Laser Ablation Millimeter-Wave Instrumentation for in Situ Exploration of the Solar System

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Laser Ablation Millimeter-Wave Instrumentation for In Situ Exploration of the Solar System

A thesis presented
by
Alexander W. Raymond
to
The School of Engineering and Applied Sciences
in partial fulfillment of the requirements
for the degree of
Doctor of Philosophy
in the subject of
Applied Physics

Harvard University
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Abstract

Determining the chemical makeup of different sites throughout the solar system is an on-going endeavor. The major portion of the thesis relates to instrumentation for determining molecular composition, but we begin on a purely scientific topic with the discussion of a numerical model of the pulsed glow discharge plasma in a laboratory experiment intended to mimic the chemistry of the upper atmosphere of Saturn’s moon Titan. Titan’s upper atmosphere contains rich organic chemistry, which is the progenitor to the aerosol haze that blankets the surface. The experiment, known as the Titan Haze Simulation (THS), is being conducted at NASA Ames Research Center. The model accomplishes two things. First, it identifies some of the reaction pathways that lead to the positive ions that have been detected using the THS time-of-flight mass spectrometer. Second, it compares the electron density and temperature of the laboratory analog with those measured by the Cassini spacecraft at Titan and establishes that the plasma environments are similar in important ways.

The next chapter of the thesis presents a detailed characterization of the Fabry-Perot cavity, which is a key component in a new miniature rotational spectrometer being developed by the Spectroscopy Lab at the Jet Propulsion Laboratory. The spectrometer, known as Spec-Chip, operates at millimeter-wave frequencies around
100 GHz and is capable of detecting the rotational transitions of polar molecules. The strength of the rotational spectroscopy approach is that it is highly specific: the spatial arrangement of the atoms in a molecule lead to a unique set of transitions that allow for the precise determination of sample makeup. We map the cavity modes, measure the quality factor, and document the detection of a new gas. The Spec-Chip is intended for deployment on space missions to measure the atmospheric or outgassing composition of planetary bodies or comets.

Spec-Chip is meant for measuring gas-phase composition; however, to expand the number of possible sites to which it might be deployed, we consider the possibility of using it to identify the volatilized products of pulsed laser ablation. Before testing the instrument directly, we describe an experiment using a laboratory-scale rotational spectrometer operated by the McCarthy Lab at the Harvard-Smithsonian Center for Astrophysics, which addresses the question: what are the conditions inside the plume created by the nanosecond ablation of a molecular solid? When volatilized by a laser, the molecular bonds of the analyte species can break to form fragments; a process that can complicate interpretation of the rotational spectrum. The nanosecond ablation of mixtures of alanine amino acid and copper powder produce several neutral molecular fragments that we detect in comparable abundance to the parent molecules. To help explain the cause of the fragmentation and identify the spatiotemporal origin of the volatilized analyte molecules, we do pump-probe shadowgraphy of the expanding ablation plume. We find that the ablation produces a shockwave moving at 5 to 15 km s\(^{-1}\) depending on the precise laser and atmospheric conditions. Using that speed, we infer the initial conditions of the laser-vaporized material and show that the
unfragmented parent molecules probably originate from material in the superheated liquid phase some time after the ablation plume has substantially cooled.

In the final part of the thesis, we demonstrate that Spec-Chip can be coupled to a laser-ablation source to detect neutral gas-phase molecules. Rotational transitions of two salts, NaCl and KCl, are measured using Spec-Chip. As with the Cu/alanine ablation in Chapter 4, we find that a significant amount of the salt is ejected in the form of microparticles, which, if fully vaporized, opens the possibility of improving the volatilization yield and the instrument sensitivity along with it. Mass spectrometry measurements of ablated salts with nanosecond and femtosecond pulses show that dissociation occurs in these materials.
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Acknowledgments

I enjoyed conducting the research reported in this thesis and am grateful to the individuals who enabled it. Eric Mazur advised the project and manages an interesting, talented group of students and scientists who I loved having as colleagues. Federico Capasso, Ronald Walsworth, and Michael McCarthy kindly served as committee members to evaluate the work. In addition to his help on the committee, the McCarthy Lab at the Smithsonian Astronomical Observatory, and in particular Kelvin Lee and Marie-Aline Martin, guided the rotational measurements of alanine and salts as well as provided considerable feedback regarding the scope and approach to that work. Brian Drouin at the Jet Propulsion Laboratory allowed me to visit and work in his group and taught me about the Fourier transform millimeter-wave techniques. Brian also provided prototypes of the Spec-Chip instrument and a considerable amount of help drafting two paper manuscripts. The value of Brian’s part identifying interesting problems for my Ph.D. project was huge, and I am grateful to him. Farid Salama and Ella Sciamma-O’Brien at NASA Ames Research Center provided a line of scientific inquiry around their Titan Haze Experiment, generously shared their experimental data, and worked closely with me to develop a chemical model. It was fun and formative working with them, and I appreciate that they were such wonderful hosts during my visit to Ames. The major portion of the research was supported by the NASA Space Technology Research Fellowship Program, through which I was mentored by Jordana Blacksberg at JPL. Jordana gave valuable guidance about developing instrumentation inside NASA in addition to hosting me during two visits to her lab, which I enjoyed very much. Finally, I would like to thank my family for their support throughout my education.
Acknowledgements

Acknowledgements of Financial Support

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Chapter 1

Introduction

1.1 Overview

With the exception of Chapter 2, which is a purely scientific inquiry into the plasma chemistry of a laboratory experiment that is an analog test for the atmosphere of the moon Titan, the major portion of this thesis examines the idea of using laser-ablation together with a rotational spectrometer as a possible means to determine the chemical makeup of condensed phases on missions to space. The Chapters are bound by the theme of exploring the chemical makeup of the solar system; its planets, moons, and small bodies. Modeling the plasma of a laboratory experiment addressing gas-phase organic chemistry in Chapter 2, and an interest in measuring charge neutral molecules, leads to a study of the characteristics of a deployable rotational spectrometer capable of measuring the neutral gas composition in Chapter 3. Considering how to expand the applications of that instrument to include condensed-phase materials that are forcibly volatilized with laser-ablation prompts an investigation of laser-induced frag-
mentation in Chapter 4, which utilizes a laboratory microwave spectrometer. Finally, incorporating the laser-ablation methods discussed in Chapter 4, a demonstration of the deployable rotational spectrometer coupled to a laser-ablation source is presented in Chapter 5.

1.2 Organization of the dissertation

Chapter 2 discusses a numerical simulation of the Titan Haze Simulation (THS) experiment, which is a part of the COsmic SImulation Chamber (known as COSmIC) at NASA Ames Research Center. The numerical model is meant for interpreting the chemical pathways that lead to the experimental mass spectra acquired in the THS laboratory experiments and for comparing the electron density and temperature of the THS plasma to observations made at Titan by the Cassini spacecraft. The THS plasma is a pulsed glow-discharge experiment designed to simulate the reaction of N$_2$/CH$_4$-dominated gas in Titan’s upper atmosphere. The transient, one-dimensional model of THS chemistry tracks the evolution of more than 120 species in the direction of the plasma flow. As the minor species C$_2$H$_2$ and C$_2$H$_4$ are added to the N$_2$/CH$_4$-based mixture, the model correctly predicts the emergence of reaction products with up to five carbon atoms in relative abundances that agree well with measured mass spectra. Chemical growth in Titan’s upper atmosphere transpires through ion-neutral and neutral-neutral chemistry, and the main reactions involving a series of known atmospheric species are retrieved from the calculation. The model indicates that the electron density and chemistry are steady during more than 99 percent of the 300-µs long discharge pulse. The model also suggests that the THS ionization fraction and
electron temperature are comparable to those measured in Titan’s upper atmosphere. These findings reafﬁrm that the THS plasma is a controlled analog environment for studying the first and intermediate steps of chemistry in Titan’s upper atmosphere.

Chapter 3 presents a new miniature spectrometer, called Spec-Chip, currently under development at the Jet Propulsion Laboratory, which is designed for making \textit{in situ} measurements of gases and could be deployed at various sites throughout the solar system including, potentially, in Titan’s atmosphere. The design is based on the pulsed Fourier transform method of Balle-Flygare but operates at higher frequency than traditional microwave implementations. A semi-confocal Fabry-Perot cavity operating between 94 and 104 GHz is an essential part of the new technology and is characterized in detail. The new device measures gas or volatile composition \textit{in situ}, and the cavity has a nominal volume of 12 cm$^3$, which is 200 times smaller than cavities operating at comparable frequencies in laboratory gas spectrometers. Scans of mode amplitude are presented as a function of mirror spacing and transmitter frequency. Primary (TEM$_{00}$) and secondary (TEM$_{10}$) modes are both observed and are matched to an eigenmode calculation. The modes are well-behaved and have quality factors in the range of 1000-6000, which is a desirable compromise between field strength and mode width. Measurements of pulse bandwidth versus duration agree with time-bandwidth product predictions. Measurements of rotational transitions in N$_2$O and CH$_3$OH are plotted at various pressures and collisional broadening is resolved at mTorr pressures. Through these gas detections, we demonstrate that it is possible to significantly reduce the size of cavity spectrometers for \textit{in situ} deployment. The new Spec-Chip device opens new possibilities for molecular sensing in pollution.
Chapter 1: Introduction

monitoring, planetary science, and other fields.

The miniature gas spectrometer in Chapter 3 can detect freely-rotating molecules within the Fabry-Perot cavity. The number of potential sites where the spectrometer could be deployed are increased by coupling it with a laser-ablation source that forcibly-volatilizes solids. The laser-ablation process can alter the molecular composition of the target species by ionization and fragmentation. Therefore, before coupling a laser source to the Spec-Chip cavity in Chapter 5, an investigation of the thermochemistry and fragmentation of a nominal organic species is done in Chapter 4. Solid alanine is volatilized by nanosecond laser ablation but not without fragmenting some of the parent molecules. The extent and cause of laser fragmentation of molecular solids like alanine is an open problem that we address in this study. We prepare alanine samples in copper binder; a condensed-phase system that allows us to control the metal-versus-organic character of our targets and to leverage prior knowledge about the conditions of Cu laser plasma. Using rotational spectroscopy, we observe multiple neutral molecular fragments and find that the fragment and alanine yields depend linearly on fluence. Comparing shadowgraph images of the shockwave with numerical simulation suggests that the initial temperature and pressure inside the ablation plume are on the order of tens of $10^3$ K and GPa, respectively. At these conditions, kinetic analysis shows the parent alanine should be completely fragmented. We hypothesize that the intact volatilized alanine molecules originate not from the initial ablated mass but from the surface of the fluidized target during a brief instant as the it cools between the threshold temperature for dissociation and the boiling point. For our compacted targets, we find that a significant mass of particles are
ejected from the sample during ablation depending on the composition and bounding gas. Imaging shows that the ejected material spans vapor, liquid, and solid states.

