in equation 1-2 becomes negligible as the spacecraft velocity becomes high. This difference in the conductance of molecules entering the antechamber versus the conductance of molecules leaving the antechamber then leads to the mass dependent ram pressure enhancement in spacecraft closed sources.

This enhancement is mass dependent, meaning the closed source response is greater for species of higher molecular weights. The closed source normalized sensitivities $S_n$ for a species $s$ of mass $m_s$ and electron ionization cross section at 70 eV $\sigma_s$ can be approximated to first order through interpolation of the normalized sensitivities of argon and krypton. Equation 1-3 shows how the sensitivity of the closed source depends on the mass of the incoming neutrals,

$$S_a = S_n \times C_{RF}(m_s) \times \sigma_s$$

(1-3)

where $S_a$ is the absolute sensitivity, $S_n$ is the normalized sensitivity, $C_{RF}$ is the sensitivity correction factor (0.71 if $m_s$ is $<$20.5 or 1 if $m_s$ is $>$20.5), $m_s$ is the mass of species $s$, and $\sigma_s$ is the
electron ionization cross section at 70 eV. This also means that molecules of high molecular weights, which are only present in very trace amounts throughout space, can be seen as a result of this higher sensitivity in the closed source inlet. The signal varies approximately with the cosine of the angle of attack (and is optimized for angles <90°) and is proportional to the product of the spacecraft velocity and the square root of the ratio of molecular weight divided by the gas temperature, as seen in equations 1-4 and 1-5:

\[ n_{s,i} = n_{a,i} \sqrt{\frac{T_{a,i}}{T_{s,i}}} (\exp{-S_i^2} + \sqrt{\pi}S_i(1 + \text{erf}S_i)) \] (1-4)

Where \( S_i = \frac{V \cos(\alpha)}{c_i} \) and \( c_i = \sqrt{\frac{2kT_{a,i}}{m_i}} \) (1-5)

In these equations, \( n \) is the number density, \( T \) is the temperature, where \( a \) is the ambient gas and \( s \) is the gas in the source, \( i \) is representative of the gas species, \( V \) is the apparent velocity of the incoming neutral molecules, \( \alpha \) is the angle of attack, \( c_i \) is the most probable speed of the ambient gas particles, and \( K \) is Boltzmann’s constant. A balance in the conductances of incoming gas particles, which are traveling at spacecraft velocity, and outgoing gas particles, which are traveling at thermalized velocities, through the inlet aperture is what determines the number density in the antechamber. All these values (ion source density, the conductances of incoming and outgoing molecules, and ambient density) can be predicted from kinetic theory.

Due to the high-velocity interactions that, of necessity, must occur between neutral molecules and the walls of the inlet antechamber, many problems develop in any analysis performed from closed source data. These high-velocity neutral collisions are required to thermalize the molecules, which allows them to reach thermal and energetic equilibrium with the instrument before being introduced into the mass spectrometer. However, such high impacts cause extensive vibrational excitation of the molecules. For example, when a spacecraft is
travelling at 11.6 km/s, a simple kinetic energy calculation reveals that the amount of energy the colliding neutral contains is about 0.7 eV/amu, irrespective of any translational-to-vibrational energy efficiency.\textsuperscript{1} However, if 14% of this initial kinetic energy is transferred into vibrational energy in the neutral, this equates to about 4.34 eV of acquired vibrational energy for CO\textsubscript{2}. Molecules with even higher molecular weights, such as hexane at 86 amu, would have even more added vibrational energy. In addition, the collisions of high energy neutral molecules and dissociated radical species with the ion source walls then cause a cascade of sample gases and small recombination products, such as O\textsubscript{2}, CO\textsubscript{2}, and H\textsubscript{2}, to be released from the inlet surfaces.\textsuperscript{31,32} This release of contaminant gases can cause severe problems in measuring the atmospheric compositions of the planets.

Unimolecular dissociation caused by high-energy impacts with the antechamber walls is not the only cause of error in analyses of closed source data. Wall effects, such as adsorption and recombination on the metal surfaces of the closed source antechambers, are also a hindrance to correct analysis of atmospheric composition after high velocity impacts. Von Zahn et al.\textsuperscript{1} point out that there is a difficulty in measuring molecular gases (and especially reactive gases, such as H and O) because they tend to adsorb or chemically react to the ion source walls. Initially, when the wall surfaces are clean, they act as a sort of chemical sink for reactive gases. If the ion source surfaces are not saturated with gases, the incoming ambient gas sample displaces these adsorbed gases and give rise to additional, unwanted signals in mass spectrometer measurements. They also state that so much CO from the ambient CO\textsubscript{2} and miscellaneous background is produced inside the ion sources that a reliable correction for these interferences is difficult. Pelz et al.\textsuperscript{20} mention that closed source instrument results have been questioned because the possibility exists that atomic oxygen can be removed from the surface by conversion to carbon dioxide and other
oxide forms.\textsuperscript{33} OGO-6 results showed that following three weeks’ exposure to space, ambient oxygen was converted to molecular oxygen in the closed source antechamber.\textsuperscript{34,35} In addition, ambient oxygen densities determined from closed source instruments disagree with those measured by open sources.\textsuperscript{36}

The background count rate due to other gases adsorbed on source antechamber surfaces may cause interferences at some mass numbers, especially below 50 Daltons. The interference at some mass numbers by other ambient gases present in high concentrations on the antechamber surfaces presents a problem in subsequent analysis,\textsuperscript{17} such as mistaking CO\textsubscript{2} at 44 amu for propane or N\textsubscript{2}O, \textsuperscript{13}C for \textsuperscript{12}CH at 13 amu, and N\textsubscript{2} at 28 amu for CO. Istomin (personal communication to U. von Zahn) has mentioned that at high altitudes and low temperatures, cloud particles and condensable gases like water vapor may perhaps become attached to the internal surfaces of the inlet. At low altitudes and higher temperatures, these species may detach again from the walls and be liable to introduce a bias in the data.\textsuperscript{1} As such, surface reactions and effects must be understood to interpret atmospheric measurements accurately.\textsuperscript{37}

\textbf{1.4 Representative Selection of Previous Missions and Their Results}

Earth and the Moon

Among the first uncrewed spacecraft to be equipped with a closed source, the Atmosphere Explorer-C mission, also called Explorer 51, was launched in December 1973. It was designed to measure \textit{in situ} the spatial distribution, temporal changes, and concentrations of neutral species found in the Earth’s atmosphere. Especial emphasis was given to the study of hydrogen, helium, oxygen, nitrogen, and argon, all with masses below 44 amu. A Bennett ion mass spectrometer and an open-source neutral mass spectrometer were among the instruments
used to carry out the objectives of the mission. The use of both a closed neutral source and an open neutral source combined with a Bennett ion mass spectrometer allowed for direct comparison of the results from the two sources and provided valuable insight for future missions into such measurement techniques. Unlike the modern, dual-source inlet, these two instruments were not in contact with each other, meaning they were on separate places on the spacecraft. The overall design of the Atmosphere Explorer-C spacecraft can be seen in Figure 1-3.\textsuperscript{38,39}

Continuing the mission begun by Explorer 51, the Atmosphere Explorer-D (Explorer 54) and Atmosphere Explorer-E (Explorer 55) spacecraft were launched in October 1975 and November 1975, respectively, and contained much the same payload and had much the same
design as did Atmosphere Explorer-C. While Explorer 54 did not contain a Bennett ion mass spectrometer, Explorer 55 had the exact same instrumental setup as did Explorer 51. As continuations of the Explorer 51 mission, Explorer 54 and Explorer 55 had the same scientific objectives. However, they were inserted into orbit at different latitude regions, with Explorer 54 sampling the high latitude regions and Explorer 55 sampling the low latitude and equatorial regions. The closed source on all three of these spacecraft contained gold-plated stainless steel thermalizing chambers and ion sources attached to hyperbolic rod quadrupole mass analyzers. Sampled gas molecules entered the chamber through a knife-edge orifice and were then directed through an electron impact ionization source into the mass analyzer and then through a 90° turn to the off-axis electron multiplier. The mass range of all three explorer missions was 1-44 amu with a dynamic range of greater than 10⁷ and a mass resolution of about 1 amu.³⁸,⁴⁰,⁴¹

There were two additional missions that were very similar in design and mission objectives to the Atmosphere Explorer-C, -D, and -E missions. The Dynamics Explorer-1 and Dynamics Explorer-2 (Explorer 62 and Explorer 63) missions were both launched and inserted into Earth’s atmosphere in August 1981. Figure 1-4 shows the general spacecraft design of Explorer 62 and Explorer 63, which is identical to Explorer 51, 54, and 55. Their objectives were to investigate the strong interactive processes coupling the hot, tenuous, convecting plasmas of the magnetosphere with the cooler, denser plasmas and gases present in the ionosphere, upper atmosphere, and plasmasphere. As such, unlike the Explorer 51, 54, and 55 missions, which sampled atmospheric gases at regions of the Earth based on latitude, the Dynamics Explorer missions were inserted into polar coplanar orbits based on altitude, with Explorer 62 (DE-1) sampling gas at high atmospheric altitudes, and Explorer 63 (DE-2) sampling gas at low atmospheric altitudes. These coplanar orbits allowed the different layers of the atmosphere, along
with their coupled processes, to be studied simultaneously. Explorer 62 contained fewer scientific instruments than did either the Atmosphere Explorer spacecraft or the Dynamics Explorer-2 spacecraft, which is the only one of these two missions that contained a closed source for neutral analysis, called the Neutral Atmosphere Composition Spectrometer. This instrument was identical in design to the closed source flown on all previous Explorer missions.\textsuperscript{42,43}

Figure 1-4: A photograph of the Dynamics Explorer-1 (top) and Dynamics Explorer-2 (bottom) spacecraft. As can be seen, both spacecraft had the same design. The instrument panels can be seen facing the camera. There were more instruments on the Dynamics Explorer-2 spacecraft, hence the need for more used space on the panel. Reprinted with permission from Williams et al., https://nssdc.gsfc.nasa.gov/nmc/spacecraft/display.action?id=1981-070A. © 2022 National Aeronautics and Space Administration.

The Lunar Atmosphere and Dust Environment Explorer (LADEE) was launched in September 2013 and was inserted into orbit around the Moon’s equator. Its scientific mission was three-fold; first, it was designed to determine the global density, composition, and time
variability of the lunar atmosphere; second, a study was undertaken to determine the composition of the diffuse emissions above the surface of the Moon that were seen by the Apollo astronauts; and third, the spacecraft documented the size and frequency of dust impactors around the Moon. The Neutral Mass Spectrometer (NMS) onboard LADEE, as seen in Figure 1-5, performed such

![Closed and Open Ion Source Assemblies](https://spaceflight101.com/ladee/science-instruments/)

Figure 1-5: A photograph of the closed ion source and open ion source assembly from the LADEE spacecraft. The closed source, on top, contains a spherical antechamber for thermalization of neutrals and a transfer tube to guide the molecules into the mass spectrometer, whereas molecules entering from the open source, gold color, below the closed source, enter the ionization region of the mass spectrometer directly. Reprinted with permission from https://spaceflight101.com/ladee/science-instruments/. © 2022 National Aeronautics and Space Administration.

in situ measurements of atmospheric atoms and molecules. To accomplish this goal, the NMS contained both an open source, for the analysis of ions and reactive neutrals, and a closed source, for small, non-reactive neutrals. This closed source contained a spherical antechamber and transfer tube made of titanium. The transfer tube guided the thermalized molecules into an
electron beam ionization region, which then opened into a quadrupole mass analyzer. The quadrupole mass analyzer had a dynamic range of around $10^8$, unit mass resolution, and a mass range of 2-150 amu.44 Using the NMS, scientists found numerous neutral species, such as CO$_2$, CO, H$_2$O, and N$_2$, and determined that helium, argon, and neon were the dominant species in the lunar atmosphere.45,46

Mars

The Mars Atmosphere and Evolution (MAVEN) mission, launched in November 2013 and inserted into Martian orbit in 2014 at an orbital velocity around 5 km/s, was designed to study the structure and composition of the upper neutral atmosphere of Mars. The scientific mission objectives included measuring isotopic ratios, including the profiles of helium, oxygen, nitrogen, CO, CO$_2$, NO, and argon as well as their major isotopes, and the measurement of thermal and supra-thermal ions. All of this was done to produce models to describe the escape of the atmosphere around Mars both past and present and the evolution of the dry, windy Martian climate.27 Much like many of the preceding missions, the Neutral Gas and Ion Mass Spectrometer (NGIMS) onboard MAVEN was equipped with both an open source and a closed source for atmospheric analysis. This closed source contained a titanium spherical antechamber connected to an electron ionization source and a hyperbolic rod quadrupole mass spectrometer through means of a titanium transfer tube.47 Figure 1-6 shows the general design of the mass spectrometer system of the NGIMS. The dynamic range of the MAVEN NGIMS was around $10^8$ with unit mass resolution and a mass analyzer range of 2-150 amu.
Figure 1-6: The design of the Neutral Gas and Ion Mass Spectrometer (NGIMS) instrument aboard the Mars Atmosphere and Evolution (MAVEN) Mission. The closed source, far left, is made of titanium, and allows neutrals to thermalize before entering the electron impact ionization source of the mass spectrometer. The big green box in the background is all the electronics necessary for instrument power. Reprinted with permission from https://mars.nasa.gov/resources/5186/neutral-gas-and-ion-mass-spectrometer-for-maven-spacecraft/. © 2022 National Aeronautics and Space Administration.