In Chapter 5, we demonstrate that the Spec-Chip can be used to detect laser-ablated molecules. Rotational transitions of two neutral salts, NaCl and KCl, are reported. These and other alkali halides are possible indicators of water-rock interaction in the subsurface oceans of icy moons and are species of interest in future planetary missions. Additionally, they are a simple molecular system for understanding the physical chemistry of laser-ablation. Laser ablation is a technique for volatilizing condensed-phase samples for chemical analysis. Compared with molecular beams in laboratory experiments, direct sampling of the laser ablation plume is a messy process since ionization and dissociation resulting from the ablation event alter the composition target species. In a first experiment, the Spec-Chip is used together with a nanosecond ablation source. Two detections are reported. In a second experiment, a quadrupole mass spectrometer is used to search for ion formation in the ablation plume. For nanosecond pulses, we observe positive ions in the ablation plume. Increasing the intensity of the pulses by operating in the femtosecond regime produces atomic ion fragments as well as ion clusters although no detectable diatomic parent ions.

Chapter 6 summarizes the work and recommends paths for future investigation.
Chapter 2

A Model of Titan-like Chemistry to Connect Experiments and Cassini Observations

2.1 Introduction

Ultraviolet radiation and energetic particle bombardment ionize and dissociate the predominantly nitrogen- and methane-composed upper atmosphere of Saturn’s moon Titan, leading to the formation of more complex reaction products and trace fragments. Some of those species aggregate into particles, which affect the radiation budget and climate. As the organic particles migrate downward, they eventually precipitate onto the surface. The stratigraphy of that deposited organic material, accumulating over geological timescales, might contain information about the history of Titan’s atmosphere [1]. Those same deposits would also represent interesting pre-
biotic scenarios if they were to interact with liquid methane, ethane \([2, 3]\) or episodic liquid water formed, for example, by an asteroid impact \([4]\). Knowing how particular organic species form in the upper atmosphere is an important part of understanding the overall inventory of organic material at Titan, past and present.

The Cassini mission has made \textit{in situ} measurements of the upper atmosphere during many flybys. Interpretation of those data relies on a combination of atmospheric modeling \([5–11]\) as well as laboratory studies \([12, 13]\). The ionization, dissociation and reaction of nitrogen-methane mixtures are complicated processes. The goal of the Titan Haze Simulation (THS), a part of the COsmic SImulation Chamber (known as COSmIC) at NASA Ames Research Center, is to mimic these processes in a controlled laboratory environment to learn how they happen.

The THS experiment comprises a pulsed glow discharge plasma that induces chemistry between \(N_2\) and \(CH_4\) and simulates Titan’s atmospheric chemistry at low, Titan-like temperature (below 200 K) \([14–16]\). The strength of the experiment is the control with which the large molecular mass products can be repressed or produced depending on the precursor mixture. The precursor gases expand at high speed through a plasma channel where they are partially ionized to initiate chemistry. As the reacting mixture exits the plasma channel, it expands freely to very low pressure halting further chemistry. By adding different precursor gases in minor concentrations to express particular chemical pathways, the initial and intermediate stages of chemical growth and haze formation in \(N_2/CH_4\)-based plasma can be investigated \([15–17]\).

The present paper describes a new transient, one-dimensional chemical network model of the THS plasma and compares calculated results to experimental mass
spectra and electrode current measurements. Using the model, we deduce difficult-to-
measure properties like the distribution of electron density and temperature inside the
plasma channel and the equilibration time after the discharge pulse begins. Finally,
model predictions of ionization fraction and electron temperature for the laboratory
plasma are compared to measurements of Titan’s atmosphere made by the Cassini
spacecraft. Modeling the laboratory experiment is a key step in determining the
fidelity of the THS plasma experiment as an analog to Titan’s atmosphere above about
950 km and for identifying the chemical pathways leading from ions and fragments
to large organic species.

2.2 Model Description

A fluid mechanical approach is used to model the THS plasma [18,19]. The electron
density and electron energy density are calculated from

\[
\frac{\partial n_e}{\partial t} - \nabla \cdot [(\mu_e \cdot E)n_e + \nabla (D_e n_e)] = R_e \tag{2.1}
\]

\[
\frac{\partial n_\varepsilon}{\partial t} - \nabla \cdot [(\mu_\varepsilon \cdot E)n_\varepsilon + \nabla (D_\varepsilon n_\varepsilon)] + E \cdot [(\mu_e \cdot E)n_e + \nabla (D_e n_e)] = S_\varepsilon. \tag{2.2}
\]

In these equations, the subscripts \(e\) and \(\varepsilon\) refer to electrons and electron energy,
respectively. The variable \(\mu\) is the electron mobility [20], \(D\) is the diffusivity, \(E\) is
the electric field, \(R_e\) is the source term for electrons, and \(S_\varepsilon\) is the energy source term
that accounts for inelastic collisions. The concentrations of heavy species (i.e., atoms,
molecules and their ions) are obtained from
\[ \rho \frac{\partial \omega_k}{\partial t} + \rho (u \cdot \nabla) \omega_k = \nabla \cdot \left[ \rho \omega_k D_k \frac{\nabla \omega_k}{\omega_k} - z_k \mu_k E \right] + R_k, \]  

(2.3)

where \( \omega_k \) is the mass fraction of the \( k \)th heavy species and \( R_k \) is the source term for heavy species. A mixture-averaged diffusion coefficient, \( D_k \), is included in the calculations using a nominal cross section for each species; however, the model is insensitive to its precise value because the supersonic expansion dominates the flow. The source term is obtained by solving a network of chemical rate equations.

The spatial derivatives are calculated along the \( x \)-axis of the plasma channel (Fig. 2.1). Previous modeling of the plasma channel considered two-dimensions \([18, 19]\). We reduce the dimensionality in favor of a larger chemical network as is commonly done in the Titan climate modeling. Consequently, the anode and inlet occupy the same position in the domain (\( x = 0 \) mm). Similarly, the cathode and outlet are at the same position (\( x = 1.5 \) mm). To model the combined influence of the electrodes and flow on the concentration of the heavy species, we adopt the following approach. The initial and inlet mixing ratios of heavy species are the nominal mixture values, \( e.g., 0.9 \text{N}_2 \) and \( 0.1 \text{CH}_4 \) for 90:10 \text{N}_2/\text{CH}_4 and zero for all other species except for a small number of \( \text{N}_2(X,v = 0)^+ \) ions added to ensure the initial mixture is quasi-neutral with respect to the seed electrons. These nitrogen ions are in low enough concentration that they do not significantly affect the flow or the chemistry. The trace species created in the channel, which could in principle diffuse upstream, are treated as blocked (\( i.e., \partial w_k/\partial x = 0 \)). Such a condition is reasonable given the high speed of the incoming flow, which tends to push the reaction products downstream. Since ions near the inlet diffuse into the anode, a surface reaction is added to the inlet
Chapter 2: A Model of Titan-like Chemistry to Connect Experiments and Cassini Observations

boundary, which is effectively a point sink/source term. In a similar way, an open boundary condition and a point surface reaction are applied at the outlet/cathode to account for heavy species loss, neutralization of ions, and the generation of secondary electrons. The surface reaction accomplishes two things: i) it neutralizes ions (e.g., $\text{C}_2\text{H}_2^+ \rightarrow \text{C}_2\text{H}_2$) and ii) it produces secondary electrons at a rate determined by the secondary emission coefficient, which we specify as 0.025 [21].

The rate constants of the surface reactions are determined according to [22]:

$$k_s = \frac{\gamma_k}{4\Gamma (1 - \gamma_k/2)} \sqrt{\frac{8RT}{\pi M_k}},$$  \hspace{1cm} (2.4)

where $R$ is the ideal gas constant, $T$ is the local temperature, $M_k$ is the molar mass of the $k^{th}$ ion, and $\Gamma$ is the surface site concentration. As a first approach, we adopt unity sticking coefficients ($\gamma_k$) because our main focus is the plasma chemistry although more detailed wall chemistry could be modeled as part of future work. To compensate for uncertainties surrounding the surface chemistry and the simplified one-dimensional geometry, the abundances we report are those slightly upstream from the cathode at 1.496 mm; a value that we find gives good agreement with experiment.

At Titan, chemistry occurs through ion-neutral [23] and neutral-neutral reactions [9, 11, 13]. In the THS plasma, reactions are initiated by electron impact and involve the different molecular precursors present in the initial gas mixture: $\text{N}_2$ and $\text{CH}_4$, but also more complex species that have been detected as trace constituents on Titan, like $\text{C}_2\text{H}_2$ or $\text{C}_2\text{H}_4$. The ions and fragmentation products of those electron impacts then feed a network of ion-neutral and neutral-neutral reactions. In the model, the kinetics of the electron impact reactions are handled by integrating the electron
cross sections for the chosen precursor gases over the electron energy density function. For simplicity, we have limited the analysis to four precursor gases: $N_2$, $CH_4$, $C_2H_2$, and $C_2H_4$. The kinetics for ion-neutral and neutral-neutral reactions are modeled using constant, or in some cases temperature-dependent, rate coefficients. The chemical network adopted for this study is tabulated in the Appendix. The large network is needed in order to explain the trace chemistry happening in the THS plasma across a range of precursor mixtures and was developed by combining reactions from sev-
eral previous studies (e.g., [24, 25]) then adding additional reactions to improve the agreement at particular masses in the spectra. Although some of the rate coefficients for reactions compiled from the various sources are for regimes that do not strictly apply to the temperature and pressure of the THS plasma, given the large number of chemical paths included in the network, the majority of peaks are unaffected by the precise rate coefficient of a particular reaction. As the model is further constrained by future experiments, involving either different precursor gases or measurements of the neutral chemistry, reactions can be adjusted or added to the network to enhance the level of agreement.

The electric field affects the transport of charged species and is obtained by solving Poisson’s equation subject to the anode and cathode potentials at the boundaries. The domain modeled is the 1.5-mm wide, 0.4-mm tall plasma channel inside the THS discharge nozzle shown in Fig. 2.1. In practice, the electrons that seed the breakdown probably originate from thermionic emission at the cathode [26]. Because the cathode temperature distribution is challenging to quantify in the pulsed jet experiments, we choose to use an initial seed electron density of $10^7$ cm$^{-3}$ with 25 meV mean energy, which corresponds to about $6 \times 10^5$ room temperature electrons. The breakdown characteristics are insensitive to these initial values.