Results from the NGIMS confirm many of the results that have been acquired from various ground-based techniques. For example, Mahaffy et al. point out that the combination of isotopic measurements of gases trapped in glassy inclusions and orbital spectroscopic detection of only a few surface carbonates show that the atmosphere of Mars has thinned significantly since initial detection. In addition, these results also show that the atmosphere has escaped much more quickly than replenishment from the loss of surface reservoirs has occurred. Recent in situ measurements from the Curiosity Rover (among others) are consistent with these findings. They show an atmospheric composition of $^{13}\text{C}$ and $^{18}\text{C}$ in CO$_2$ in the atmosphere of 46\% and 48\%,
respectively,\textsuperscript{49} a mixing ratio of $^{36}\text{Ar}/^{38}\text{Ar}$ of about 5.2,\textsuperscript{50} and a D/H mixing ratio in atmospheric water of about 5000\%.\textsuperscript{51} In each of these cases, there is an obvious enrichment in the atmosphere of the heavier isotope.\textsuperscript{27}

Saturn

Perhaps the longest and most successful previous mission to a planetary system, the Cassini-Huygens mission launched from Cape Canaveral in October 1997 and was inserted into Saturn’s orbit in July 2004. The Huygens probe then detached from the Cassini spacecraft in December 2004 and landed on the surface of Titan, the largest moon of Saturn, in January 2005. During its nearly 20-year mission, Cassini provided a wealth of knowledge about the structure and composition of Saturn and its rings, about the atmospheric composition of many of its icy moons, including Iapetus, Titan, and Enceladus, with their clouds, hazes, and plumes, and about the dynamic behavior of Saturn’s atmosphere and magnetosphere.\textsuperscript{17,52-54} The closed source inlet of Cassini was based on similar sources found on the Atmosphere Explorer-C, -D, and -E missions, as well as the Dynamics Explorer-1 and -2 missions. A picture of the actual closed and open ion source used on Cassini can be seen in Figure 1-2. It contained a titanium antechamber with a 5 cm diameter to thermalize neutrals before they entered the hot-filament electron gun (electron impact) ionization region of the instrument. Molecules ionized in the source would then be directed through a hyperbolic rod quadrupole mass analyzer through a 90° turn into the detector.\textsuperscript{17} The quadrupole onboard Cassini had unit mass resolution with a mass range of 1-99 amu, which was smaller than many of the closed source instruments developed since, and a dynamic range of about $10^8$. 
Comets and Other Celestial Bodies

A different mission than most of those mentioned, the Comet Nucleus Tour (CONTOUR) mission was designed to investigate and measure the chemical and isotopic composition of neutral and ion species in the nuclear coma and dust tails of three comets, Encke, Schwassmann-Wachmann 3, and d’Arrest. In performing these measurements, scientists hoped that CONTOUR would provide an understanding of the relative abundances of H₂O, CH₄, CO₂, NH₃, and H₂S in cometary comas, which would provide the best possible record of conditions present in the outer solar nebula early in its history. In addition to the three comets mentioned, it was also hoped that there would be a possibility of approaching a fourth, newly discovered comet during the mission. CONTOUR was launched in July 2002, but, unfortunately, the spacecraft was lost during an August 2002 injection maneuver. As such, there are no results from the mission. The spacecraft mass spectrometer onboard CONTOUR, however, contained a closed source, with a spherical antechamber made of titanium and a hyperbolic rod quadrupole mass analyzer. The ions would be created using electron impact and then enter the mass analyzer, which had unit mass resolution and one of the largest mass ranges of 1-294 amu.

Another failed mission that would have utilized a closed source, Nozomi (Planet B) was built by the Institute of Space and Astronautical Science in Tokyo, Japan and launched in July 1998. It was designed to study the upper atmosphere of Mars and its interaction with the solar wind. Instruments on the spacecraft were designed to measure the structure, composition, and dynamics of the ionosphere, aeronomy effects of the solar wind, the escape of atmospheric constituents, the intrinsic magnetic field, the penetration of the magnetic field from the solar wind, the structure of the magnetosphere, and the dust in the upper atmosphere and even in orbit around the planet. The closed source was part of the Neutral Mass Spectrometer (NMS) onboard.
the instrument. It contained a titanium antechamber and transfer tube, and guided neutral molecules from the planetary atmosphere through the electron impact ionization source into a quadrupole mass analyzer. Although the spacecraft instruments were able to briefly transmit useful measurement data on light in interplanetary space, the insertion into Martian orbit was unsuccessful and, as such, no data was acquired from the closed source as part of the NMS.

Future Planned Missions

In addition to the launched and completed missions previously discussed, there are two planned missions (both to the Jovian system) that will have instruments very similar to those used on past missions. These missions are the Jupiter Icy Moons Explorer (JUICE), funded and designed by the European Space Agency (ESA), which is projected to launch in April 2023, and the Europa Clipper, funded and designed by the National Aeronautics and Space Administration (NASA), which is projected to launch in October 2024. JUICE is designed to study the atmosphere and environment of Jupiter through detailed observations and will also include characterization of Ganymede, Europa, and Callisto, three of the icy moons of Jupiter. These moons are considered “icy” worlds because they are believed to have subsurface oceans that could provide the means necessary for potential habitation. The JUICE spacecraft will be equipped with the Particle Environment Package (PEP), which will be the primary instrument suite used for investigation of the atmospheres and plasma environment of the icy moons. As part of the PEP, the Neutral Gas and Ion Mass Spectrometer (NIM) onboard JUICE will allow for the determination of the neutral gas composition and also the ion makeup of each atmosphere.
Figure 1-7: A schematic of the NIM instrument onboard the JUICE mission spacecraft. The closed source, (th-Mode) at the top, is attached to the time-of-flight mass analyzer by means of the open source (n-Mode and i-Mode) and hot filament electron ionization source. This will be the first space instrument to use a time-of-flight mass analyzer attached to a dual ion source inlet. Reprinted with permission from Fohn, M. et al., https://presentations.copernicus.org/EGU2020/EGU2020-2955_presentation.pdf. © 2020 European Sciences Union.

Figure 1-7 shows a simple schematic of the NIM instrument,\textsuperscript{60} which contains a dual closed source and open source attached to a time-of-flight (TOF) mass analyzer. The closed source contains a spherical titanium antechamber with a $10/3 \pi$ steradian field of view. This chamber is then attached to the open source and the electron ionization source. All ions are then introduced into the mass analyzer, which is different than those found on previous missions in that it uses a time-of-flight mass analyzer system with an ion mirror to increase the flight distance, giving the instrument a total length of about 360 mm. NIM is designed to measure
masses up to 1000 amu, but only masses up to about 100 amu are expected to be found. There is also a density enhancement in the closed source, which allows the signal to increase as the velocity of the incoming neutrals increases.\textsuperscript{61}

The Europa Clipper has a very similar purpose – to orbit Jupiter and perform many flybys of the moon Europa. Unlike JUICE, which plans to also study Ganymede and Callisto, the Europa Clipper is designed to focus its study on Europa. The Mass Spectrometer for Planetary Exploration/Europa (MASPEX), which will fly onboard the Clipper, has significantly improved performance over existing instruments. This includes a dynamic range of $10^9$ in a one second

![Figure 1-8: At top, a picture of the Mass Spectrometer for Planetary Exploration/Europa (MASPEX) instrument onboard the Europa Clipper. This time-of-flight mass spectrometer is longer than the one used on JUICE, but contains two reflectrons, rather than one, for an even longer drift region. This instrument will have a very high sensitivity and a high mass resolution and allow detection of heavy organic molecules with molecular weights of around 1000 amu. Reprinted with permission from Bolles, D. https://science.nasa.gov/technology/technology-highlights/supported-instruments-search-evidence-life-europa. © 2017 National Aeronautics and Space Administration.](image)

period, an extended mass range of greater than 1000 amu to allow for the analysis of any heavy organic molecules that may be present, a sensitivity as low as 1 ppt (with cryotrapping) and a
mass resolution of greater than 30,000 $\text{M}/\Delta \text{M}$.\textsuperscript{62} Such high sensitivity and resolution will allow
for unambiguous determination of the isotopes of volatile molecules, including CH$_4$, H$_2$O, NH$_3$, CO, N$_2$, CO$_2$, and small organic compounds from complex atmospheric mixtures. It will also be
able to measure trace compounds that may be present, such as argon, krypton, xenon, and their
isotopes.\textsuperscript{63} Figure 1-8 contains both a picture and a schematic of the mass spectrometer,\textsuperscript{62} which
shows that MASPEX will contain a closed source. This closed source will have a titanium
antechamber and transfer tube and will rely on electron ionization to introduce all the molecules
in a sample into the mass analyzer. Like its JUICE counterpart, MASPEX will also contain a
time-of-flight mass analyzer, with two reflectrons around the drift region for significantly longer
drift time, as the instrument itself will be roughly 400 mm long.\textsuperscript{63}

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2 A Microchannel Thermalization Inlet Design to Reduce Molecular Fragmentation in Orbital and Flyby Closed-Source Mass Spectrometers

** Note: This chapter was published as a complete, stand-alone manuscript in *Planetary and Space Science* in July 2019 and was written by Brandon M Turner, Anupriya, Sandra Osburn-Staker, Abraham De la Cruz, Parker Crowther, Logan R. Sweet, Eric T. Sevy, and Daniel E. Austin. Minor changes to correct errors in grammar and punctuation have been performed throughout the chapter to bring it into uniformity with the design and structure of the rest of the dissertation. **

2.1 Abstract

Closed-source mass spectrometers rely on thermalization of neutral molecules, which are intercepted at a high velocity relative to the spacecraft. However, encountered molecules generally impact with enough kinetic energy to drive chemical modification, obscuring the identity of native compounds. We describe a novel inlet design that reduces dissociation and other chemical changes to sampled species by quenching the impact energy faster than the dissociation process. The inlet consists of a parallel array of microchannels. Impinging molecules experience the same number and type of thermalizing collisions as in a conventional closed-source inlet, but the process is several orders of magnitude faster than it is in prior designs due to the short distance between successive impacts. Preliminary calculations using the representative molecule hexane show that the lowest energy pathway to dissociation is breaking one of the carbon-carbon bonds and that vibrationally excited neutrals survive intact only a short time after the initial impact. The *ab initio* and density functional theory calculations described here show that lifetimes of impact-induced, vibrationally excited states depend on impact velocity, molecular weight, and molecular bonding and, for hexane, are in the range of $10^{-4}$ to $10^{-10}$ seconds for encounter velocities of 9 to 13 km/s, assuming a translational-to-vibrational energy conversion of 14%. For all molecules, the microchannel thermalization inlet allows encounter velocities at least 1.3 times higher than a conventional thermalization inlet for a given level of fragmentation. With hexane, for instance, fragmentation in the microchannel inlet is negligible at velocities of 11 km/s, whereas a conventional inlet starts experiencing fragmentation of hexane at 8.5 km/s. Ram pressure enhancement is maintained using this novel inlet, preserving the improved sensitivity of closed-source designs. The microchannel thermalization inlet reduces all types of impact-induced chemical changes, including racemization, isomerization, and rearrangement, for any encounter velocity.

Keywords: impact fragmentation, closed source mass spectrometers, thermalization
2.2 Introduction

Mass spectrometers have proven to be among the most important instruments for understanding and characterizing the unique chemical composition of solar system environments. They have been included on several planetary orbiter,\textsuperscript{1,\textbf{3}} descent,\textsuperscript{4,\textbf{6}} and lander missions\textsuperscript{7-\textbf{9}} during the past 50 years, probing both ion and neutral particles and providing detailed chemical and isotopic information for a wide variety of sample types with excellent sensitivity. Mass spectrometers have been successfully used to investigate the atmospheres of Mars,\textsuperscript{1,\textbf{10-12}} Venus,\textsuperscript{3,\textbf{13}} Jupiter,\textsuperscript{14,\textbf{15}} and Saturn,\textsuperscript{16} along with its moons,\textsuperscript{17,\textbf{18}} as well as comets.\textsuperscript{19-\textbf{23}}

Such mass spectrometric investigations have been able to make discoveries of key importance, such as demonstrating the presence of water and inorganic carbonates and elucidating the gaseous composition on the surface of Mars.\textsuperscript{7,\textbf{11}} Other discoveries which drew wide attention were the presence of water with a high deuterium-to-hydrogen (D/H) ratio and an excess of noble gases in the atmosphere of Venus,\textsuperscript{13} the presence of small hydrocarbons and noble gases in the Jovian atmosphere,\textsuperscript{24} and the presence of small hydrocarbons and molecular gases like H\textsubscript{2} and CO\textsubscript{2} in the atmospheres of the moons of Saturn.\textsuperscript{25}

As with other \textit{in situ} measurement techniques, mass spectrometers must be in physical contact with samples to make measurements. For flyby and orbiter instruments, neutral molecules must be collected as they pass into the inlet at relatively high velocities. The neutral atoms and molecules are first ionized, then analyzed using one of many types of mass analyzers, such as time-of-flight,\textsuperscript{19,\textbf{21,26}} quadrupole,\textsuperscript{1,\textbf{7,10,27}} and a variety of ion traps.\textsuperscript{23,\textbf{28,29}} Two types of inlet have been in common use for several decades: the “open source”, in which neutral species are directly ionized and focused into the instrument without contact with any instrument.
surfaces; and the “closed source”, in which neutrals are collected in a small chamber, thermalized, and then diffused into the ionization region.\textsuperscript{1,30-33}

A closed source provides a significant improvement in sensitivity due to a ram pressure enhancement inside the source.\textsuperscript{24,33} The high incoming velocity and, hence, kinetic energy of neutral species is dissipated in the source through multiple collisions with the chamber walls, eventually reaching thermal equilibrium with the walls. Ram pressure enhancement is a result of the much lower velocity of thermalized neutrals leaving the closed source compared with the high velocity of incoming neutrals. As such, the ram pressure enhancement increases with the molecular mass and the encounter velocity and depends on the incident angle and the relative conductances of neutrals entering and leaving the front of the inlet or leaving toward the ionizer. Reactive gases including atomic oxygen and atomic nitrogen, however, are lost due to reaction with the walls of the chamber and cannot be analyzed. An open source allows neutrals to be ionized without having had any interactions with a surface, but the sensitivity is lower than in a closed source. Some flight instruments, such as the Ion and Neutral Mass Spectrometer (INMS) onboard the Cassini-Huygens spacecraft, have included both types of inlet\textsuperscript{16} with a shared mass analyzer.

A conventional closed source chamber is shown in Figure 2-1. Neutrals enter the source and strike the chamber wall with a velocity roughly equal to the velocity of the spacecraft relative to the ambient atmosphere or planetary surface. The initial kinetic energy of the impact is lost through multiple collisions with the chamber walls.\textsuperscript{34} Due to this transfer of energy, this chamber is sometimes referred to as a thermalization chamber. It is also referred to as an antechamber because it precedes the ionization region of the mass spectrometer.
The Cassini mission provided a wealth of data about Saturn, its rings, and several of its moons. Recent publications have revealed that the INMS instrument, despite having only a modest mass resolution and mass range, has given clear indication of the presence of organics in the exospheres of Titan and the plumes of Enceladus as sampled and measured during several flybys.\textsuperscript{25,35-38} Of special interest are the results from the more than ten flybys to Enceladus, each varying in encounter velocity, where the plume was found to be predominantly composed of H\textsubscript{2}O, CO\textsubscript{2}, CH\textsubscript{4}, NH\textsubscript{3}, and H\textsubscript{2} as the abundant species and several trace species that included complex organics. The presence of potential organics identified as C-, N-, O- and NO- bearing hydrocarbons was confirmed during lower velocity flybys, though with significant ambiguity in the results.\textsuperscript{30}

A first-principles-based reactive molecular dynamics simulation study by Jaramillo-Botero et al.\textsuperscript{39} demonstrated that significant chemical changes, such as molecular fragmentation, may occur during high velocity encounters in flyby missions. These chemical changes are driven by high velocity impact-induced fragmentation occurring in the antechamber and can lead to
incorrect identification. The simulations predicted that variations in the fraction of small molecules, such as H₂, O₂, H₂O, CO₂, and CO, would occur as a function of impact energy, consistent with the variations found in INMS data. The simulation study also showed that increasing impact velocity led to fewer impactor molecules remaining intact after a collision. The study concluded that a single neutral-surface impact may be enough to break apart some molecules even at flyby velocities as low as 5 km/s, the lowest speed studied in the simulations, while fragmentation patterns do not differ significantly at encounter velocities higher than 20 km/s.

When neutral molecules collide at high velocity with the walls of a conventional antechamber, the collision converts some of the translational kinetic energy to vibrational energy in the molecule. Energy is also converted to rotational modes, phonon modes of the surface, and recoil translational energy of the molecule. If the acquired vibrational energy in the molecule is greater than the strength of any bonds in the molecule, the molecule can dissociate. The lifetime of this vibrationally excited state can be predicted using standard chemical kinetics, such as transition state theory, and depends on both the amount of excess energy within the molecule and the time it takes for the excess vibrational energy to be statistically redistributed throughout all the bonds of the molecule. Successive collisions with the chamber walls cause a loss of energy from the molecules into the walls and reduces the vibrational excitation of the molecules. In the conventional antechamber, successive collisions with the wall, and, hence, thermalization occur on a timescale of tens to hundreds of microseconds. However, for high velocity impacts, molecular dissociation occurs faster than this. By comparison, ions formed in an electron ionization source, with only a few to a few tens of eV of internal energy, typically dissociate on a timescale of microseconds.⁴⁰
The fraction of impact kinetic energy that is converted to vibrational modes of a recoiling molecule has not been experimentally characterized for any molecules at velocities relevant to spacecraft encounters. However, this property has been measured for impacts of polyatomic ions on surfaces and is typically between 13% and 20%, with some variation depending on the properties of the molecule and surface. In this study, we use 14% because it lies within, but at the low end of, this cited range of efficiencies of energy transfer to account for the relative stiffness of the surface material. The 14% efficiency is in reference to the amount of precollision energy - initially almost all translational energy - that is transferred to vibrational modes of the molecules upon collision. To illustrate the energy available for bond dissociation due to a molecular impact, Figure 2-2 shows vibrational energy as a function of encounter velocity for several representative molecular weights, assuming 14% efficiency of translational-to-vibrational conversion and assuming a single impact only. Even at modest velocities and relatively low

![Figure 2-2: Vibrational energy available after a normal-incident molecule-surface impact. Each line represents a different molecular weight, as indicated. The flat line at 3.91 eV is the typical C-C bond dissociation energy, shown for comparison. Reprinted with permission from Turner, B.M. et al. Planet. Space Sci. 2019, 172, 1-7. DOI: https://doi.org/10.1016/j.pss.2019.04.009. Copyright © 2019 Elsevier, Ltd.](image-url)
molecular weights, the vibrational energy exceeds the typical energy of a carbon-carbon bond (3.91 eV). Although the energy is not located on a single bond, when the total molecular vibrational energy is above the dissociation energy of a single bond, the molecule has sufficient energy to dissociate with some finite lifetime.

An additional complication is that unimolecular dissociation of neutral molecules typically produces two radical fragments. After thermalization, these unstable radical molecules will stick to the walls of the antechamber and will either not be detected at all or will be detected only after recombination with another radical, such as atomic hydrogen. When this happens, the molecules entering the ionization region are not the same as those that entered the antechamber. Hence, by the time the neutral species are presented to the ionization region of the mass spectrometer, the original composition will have been significantly altered, leading to incorrect identification, even with a high-performance mass analyzer.

The present paper proposes a hardware solution to reduce such impact fragmentation while retaining the benefits of a closed ion source. The solution is based on the idea that if vibrationally excited neutrals can be cooled or thermalized faster than their dissociative lifetimes, few of them will dissociate. This can be realized if the rebounding molecule only has to travel a short distance between successive impacts. Thus, an inlet consisting of an array of microchannels allows rapid thermalization and could replace the conventional, spherical antechamber. Because of the narrow channels, the time between successive collisions is much shorter, and the neutral molecules thermalize on a timescale of tens to hundreds of nanoseconds rather than tens to hundreds of microseconds. As a result, the new microchannel thermalization inlet reduces the fragmentation of molecules that impact at high velocities.
In addition, it retains the benefits of a ram pressure enhancement to sensitivity. The channels are designed such that molecules enter with a high temperature and a high conductance and then exit the channels, after thermalization, with a lower temperature and a lower conductance. This difference between the conductance as they enter the channels and the conductance as they leave the channels is what creates the ram pressure enhancement to sensitivity and is maintained in the new microchannel thermalization inlet. The benefits of such an inlet apply to any orbital or flyby velocity and enable the detection of volatile and semi-volatile molecules that were previously undetectable due to impact fragmentation. This work can be extended to use with mass spectrometers on future planetary orbiter and flyby explorations.

2.3 Inlet Design

Figure 2-3: The design of the microchannel thermalization inlet, consisting of an array of channels, nominally 0.25 mm long and 10 microns in diameter. The plate can be any shape (left figure) and will be attached to the front of a chamber (right figure) where the molecules will collect before ionization. Reprinted with permission from Turner, B.M. et al. *Planet. Space Sci.* **2019**, *172*, 1-7. DOI: https://doi.org/10.1016/j.pss.2019.04.009. Copyright © 2019 Elsevier, Ltd.
The microchannel thermalization inlet (Figure 2-3) is simple in design, consisting of an array of channels in a plate of any shape made of suitable material, nominally stainless steel, although a variety of metals or ceramics would work. Molecules undergo a high kinetic energy initial impact like those that occur in a conventional antechamber, and subsequent impacts are likewise similar in terms of both number and energy. However, the thermalizing collisions along the walls of the channel occur at a higher frequency on a timescale of tens to hundreds of nanoseconds. This energetically cools the molecules orders of magnitude faster than in the conventional antechamber and faster than the dissociative lifetimes of many of the associated vibrationally excited neutrals.

The channel diameter governs the thermalization time and must be as small as possible without limiting the conductance of molecules to the ionizer. The aspect ratio of the channels influences the response time of the instrument, but the channels must be sufficiently long that thermalization is complete, or at least partially complete, as molecules emerge from the end of the channels. The channels are angled slightly from the ram direction so that impacts occur deep inside each channel. Because the surface of each channel wall is rough on the microscopic scale (albeit possibly smooth on the molecular scale), impact angle will have little effect on energy transfer, and the average scatter angle off the channel walls will not be specular. Adsorption and desorption do not occur at these high energies, but they do occur later as the molecules approach thermal energies.

The microchannel thermalization inlet is notably similar in structure to the common microchannel plate (MCP) electron multiplier detectors; however, the function and material are quite different for the present application. Although MCPs are generally made using lead glass, recent efforts have produced similar structures using silicon, aluminum oxide, and metals like
nickel and electroplated copper.\textsuperscript{46} Similarly, other recent efforts have produced similar structures in metal using a variety of lithographic methods, including UV-LIGA,\textsuperscript{46} electroforming,\textsuperscript{47} and photolithographic etching.\textsuperscript{44} The aspect ratio needed for neutral thermalization will also drive the selection of fabrication method. For instance, UV-LIGA does not produce channels with a high aspect ratio, although work is being done to improve the aspect ratios achievable with this method.\textsuperscript{46} In all cases, channels can be constructed with micro-scale diameters, ranging from 0.02-0.5 μm with photolithography\textsuperscript{45} to 10 μm or more with UV-LIGA.\textsuperscript{46} Future testing will determine the suitability of these materials and fabrication techniques for a flight-qualified inlet. At this point, optimal materials for this application have not yet been determined.

2.4 Theoretical Analysis of Performance

The microchannel thermalization inlet is expected to reduce or eliminate fragmentation for those vibrationally excited, recoiling molecules with lifetimes in the range of nanoseconds to microseconds. To determine lifetimes for compounds of interest under a given range of incident velocities, theoretical calculations have been performed using transition state theory (TST) to calculate rate constants as a function of temperature. The purpose in performing these calculations was to determine both dissociative lifetimes and thermalization timescales of representative neutral molecules, such as hexane. These calculations also help in determining likely fragmentation pathways in these molecules. Based on previous experimental measurements with ion-surface impacts,\textsuperscript{41} we assumed that approximately 14% of the initial kinetic energy transfers into the vibrational modes of a molecule during a collision with a surface.
One difficulty in performing theoretical calculations on unimolecular dissociation reactions is that there is no clearly defined transition state in the reaction mechanism. As such, the transition state must be assumed, which was done by simulating the breaking of a bond in the molecule to find the reaction barrier. For hexane, this meant breaking the molecule at the energetically weakest bond, which according to calculations would be either the C₂-C₃ or the C₄-C₅ bond. This would create an ethyl radical and a butyl radical, according to equation (2-1):

\[ \text{C}_6\text{H}_{14} \rightarrow \cdot\text{C}_2\text{H}_5 + \cdot\text{C}_4\text{H}_9 \]  

(2-1)

The next lowest energy bond is the C₃-C₄ bond, which would create two propyl radicals upon dissociation, according to equation (2-2):

\[ \text{C}_6\text{H}_{14} \rightarrow \cdot\text{C}_3\text{H}_7 + \cdot\text{C}_3\text{H}_7 \]  

(2-2)

As both dissociation pathways are very close in energy, separated by about 0.14 eV, incoming neutral hexane molecules with high energy could easily follow either pathway, causing the perceived dissociation to be faster and decreasing the expected dissociative lifetimes of the molecules. Therefore, the dissociative lifetimes determined in this analysis for hexane are likely upper limits.

To determine the fraction of hexane molecules that survive impact as a function of flyby velocity, we first calculated the rate constant for dissociation of hexane as a function of temperature using transition state theory, according to equation (2-3),

\[ k_R(T) = \kappa \frac{kT}{h} N_A \frac{q^\dagger}{q} e^{-\Delta E/kT} \]  

(2-3)
activated complex and the reactant, respectively.\textsuperscript{48} To calculate the partition functions of the reactant and the transition state, we first performed a geometry optimization on the reactant and searched for the transition state geometry using Gaussian-09.\textsuperscript{49} Both were done using DFT with a B3LYP functional and a 6-31G* basis set. Vibrational frequencies, as well as moments of inertia, were calculated by performing an anharmonic vibrational energy calculation. Again, this was done using Gaussian-09 using DFT with a B3LYP functional and a 6-31G* basis set. The partition functions of the reactant and the activated complex were then calculated using those vibrational frequencies and moments of inertia.