The velocity, density and temperature of the heavy species have been modeled previously [19, 27] and used as uncoupled inputs to the THS model. The velocity of the gas in the plasma channel reaches more than 400 m s$^{-1}$, so the residence time is about 3.5 µs; short enough to mitigate wall effects since the time for a molecule to randomly move from the center of the channel to the wall is on the order of 8 µs.
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The short residence time is what enables the THS experiment to specifically address the initial and intermediate stages of the chemistry avoiding further processing of the products that would be more complicated to interpret. The temperature and number density inputs for the 90:10 N₂/CH₄ plasma are compared with values for Titan’s upper atmosphere in Fig. 2.2. The temperature of gas in Titan’s ionosphere is about 150 ± 15 K depending on latitude and other factors [28]. Fig. 2a shows that the gas temperature in the THS nozzle is comparable. The THS molecular number density (Fig. 2b) is, however, significantly greater than Titan’s upper atmosphere. At Titan, three-body reactions of species with three carbon atoms, for example, are significant in the stratosphere (42–310 km) [5], or between about 1×10¹⁹ and 3×10¹⁵ cm⁻³, respectively [29]. The density designed in the THS plasma, which corresponds to the upper-end of Titan’s stratosphere, is necessary to produce enough reaction products to be detected by a reflectron time-of-flight mass spectrometer (Re-TOF-MS). Although the THS density is on the cusp of where three-body reactions could become significant, the level of agreement the model achieves with the mass spectra is the gauge by which we evaluate their importance.

The assumptions made in the model and comparison to experimental results are:

1. one-dimensional flow
2. reactions at the outlet of the plasma channel are terminated by expansion to low pressure
3. condensation and particle formation do not significantly alter the ion chemistry

13
Figure 2.2: a) temperature and b) precursor number density inputs to the THS calculation for the 90:10 N$_2$/CH$_4$ mixture together with values for Titan’s atmosphere. Arrows point to the relevant horizontal axes. THS calculation and observations have a shared vertical axis. Temperature and density are adapted from [13] and [28,29], respectively. Modeled THS properties are from [27].

4. the number density of the major species (N$_2$) is unaffected by the discharge
5. the temperature of the heavy species is unaffected by the electron population

6. the velocity, temperature and pressure profile are dominated by the N\textsubscript{2} and are taken to be the same for all mixtures considered

7. isotopomers and negative ions are ignored.

Although previous models of the COSmIC argon plasma are two-dimensional [18,19], a simpler one-dimensional model is adopted in this work in order to handle the parameterization of the large number of reactions occurring in the N\textsubscript{2}/CH\textsubscript{4} plasma. Comparisons to the [18] results for the one-dimensional model with argon precursor yield agreement well within the uncertainty observed for experimental comparisons. The Maxwellian assumption for electron energy distributions has been used in models of Titan’s atmosphere and is consistent with measured electron spectra [30]. The assumption that the temperatures of the heavy species is governed by the flow and not by the electron population was justified by fits to nitrogen visible emission that gave a maximum neutral temperature of 200 K in the plasma discharge [16], and is consistent with models of other cold plasmas [31]. [32] showed that vibrationally excited states of nitrogen affect the excited state molecule and ion populations for a glow discharge with similar electron density and pressure as the THS plasma, but only at millisecond time scales that do not apply to the μs-time-scale reaction mechanisms that exist here. The energy of the electron population is, however, coupled to the heavy species through momentum transfer collisions involving nitrogen.
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2.3 Experimental Description

The THS plasma is a pulsed glow-discharge [14]. Details about the THS setup can be found in [15–17]. They are briefly outlined here. The geometry of the discharge nozzle is shown in Fig. 2.1. Precursor gas feeds into a 100-mm long, 127-µm tall entrance slit during a 1300-µs long pulse at 2000 sccm average flow rate. The copper plate containing the slit forms the anode. From there, the precursor gas flows into the plasma channel, which is a 1.5-mm wide, 0.4-mm tall region bounded by two insulating alumina plates. At the outlet of the plasma channel, two knife-edge elkonite (90 percent Tungsten, 10 percent copper) conductors form the cathode. 600 µs after the gas pulse begins, the cathode is driven to negative high-voltage for about 300 µs to induce the discharge. The electric field accelerates free electrons in the plasma channel to eV-level energies inducing electron-impact ionization and dissociation.

Polarized skimmers attract and skim the positive ions present in the plasma plume exiting the discharge channel into the Re-TOF-MS attached to the vacuum chamber and facing the slit. Positive ions are orthogonally accelerated using a 200-V pulsed voltage on a repeller plate to separate each species according to its mass-to-charge ratio. They are then focused onto a microchannel plate detector, which records the time of arrival. Time-domain spectra are converted to mass spectra using a calibration based on argon and nitrogen plasmas. The heights of the peaks reported at a particular mass-to-charge ratio correspond to the area of the time-domain peaks calculated from Gaussian fits.
Chapter 2: A Model of Titan-like Chemistry to Connect Experiments and Cassini Observations

2.4 Results and Discussion

Figure 2.3 shows the experimental and calculated mass spectra for four mixtures at –800-V cathode potential. The same chemical network was used for the calculations of all four spectra, so the different products that arise in each case are expressions of different chemical pathways that result when new precursors are added. The intensities are relative to a primary constituent: either mass 28 (N$_2^+$ for the N$_2$ plasma) or 16 (CH$_4^+$ for all other mixtures). The lower-limit on the vertical axis is the nearest decade below the minimum abundance extracted from the Re-TOF-MS spectra. Changing the mixture from N$_2$/CH$_4$ to N$_2$/CH$_4$/C$_2$H$_x$ increases the number of high-mass ions. The model correctly predicts that the chemistry is truncated due to the short residence time of the gas in the active region of the plasma discharge (between anode and cathode) followed by the expansion to low pressure that halts any further chemistry in the afterglow. For small molecular precursors, we do not predict the production of very large molecules. This finding illustrates that the THS pulsed plasma is a tool for studying the initial and intermediate stages of Titan-like chemistry. Table 2.1 lists the relative abundances for the experimental and modeled spectra. The ions associated with each prediction from the model are listed. The peaks at $M/Z = 14$ and 28 contain contributions from more than one ion: CH$_2^+$ and N$^+$ for mass 14 and HCNH$^+$, C$_2$H$_4^+$, and N$_2^+$ for mass 28.
Figure 2.3: Comparison of experimental and calculated THS mass spectra for different nitrogen-based mixtures at −800-V cathode potential.
Table 2.1: Experimental (bold) and modeled (in parenthesis) mass spectra relative abundances for –800-V cathode potential normalized by $m/z = 16$ for the each mixture.

<table>
<thead>
<tr>
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<th>85:10:5</th>
<th>85:10:5</th>
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<td></td>
<td>$\text{N}_2/\text{CH}_4$</td>
<td>$\text{N}_2/\text{CH}_4/\text{C}_2\text{H}_2$</td>
<td>$\text{N}_2/\text{CH}_4/\text{C}_2\text{H}_4$</td>
</tr>
<tr>
<td>12</td>
<td>- (-)</td>
<td>- (0.035 C$^+$)</td>
<td>- (0.005 C$^+$)</td>
</tr>
<tr>
<td>13</td>
<td>0.017 (0.054 CH$^+$)</td>
<td>- (0.033 CH$^+$)</td>
<td>0.020 (0.055 CH$^+$)</td>
</tr>
<tr>
<td>14</td>
<td>0.528 (0.091 CH$_2^+$), 0.149 N$^+$)</td>
<td>0.245 (0.094 CH$_2^+$), 0.128 N$^+$)</td>
<td>0.500 (0.123 CH$_2^+$)</td>
</tr>
<tr>
<td>15</td>
<td>2.582 (4.948 CH$_3^+$)</td>
<td>1.568 (3.675 CH$_3^+$)</td>
<td>2.321 (4.087 CH$_3^+$)</td>
</tr>
<tr>
<td>16</td>
<td>1.000 (1.000 CH$_4^+$)</td>
<td>1.000 (1.000 CH$_4^+$)</td>
<td>1.000 (1.000 CH$_4^+$)</td>
</tr>
<tr>
<td>17</td>
<td>0.329 (3.187 CH$_5^+$)</td>
<td>0.153 (1.299 CH$_5^+$)</td>
<td>0.231 (1.213 CH$_5^+$)</td>
</tr>
<tr>
<td>24</td>
<td>- (-)</td>
<td>- (0.127 C$_2^+$)</td>
<td>- (0.009 C$_2^+$)</td>
</tr>
<tr>
<td>25</td>
<td>- (-)</td>
<td>0.210 (0.573 C$_2\text{H}^+$)</td>
<td>0.073 (0.031 C$_2\text{H}^+$)</td>
</tr>
<tr>
<td>26</td>
<td>- (-)</td>
<td>5.874 (2.469 C$_2\text{H}_2^+$)</td>
<td>1.234 (1.005 C$_2\text{H}_2^+$)</td>
</tr>
<tr>
<td>27</td>
<td>0.084 (-)</td>
<td>0.494 (0.954 C$_2\text{H}_3^+$)</td>
<td>3.937 (1.847 C$_2\text{H}_3^+$)</td>
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Continued on next page
Table 2.1 – continued from previous page