Partition functions for the reactants were calculated using the program paradensum.\textsuperscript{50} Sums and densities of states describe the number of energetic states (vibrational, electric, rotational, translational) per interval of energy at each energy level available to be occupied. A high density of states shows many possible states are available for occupation at that energy level. A low density of states means that no or very few states can be occupied at that energy level. On the other hand, the program parsctst uses semi-classical transition state theory (SCTST),\textsuperscript{51} to calculate the cumulative reaction probability (CRP) of the transition state of the dissociation reaction of each molecule. Program parsctst calculates the partition functions for the transition state of each molecule.

Due to the high translational velocities, rather than using rate constants as a function of temperature, it is more convenient to consider the hexane dissociation rate constants as a function of vibrational energy gained during impact. To determine how the vibrational energy gained corresponds to temperature, we first calculated the vibrational energy per mode at a given temperature, using equation (2-4),

\[
E_i = \sum_n \nu_i (n + \frac{1}{2}) e^{-\nu_i (n + \frac{1}{2})/kT}
\]  

(2-4)
where both the vibrational frequency and $kT$ are in units of cm$^{-1}$. The total vibrational energy was then found by summing the energy of all the normal modes, as in equation (2-5).

$$E_{vib} = \sum_i E_i$$  \hspace{1cm} (2-5)

The vibrational energy gained at a given temperature was then found by taking the difference of the energy at the temperature and the vibrational energy at 10K, which is essentially the zero-point energy. If 14% of the precollision energy,$^{41}$ which is almost all translational energy, is transferred to the molecule upon collision, we calculated an initial velocity using equation (2-6) and equation (2-7):

$$\Delta E_{vib} = 0.14 \times E_{trans}(initial)$$  \hspace{1cm} (2-6)

$$E_{trans}(initial) = \frac{1}{2}mv^2(initial)$$  \hspace{1cm} (2-7)

To find the fraction of molecules that survive the time between the first collision and the second collision, we need to know the velocity of hexane following the first collision. This is found assuming that 14% of the initial energy is transferred to vibrational energy of the hexane and that an additional 10% is transferred either into molecular rotations or the surface.$^{52-55}$ The translational energy following the first collision is then found using equation (2-8):

$$E_{trans}(final) = 0.76 \times E_{trans}(initial) = \frac{1}{2}mv^2(final)$$  \hspace{1cm} (2-8)

Using this velocity, we calculated the time required for a molecule to travel the distance either between the walls of the conventional 5 cm antechamber or between the channel walls of the 10 μm microchannel thermalization inlet. Then, assuming the dissociation of hexane is unimolecular and, therefore, first order, we calculated the fraction of incoming neutral molecules that survive into the ionization region based on the time needed to travel the distance between subsequent collisions, using equation (2-9):
\[
\frac{[\text{Hexane}]}{[\text{Hexane}]_0} = e^{-k_R t}
\]  

(2-9)

After the first collision, molecules will have significant energy in both translational and vibrational modes, but this model does not allow us to predict whether the vibrational energy will increase or decrease during the second collision.

2.5 Results and Discussion

The calculated fraction of molecules that survive the time between the first and second collisions for hexane as a function of the spacecraft flyby velocity is plotted in Figure 2-4 for both the 5 cm antechamber and the 10 µm microchannel thermalization inlet. Below a flyby velocity of 8.5 km/s, essentially all the hexane molecules sampled by an inlet with a 5 cm antechamber are expected to survive, while above 10 km/s, all hexane molecules that enter such an inlet are expected to dissociate after the initial impact. In contrast, essentially all hexane molecules that enter a probe with the proposed 10 µm microchannel inlet at velocities of less than 11 km/s are expected to survive, while above 13 km/s, all hexane molecules entering the spacecraft with a 10 µm microchannel inlet are expected to dissociate. Under these conditions, the microchannel inlet extends the range of useable velocities for detection of hexane by a factor of 1.3. Interestingly, the onset of dissociation for the 5 cm inlet, as shown in Figure 2-4, occurs at a slightly higher velocity (8.5 km/s) than the point at which the total vibrational energy from impact exceeds the typical bond dissociation energy (at 7.6 km/s) shown in Figure 2-2.

Molecules with a slight excess of vibrational energy beyond the bond dissociation energy will dissociate, but at a slow rate and with a very long lifetime. In this case, thermalization even in the 5 cm antechamber occurs more quickly than this dissociation and the molecule remains intact.
For this analysis, hexane is a representative compound; other compounds likely dissociate under similar high-velocity conditions, and the fragmentation would be similarly reduced with the microchannel inlet. This analysis also shows that at the high velocities of some Cassini flybys, no hexane could have survived intact within the antechamber. Other compounds may have been similarly affected. However, dissociation thresholds and lifetimes of other compounds are yet to be determined.

The dissociation lifetimes of other compounds will differ from those of hexane because of different impact kinetic energy (mass dependent) and different molecular bonding, but all compounds should qualitatively follow the trends shown in Figure 2-4. For the range of incident velocities corresponding to microsecond lifetimes, faster thermalization will significantly reduce fragmentation. At higher velocities, fragmentation will occur in both inlets. At lower velocities,
fragmentation is not expected to occur. Likewise, for translational-to-vibrational conversion rates different from 14% (e.g., different material used for surface impact), the same general trends of Figure 2-4 are expected. Thus, for a given velocity, some compounds may fragment while others may not, and the effect must be evaluated for all compounds of interest. When impact velocities and molecular weights of interest are so high that shattering impacts occur,\textsuperscript{56} however, rapid thermalization is no longer possible.

Materials that give a lower translational-to-vibrational transfer efficiency (i.e., materials with less stiffness to molecular impacts) should also reduce fragmentation for any inlet design or velocity range. In this case, molecules impacting at any given velocity will have less vibrational excitation, resulting in a longer dissociative lifetime. Although such materials would also benefit the conventional thermalization antechamber, a combination of a suitable material with the new microchannel thermalization design would further enhance the results presented above.

Neutrals that impact on the solid material on the front of the plate (between channels) will rebound back out into space and will not be sampled. Only molecules that enter the channels and undergo rapid thermalization will make it to the ionizer. Thus, the mass spectrometer will only detect material that has been rapidly thermalized. In contrast, lining the inside surface of a conventional antechamber with a microchannel or micro-/nano-scale porous material will produce and capture fragments of the neutrals that impacted on the front surface between the channels or pores and will give erroneous results.

Narrower channels would be expected to reduce the thermalization time and allow larger molecules and/or higher velocities to collide without fragmentation. However, considerations of channel aspect ratio and conductances are important for practical implementation. Thus, the channels cannot be arbitrarily small, and a nano-pore would require the material to be extremely
thin. The width of the channels determines the effectiveness of the microchannel thermalization inlet to adequately, and completely, thermalize incoming neutrals. Wider channels allow more molecules to enter and proceed through to the mass spectrometer. However, the ability of the channels to thermalize the neutrals is diminished as the width of the channels increases, likewise increasing the amount of fragmentation that occurs in the incoming neutrals. In contrast, the narrower the channels, the greater the speed of thermalization and the greater the range of molecules that will stay intact into the mass spectrometer. A narrower channel, however, inhibits the time response of the inlet unless the channels are thin. Unfortunately, thinner channels are more fragile, increasing the need for structural support. As such, a channel diameter of 10 μm can ensure rapid thermalization within the inlet while still maintaining the significant ram pressure enhancement, and the inlet will still be robust enough for use on flyby and orbiter space missions. The value of 10 μm used in this study was chosen as an order-of-magnitude starting point for the proposed design and as a baseline to demonstrate the effect. Channels of this size are achievable using current fabrication techniques, and this value provides the needed aspect ratio for ram pressure enhancement with a reasonable thickness for the inlet structure. Further work is needed to optimize specific inlet dimensions and should include factors such as required sensitivity of an instrument for a given mission and science target.

As expected, the microchannel thermalization inlet has a shortened timescale between successive collisions. Molecules colliding with the walls of the microchannel thermalization inlet do so at a faster rate with respect to the thermalization antechamber of the INMS onboard Cassini. Therefore, we expect significant improvement in the speed with which molecules will thermalize using this new inlet design. More molecules will then reach the ionization region of flyby and orbiter mass spectrometers intact.
2.6 Conclusion

A microchannel thermalization inlet would counteract the impact-induced fragmentation of the conventional closed ion source. It has been shown that the time between thermalizing collisions in such an inlet is significantly reduced and allows energetically excited molecules to quickly thermalize. This rapid thermalization reduces the amount of fragmentation that occurs in neutral molecules and allows more of them to reach the mass spectrometer intact, improving analysis of planetary exospheres and surfaces. The microchannel thermalization inlet also maintains a significant improvement to sensitivity due to a ram pressure enhancement. This reduced rate of fragmentation and the improved sensitivity apply to molecules of numerous molecular weights and at a larger range of encounter velocities. This inlet would enable a much better variety of compounds to be identifiable in closed ion sources on future orbiter and flyby missions. Using the new microchannel thermalization inlet, previously undetectable large compounds of astrobiological importance, such as amino acids and large organics, can be identified in tenuous space environments.

2.7 References


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3 Dissociative Scattering in High-Velocity Molecule-Surface Impacts: Astrobiological Implications for Closed-Source Mass Spectrometer Sampling

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3.1 Abstract

A theoretical study of impact-induced, high-velocity dissociation of \( n \)-alkane molecules using density functional theory and microcanonical transition state theory provides insight into the breadth and scope of chemical changes that occur after the high-velocity collisions typical of spacecraft-molecule encounters. Of key concern is how the molecular weight influences the extent of dissociation, as a higher molecular weight provides more initial energy during surface collisions in the thermalization chamber or “closed source” inlet of a spacecraft-based mass spectrometer. Calculations show that for the series of \( n \)-alkanes up to \( n=16 \), the velocity above which dissociation occurs is independent of the molecular weight of the molecule. Assuming 14% of the incoming translational kinetic energy is converted to vibrational energy in the incident molecule, a spacecraft velocity of 7.3 km/s results in half of the molecules dissociating between the first and any subsequent impacts with the thermalization chamber surface. The range of velocities at which a portion of incident molecules dissociate has a standard deviation of \( \pm 0.7 \) km/s. These values are strong functions of the surface properties and the resulting conversion efficiency of translational-to-vibrational energy. Although a higher molecular weight increases the impact energy and the resulting vibrational energy of the incident molecule, for the molecules studied, increased molecular weight also increases the number of bonds and vibrational modes of the molecule, which balances the dissociation lifetime. This trend is expected to hold for larger compounds, such as astrobiologically relevant fatty acids, amino acids, and larger hydrocarbons that may be sampled in orbiting or flyby missions. Additionally, understanding such dissociation reactions provides insight into potential fragments of native species that could be found in mass spectral composition analyses. It also provides a basis for improving the design of closed source inlets to increase the dissociative lifetimes and increase survivability of molecules of interest, thereby facilitating discovery and characterization.

Keywords: unimolecular dissociation, high-velocity impacts, dissociative rate constants, microcanonical transition state theory, closed ion source inlets
3.2 Introduction

Of prime interest and import to space research is better characterizing the unique chemical constituents and processes in the various planetary environments in the outer Solar System. Such chemical processes include the subsurface ocean and ejecting plumes on Enceladus,$^1$ the volcanic activity on Io,$^2$ and the formation of liquid methane and ethane seas on Titan.$^3$ Understanding these processes may provide deeper insight into the origins of the universe, further knowledge about the formation of the Solar System, and a better understanding of the requirements for habitability away from Earth. Without analytical techniques that can study the composition of the atmospheres, surfaces, and sub-surfaces of planetary bodies, however, it is difficult to determine possible habitable zones or important chemical processes in harsh space environments. As such, mass spectrometry is a powerful analytical tool for exploring atmospheres and surfaces throughout the Solar System.

Mass spectrometers aboard flyby and orbiter missions, which can obtain atmospheric samples and subsequently determine their composition, have become essential for space exploration. Another advantage of flyby and orbiter spacecraft is that they can sample from multiple locations during the same mission. Examples of previous flyby or orbiter missions are Cassini-Huygens, which travelled to the Saturnian system and provided glimpses of the chemistry of Jupiter along the way,$^4,5$ Galileo, which travelled to the Jovian system, but also studied an asteroid and a comet,$^2,6,7$ and Pioneer Venus and Magellan, which travelled to Venus to study both the atmosphere and the surface of the planet.$^8,9$ In each of these referenced missions, a closed ion source inlet was used to collect neutral gas molecules before they entered the ionization region of the instrument mass spectrometer.
Use of a closed ion source dates to the 1960s, when they were included on the mass spectrometers of the Orbiting Geophysical Observatory (OGO)-6 and SanMarco-3 satellites to study the magnetosphere of the Earth.\textsuperscript{10} It was particularly useful for the detection of chemically inert species, which allowed for the determination of gas density in an ambient atmosphere.\textsuperscript{11} Waite et al.\textsuperscript{4} and Mahaffy et al.\textsuperscript{12} describe a typical closed ion source inlet, which contains a spherical antechamber, usually made of metal, connected to an ionization source by means of a long transfer tube, as seen in Figure 3-1.\textsuperscript{12} Sampled gas molecules enter the antechamber through

Figure 3-1: The design of the dual inlet ion source from the Mars Atmosphere and Volatile Evolution (MAVEN) Mission spacecraft, showing a closed ion source, at the top, with a spherical antechamber and a long transfer tube, and an open ion source, just below. Reprinted with permission from Mahaffy, P.R. et al., Space Sci. Rev. 2014, 195, 49-73. DOI: https://doi.org/10.1007/s11214-014-0091-1. © 2014 Springer Nature
a small entrance aperture and then collide with the antechamber walls. After many successive collisions with the walls, incoming neutral molecules can thermally equilibrate with the walls of the antechamber and then enter the transfer tube to the ionization region of the mass spectrometer. The biggest advantage of using a closed ion source is a significant ram pressure enhancement, which leads to a heightened sensitivity and an improved limit of detection in the instrument.\textsuperscript{13,14} The higher sensitivity of the closed ion source is much better for identifying larger, lower-abundance molecules such as astrobiologically relevant or complex organic molecules. However, a problem inherent in using closed source inlets is that these high-velocity impacts collisionally excite neutral molecules that, in many instances, may dissociate before the mass spectrometer can analyze them.