<table>
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<th>m/z</th>
<th>m/z 90:10</th>
<th>m/z 85:10:5</th>
<th>m/z 85:10:5</th>
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<td>N&lt;sub&gt;2&lt;/sub&gt;/CH&lt;sub&gt;4&lt;/sub&gt;</td>
<td>N&lt;sub&gt;2&lt;/sub&gt;/CH&lt;sub&gt;4&lt;/sub&gt;/C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>N&lt;sub&gt;2&lt;/sub&gt;/CH&lt;sub&gt;4&lt;/sub&gt;/C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;</td>
</tr>
<tr>
<td>28</td>
<td>9.364 (0.069 HCNH&lt;sup&gt;+&lt;/sup&gt;, 0.142 C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;+&lt;/sup&gt;, 13.532 N&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;+&lt;/sup&gt;)</td>
<td>11.788 (0.082 C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;+&lt;/sup&gt;, 10.853 N&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;+&lt;/sup&gt;)</td>
<td>20.988 (8.492 C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;+&lt;/sup&gt;, 10.129 N&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;+&lt;/sup&gt;)</td>
</tr>
<tr>
<td>29</td>
<td>0.811 (10.540 C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;&lt;sup&gt;+&lt;/sup&gt;)</td>
<td>0.556 (5.355 C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;&lt;sup&gt;+&lt;/sup&gt;)</td>
<td>2.482 (5.207 C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;&lt;sup&gt;+&lt;/sup&gt;)</td>
</tr>
<tr>
<td>30</td>
<td>0.008 (-)</td>
<td>- (-)</td>
<td>0.101 (-)</td>
</tr>
<tr>
<td>38</td>
<td>- (-)</td>
<td>- (-)</td>
<td>0.450 (3.491 C&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;+&lt;/sup&gt;)</td>
</tr>
<tr>
<td>39</td>
<td>- (-)</td>
<td>0.233 (1.589 C&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;+&lt;/sup&gt;)</td>
<td>0.106 (0.418 C&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;+&lt;/sup&gt;)</td>
</tr>
<tr>
<td>40</td>
<td>- (-)</td>
<td>0.807 (0.187 C&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;&lt;sup&gt;+&lt;/sup&gt;)</td>
<td>2.667 (1.589 C&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;&lt;sup&gt;+&lt;/sup&gt;)</td>
</tr>
<tr>
<td>41</td>
<td>- (-)</td>
<td>- (-)</td>
<td>0.062 (0.078 N&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;+&lt;/sup&gt;)</td>
</tr>
<tr>
<td>42</td>
<td>- (-)</td>
<td>0.508 (1.989 C&lt;sub&gt;4&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;+&lt;/sup&gt;)</td>
<td>- (-)</td>
</tr>
<tr>
<td>50</td>
<td>- (-)</td>
<td>1.151 (4.841 C&lt;sub&gt;4&lt;/sub&gt;H&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;+&lt;/sup&gt;)</td>
<td>- (-)</td>
</tr>
<tr>
<td>51</td>
<td>- (-)</td>
<td>- (-)</td>
<td>1.151 (4.841 C&lt;sub&gt;4&lt;/sub&gt;H&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;+&lt;/sup&gt;)</td>
</tr>
</tbody>
</table>

Continued on next page
Table 2.1 – continued from previous page

<table>
<thead>
<tr>
<th>m/z</th>
<th>90:10</th>
<th>85:10:5</th>
<th>85:10:5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N$_2$/CH$_4$</td>
<td>N$_2$/CH$_4$/C$_2$H$_2$</td>
<td>N$_2$/CH$_4$/C$_2$H$_4$</td>
</tr>
<tr>
<td>52</td>
<td>- (-)</td>
<td>0.047 (-)</td>
<td>- (-)</td>
</tr>
<tr>
<td>53</td>
<td>- (-)</td>
<td>- (0.011 C$_4$H$_5^+$)</td>
<td>0.284 (0.302 C$_4$H$_5^+$)</td>
</tr>
<tr>
<td>54</td>
<td>- (-)</td>
<td>- (-)</td>
<td>0.110 (0.358 C$_4$H$_6^+$)</td>
</tr>
<tr>
<td>55</td>
<td>- (-)</td>
<td>- (-)</td>
<td>0.241 (5.640 C$_4$H$_7^+$)</td>
</tr>
<tr>
<td>65</td>
<td>- (-)</td>
<td>0.035 (0.206 C$_5$H$_5^+$)</td>
<td>- (0.001 C$_5$H$_5^+$)</td>
</tr>
<tr>
<td>67</td>
<td>- (-)</td>
<td>- (-)</td>
<td>0.105 (0.952 C$_5$H$_7^+$)</td>
</tr>
<tr>
<td>69</td>
<td>- (-)</td>
<td>- (-)</td>
<td>0.057 (0.362 C$_5$H$_9^+$)</td>
</tr>
<tr>
<td>76</td>
<td>- (-)</td>
<td>0.066 (-)</td>
<td>- (-)</td>
</tr>
<tr>
<td>77</td>
<td>- (-)</td>
<td>0.032 (-)</td>
<td>- (0.002 C$_6$H$_5^+$)</td>
</tr>
<tr>
<td>79</td>
<td>- (-)</td>
<td>- (-)</td>
<td>- (0.062 C$_6$H$_7^+$)</td>
</tr>
</tbody>
</table>
Several features of the modeled spectra suggest that the model includes key aspects of the chemistry occurring inside the THS analog environment. In the nitrogen plasma, the $\text{N}^+ / \text{N}_2^+$ and $\text{N}_3^+ / \text{N}_2^+$ abundance ratios are in good agreement with experiment; the $\text{N}^+$ and $\text{N}_3^+$ ions are around two orders of magnitude less abundant than the $\text{N}_2$ ion. When methane is added to the mixture, C1 and C2 series appear, \emph{i.e.}, species with one and two carbon atoms, respectively. The appearance of C2 ions indicates that bimolecular chemistry involving the CH$_4$ ions and fragments occurs, but because the flow rapidly expands to low pressure, the C1 and C2 products do not participate in reactions that would form C3 or higher-order ions; however, by seeding the N$_2$/CH$_4$ with acetylene or ethylene, the C3, C4 and C5 peaks do emerge. In both the experiment and model of the N$_2$/CH$_4$/C$_2$H$_x$ mixtures, the ion abundances nominally peak at the C2 series then decrease with increasing $M/Z$. Different sets of C4 and C5 peaks are predicted for the N$_2$/CH$_4$/C$_2$H$_2$ and N$_2$/CH$_4$/C$_2$H$_4$ mixtures, and, for the most part, each of those sets matches the peaks found in the experiment. Moreover, the positive ions observed in the THS laboratory spectra are in the same range as the mean positive ions measured by Cassini. [33] have showed that the effective ion mass in the upper atmosphere varies exponentially with altitude from about 25 amu at 1400 km to 60 amu at 1000 km, and the THS mass spectra presented contain peaks from 12 to 78 amu.

There are a few instances of disagreement between the calculated and measured spectra, which are worth mentioning. Masses 52, 76 and 77 in the N$_2$/CH$_4$/C$_2$H$_2$ mixture are nonzero in the experiments, but the model does not predict appreciable ion abundances for those masses. Possible sources of these experimental peaks include
HC$_3$NH$^+$/C$_2$N$_2^+$, C$_6$H$_4^+$/C$_5$H$_2$N$^+$, and C$_6$H$_5^+$/C$_5$H$_3$N$^+$, respectively [15]. Reactions that produce these species have been included in the network, but either the rate coefficients are insufficient to account for the measured yields or these species are created by reactions that are not included in the existing surveys and astrochemistry databases. Masses 51 and 79 in the N$_2$/CH$_4$/C$_2$H$_4$ mixture are nonzero in the model but do not appear in the experiments. These modeled peaks correspond to C$_4$H$_3^+$ and C$_6$H$_7^+$, respectively, and the network includes reactions that consume both of these species. For the N$_2$/CH$_4$/C$_2$H$_4$ mixture, the calculated relative abundance of mass 55 (C$_4$H$_7^+$) is about two orders of magnitude greater than in the experiments, which suggests either the production (Reaction 158 in the Appendix) or loss (Reaction 280) mechanism is inaccurate. While future measurements and the inclusion of additional reactions might be necessary to improve the agreement, the majority of the peaks in the calculated mass spectra are within an order of magnitude of the experimental values, which, considering the complexity of the plasma, suggests that much of the physics and chemistry of the THS experiment are represented by the model.

When comparing the experimental and calculated mass spectra, several possible sources of error exist. First, while the agreement between model and experiment is good and is beginning to yield new understanding about the THS plasma, the chemical network probably does not contain all the reaction pathways that occur, and additional experiments will be required to improve it. For example, like some of the studies from which we have compiled the chemical network, we have not systematically included charge exchange reactions, which are not significant in Titan’s upper atmosphere [34] although it is possible such reactions could happen in the THS ex-
periment. Second, the rate coefficients come from many different literature sources; each with its own intrinsic error that contributes to the overall uncertainty. It is well documented that uncertainty propagation in large chemical networks can lead to significant variation in predicted products [35,36]. In their modeling of Titan’s atmospheric column, [37] showed that uncertainty of 20 percent in kinetics rates distributed randomly over the network leads to spreads of at least two orders of magnitude in C3 predictions. Even in controlled laboratory analog experiments, disagreement by an order of magnitude for individual species is common, see for example [38]. Third, discrepancies between calculated and measured mass spectra could come from non-uniform skimming of the ions in the Re-TOF-MS optics. Finally, it is likely that some species are scavenged by particle nuclei in the formation of haze particles [16]. This process has been proposed as a sink for hydrogen fragments [39]. Agreement between the experimental and calculated spectra is not perfect, but considering the many assumptions and uncertainties that go into a model of this kind, the semi-quantitative level of agreement it achieves is promising.

The ratios of abundances for masses $M/Z$ 28:16 and 26:16, whose peaks are primarily dominated by $\text{N}_2^+/\text{CH}_4^+$ and $\text{C}_2\text{H}_2^+/\text{CH}_4^+$, respectively, are listed in Table 2.2. The 28:16 ratios from experiments and calculations differ by about 10 percent or less and follow consistent trends: the ratio decreases by 10–20 percent when $\text{C}_2\text{H}_2$ is added but increases by 30–60 percent when $\text{C}_2\text{H}_4$ is added. The 26:16 ion ratios also agree within a factor of about two or better. This agreement of the ion ratios is quite close considering the abundances are unconstrained and increase many orders of magnitude during breakdown from essentially zero. This observation indicates that
Chapter 2: A Model of Titan-like Chemistry to Connect Experiments and Cassini Observations

the electron impact reactions used for those species, which initiate the chemistry in
the THS system, are reasonably correct. The agreement of the acetylene ion ratio
(26:16) in model and experiment is, in particular, important because acetylene is
among the most prominent photolysis products in Titan’s atmosphere [40].

Table 2.2: \( \text{N}_2^+ / \text{CH}_4^+ [M/Z = 28/16] \) (and \( \text{C}_2\text{H}_2^+ / \text{CH}_4^+ [26/16] \)) abundance ratios for different mixtures at –800-V cathode potential in the THS experiments and model.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Experiment</th>
<th>Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>90:10 ( \text{N}_2 / \text{CH}_4 )</td>
<td>13.1 (0.00)</td>
<td>13.7 (0.00)</td>
</tr>
<tr>
<td>85:10:5 ( \text{N}_2 / \text{CH}_4 / \text{C}_2\text{H}_2 )</td>
<td>11.8 (5.87)</td>
<td>10.9 (2.47)</td>
</tr>
<tr>
<td>85:10:5 ( \text{N}_2 / \text{CH}_4 / \text{C}_2\text{H}_4 )</td>
<td>21.0 (1.23)</td>
<td>18.6 (1.01)</td>
</tr>
</tbody>
</table>

An important reason for modeling the THS plasma is identifying the pathways
of chemical growth. Tables 2.3 and 2.4 list the dominant production and loss re-
actions, respectively, for a set of species. The neutral versions of these species have
each been identified in Titan’s upper atmosphere [28, 41]. The values of the calcu-
lated reaction rates are listed if larger than \( 1 \times 10^{-6} \) mol m\(^{-3}\) s\(^{-1}\). For the experimental
conditions considered, the model predicts that neutral \( \text{C}_2\text{H}_2 \) production is only appre-
ciable in the mixture that already contains acetylene precursor through the reaction
of \( \text{C}_4\text{H}_2 \) with \( \text{C}_4\text{H}_3^+ \), which are themselves reaction products that, at Titan, might
be derived through other chemical pathways. \( \text{C}_2\text{H}_2 \) is destroyed mainly by reactions
with \( \text{C}_2\text{H}_2^+ \) ions or \( \text{CH}_x^+ \) fragments. Neutral \( \text{C}_2\text{H}_4 \) exhibits large production rates
for all the precursor mixtures since its formation pathway involves \( \text{CH}_4 \) and the CH
fragment, which are both abundant. Nitrogen incorporation is an important part of the haze chemistry of Titan [42]. HCN has been detected in Cassini Composite Infrared Spectrometer observations at 713 cm$^{-1}$ [43]. Although its abundance is seasonal, modeled concentrations of HCN nominally peak near the mesopause at around $10^8$ cm$^{-3}$ [10], and HCN mixing ratios are highest in the ionosphere where they are between 0.1 and 1 percent [37]. According to Hébrard et al.’s network, the dominant pathways for HCN production in the upper atmosphere are HCNH$+$H$\rightarrow$HCN$+$H$_2$ and N$+$CH$_3$$\rightarrow$HCN$+$2H. In the THS plasma, various paths for nitrogen incorporation are included in the chemical network including N$^+$ reactions with CH and CH$_4$ leading to CN$^+$ and HCNH$^+$ as well as the dominant neutral mechanisms highlighted by Hébrard et al. The model suggests that the neutral pathway, N$+$CH$_3$, is a dominant source of HCN for each of the N$_2$/CH$_4$/C$_x$H$_y$ mixtures. The reason is that atomic nitrogen and CH$_3$ are abundant products from the precursor fragmentation. The HCNH$+$H pathway is less productive since HCNH must first be formed from the fragments. The model also suggests that once formed, HCN is stable; subject only to small rates of charge transfer with N$_2$$\tilde{a}$(X,$v$ = 0)$^+$ or reaction with the C$_2$H$_5^+$ ion.
Table 2.3: Calculated production (mol m\(^{-3}\) s\(^{-1}\)) of species at –800-V cathode potential whose neutral counterparts have been observed in Titan’s upper atmosphere. The larger value at either the midpoint or outlet is reported.

<table>
<thead>
<tr>
<th>Species</th>
<th>90:10</th>
<th>85:10:5</th>
<th>85:10:5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N(_2)/CH(_4)</td>
<td>N(_2)/CH(_4)/C(_2)H(_2)</td>
<td>N(_2)/CH(_4)/C(_2)H(_4)</td>
</tr>
<tr>
<td>C(_2)H(_2)(^+)</td>
<td>-</td>
<td>e+C(_2)H(_2)→2e+C(_2)H(_2)(^+)</td>
<td>e+C(_2)H(_4)→2e+H(_2)+C(_2)H(_2)(^+)</td>
</tr>
<tr>
<td></td>
<td>(&lt; 10(^{-6}))</td>
<td>(0.30)</td>
<td>(0.024)</td>
</tr>
<tr>
<td>C(_2)H(_4)(^+)</td>
<td>CH(_4)+CH(_2)(^+)→H(_2)+C(_2)H(_4)(^+)</td>
<td>CH(_4)+CH(_2)(^+)→H(_2)+C(_2)H(_4)(^+)</td>
<td>e+C(_2)H(_4)→2e+C(_2)H(_4)(^+)</td>
</tr>
<tr>
<td></td>
<td>(0.41)</td>
<td>(0.40)</td>
<td>(1.0)</td>
</tr>
<tr>
<td>C(_3)H(_4)(^+)</td>
<td>-</td>
<td>CH(_4)+C(_2)H(_2)(^+)→H(_2)+C(_3)H(_4)(^+)</td>
<td>CH(_4)+C(_2)H(_2)(^+)→H(_2)+C(_3)H(_4)(^+)</td>
</tr>
<tr>
<td></td>
<td>(&lt; 10(^{-6}))</td>
<td>(28.)</td>
<td>(10.)</td>
</tr>
<tr>
<td>C(_4)H(_2)(^+)</td>
<td>-</td>
<td>C(_2)H(_2)+C(_2)H(_2)(^+)→H(_2)+C(_4)H(_2)(^+)</td>
<td>C(_2)H(_4)+C(_2)H(^+)→H+H(_2)+C(_4)H(_2)(^+)</td>
</tr>
<tr>
<td></td>
<td>(&lt; 10(^{-6}))</td>
<td>(34.)</td>
<td>(0.23)</td>
</tr>
<tr>
<td>HCN(^+)</td>
<td>HCN+ N(_2)(X,v=0)(^+)→</td>
<td>HCN+N(_2)(X,v=0)(^+)→</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>N(_2)(X,v=0)+HCN(^+) (3.4×10(^{-6}))</td>
<td>N(_2)(X,v=0)+HCN(^+) (1.3×10(^{-6}))</td>
<td>(&lt; 10(^{-6}))</td>
</tr>
</tbody>
</table>
Table 2.3 – continued from previous page

<table>
<thead>
<tr>
<th>Species</th>
<th>90:10 (\text{N}_2/\text{CH}_4)</th>
<th>85:10:5 (\text{N}_2/\text{CH}_4/\text{C}_2\text{H}_2)</th>
<th>85:10:5 (\text{N}_2/\text{CH}_4/\text{C}_2\text{H}_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{C}_2\text{H}_2)</td>
<td>- ((&lt; 10^{-6}))</td>
<td>(\text{C}_4\text{H}_2/\text{C}_4\text{H}_3^+\rightarrow\text{C}_2\text{H}_2/\text{C}_6\text{H}_3^+) ((0.017))</td>
<td>(\text{C}_3\text{H}_4/\text{C}_3\text{H}_4^+\rightarrow\text{C}_2\text{H}_2/\text{C}_4\text{H}_6^+) ((8.7\times10^{-6}))</td>
</tr>
<tr>
<td>(\text{C}_2\text{H}_4)</td>
<td>(\text{CH}+\text{CH}_4\rightarrow\text{C}_2\text{H}_4+\text{H}) ((0.23))</td>
<td>(\text{CH}+\text{CH}_4\rightarrow\text{C}_2\text{H}_4+\text{H}) ((0.14))</td>
<td>(\text{CH}+\text{CH}_4\rightarrow\text{C}_2\text{H}_4+\text{H}) ((0.20))</td>
</tr>
<tr>
<td>(\text{HCN})</td>
<td>(\text{N}(\text{S})+\text{CH}_3\rightarrow\text{HCN}+\text{H}_2) ((0.064))</td>
<td>(\text{N}(\text{S})+\text{CH}_3\rightarrow\text{HCN}+\text{H}_2) ((0.033))</td>
<td>(\text{N}(\text{S})+\text{CH}_3\rightarrow\text{HCN}+\text{H}_2) ((0.024))</td>
</tr>
</tbody>
</table>
While not included in Tables 2.3 and 2.4, the model predicts the rates of ion neutralization at the cathode surface are comparable to the electron-impact ionization rates integrated along the plasma channel. The neutralization rates at the anode are negligible, which is expected since very few of the ions produced in the plasma channel diffuse upstream against the flow. Although the rates we predict at the cathode are likely over-estimated, the agreement between the modeled and experimental mass spectra suggests the present treatment is suitable for the purpose of analyzing the plasma-phase chemistry. In future work, we hope to use the model to study possible chemistry induced by reactions at the surface, and for that, more detailed treatment of the cathode surface sticking as well as devising a means of experimentally distinguishing the surface reaction products will be needed.
Table 2.4: Calculated loss (mol m\(^{-3}\) s\(^{-1}\)) of species at –800-V cathode potential whose neutral counterparts have been observed in Titan’s upper atmosphere. The larger value at either the midpoint or outlet is reported.

<table>
<thead>
<tr>
<th>Species</th>
<th>90:10</th>
<th>85:10:5</th>
<th>85:10:5</th>
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</thead>
<tbody>
<tr>
<td>N(_2)/CH(_4)</td>
<td>N(_2)/CH(_4)/C(_2)H(_2)</td>
<td>N(_2)/CH(_4)/C(_2)H(_4)</td>
<td></td>
</tr>
<tr>
<td>C(_2)H(_2^+)</td>
<td>-</td>
<td>C(_2)H(_2^+)+C(_2)H(_2^+)\rightarrow H+C(_4)H(_3^+)</td>
<td>CH(_4^+)+C(_2)H(_2^+)\rightarrow H+2+C(_3)H(_4^+)</td>
</tr>
<tr>
<td></td>
<td>(&lt; 10(^{-6}))</td>
<td>(70.)</td>
<td>(10.)</td>
</tr>
<tr>
<td>C(_2)H(_4^+)</td>
<td>C(_2)H(_4^+)+C(_2)H(_4^+)\rightarrow H+C(_4)H(_7^+)</td>
<td>C(_2)H(_2^+)+C(_2)H(_4^+)\rightarrow CH(_3^+)+cl-C(_3)H(_3^+)</td>
<td>C(_2)H(_4^+)+C(_2)H(_4^+)\rightarrow H+C(_4)H(_7^+)</td>
</tr>
<tr>
<td></td>
<td>(6.1\times10(^{-6}))</td>
<td>(0.90)</td>
<td>(19.)</td>
</tr>
<tr>
<td>C(_3)H(_4^+)</td>
<td>-</td>
<td>N(S)+C(_3)H(_4^+)\rightarrow H(_2^+)+HC(<em>3)NH(</em>+)</td>
<td>N(S)+C(_3)H(_4^+)\rightarrow H(_2^+)+HC(<em>3)NH(</em>+)</td>
</tr>
<tr>
<td></td>
<td>(&lt; 10(^{-6}))</td>
<td>(0.0015)</td>
<td>(2.7\times10(^{-4}))</td>
</tr>
<tr>
<td>C(_2)H(_2)</td>
<td>-</td>
<td>C(_2)H(_2^+)+C(_2)H(_2^+)\rightarrow H+C(_4)H(_3^+)</td>
<td>C(_2)H(_2^+)+CH(_3^+)\rightarrow H(_2^+)+cl-C(_3)H(_3^+)</td>
</tr>
<tr>
<td></td>
<td>(&lt; 10(^{-6}))</td>
<td>(70.)</td>
<td>(0.0057)</td>
</tr>
<tr>
<td>C(_2)H(_4)</td>
<td>C(_2)H(_4^+)+CH(_5^+)\rightarrow CH(_4^+)+C(_2)H(_5^+)</td>
<td>C(_2)H(_4^+)+C(_2)H(_2^+)\rightarrow H+C(_4)H(_5^+)</td>
<td>C(_2)H(_4^+)+C(_2)H(_5^+)\rightarrow CH(_4^+)+C(_3)H(_5^+)</td>
</tr>
<tr>
<td></td>
<td>(0.0028)</td>
<td>(1.9\times10(^{-5}))</td>
<td>(53.)</td>
</tr>
</tbody>
</table>