Because flyby and orbiter spacecraft must travel at high velocities to reach the outer stretches of the Solar System in a timely manner and high velocities are needed for orbiting, neutral molecules that enter the closed ion source undergo a high-energy, high-velocity impact within the antechamber. These high-velocity impacts create challenges in the mass spectral analysis performed on such spacecraft. During such high-velocity impacts with the antechamber walls in closed ion source inlets, many surface-molecule interactions and processes may occur. Teolis et al.\textsuperscript{15} pointed out that water easily adsors onto the titanium surface of closed source inlets, whereas volatile molecules rapidly enter the ionization region of the mass spectrometer. Cui et al.\textsuperscript{16} studied extensively how the number density of molecules that enter the closed source antechamber from the atmosphere of a planetary body can influence wall effects and heterogeneous surface chemistry within the antechamber. Vuitton et al.\textsuperscript{17} have shown that the majority of the C\textsubscript{6}H\textsubscript{6} (benzene) molecules detected by the Cassini INMS in the Saturnian system
are likely formed on the chamber walls through recombination of C₆H₅ radicals with atomic H. In addition, the peak near channel 90, which represents C₇H₈, is a feature that can likely be explained by wall effects. Wall effects have also been used to argue for the detection of NH₃,₁⁵ which arises from atomic N and atomic H radicals in the atmosphere of Titan. Lastly, the recombination of radicals on the chamber walls has even been hypothesized in previous analysis of mass spectrometer data, which has been used to derive the densities of atomic N in the Venusian atmosphere.¹⁸

Although the chemistry of ions is different from the chemistry of neutrals, work with surface-induced dissociation (SID) of ions may provide insight into the chemistry of neutral molecules at such high velocities. Several groups¹⁹-²³ have studied impacts of ions with surfaces to probe how surface material affects the amount of dissociation that occurs due to collisions. SID experiments have shown that the amount of dissociation is highly influenced by the material with which the molecule collides. Softer surfaces, such as self-assembled monolayers (SAM), reduce the amount of dissociation caused by impacts because they result in less translational-to-vibrational energy transfer from within incoming molecules and more energy deposited into the surface. On the other hand, harder, more stiff surfaces, such as metals, increase the amount of dissociation caused by impacts because they result in a higher translational-to-vibrational energy conversion and less energy deposited into the surface. The velocities to which these ions have been accelerated have also influenced the amount of dissociation that occurs because of a collision with a surface. In these studies, higher velocities led to more dissociation. As such, the more energy that is transferred to vibrational degrees of freedom during the collision, the greater the rate of dissociation that will result from an impact.
In addition to work with ions, some theoretical work has been done to study how high-velocity impacts affect mass spectral analysis through dissociative scattering of larger molecules into more abundant, smaller molecular moieties. Jaramillo-Botero et al.\textsuperscript{24} have studied how the substantial fragmentation that likely occurs after a high-velocity impact in a closed ion source inlet antechamber complicates interpretation of data from the Cassini INMS. They found that even at relatively low velocities of about 5 km/s, molecular fragmentation caused by dissociation must be considered. Jaramillo-Botero et al.\textsuperscript{25} have also performed simulations to explore how hypervelocity impacts affect fragmentation of amino acid and fatty acid organic biosignatures over a range of velocities (1-12 km/s). They found that the fragmentation fraction is a sensitive function of velocity, impact angle, molecular structure, and impact surface material. Previous work by our group\textsuperscript{26} focused on how the dissociation of hexane occurred at a wide range of encounter velocities. To study the effect molecular weight has on the dissociation of neutral molecules following high-velocity impacts, this current work expands our previous study to include alkanes of both higher and lower molecular weights than hexane. However, this study only probes the molecular weight effect on the threshold velocity at which the weakest bond of an incoming $n$-alkane molecule dissociates. As such, the effect of excess energy within the colliding neutrals is not considered.

The high-velocity, high-energy fragmentation processes of astrobiologically important molecules, such as fatty acids, amino acids, and sugars, which are relatively large molecules, are not well understood. How the increased molecular weight of such molecules affects the amount of dissociation that occurs after such collisions is important to consider in current and future space missions. After a high-velocity impact, these large molecules contain a high amount of internal energy. If allowed to remain in this energetically excited state, these larger molecules
can readily dissociate into radical species that recombine to form many more naturally abundant, smaller molecules, such as carbon dioxide, water, and small n-alkane molecules. Due to the increased energy caused by high-velocity impacts, when a mass spectrometer used during a flyby or orbiter mission detects these smaller molecules, it is hard to determine what fraction arises from the rapid unimolecular dissociation of these astrobiologically relevant molecules and what fraction is naturally present in the native environment.

Here, a theoretical approach is employed to study the dissociative effect of surface collisions with neutral molecules of higher molecular weights. This includes a study of the likely dissociation pathways of alkane molecules, ranging from small (ethane - C₂) to relatively large (hexadecane - C₁₆). Analyzing a homologous series, such as the n-alkanes, from low to high molecular weight shows how an increase in the molecular weight influences dissociation of molecules at the high velocities reached during flyby or orbiter sampling. Such an analysis examines how neutral molecules of higher and higher molecular weights are likely to dissociate at a range of encounter velocities. The analysis described here will allow for more accurate deconvolution of compounds found in composition analyses performed during future flyby and orbiter space missions. In addition, the data shown will allow extrapolation of similar effects in a greater host of molecules, with different functional groups and even higher molecular weights.

3.3 Methods

The general method for these calculations, which has been published elsewhere,²⁶ is to use dissociative rate constants of n-alkane molecules calculated using microcanonical transition state theory (TST) to determine the survivability of incoming neutral alkane molecules in closed source antechambers as a function of impact velocity. It consists of three basic parts: first, a
calculation of dissociation energy and transition states for each C—C bond breakage product channel (C—H bond breakage channels are not considered because they have a much higher activation energy for dissociation than do C—C bond breakage channels); second, the determination of vibrational frequencies and moments of inertia for both the reactant and activated complex for each product channel; and finally, the calculation of the reaction rate constant for each product channel and the overall unimolecular rate constant for the dissociation of each n-alkane in this study using TST. These reaction rate constants are calculated as a function of internal energy deposited in the molecule during a collision, and the results are then analyzed to determine the fraction of incoming neutral alkanes that are expected to dissociate between the initial high-velocity impact and a second impact with the surface given the dimensions of typical closed ion source inlet antechambers.

Quantum computational methods were used to determine the dissociation energy and the transition state for a given reaction channel. A geometry optimization of the reactant was performed using Gaussian-09 and density functional theory (DFT) with a B3LYP functional and a 6-31G* basis set. To simulate the dissociation of a bond in any of the possible dissociation pathways, the length of the C—C bond was constrained at various lengths between 1 Å and 10 Å and the remaining bond lengths and angles were allowed to relax to their lowest energy geometry. To obtain more accurate energies for these optimized geometries along the potential energy surface for the elongation and eventual breaking of the C—C bond, a single-point energy calculation was performed using each of the geometry-optimized species with various C—C bond lengths using Gaussian-09 at the CCSD(T) level of theory with a 6-31G* basis set.

A representative potential energy surface calculated for this system is shown in Figure 3-2. As the bond is lengthened, energy increases and eventually peaks before reaching an asymptotic
value. The minimum energy point at around 1.5 Å is the minimum energy of the reactant, while the asymptotic value is the energy of the two radical product species. The maximum shown at around 3.5 Å in the figure is the energy of the activated complex or transition state between reactant and product. The difference in energy between the minimum and the transition state is used as the dissociation energy. For each reactant channel (methyl, ethyl, etc.) for the \textit{n}-alkanes studied here, this energy value was around 3.85 eV. This value compares well with the average bond enthalpy for a typical C—C bond (3.91 eV),\textsuperscript{29} which is slightly smaller than the activation energy expected, as the bond enthalpy represents a difference between the minimum of the potential and the asymptotic value, and the calculated average bond enthalpy is typically determined at 298.15 K. This reaction is what is referred to as a “barrierless” reaction, where
there is no clearly defined transition state, and it must generally be assumed. However, in such
reactions, energetic barriers for recombination occur when there is rearrangement of the products
after relaxation.\textsuperscript{30} For example, when a C—C bond in ethane breaks to form two methyl radicals,
the products need to relax to the lower energy, flat (trigonal planar) geometry. Because the
graphology of the atoms then must change, a barrier to recombination arises. This barrier can be
small, but, nevertheless, it is present. When the two methyl radicals are subsequently brought
back together, there must be an increase in energy to revert them from their trigonal planar
geometry back to their original trigonal pyramidal geometry.

The optimized geometries for the reactant minimum and the transition state maximum
were then used to calculate the vibrational frequencies and moments of inertia of each species.
Vibrational frequencies were calculated using DFT in Gaussian-09 with a B3LYP functional and
a 6-31G* basis set. Transition states are confirmed when the geometry assumed to be the
transition state based on the potential energy surface calculations has only one imaginary
frequency, or negative force constant, which defines the transition state. Moments of inertia were
then calculated using NW-CHEM code by performing a single-point energy calculation using the
geometries of the reactant minimum and the activated complex. These were also DFT, B3LYP
calculations with a 6-31G* basis set. A program written by this group (Appendix A) using TST
was then used to calculate the dissociation rate constants for each product channel of each \( n \)-
alkane, as well as the overall unimolecular rate constant (\( k_{\text{uni}} \)) and reactant lifetime (\( \tau \)). Using the
5 cm diameter of the antechamber as the distance between successive collisions, the rate constant
was then used to determine the fraction of incoming alkane molecules that will survive from the
first high-energy, high-velocity impact to the second impact. This fraction then serves as the
upper limit of surviving alkane molecules, as there will be a distribution of distances between the
first and second collisions, all of which will be shorter than the full diameter of the antechamber. In addition, no other collisions beyond surface-molecule impacts are taken into consideration, as the mean free path of alkane molecules in closed ion source inlets is on the order of tens of kilometers,\textsuperscript{14} which is much greater than the 5 cm diameter of the antechamber.

Dissociative rates and lifetimes describe the average amount of time an excited molecule will survive before it undergoes unimolecular dissociation. The more energetically excited a molecule becomes after a collision, the more rapidly it will undergo homolytic cleavage into two constituent radicals. Although improbable, in some situations with a near perpendicular impact angle, all the acquired vibrational energy from the collision could be focused into one bond almost immediately. Such shattering impacts\textsuperscript{31} cause dissociation to occur on a timescale much faster than the calculated dissociative lifetime. These situations, then, provide the lower bound on the dissociative lifetimes of neutral \textit{n}-alkanes. Most collisions will have a shallower impact angle, so there will be less energetic excitation and the dissociative lifetime will be longer. As a result, in any high-velocity collision between a molecule and an antechamber, there is a range of dissociation lifetimes that could occur as the energy partitions differently into vibrational modes in the molecule. For this analysis, molecules are assumed to undergo internal vibrational redistribution (IVR) before dissociation occurs. As such, the results adequately describe an upper bound on the dissociative lifetimes of neutral \textit{n}-alkanes after such collisions.

Of further note, depending on impact conditions, such as the surface material, impact angle, and orientation of the molecule during the impact, a significant amount of the initial translational energy is lost during a collision. Roughly 10\% of the initial kinetic energy is lost to the surface and, for this study, 14\% is assumed to be converted to internal energy. Based on work done by other groups using SID,\textsuperscript{19-23} an energy transfer efficiency of 14\% is a safe and
reasonable assumption to use to describe the energetic effect a metal surface would have on a molecule that impacts at a shallow (<45°) angle. However, the energy loss to the surface and the T-to-V conversion rate can both vary with changes to the smoothness of the metal surface of the antechamber. As the smoothness of antechamber walls improve, the effects of the orientation of the incoming molecules and the angle at which they collide will become more evident.25

Due to the loss of kinetic energy, the molecule will have a lower velocity after the collision and will travel more slowly to the second collision, impacting with less energy than before. The fraction of alkane molecules that survive this initial high-energy collision is then found by comparing the amount of time it takes for the molecule to undergo a subsequent surface collision and the dissociative lifetime. If the time between collisions is shorter than the dissociative lifetime, the molecule remains intact after the initial collision and will reach the second collision, during which it loses additional energy. This process continues until the molecule thermally equilibrates with the walls of the antechamber and either adsorbs to the antechamber walls, recombines with other molecules or radicals, and later desorbs before entering the transfer tube or travels directly through the transfer tube into the ionization source of the mass spectrometer. The mass spectrometer then provides a signal that relates directly to native chemical species, rather than fragmented species derived from native molecular species. These spectra can then be convoluted with spectral patterns of known ionization fragmentation to produce an accurate determination of atmospheric composition.

3.4 Results and Discussion

Dissociative Rate Constants
Dissociative rate constants for C₂ (ethane) through C₁₆ (hexadecane) were calculated as a function of internal energy added from a single collision with a surface. A dissociative rate constant describes the probability of a molecule to undergo unimolecular dissociation into fragments, such as methyl, ethyl, or propyl radicals in the case of neutral alkane molecules.

Figure 3-3 shows the dissociative rate constants of each of the alkanes studied here as a function of how much energy is added to vibrational modes of the molecule after a high-velocity impact. Energy added is related to the initial velocity of the spacecraft in relation to the molecule, assuming a translational-to-vibrational energy conversion factor of 14%. Figure 3-3 has no crossover points, signifying that energy is added to each alkane molecule in a stepwise manner, without regard to molecular weight. However, when the energy axis in Figure 3-3 is converted to velocities using the equation \( E_{\text{kin}} = \frac{1}{2}mv^2 \), the mass of each specific alkane used in the
calculation shifts the graph for that alkane differently and crossover points between the rate constant curves of the alkanes develop. These “crossover points” are where the dissociation of

![Graphs showing dissociative rate constants of alkanes as a function of encounter velocity.](image)

Figure 3-4: The dissociative rate constants of alkanes as a function of encounter velocity. A small alkane (ethane, in blue), two intermediate alkanes (hexane, in black, and decane, in green), and one large alkane (tetradecane, in red) were chosen in the top graph to show how the rate constant changes depending on the molecular weight of the alkane. As can be seen in the graph, the rate constant values are all similar at approximately 7.5 km/s and the rate constants for each alkane cross one another at some point near this threshold. To better show how each of the rate constant lines cross each other, the bottom graph shows a close-up of the region around 7.5 km/s.
two unique alkanes occurs at the same rate and on the same timescale. Figure 3-4, then, shows the dissociative rate constants of each of the alkanes as a function of the encounter velocity. As can be seen, the crossover points between the alkanes each occur around a velocity of 7.5 km/s, meaning that at a velocity around 7.5 km/s, each alkane will dissociate in roughly the same amount of time.

Energy and Influence of Increased Molecular Weight

For each reactant channel (methyl, ethyl, etc.) for the \( n \)-alkanes studied here, the calculated bond dissociation energy value \( (E_a) \) was around 3.85 eV. Using physical laboratory experiments, Blanskby and Ellison\(^{29}\) determined the C—C bond enthalpy in alkanes to be roughly 3.91 eV. Once enough energy is transferred into a dissociative vibrational mode of the

![Figure 3-5: Vibrational energy available in neutral \( n \)-alkanes after a normal-incident molecule-surface impact assuming 14% of the initial translational energy transfers into vibrational energy within the molecule. Each line represents any molecule of a certain molecular weight, as indicated. The flat line at 3.91 eV is a typical C-C bond dissociation energy, shown for comparison.](image)
neutral to surpass $E_a$, the molecule can dissociate. The total kinetic energy increases as the molecular weight of the alkane increases. This effect, according to the equation $E_{kin} = \frac{1}{2} m v^2$ and assuming a 14% T-to-V energy conversion rate, is shown in Figure 3-5. If this graph is adjusted to instead show the exact velocity at which onset of dissociation occurs according to molecular weight, the results show a downward trend, as seen in Figure 3-6. With more energy available during a collision at a similar velocity, due to a higher molecular weight, more energy is transferred into vibrational modes of incoming neutral molecules, allowing the activation

Figure 3-6: The velocity at which any dissociation of a neutral $n$-alkane molecule occurs as a function of the molecular weight of the alkane with a 14% efficiency of energy transfer. According to $E_{kin} = \frac{1}{2} m v^2$, a molecule with a higher molecular weight will provide more energy into vibrational modes of the molecule and will cause dissociation to occur at lower velocities. This graph shows the trend for the n-alkanes through icosane ($C_{20}$), at which point it seems the velocity at which dissociation first occurs seems to be reaching an asymptotic value.
energy for bond dissociation of a C—C bond to be achieved more rapidly. As such, if a
difference in molecular weight was the most important factor to consider for unimolecular
dissociation in closed ion sources, as the molecular weight increased, the amount of dissociation
should likewise increase. However, our results show that this is not the case, which means other
factors must be considered in such analyses.

Number of Energetic Modes (Energy Partitioning)

As each successive alkane molecule has an additional -CH₂- unit, there are more bonds,
and, hence, more vibrational modes in the molecule. Having more energetic modes means there
are more places to store energy in the molecule and the transferred internal energy takes longer
to focus into one bond. This increases the dissociative lifetime and, for a given amount of
energy, makes it more likely that the molecule will survive the initial high-energy collision and
make it into the ionization region of the mass spectrometer. Two higher-energy C—H bonds
(bond enthalpy, 4.38 eV)²⁹ are added, whereas only one lower-energy C—C bond (bond
enthalpy, 3.91 eV)²⁹ is added. As C—C bonds are weaker, one of them is much more likely to
break in this process. But, two higher-energy bonds are also added, which allows more of the
vibrational energy to be distributed into the C—H bonds and reduces the amount of energy
available to partition into the C—C bonds. This reduces the overall amount of energy available
for distribution into the dissociative bonds of the molecule.

Dissociative Pathways

With the addition of a -CH₂- group, each alkane molecule gains an additional dissociation
pathway. For example, an ethane molecule can only dissociate into two methyl radicals, as seen
in equation (3-1):
$H_3C - CH_3 \rightarrow 2(\cdot CH_3)$ \hspace{1cm} (3-1)

Hexane, however, has five C—C bonds. This means that there are five places within the molecule where dissociation is essentially equally likely to occur. Only three of these dissociative pathways are unique, however, as two of the pathways could occur twice from equivalent C—C bonds. Accordingly, hexane has two equivalent C—C bonds that dissociate into a methyl radical and a pentyl radical, as seen in equation (3-2), two equivalent C—C bonds that dissociate into an ethyl radical and a butyl radical, as seen in equation (3-3), and one C—C bond that dissociates into two propyl radicals, as seen in equation (3-4):

$H_3C(CH_2)_4 - CH_3 \rightarrow H_3C(CH_2)_3H_2C \cdot + \cdot CH_3$ \hspace{1cm} (3-2)

$H_3C(CH_2)_3 - CH_2CH_3 \rightarrow H_3C(CH_2)_2H_2C \cdot + \cdot CH_2CH_3$ \hspace{1cm} (3-3)

$H_3C(CH_2)_2 - (CH_2)_2CH_3 \rightarrow 2(\cdot CH_2CH_2CH_3)$ \hspace{1cm} (3-4)

As each C—C bond in the alkane requires roughly the same amount of energy to dissociate, some combination of these four radicals will be produced after high-velocity impacts with a surface. Each additional pathway provides more places where a molecule could potentially break and, as such, the dissociative rate constant for each unique pathway must be taken into consideration. At very high velocities (>20 km/s), even at a low energy transfer efficiency of 5%, there is enough internal energy transferred into the molecule after a collision that any C—C bond in the molecule could break. As such, molecules detected by a spacecraft mass spectrometer travelling at these speeds would be small fragments or products of subsequent reactions rather than native, intact chemical species.

50% Dissociation Velocities
Figure 3-7 shows a plot of the velocity at which half of the incoming neutral alkanes would be expected to dissociate between the first and second collisions as a function of molecular weight. As can be seen, this velocity is essentially constant for all molecular weights studied. The 50% survival velocity for the alkanes studied here is approximately 7.5 km/s. While the uncertainty in energy calculations for reactants and transition states is 0.5% or less, the uncertainty in calculated activation energies can be much larger. Single point energies calculated using Hartree-Fock have typical errors of 0.5% for small molecules, while energies calculated at the CCSD(T) level of theory performed here have even smaller error. To account for this, we have used an uncertainty in the calculated values of activation energy of ±5%, which is a generous upper bound for the uncertainty in the calculated values of activation energy and provides a range of likely velocities for dissociation shown by the error bars in Figure 3-7. These
error bars provide a 50% dissociation velocity range for each neutral \( n \)-alkane of ±0.3 km/s. The velocity is clearly constant in that range of worst-case uncertainty. Indeed, the scatter in the 50% survival velocity is much smaller than the velocity range obtained using ±5% uncertainty of activation energy, suggesting that the uncertainty in the calculated activation energy is indeed much smaller than ±5%.

In addition, each of the factors previously discussed plays an important role in determining how much dissociation will occur. A greater molecular weight leads to more energy transferred into internal energy within the molecule, which should decrease the dissociative lifetime of neutral molecules and cause more widespread dissociation. However, there are more energetic modes into which this converted energy can partition. In addition, each successively larger alkane molecule contains two additional C—H bonds, which require almost 0.5 eV more energy per bond to dissociate than do C—C bonds.29 This means that even more internal energy must be added to the molecule before enough energy will partition into a C—C bond to cause dissociation. The dissociative lifetime of the alkane molecules increases, offsetting the decrease in the dissociative lifetime caused by the increase in the overall internal energy acquired from the first, high-velocity collision in the antechamber.

The results in Figure 3-8 show varying levels of calculated survivability of neutral alkanes, ranging from 99.99% of the molecules surviving the first collision to only 0.01% of the incoming neutral alkane molecules surviving the initial collision. It is interesting to note in Figure 3-8 that if the lines are extended, they seem to converge to a molecular weight of about 1200 amu and an encounter velocity of about 8 km/s. Said another way, at a velocity above 8 km/s, very few (0.01% or fewer) molecules of high molecular weight (>1000 amu) with dissociation energies and a number of vibrational modes similar to the neutral \( n \)-alkane
Figure 3-8: The velocity at which a certain amount of incoming neutral alkane molecules will survive the initial collision in a closed source antechamber as a function of molecular weight. Each line represents a different survival percentage, ranging from 99.99% of the incoming molecules surviving (dark purple line, at bottom) to only 0.01% of the incoming neutrals surviving (green line, at top). The other lines are 99.9% survival (gold yellow), 99% survival (blue), 90% survival (orange), 50% survival (black), 10% survival (light gray), 1% survival (light purple), and 0.1 % survival (light blue), as indicated.

molecules studied here will survive the initial high-velocity impact to the second collision and, as such, will not be accounted for in any subsequent mass spectral analysis. This finding is important because previous space missions to the outer planetary systems were often travelling at velocities higher than 8 km/s when measurements were taken. As such, all experimental data
acquired during these missions would have significant contributions from impact-induced unimolecular dissociation.

Efficiency of Energy Transfer

One of the largest unknown variables of these studies is how much of the initial kinetic energy of the molecule is transferred into vibrational energy during a collision with the surface.

Figure 3-9: The range of velocities where unimolecular dissociation of neutral alkane molecules occurs. Each shaded region represents a Gaussian distribution (where the darker middle of each region is the average of the distribution) of encounter velocities within a certain efficiency of energy transfer where dissociation will occur after the first collision. The orange shaded region corresponds to a 5% energy transfer efficiency, the green shaded region corresponds to a 14% energy transfer efficiency, and the blue shaded region corresponds to a 25% energy transfer efficiency. As can be seen, even at velocities as low as 4 km/s, small alkane molecules will dissociate if the energy transfer efficiency is 25%.

Previous work with collision-induced dissociation (CID) and surface-induced dissociation (SID) done by other groups\textsuperscript{19-23} helps describe certain conditions that determine the efficiency of
energy transfer. With harder surfaces, such as metals, the efficiency of energy transfer is generally much higher, even in glancing collisions, and dissociation occurs at much lower velocities, as seen with the bottom, blue-shaded region in Figure 3-9. With softer surfaces, such as self-assembled monolayers (SAMs), the efficiency of energy transfer is significantly reduced, even in more direct impacts, and dissociation occurs at much higher velocities, as seen with the top, orange-shaded region in Figure 3-9. The middle, green-shaded region in Figure 3-9 represents a 14% efficiency of translational-to-vibrational energy conversion, which was used throughout this study. Another important factor to consider in the determination of the efficiency of energy transfer in such high-velocity impacts is the angle of the inlet or antechamber relative to the ram direction of the spacecraft.

Figure 3-9 shows graphically how the survival of incoming n-alkane molecules depends on the efficiency of transfer from translational energy to vibrational energy. It shows the range of velocities at which unimolecular dissociation of such molecules will occur in the closed ion source inlet antechamber. Each shaded region represents a Gaussian distribution where the darker middle of the shaded band is the average velocity. As can be seen, regardless of whether the collision results in a 5% efficiency, a 14% efficiency, or a 25% efficiency, the velocity at which half of the incoming, neutral n-alkane molecules dissociate is essentially the same.

Future space missions are planning to use a closed ion source inlet with a spherical antechamber as previously described. It is expected that similar results will come from such missions, with uncertainty not in what molecules are found, but in whether the results of composition analyses show native chemical species from the atmosphere or dissociation products from larger neutral molecules. For example, Figure 3-9 shows that with a 25% efficiency of energy transfer, even at velocities as low as 4.5 km/s, the projected velocity of the proposed
Europa Clipper, there will likely be significant dissociation of neutral alkane molecules before mass spectral analysis. In addition, even at a 5% efficiency of energy transfer, molecules with different chemical bonds (i.e., alkenes, alkynes) and different functional groups (i.e., fatty acids, amines) will still undergo significant fragmentation even at moderate speeds (>10 km/s).