Continued on next page
Table 2.4 – continued from previous page

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<th>85:10:5</th>
<th>85:10:5</th>
</tr>
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<tr>
<td></td>
<td>N₂/CH₄</td>
<td>N₂/CH₄/C₂H₂</td>
<td>N₂/CH₄/C₂H₄</td>
</tr>
<tr>
<td>C₄H₂</td>
<td>-</td>
<td>C₄H₂+C₂H₅⁺→C₂H₄+C₄H₃⁺</td>
<td>C₄H₂+C₂H₅⁺→C₂H₄+C₄H₃⁺</td>
</tr>
<tr>
<td></td>
<td>(&lt; 10⁻⁶)</td>
<td>(0.085)</td>
<td>(1.8×10⁻⁴)</td>
</tr>
<tr>
<td>HCN</td>
<td>HCN+C₂H₅⁺→</td>
<td>HCN+ N₂(X,v=0)⁺→</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>C₂H₄+HCNH⁺ (4.0×10⁻⁶)</td>
<td>N₂(X,v=0)+HCN⁺ (1.3×10⁻⁶)</td>
<td>(&lt; 10⁻⁶)</td>
</tr>
</tbody>
</table>
Figure 2.4: Comparison of experimental and calculated THS anode currents for different precursors.

Figure 2.4 shows the experimental and calculated anode currents. Argon is included as a check since it has a different collisional cross section than N$_2$ or the precursor hydrocarbons. For the cathode potentials considered, the anode current is linear and exhibits relatively modest variation with composition in the range of 100 mA at –1000 V. The experimental and calculated values are within a factor of about two. The small discrepancy could be a result of transverse gradients in the electric or density fields, which are not captured by the one-dimensional model.

The electron population initiates the chemistry, so accurate modeling of the electron physical properties is important. Agreement of the modeled and experimental anode currents is a first indication that the predicted electron densities are correct. The insensitivity of the anode current to the mixture used is an important observation. Adding minor constituents like acetylene or ethylene allows chemical pathways to be
probed under the assumption that the plasma properties are not drastically altered by their presence. Because the anode current is roughly the same for the $\text{N}_2$ and $\text{N}_2/\text{CH}_4$, the electron densities are likely similar. Consequently, the electron impact reactions that initiate the chemistry probably vary mostly due to the partial pressures of molecules in the flow not due to the electron density. Another reason the predicted electron density is probably correct is that the relative abundances for the primary ions ($\text{N}_2^+/	ext{CH}_4^+$ and $\text{C}_2\text{H}_2^+/	ext{CH}_4^+$) are in agreement. The electron densities must also therefore be in agreement according to the principle of quasi-neutrality.

The calculated electron density distribution at times near breakdown is plotted in Fig. 2.5 for a particular mixture and potential. As the magnitude of the negative cathode voltage increases, the electric field in the plasma channel induces electron migration toward the anode (inlet). The electron density increases by many orders of magnitude within the first $0.15$ $\mu$s after the beginning of the discharge to more than $10^{12}$ cm$^{-3}$. The breakdown is therefore essentially instantaneous compared to the $300-\mu$s duration of the discharge. By $0.3$ $\mu$s, the electron density distribution equilibrates, reaching a steady state, and is relatively constant across the plasma channel except near the cathode where it falls by more than two orders of magnitude. The decrease in electron density near the cathode is expected by analogy to static discharges [14] and is commensurate with what is observed on-axis in two-dimensional modeling of the COSmIC plasma channel [18,19].

The calculated steady-state voltage distribution within the plasma channel is shown in Fig. 2.6 for the various precursor gases with $-800$-V cathode potential. As a result of shielding, the voltage is fairly constant across most of the plasma channel.
Near the surface of the cathode, ion bombardment yields a lower potential, which depends on the precursor mixture: \(-125\) V for nitrogen gas compared with \(-80\) V for \(\text{N}_2/\text{CH}_4/\text{C}_2\text{H}_4\). The voltage gradient near the cathode is consistent with the decrease in electron density observed in that region (Fig. 2.5), which corresponds to a larger Debye length and reduced shielding.

In addition to calculating parameters that can be compared to experimental measurements for validation of the model or that can give us insight into operating parameters that are not measureable in the laboratory, the model allows us to follow the evolution in time of the different species produced by the chemistry occurring in the THS plasma cavity. Figure 2.7 shows the transient mixing ratios of ions at the outlet for the \(\text{N}_2/\text{CH}_4/\text{C}_2\text{H}_2\) mixture driven by \(-800\)-V cathode potential. These calculated abundances are all trace quantities at the ppm level and are grouped according to the number of carbon atoms. They show that during breakdown, the ion mixing
Figure 2.6: Calculated voltage distribution across the plasma channel for different precursors at −800-V cathode potential.

ratios increase by many orders of magnitude then are constant after approximately 3.5 µs, which nearly corresponds to the residence time of the gas flowing through the channel. Similarly, Fig. 2.8 shows the modeled time-dependent mixing ratios of neutral species for the same conditions as Fig. 2.7. The evolution of the neutral nitriles differs from their corresponding ions because HCNH$^+$ feeds many reactions that make HCN, which changes the abundance of both species compared with Fig. 2.7; however, the neutral hydrocarbon species generally have similar time dependence to their ion counterparts except the abundance is about two orders of magnitude greater. This correspondence derives from neutralization by impact with the cathode. Whether or not these neutralization rates are realistic for the THS experiment will require measurement of the neutral species, which is not possible with the current configuration of the THS setup because ions of the precursor gas saturate the detector. Future measurements of the neutrals should be possible given their large abundances and
will impose additional constraints on the THS chemical network.

Modeling the trace species formation inside the plasma channel is important. The time dependence of the chemistry is difficult to measure directly because the plasma beam is dispersed inside the Re-TOF-MS optics. Using the model, we find that the plasma achieves chemically steady conditions over most of the discharge. The ion equilibration time suggests the THS flow is steady during more than 99 percent of the discharge time. The faster equilibration time for electrons suggest that the trace species chemistry has little effect on the overall electron population. Other slow-flow plasmas (e.g., [31]) have shown that chemistry continues many seconds into steady discharges. In addition to truncating the chemistry by expanding to low temperature, the short residence time in the THS plasma channel limits the electron dosage and avoids complicated further processing of newly formed products.

Figures 2.9 and 2.10 compare calculated electron abundances of the THS plasmas with Cassini measurements of Titan’s upper atmosphere. In Fig. 2.9, the steady electron number density for the plasma channel is plotted with Cassini radio and plasma wave science (RPWS) data from [44]. The THS electron density is many of orders of magnitude greater than the upper atmosphere of Titan, which is approximately $10^3 \text{ cm}^{-3}$ at 1000 km. The ionization fractions, however, are comparable in the THS plasma and Titan’s upper atmosphere. Figure 2.10 shows that the THS ionization fraction varies between about $10^{-8}$ and $10^{-5}$ depending on the position in the channel and precursor gas. The ionization fraction at Titan increases from about $10^{-7}$ at 1000 km to more than $10^{-5}$ at 1400 km. The Titan data was calculated using the electron number density published by [44] along with an approximate neutral number
Figure 2.7: THS ion abundances calculated at the outlet for 85:10:5 N$_2$/CH$_4$/C$_2$H$_2$ mixture with −800-V cathode potential.
Figure 2.8: THS neutral abundances calculated at the outlet for 85:10:5 N$_2$/CH$_4$/C$_2$H$_2$ mixture with -800-V cathode potential.
Figure 2.9: Calculated THS electron density versus position at -800-V cathode potential for various precursors compared with Cassini high-altitude RPWS data [44]. Arrows point to the relevant horizontal axes. THS calculation and observations have a shared vertical axis. Scatter in the observational data is represented by the shaded region.

density that comes from a sum of the nitrogen and methane neutrals measured by the Ion and Neutral Mass Spectrometer (INMS) on Cassini [28].

Figure 2.11 shows the electron temperature for the plasma channel and Titan’s upper atmosphere. The trace for Titan is corroborated by an isolated observation at a solar zenith angle of about 10 degrees when the electron temperature at 1200 km was observed to be about 1 eV, increasing to approximately 1.1 eV at 1350 km [45]. The THS electron temperature over most of the plasma channel falls within the range of the scattered observational data above about 1300 km for the four different mixtures plotted: about 1 eV over most of the plasma channel, spiking to approximately 5 eV near the cathode.

Figures 2.9 through 2.11 help to establish the degree to which THS experiments
may be extrapolated to Titan. Nominally, UV and EUV are responsible for about 90 percent of the ionization in Titan’s upper atmosphere, and about 10 percent is due to magnetospheric electrons [6]. While ionization in the THS plasma is dominated by electron-impact reactions, the agreement of the ionization fraction and mean electron temperature between the THS experiment and observational data collected by Cassini implies that the glow discharge is a favorable ionization source for stimulating chemistry in the analog experiments. Furthermore, the comparable ionization fraction in the THS experiment and Titan’s ionosphere implies that the importance of ion-neutral and neutral-neutral reactions might be similar in these two plasmas. The neutral (and electron) number density is many orders of magnitude greater in the THS experiment than in Titan’s upper atmosphere; however, the THS density is
Figure 2.11: Calculated THS electron temperature versus position at −800-V cathode potential for various precursors compared with Cassini high-altitude RPWS/INMS data [44]. Arrows point to the relevant horizontal axes. THS calculation and observations have a shared vertical axis. Scatter in the observational data is represented by the shaded region.
at or perhaps below the limit of where we expect three-body reactions to occur, and the level of agreement between model and THS experiment implies that they are not dominant; at least not across the species we track. Also, it is possible that the greater number density combined with short residence time leads to a more realistic degree of reaction in the THS experiment than would occur at lower density. To see why this could be true, consider a hypothetical electron impact reaction involving CH$_4$. The roughly $10^8$ and $10^{12}$ times greater density of electrons and CH$_4$, respectively, in THS compared to Titan’s upper atmosphere yields a reaction rate that is 20 orders of magnitude faster, nominally. The lifetime of CH$_4$ in Titan’s atmosphere is on the order of 20 million years [46, 47]. The ratio of that atmospheric lifetime to the THS plasma channel residence time is about $10^{20}$. The extent of a particular reaction should therefore be comparable at the order-of-magnitude level between the Titan and THS cases.