There are several solutions to the dissociation problem in closed ion source inlets. Flying the spacecraft at slower velocities would reduce the initial kinetic energy and provide less internal energy after molecules collide with a surface, regardless of the translational-to-vibrational transfer efficiency. In addition, choosing a softer impact material for the surface would reduce the T-to-V conversion efficiency altogether, reducing the amount of energetic excitation of incoming neutral alkane molecules, further reducing dissociation. Having an inlet with a shorter distance between successive collisions, as in the microchannel thermalization inlet proposed in a previous publication by this group,26 reduces the path of the excited neutral and allows thermalizing collisions to occur more rapidly. Regardless of what solutions are implemented for surface material or surface stiffness, however, the dissociation of higher molecular weight compounds will be roughly the same as for small compounds. As such, if the dissociation problem is solved for smaller compounds, it will also be solved for larger compounds.

3.5 Conclusion

The work presented here expands the work previously done by this group26 on dissociation calculations of alkane molecules. It was found in the current study that as the molecular weight of each alkane increases, the velocity at which half of the incoming alkane molecules will likely survive the initial high-velocity impact remains essentially constant. Several factors influence the
amount of dissociation that occurs after such collisions: the added translational energy due to an increased molecular weight; the increased number of bonds, which add more energetic modes to each alkane; the number of dissociative pathways increasing with each additional -CH₂- group; the efficiency of energy transfer after the collision; and how the dissociative rate constants change as the molecular weight increases. This study shows that an increase in molecular weight is not the primary determinant in how many neutral alkane molecules dissociate in the antechamber of the closed ion source inlet. In addition, the flat curve of dissociation behavior as a function of molecular weight is the case regardless of the assumptions made about the T-to-V conversion rate. As such, there are three main solutions to the dissociation problem in closed ion sources: 1) fly future spacecraft missions at lower velocities; 2) reduce the T-to-V conversion efficiency by using a softer impact material for the antechamber walls or changing the angle of the antechamber orifice; and 3) reduce the pathlength of the excited neutral after the initial, high-energy collision by using a different inlet design, such as the proposed microchannel thermalization inlet.

3.6 References


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Towards a Greater Understanding of Dissociation After High-Velocity Impacts: Comparing Theory to Experimental Data

4.1 Abstract

Theoretical calculations using neutral \( n \)-alkanes have provided much information about dissociative processes in closed ion sources. Such calculations have shown that unimolecular dissociation is widespread in such closed sources and causes significant errors in the determination of atmospheric compositions. However, the theoretical results indicate that molecular weight is not the only factor in determining how widespread this dissociation is. The current work has only been performed using the first collision in the antechamber and only for the \( n \)-alkane family.

Further work will study the effect that different molecular moieties, such as the carboxyl (-COOH), alcohol (-OH), and amine (-NH\(_2\)) functional groups, have on the dissociation of neutral molecules after a high velocity, high energy thermalizing collision. Decomposition and dissociation of the carboxyl and amine functional groups, especially, could cause significant amounts of carbon dioxide (CO\(_2\)), carbon monoxide (CO), and ammonium (NH\(_3\)) to form and significantly increase their concentrations in mass spectral analyses in space.

In addition, further work will be done to analyze the amount of dissociation after multiple collisions. During successive collisions, neutral molecules will gain additional vibrational energy, which will increase the amount and the rate of dissociation in closed source inlets. Determining both the amount of additional vibrational energy gained in each collision and how that additional energy affects the dissociation patterns of neutral molecules in closed source antechambers can show how many collisions are required and how often those collisions must occur for molecules to remain intact. This information will shape future inlet designs that will reduce or eliminate molecular fragmentation in closed source inlets, such as the proposed microchannel thermalization inlet.

Lastly, applying the theoretical results to laboratory experiments can provide additional evidence for dissociation in closed ion source inlet antechambers. Physical laboratory experiments can also provide a way to test the effectiveness of hardware solutions that try to reduce or eliminate such widespread unimolecular dissociation.

Keywords: dissociation, microchannel thermalization inlet, carbon dioxide
4.2 Future Work

Current Theoretical Efforts

Two additional projects to understand more specific effects and processes of high-velocity dissociation are currently underway. The first undertakes a similar theoretical approach applied to the \( n \)-alkane molecules to understand better the dissociation of \( \text{CO}_2 \) into its CO and O constituents. Rate constants for the dissociation of \( \text{CO}_2 \) into CO and O can be determined. Much like the alkanes previously studied, this reaction has multiple potential pathways. Although there is only one unique bond in \( \text{CO}_2 \) (two \( \text{C}=\text{O} \) bonds), depending on the parameters of the reaction, the molecule can follow the higher energy dissociation pathway and homolytically cleave into ground state CO and ground state oxygen; or the molecule can follow the lower energy dissociation pathway and homolytically cleave into ground state CO and triplet state oxygen.\(^{1-3}\) As there are two potential dissociation pathways, one with more energy than the other, each needs to be further studied and correlated with the other to determine which pathway dominates in high-energy situations and how that changes the dissociative rate constants. Determining the energies of dissociation in each case, along with where the potential energy surfaces cross each other, will show how much such intertwined dissociative processes can influence the perceived \( \text{CO}_2/\text{CO} \) ratios and \( \text{O}_2/\text{O} \) ratios found in previous closed source space missions.

The second additional project to delve deeper into high-velocity impact dissociation is to look at what happens after the first collision. The present study used only the time between the first and second collisions to determine if a molecule would survive intact into the ionization region of the mass spectrometer. However, Carignan et al.\(^4\) point out that most incoming neutral molecules will undergo many collisions in the closed source before being analyzed by a
spacecraft mass spectrometer. It is unknown how many collisions occur between an incoming neutral molecule and the walls of a closed source antechamber and transfer tube before analysis in the mass spectrometer occurs. During successive collisions, the molecule gains additional vibrational energy while losing additional translational energy, both to the wall surface and into vibrational modes. However, neutral molecules will likely only gain additional vibrational energy from some small number of successive collisions and then the vibrational energy will also start to be lost upon further collisions with the antechamber walls. As such, as molecules undergo further collisions in the antechamber, they may not only become more vibrationally excited, but they may also ultimately travel slower to the next collision. This slower translational speed means that each colliding molecule spends more time in an excited state and is more likely to dissociate after successive collisions than after the initial collision. One goal of future work is to determine how many collisions need to occur before the molecule will thermally equilibrate with the walls of the antechamber (where essentially no further energy is lost or gained after a collision), and the molecule is energetically cold enough to halt all further dissociations.

Future Theoretical Efforts

Future theoretical work with dissociative rate constants of molecules after a high-velocity impact is a two-fold project. First, and most important, is performing similar calculations as those described in this work on molecules that have a variety of functional groups. Among the functional groups that could provide the most insight into not only the results from previous space missions, but also many future space missions, are carboxylic acid groups, with their definitive -COOH moiety, and amino acids, with both a -COOH moiety and an amine (NH₂) moiety. Molecules containing a -COOH group, such as a fatty acid, could form a carboxylic
group upon dissociation, which could then lose its hydrogen atom to become CO$_2$. Additional processes of CO$_2$ production, such as this dissociative process, could lead to the discrepancies found in the results from Cassini INMS.$^{5-7}$ As these molecules are important potential biomarkers, a presence of stable concentrations of CO and CO$_2$ in a space environment could indicate future or past habitability in that location. There have also been discrepancies discovered with other mixing ratios,$^{8,9}$ some of which may be influenced by CO$_2$ and CO. In addition, NH$_2$ could dissociate from an amino acid (or other nitrogen containing compound) and then recombine with a hydrogen atom on the surface of a closed source antechamber to become ammonia, NH$_3$, or even ammonium, NH$_4^+$, which could also help explain the presence of NH$_3$ in places where it was not expected or discrepancies in determined concentrations.$^{5,10}$ Further theoretical work with these two functional groups could provide clues as to how these molecules may have been created during the formation processes of the Solar System.

What makes such molecules particularly interesting to study is that any molecules containing a heteroatom, any atom that is not carbon or hydrogen, have different chemistry than their purely hydrocarbon counterparts. This is due, in part, to the electronegativity of the individual heteroatoms. For example, a C—C bond where one of the carbon atoms is also bonded to an oxygen atom, as is the case in ethanol, tends to be weaker than a C—C bond with both carbon atoms only bonded to hydrogen. This is due to the electronegative oxygen atom stealing electron density from the neighboring C—C bond. The C—C bond in ethane contains roughly 3.91 eV of energy, whereas the C—C bond in ethanol contains roughly 3.78 eV of energy.$^{11}$ While not significantly different, the lower bond energy of a C—C—O bond makes any molecule with a functional group containing a C—O bond easier to dissociate than their similar $n$-alkane counterpart. As such, small molecules found in planetary atmospheres that
contain a C—O bond, such as CO₂ or CO, could arise from dissociation of larger, complex hydrocarbons that contain a carboxylic acid, ketone, ester, or aldehyde functional group.

Nitrogen, on the other hand, strengthens the neighboring C—C bond. Although the electronegativity of nitrogen is close to that of the electronegativity of carbon, a stronger C—C bond in nitrogen-containing compounds is due to the nitrogen atom donating electron density into the neighboring C—C bond. In addition, the triple bond of C—N has delocalized electron density, which strengthens the bonds in the entire molecule, much like in an aromatic ring, and makes it harder for such molecules to dissociate. As such, C—C—N bonds tend to be much stronger than C—C—O or C—C—C bonds. For example, as previously mentioned, the bond dissociation energy of the C—C bond in ethane is roughly 3.91 eV. The bond dissociation energy of acetonitrile, however, where a C—C bond with one of the carbon atoms bonded to a nitrogen, is roughly 5.43 eV, nearly 1.5x stronger than the C—C bond in the similar n-alkane. As such, it would take much more energy transferred into vibrational modes during collisions at much faster encounter velocities for neutral molecules containing a C—N bond to dissociate. Although the C—N bond is not the weakest bond in the molecule, it makes every neighboring bond, even C—C bonds, stronger, causing a higher barrier for dissociation and making molecules containing C—N bonds more likely to be observed in planetary exospheres.

Another goal of future theoretical work is to expand the alkane study to include alkenes and alkynes, that have stronger C—C bonds than their alkane counterparts. These stronger C—C bonds come in the form of double and triple bonds, which require more energy to dissociate as multiple bonds must be broken simultaneously. C=C and C≡C bonds in and of themselves are stronger, which makes a molecule much less likely to dissociate after a high-energy impact in a closed source antechamber. A typical C≡C bond contains roughly 6.33 eV of energy and a C≡C
bond contains roughly 8.65 eV of energy. Work published by Yu-Ran Luo\textsuperscript{11} has even shown that proximity to a multiple bond, as seen previously with C—N bonds, can strengthen neighboring C—C bonds. For example, the C—C bond where one of the carbons is bonded to another carbon with a multiple bond, such as in 1-butene and 1-butyne, has a higher bond dissociation energy than in their \textit{n}-alkane counterpart. This means that the C—C—C bond in butane contains roughly 3.91 eV of energy, whereas the C—C=C bond in 1-butene contains roughly 4.33 eV of energy and the C—C≡C bond in 1-butyne contains nearly 5.38 eV of energy!\textsuperscript{11}

Much like the C—H bonds of \textit{n}-alkanes, which require more energy to dissociate than C—C bonds, these higher energy bonds (C—C—N, C—C=C, C—C≡C) can absorb more of the vibrational energy acquired during a high-velocity, high-energy impact as it distributes through the molecule and will cause a decrease in the amount of dissociation that occurs. It will take the transferring vibrational energy longer to focus into a weaker bond, such as a C—C—C bond or a C—C—O bond, and the dissociative lifetime will increase accordingly. These differences in dissociation energy equate to an increase in the dissociation velocity of only about 0.25 km/s (from alkanes to alkenes) and only an additional 0.5 km/s (from alkenes to alkynes) before a significant number of molecules containing such bonds would dissociate. As such, at similar velocities to those flown in previous space missions, any molecules detected in mass spectral analyses containing multiple bonds would arise from native species present in the planetary atmosphere, rather than from dissociative products.

Two other things should be considered in such analyses. First, IR data has shown abundances of each of these classes of compounds at other planets. Water is an astrobiologically important molecule because it can allow life to flourish. Many minor planetary bodies, including Europa, Enceladus, Callisto, and Ganymede, have either been proven to contain water (usually in
the form of ice) on or under its surface or in the atmosphere or are believed to contain large water oceans under their surface. Water contains a hydroxyl (-OH) group, which can also form from the dissociation of larger molecules. Fatty acids and amino acids contain a carboxyl (-COOH) group, from which the astrobiologically important CO and CO₂ can form. CO₂ especially could be a bioproduct of biological processes, such as aerobic respiration, and could signify life or possible habitable zones. So, being able to observe these compounds in the atmospheres and on the surfaces of planetary bodies both major and minor would be important. A further knowledge of dissociation pathways of molecules containing such groups would help in the convolution of mass spectra from such places.