There are plans to measure neutrals in future THS experiments, which will further constrain the THS chemical network. Many of the neutral species that have been detected at Titan [13, 28, 41], are included in the present version of the model: C$_2$H$_2$, C$_2$H$_4$, C$_2$H$_6$, C$_3$H$_4$, C$_4$H$_2$, C$_6$H$_6$, CH$_3$CN, C$_2$H$_5$CN, C$_2$N$_2$, H$_2$, HCN, and HC$_3$N. With the exception of masses 41 and 52, which we suspect are probably not CH$_3$CN$^+$ and C$_2$N$_2$$^+$, respectively, but C$_3$H$_5^+$ and C$_4$H$_4^+$, respectively, in the mixtures presently discussed based on Ar/N$_2$ substitution, and mass 78 (benzene), the positive ions of all these species are observed in the THS experiments making it likely that their neutral counterparts are also involved in the chemistry.

Negative ions at Titan have attracted a lot of attention [30, 48–50], and the
Chapter 2: A Model of Titan-like Chemistry to Connect Experiments and Cassini Observations

THS experiment will be reconfigured to study them in the future. Negative ions were unexpected at high altitudes, and they affect Titan’s nighttime electric field, which affects the rate that positive ions are lost to Saturn’s magnetosphere [30]. Negative ion densities in the ionosphere measured by CAPS-ELS range from approximately $10^{-1}$ to $10^{1}$ cm$^{-3}$ binned across many $M/Z$. This is less than the density of small, positive ions measured by INMS at 1000 km (e.g., 200 cm$^{-3}$ for $M/Z$ 52 [25]). [49] compared the electron negativities of a handful of Titan-relevant molecules. Of those, $C_2H$ and CN, both with large electronegativity, are tracked in the THS model. $C_2H$ occurs in modest abundance, about three times the density of $N_2(X,v = 0)^+$ for the 85:10:5 $N_2$/CH$_4$/C$_2$H$_2$ mixture at $-800$ V. If a significant fraction of these molecules participate in electron attachment, they could have an effect on the plasma properties. At Titan, the $C_2H^-$/$C_2H$ relative abundance is on the order of $10^{-5}$ [25]. Some other species have a higher proportion of negative ions; for instance, $CN^-$/$CN$ is about $10^{-2}$. Negative ions may be important in the THS experiment because i) PAHs and cyanoaromatics, possible primary particles in aerosol formation [41], have large electronegativities and ii) because the negative charge affects ambipolar diffusion.

Tholins are produced in THS experiments [16], and they have been characterized. Because these particles are produced in small quantities, we have considered their influence on chemical species loss to be negligible; however, future iterations of the model could be used to deduce how tholins are synthesized. While some pathways for solids formation have been proposed [7–9], determining what gases contribute to particle nucleation and growth is an active area of research. In general, the aerosol mass spectra are complicated and vary significantly with the type of precursor mix-
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ture [1, 51–53]. Even trace quantities of precursor gases (e.g., 10 ppm benzene) can strongly affect the composition and morphology of the solids [54]. In future work, we hope to extend the THS model to include particle formation and to leverage the controlled, truncated chemistry of the THS experiment to explore the species that participate in preliminary particle formation.

2.5 Conclusion

We presented a new model of the Titan Haze Simulation plasma. Comparisons of the mass spectra and anode current demonstrate that the model is in good, semi-quantitative agreement with measurements. Calculations confirm that chemistry is truncated by the short residence time of the flowing gas in the plasma channel, which is a characteristic feature of the THS experiment. The ionization fraction and electron temperature predicted by the model are commensurate with those for Titan’s upper atmosphere, which reaffirms that the glow discharge is a good analog environment for studying Titan chemistry. In the present model, condensation of saturated hydrocarbon and nitrile products is ignored. Future measurements and analysis of the neutral molecules might allow us to determine which species are (super)saturated and thus identify which species might lead to particle growth by condensation, or to deduce which molecules might participate in polymerization. We hope to test the model against additional minor precursors, like HCN, in the future. These steps will allow us to refine the chemical network and continue addressing questions about the inventory of organic molecules in Titan’s atmosphere.
Chapter 3

Miniature Cavity for In Situ
Millimeter Wave Gas Sensing

3.1 Introduction

*In situ* measurements of point gas sources are important for planetary and sample return missions. Gas sensing at microwave, millimeter or sub-millimeter wavelengths yields precise determination of molecular and isotopic content based on the frequency dependent absorption of narrow rotational transitions at low pressure. The invention of cavity-based pulsed microwave techniques [55] enabled accurate measurement of molecular structure. These techniques have been improved over the years to detect small quantities of reactive species in discharge plumes [56] and even chiral molecules [57]. In general, rotational spectroscopy is a long-standing field [58] that is experiencing a resurgence as an analytical technique because of some recent technological advances [59–61] that have reduced measurement time and improved sample
preparation. The main strength of rotational spectroscopy is the high resolution and accuracy attainable for individual transition frequencies leading to precise identification for each polar species including differentiation of isomers and isotopologues. The mechanics that govern those transition frequencies are written out in Appendix B.

The Jet Propulsion Laboratory has pursued various kinds of in situ spectrometers in the millimeter (mm) and sub-millimeter (sub-mm) regimes to address the need to characterize the chemical and organic makeup of the solar system [62, 63]. The in situ devices are enabled by multiplier chain sources, which are compact and more efficiently operated than backward wave oscillators or klystrons [64,65] and are therefore able to streamline requirements for remote deployment. Early targets for an in situ sub-mm absorption spectrometer operating around 300 and 600 GHz were 2 liters, 20 watts, and 10 kilograms [66]. Drouin et al. [67] reported measurements of a plasma mixture made using a 600 GHz instrument that roughly met those goals.

Recently, a first gas detection was reported with a new spectrometer design based on a pulsed Fourier transform millimeter-wave (FTmmW) approach incorporating a Fabry-Perot resonator cavity [68]. The cavity accumulates energy so that very little input power is required to pump rotational transitions. Instrument-level power consumption is on the order of 200 mW. Synthesis, amplification and mixing of the mm-wave radiation are all handled on-chip [69] using custom CMOS electronics. Lock-loop frequencies of the new design are in the range of 92-105 GHz.

Compared with the laboratory cavity spectrometers operating at microwave frequencies, the new mm-wave cavity has two major advantages. First, the higher frequencies result in stronger transitions so target molecules need not be cooled.
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The transitions are stronger because the Boltzmann distribution has a peak at mm-wavelengths [66] for molecular masses less than about 100 amu. Second, the reduction in wavelength at high frequencies means that smaller cavity optics achieve an adequately high Fresnel number (i.e., greater than about 10 [70]) to control diffraction losses. The result, when combined with the integrated CMOS chips, is a compact, potentially space-deployable molecular sensor. The most challenging technological obstacles have been overcome in the current version of the FTmmW spectrometer, which is significantly smaller than conventional laboratory FTmmW instruments. The circuit board in the new design is approximately 10 cm by 5 cm in area, and the cavity is as small as 12 cm³ in volume: 25 mm mirror separation with a 25 mm diameter curved mirror. For comparison, Table 3.1 lists the properties of some cavity spectrometers that have been built for laboratory studies. Although the instruments in this list were not intended to be compact or deployable, the tabulation shows the magnitude of the size reduction achieved with the new device: more than 200 times smaller than the smallest pulsed Fabry-Perot cavity that has achieved a gas detection.
Table 3.1: Survey of laboratory Fabry-Perot cavities.

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Instrument</th>
<th>Gas</th>
<th>Q</th>
<th>Cavity Vol., cm$^3$</th>
</tr>
</thead>
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<tr>
<td>[71]</td>
<td>100 – 300 GHz semi-confocal cavity, klystron</td>
<td>N$_2$O</td>
<td>$3 \times 10^5$</td>
<td>4800</td>
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<td>[72]</td>
<td>150 GHz confocal cavity, beam splitter coupler</td>
<td>H$_2$O</td>
<td>$1 \times 10^6$</td>
<td>8600</td>
</tr>
<tr>
<td>[73]</td>
<td>48 – 81 GHz confocal cavity, waveguide coupler</td>
<td>O$_2$</td>
<td>$6 \times 10^4$</td>
<td>3100</td>
</tr>
<tr>
<td>[55]</td>
<td>4.5 – 18 GHz confocal cavity, pulsed excitation</td>
<td>OCS</td>
<td>$2 \times 10^5$</td>
<td>67000</td>
</tr>
<tr>
<td>[74]</td>
<td>44 – 98, 113-200 GHz confocal cavity</td>
<td>H$_2$O, O$_2$</td>
<td>$6 \times 10^5$</td>
<td>2800</td>
</tr>
<tr>
<td>[75]</td>
<td>1 – 10 GHz confocal cavity, pulsed excitation</td>
<td>many</td>
<td>$4 \times 10^4$</td>
<td>$2 \times 10^6$</td>
</tr>
<tr>
<td>[76]</td>
<td>300 GHz wire-grid polarizers</td>
<td>none</td>
<td>$1 \times 10^5$</td>
<td>2300</td>
</tr>
<tr>
<td>[77]</td>
<td>250 GHz wire-grid polarizers</td>
<td>none</td>
<td>$1 \times 10^5$</td>
<td>400</td>
</tr>
<tr>
<td>present</td>
<td>92 – 105 GHz semi-confocal cavity, CMOS</td>
<td>many</td>
<td>$2 \times 10^3$</td>
<td>12</td>
</tr>
</tbody>
</table>

*25/25 mm mirror (focal length/diameter)*

1 Here, confocal cavity means two curved mirrors.
While the cavity in the new FTmmW device is notionally similar to Fabry-Perot cavities in laboratory instruments, there are differences in the design and implementation that motivate the present Chapter. For example, the quality factor (Q-factor) that we report here is intentionally lower than those listed in Table 3.1. In the next section, we explain why. Our characterization shows that the new Fabry-Perot cavity meets the design targets for Q-factor and that the trades in sensitivity and resolution are manageable at the present form factor. Pulse bandwidth is adjusted by tuning the pulse duration in agreement with time-bandwidth product predictions. The spectra of two molecules, N\textsubscript{2}O and CH\textsubscript{3}OH, are presented as proof that a small cavity with modest Q-factor is capable of making gas detections. Planetary science and other fields that utilize in situ chemical sensing such as pollution monitoring and manufacturing might benefit from the chemically-specific measurements enabled by the technology described herein.