Formation of stable products can also drive the dissociation of certain bonds. For example, when a fatty acid dissociates, a carboxyl moiety (-COOH) is created. With loss of a hydrogen, which would happen on the metal surface of a closed source, this carboxyl group would become a very stable CO₂ molecule. In addition, internal rearrangement of the atoms and a hydrogen transfer followed by direct release of CO₂ could occur. In decomposition of carboxylic acid solids, for example, a loss of CO₂ occurs, but the hydrogen might be pulled off by a neighboring molecule first. In gas-phase ion reactions, rearrangements of vibrationally excited species are common and can lead to direct loss of neutral products, such as CO₂. In either case, the CO₂ molecule is energetically favorable to either the -COOH group or any associated radical product. In the case of alkane dissociation, two radicals are always formed in the homolytic cleavage. These radical products are not stable and will readily react with another radical or gas atom, especially hydrogen, to form a new, energetically stable molecule. A more stable product can cause a lower, or more reachable, dissociation barrier, as nature prefers the
lowest energy option. If the products formed from unimolecular dissociation are more energetically favorable overall, the reaction will proceed more often in that direction.

Experimental Data

Results from previous space missions, such as Cassini\textsuperscript{13-15} and MAVEN,\textsuperscript{16-18} show an abundance of small molecules, with benzene (C\textsubscript{6}H\textsubscript{6}) being the most abundant “larger” molecule discovered. Performing laboratory experiments to probe the dissociation patterns of a host of neutral molecules, including those with different functional groups (i.e., -COOH, -OH, -NH\textsubscript{2}), can provide insight into how such small molecules may have formed. Much work has been done to study dissociation caused after ion-surface impacts, but the chemistry of neutrals is much different, and laboratory work with neutrals impacting at high velocities is limited. With high-velocity impact dissociation so prevalent in any analysis done with a closed source instrument, it can be hard to determine accurately the concentrations of native species in planetary exospheres. Knowing beforehand the dissociative tendencies of larger molecules can help explain why there may be discrepancies in obtained molecular concentrations. Using the data from previous space missions that used closed sources and comparing those to our experimental data, we can determine likely dissociative pathways that molecules may have undergone after high-velocity collisions in closed ion sources and how that may have affected future analyses with such instruments.

After determining such information using an inlet like the conventional closed source antechamber, results can then be compared to those obtained using the new microchannel thermalization inlet, described in Chapter 2. This inlet seeks to reduce the amount of time between successive thermalizing collisions. If energetic redistribution can occur more rapidly,
even down to the same time as the dissociative lifetime of such excited molecules, then the molecule should remain intact all the way into the ionization region of the mass spectrometer. Previous work by this group, as described in Chapter 2, shows that reducing the amount of time the excited neutral molecules spend between collisions can drastically improve the number that survive such high-velocity impacts, thus reducing unimolecular impact dissociation. This improvement in the number of molecules that reach the ionization region of the mass spectrometer is roughly 1.3x, which would allow more molecules of a larger range of molecular weights to be analyzed. In reducing the amount of dissociation that occurs, a more accurate determination of the composition of atmospheric conditions in the Solar System can be found.

4.3 References


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program RateConstant

c This program calculates the rate constant for the unimolecular dissociation of
c neutral molecules during high-velocity impacts like those between a spacecraft
c and a neutral molecule in an ambient atmosphere in the Solar System. It also
c calculates the change in vibrational energy based on the change in temperature
c that occurs during the collision and finishes with the fraction of incoming
c molecules that survive after the initial high-velocity, high-energy impact.

parameter (max=20000)

dimension h(max),p(max),rate(max),tau(max) ! Arrays
dimension Evib(max),EV(max),deltaE(max) ! Arrays
dimension Etrans05(max),v05(max),Esur05(max) ! Arrays
dimension Efin05(max),vf05(max),time05(max),s05(max) ! Arrays
dimension Etrans10(max),v10(max),Esur10(max) ! Arrays
dimension Efin10(max),vf10(max),time10(max),s10(max) ! Arrays
dimension Etrans12(max),v12(max),Esur12(max) ! Arrays
dimension Efin12(max),vf12(max),time12(max),s12(max) ! Arrays
dimension Etrans14(max),v14(max),Esur14(max) ! Arrays
dimension Efin14(max),vf14(max),time14(max),s14(max) ! Arrays
dimension Etrans16(max),v16(max),Esur16(max) ! Arrays
dimension Efin16(max),vf16(max),time16(max),s16(max) ! Arrays
dimension Etrans18(max),v18(max),Esur18(max) ! Arrays
dimension Efin18(max),vf18(max),time18(max),s18(max) ! Arrays
dimension Etrans20(max),v20(max),Esur20(max) ! Arrays
dimension Efin20(max),vf20(max),time20(max),s20(max) ! Arrays
dimension Etrans25(max),v25(max),Esur25(max) ! Arrays
dimension Efin25(max),vf25(max),time25(max),s25(max) ! Arrays
double precision weight,mass,rxn,Ea,temp,kappa,q ! General Terms
double precision pi,planck,boltzk,boltzc ! Constants
double precision RIa,RIb,RIc,TSIa,TSIb,TSIc ! Moments of Inertia
double precision MIa,MIb,MIc,MTSIa,MTSIb,MTSIc ! Moments of Inertia (adj)
double precision Qrot1,Qrot2,Qrot3,QROT ! R Rot Partition Functions
double precision QrotTS1,QrotTS2,QrotTS3,QTSROT ! TS Rot Partition Functions
double precision QVIBR,QVIBiR,denR,QR ! R Vib Partition Functions
double precision QVIBTS,QVIBiTS,denTS,QTS ! TS Vib Partition Functions
double precision theta,NMR,DNM,Emin ! Emin Vib Energy Variables
double precision THT,NUME,DENO,ETOTAL ! Vib Energy Variables
integer n,T ! Whole Numbers
character*40 filein,fileout,name ! Text Strings
pi=acos(-1.0) ! 3.14159265 radians
planck=6.62607004081E-34 ! Units of: J*s
boltzk=1.38064852790E-23 ! Units of: J/K
boltzc=0.69503476630E+00 ! Units of: cm-1/K

print 01
01 format('$What is the input filename?')
read (5,*)filein
open(unit=4,file=filein,status='old')
read (4,*)name ! Name of the Reactant
read (4,*)weight ! Mass of the Reactant (amu)
read (4,*)rxn ! Activation Energy (hartree)
read (4,*)RIa ! Reac Moment of Inertia 1 (amu*A**2)
read (4,*)RIb ! Reac Moment of Inertia 2 (amu*A**2)
read (4,*)RIc ! Reac Moment of Inertia 3 (amu*A**2)
read (4,*)temp ! Assumed Temperature (kelvin)
read (4,*)kappa ! Value of kappa (k)
read (4,*)TSIa ! TS Moment of Inertia 1 (amu*A**2)
read (4,*)TSIb ! TS Moment of Inertia 2 (amu*A**2)
read (4,*)TSIc ! TS Moment of Inertia 3 (amu*A**2)
read (4,*!)n ! Number of Harmonic Frequencies

doi=1,n ! Reactant Frequencies (cm-1)
read (4,*!)h(i)
end do

do j=1,(n-1) ! Transition State Frequencies (cm-1)
read (4,*!)p(j)
end do

close(4)

c***********************************************************************
c Convert Input Values into Correct Units
c***********************************************************************
c This is converting the moments of inertia from amu*A**2 to kg*m**2

MIA=(RIA)*(1.66054E-27)*(1.0E-20)
MIB=(RIB)*(1.66054E-27)*(1.0E-20)
MIC=(RIC)*(1.66054E-27)*(1.0E-20)

MTSIa=(TSIa)*(1.66054E-27)*(1.0E-20)
MTSIb=(TSIb)*(1.66054E-27)*(1.0E-20)

MTSIc=(TSIc)*(1.66054E-27)*(1.0E-20)

c This is converting the activation energy from hartrees to cm⁻¹.

Ea=(rxn)*(2.19474E+05)*(0.95)

c This is converting the molecular mass from amu to kg.

mass=(weight)*(1.66053886313E-27)

c***********************************************************************
c Open and Start Writing to an Output File
c***********************************************************************

print 02
02 format('$What is the output filename?')
read (5,03) fileout
03 format(a40)
open(unit=14,file=fileout,status='new')

write(14,04) fileout
write(14,05) name
write(14,06) mass
write(14,07) Ea
write(14,08) kappa
write(14,09) M1a, M1b, M1c
write(14,10) MTS1a, MTS1b, MTS1c
write(14,11) temp

   do i=1,n
      write(14,12) h(i)
   end do

   do j=1,(n-1)
      write(14,12) p(j)
   end do

   04 format(/,1x,a20)
   05 format(2x,a20)
   06 format(3x,f10.5)
   07 format(3x,d10.5)
   08 format(3x,f10.5)
   09 format(3x,d10.5,2x,d10.5,2x,d10.5)
   10 format(3x,d10.5,2x,d10.5,2x,d10.5)
   11 format(3x,f10.5,/)  
   12 format(3x,f10.5)


Emin=0

do 14, i=1,n
theta=((h(i))/boltzc)
NMR=(theta*(EXP(-theta/temp)))
DNM=(1.-((EXP(-theta/temp))))
EV(i)=(boltzc*,((theta/2)+(NMR/DNM)))
Emin=Emin+EV(i)
write(14,13)theta,NMR,DNM,EV(i)
13 format(3x,d10.5,3x,d10.5,3x,d10.5,3x,d10.5)
14 end do

write(6,15)'Emin',Emin
15 format(/,3x,a5,3x,d10.5,/)
Qrot1 = sqrt(((8*(pi**2)*MIa*boltzk*T)/(planck**2)))
Qrot2 = sqrt(((8*(pi**2)*MIb*boltzk*T)/(planck**2)))
Qrot3 = sqrt(((8*(pi**2)*MIc*boltzk*T)/(planck**2)))
QROT = sqrt(pi)*Qrot1*Qrot2*Qrot3
QrotTS1 = sqrt(((8*(pi**2)*MTSIa*boltzk*T)/(planck**2)))
QrotTS2 = sqrt(((8*(pi**2)*MTSIb*boltzk*T)/(planck**2)))
QrotTS3 = sqrt(((8*(pi**2)*MTSIc*boltzk*T)/(planck**2)))
QTSROT = sqrt(pi)*QrotTS1*QrotTS2*QrotTS3
write(14,16) Qrot1, Qrot2, Qrot3
write(14,16) QrotTS1, QrotTS2, QrotTS3
write(14,17) QROT, QTSROT
16 format(3x,d10.5,3x,d10.5,3x,d10.5)
17 format(3x,d10.5,3x,d10.5,/
QVIBR = 1
do 18, i=1,n
QVIBiR = 1
denR = 1 - (EXP(-(h(i))/(boltzc*T)))
QVIBiR = 1/denR
QVIBR = QVIBR * QVIBiR
18 end do
QVIBTS = 1
do 19, j=1,(n-1)
QVIBiTS = 1
denTS=1-(EXP(-(p(j))/(boltzc* T)))
QVIBiTS=1/denTS
QVIBTS=QVIBTS*QVIBiTS

19 end do
QR=QVIBR*QROT
QTS=QVIBTS*QTSROT
q=QTS/QR
write(14,20)QVIBR, QVIBTS, QR, QTS, q

20 format(3x,d10.5,3x,d10.5,3x,d10.5,3x,d10.5,3x,d10.5)

rate(T)=(kappa)*((boltzk*T)/planck)*(q)*(EXP(-Ea/(boltzc*T)))

tau(T)=rate(T)**(-1)
ETOTAL=0
do 21, i=1,n
THT=((h(i))/boltzc)
NUME=(THT*(EXP(-THT/T)))
DENO=(1-(EXP(-THT/T)))
Evib(i)=(boltzc*((THT/2)+(NUME/DENO)))
ETOTAL=ETOTAL+Evib(i)

21 end do

deltaE(T)=ETOTAL-Emin
write(6,22)T, rate(T), tau(T), ETOTAL, deltaE(T)
write(14,22)T, rate(T), tau(T), ETOTAL, deltaE(T)

22 format(/,3x,i5,3x,d10.5,3x,d10.5,3x,d10.5,3x,d10.5,3x,d10.5,3x,d10.5,/)

23 end do

do 27, i=600,12000,10

Etrans14(i)=deltaE(i)/0.14

v14(i)=SQRT((2*Etrans14(i)*((1.602E-19)/8065.73))/mass)

Esur14(i)=Etrans14(i)*(0.10)

Efin14(i)=Etrans14(i)-deltaE(i)-Esur14(i)

vf14(i)=SQRT((2*Efin14(i)*((1.602E-19)/8065.73))/mass)

time14(i)=(0.05)/vf14(i)

s14(i)=EXP((-rate(i))*(time14(i)))*100

write(14,24)i,rate(i),tau(i),time14(i),s14(i)

write(14,25)i,deltaE(i),v14(i),Efin14(i),vf14(i)

write(6,26)i,rate(i),time14(i),v14(i),s14(i)

write(14,26)i,rate(i),time14(i),v14(i),s14(i)

24 format(3x,i5,3x,d10.5,3x,d10.5,3x,d10.5,3x,d10.5)

25 format(3x,i5,3x,d10.5,3x,d10.5,3x,d10.5,3x,d10.5)

26 format(3x,i5,3x,d10.5,3x,d10.5,3x,d10.5,3x,d10.5)

27 end do

close (14)

delrate i=1,100

delrate

delrate

delrate