3.2 Materials and Methods

3.2.1 Cavity Design

For in situ deployment, the spectrometer must be compact and low-power. At the same time, rapid acquisition across a wide bandwidth is desirable in many circumstances. Modern chirped pulse instruments are capable of rapid, wide-bandwidth measurements, but at the cost of high power consumption and high data-rates. Using a cavity enables field amplification over a moderately wide, tunable bandwidth that simultaneously reduces power consumption and data-rates. A scanning strategy is
implemented to cover a wide bandwidth. A reasonable duration for recording a spectrum of an unknown gas is, perhaps, 30 seconds. At a pulse rate of 10 kHz with 1000 spectral averages, 325 steps are needed to cover the 13 GHz instrument bandwidth in about 30 s. This mandates a mode full-width half maximum of about 40 MHz. The 40 MHz mode matches the cavity Q-factor, which is defined as

\[ Q = \frac{\omega W}{dW/dt} = \frac{f}{\Delta f} \]  

(3.1)

such that, near the \( f = 100 \text{ GHz} \) operating frequency, the cavity Q-factor should be approximately 2500 and the mode width \( \Delta f \) should be about 40 MHz. Because a cavity Q-factor of 2500 is somewhat lower than those for the laboratory instruments in Table 1, an important part of this study is determining if moderate Q-factors are able to pump molecular transitions using the CMOS amplifier technology. These cavities support multiple modes with mode numbers \( (q) \) in the range 12-15, where \( q \) is the number of wavelengths in a round-trip of the semi-confocal cavity tuned to frequency \( f \) by adjusting the mirror spacing to \( qc/(2f) \). Calculations using a resonator model including diffractive losses, as well as the Rabi formula, predict that a semi-confocal cavity with optics having a nominal 25 mm aperture are able to achieve Q-factors near the target range that are able to amplify the roughly 1mW power of a CMOS device to pump molecular transitions in less than the cavity build up time \( (qQ/f = 300 - 375 \text{ ns}) \). To get a sense for the loss factors that define the Q-factor in our design, some calculations are discussed next.

The couplers and cavity can be represented as a microwave circuit [55,78]. See a circuit schematic in, for example, Fig. 2 of reference [55]. The impedance of the
effective circuit is

\[ Z = n_{Tx}^2 R_{Tx} + R + n_{Rx}^2 R_{Rx} + i \left( \omega L - \frac{1}{\omega C} \right) \]  \hspace{1cm} (3.2)

where \( n_{Tx}^2 R_{Tx} \) and \( n_{Rx}^2 R_{Rx} \) are the transmitter and receiver resistances, respectively, and \( R, L, \) and \( C \) are the cavity circuit parameters. On resonance, the energy stored in the circuit is that stored by the inductor current, \( 1/2LI^2 \). The energy dissipation is the sum of the losses through the couplers and the unloaded cavity. These terms give

\[ Q = \frac{\omega_c L}{R(1 + \beta_{Tx}^2 + \beta_{Rx}^2)} \]  \hspace{1cm} (3.3)

where \( \omega_c \) is the resonance frequency and \( \beta_{Tx} \) and \( \beta_{Rx} \) are the coupling coefficients, e.g., \( \beta_{Tx} = n_{Tx}^2 R_{Tx}/R \), defined in Balle and Flygare’s paper [55]. Separating the parts of this result, we have

\[ \frac{1}{Q} = \frac{1}{Q_0} + \frac{1}{Q_{Tx}} + \frac{1}{Q_{Rx}} \]  \hspace{1cm} (3.4)

where \( Q_0 = \omega_c L/R \), \( Q_{Tx} = \omega_c L/(R\beta_{Tx}) \), and \( Q_{Rx} = \omega_c L/(R\beta_{Rx}) \) in terms of the equivalent circuit parameters. The unloaded Q-factor, \( Q_0 \), depends on the reflection and diffraction losses per roundtrip according to Eq 3.5,

\[ \frac{1}{Q} = \frac{1}{Q_r} + \frac{1}{Q_d} = \frac{\alpha_r}{2\pi d} + \frac{\alpha_d}{2\pi d} \]  \hspace{1cm} (3.5)

where \( d \) is the cavity length and \( \alpha_r \) and \( \alpha_d \) are the reflection and diffraction fractional losses per trip, respectively. The reflection losses are small such that \( Q_r = d/(2\delta) \) is on the order of \( 5 \cdot 10^4 \) (i.e., the skin depth \( \delta \) is about 300 nm).
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The diffraction losses for idealized eigenmodes of a spherical/planar mirror with no couplers are calculated by solving the Fresnel-Kirchoff formulation of Huygen’s principle in the manner prescribed by Huertley and Streifer [79]. The eigenvalues, $\sigma_{0n}$, are calculated for the primary and secondary modes ($n = 0, 1$) and the loss per roundtrip is obtained using $\alpha_d = 1 - |\sigma_{0n}|^2$. The assumptions in this calculation are $i$) that the cavity dimensions are large relative to the wavelength and $ii$) that the corners of the planar mirror do not contribute significantly to the modes so that the apertures can be approximated as circular. The diffraction Q-factor, $Q_d = 2\pi d/\alpha_d$, is calculated for the primary mode as a function of cavity length for three different spherical mirror geometries. The results are compared to experiments later in the paper and used to estimate the coupling efficiency.

In addition to the Q-factor analysis, eigenmode simulations of the cavity were performed to predict mode shapes and confirm resonant frequencies. Mode volumes are calculated by a volume integral over the domains where the field intensity in the cavity is greater than or equal to half the peak intensity. Molecules travelling through the mode volume can produce signal, and for fixed coupling and Q-factor parameters, the signal amplitude is proportional to the sample density [80]. Therefore, the mode volume determines the amount of a finite volatile or ablated sample that must be injected into the cavity.

3.2.2 Experimental

The spectrometer encompasses several subsystems. The device begins with a custom mm-wave transceiver made from two integrated circuits that are wire bonded
to a printed circuit board. The circuit board also contains an off-axis strip coupler structure, a microprocessor and an USB Atmega chip with loaded firmware. Low-frequency signals are fed to the transceiver chips for locking the mm-waves CMOS devices to tunable radio frequencies at a factor of 1920. The frequencies are chosen to enable an intermediate frequency (IF) between DC and a few hundred MHz. For the present experiments, RF is synthesized externally in the range of 48 to 55 MHz. New ΔΣ modulator-based fractional divider sources are being adopted, which are deployable and have kHz tunability. A CMOS switch [81] pulses the transmitter radiation, which is fed to a laser-micro-machined coupling structure on a gold-plated Duroid film that doubles as a flat end mirror. The semi-confocal cavity defined by the flat- and the spherical- end mirrors supports quasi-optical $TEM_{plq}$ modes. The printed circuit board and its integrated flat mirror are mounted on x/y- and tip/tilt-manual translation and rotation stages. The curved mirror is linearly translated in the z-direction using an encoded micrometer or piezomotor stage that has a full range of 15 mm. The curved mirrors used were glass coated in either aluminum or gold. We did not observe a significant difference between the two coatings; a finding that agrees with the expected small mirror reflection loss. Three different commercially-available curved mirror geometries are tested in the mode scans: 50/50 mm, 25/25 mm and 25/50 mm (diameter/focal length). The 25/25 mm mirror is used in the gas measurements. Figure 1a is a photograph of the printed circuit board containing mm-wave circuit components and the flat end mirror with embedded coupler. Figure 1b shows schematically how the circuit board is integrated with the rest of the spectrometer including the spherical end mirror.
The cavity mirrors are coarsely positioned on a common axis normal to one another. Fine alignment is done by repeatedly scanning the z-axis of the curved mirror through many half-wavelengths while measuring the amplitude of the transmitted signal until the baseline between modes is approximately flat and there are few or no high-order modes. With a little practice, just a few iterations are needed to align the cavity. Once aligned, we have found the shape and quality of the modes to be relatively stable with only small drifts day-to-day due to temperature change. At 100 GHz, the design Q-factor of 2500 corresponds to a FWHM of 40 MHz. At the longest cavity lengths measured (90 mm), the mode index \( q + 1 \) in the range of 31. The FWHM mirror spacing, \( \Delta \nu \approx (c/2) \left( \frac{2}{d + \Delta d/d^2} \right) (q + 1) \), gives a tolerance on the mirror spacing of 60 \( \mu \)m. The step size was less than 3 microns in each of the scanning experiments.

The new spectrometer operates in the time-domain. A short pulse of radiation is transmitted into the cavity to excite molecular dipoles. The signal at the receiver is down-converted with a mixer pumped at a frequency close (around 100 MHz) to the transmitter frequency. The resulting intermediate frequency is then Fourier transformed to yield the rotational spectrum. Conventionally, the free induction decay of the radiating molecules is measured by positioning the Fourier transform gate after the pulse because doing so eliminates source noise from the measurement. If source noise is not too great, the transform gate can be moved partially into the transmitter pulse. This approach is useful for molecules with short transit times or short-lived rotational transitions and is how the detections in the present Chapter were done. Presently, the signal leaving the receiver is processed off-chip. In the amplitude
measurements used to deduce Q-factor, the time domain signal in Fig. 3.1 is fed to a low-barrier Schottky diode detector crystal and lock-in amplifier. A switch frequency of 1 kHz is used to trigger pulses on the chip and the lock-in although we have found the spectrometer operates just as well at tens of kilohertz. Free induction decay signals of molecular gases are Fourier transformed off-chip using a 1 GHz bandwidth oscilloscope. An on-chip fast-Fourier transform (FFT) module is in formulation. The mode measurements presented were performed in air at ambient temperature and pressure. The N\textsubscript{2}O and CH\textsubscript{3}OH gas lines were measured at low pressure with an identical spectrometer.

For systematic instrumentation tests with sample gases, we chose two well characterized species with spectra in the instrument bandwidth. The first, nitrous oxide, or N\textsubscript{2}O, is a colorless gas with a dipole moment of 0.16 Debye. The main isotopologue, \textsuperscript{14}N\textsubscript{2}\textsuperscript{16}O, has transition at 100.49174 GHz. Nitrous oxide was streamed through the vacuum chamber following a gas regulator and needle valve. This gas, having a weak dipole moment, is fairly representative of the worst case scenario for pulse echo detection, for which the excitation pulse must achieve sufficient pumping prior to the cavity build-up time. As expected, the optimal pulse lengths were equivalent to this time. Being a linear molecule with a partition function of 563.5, the signal strengths under a variety of conditions are tens of microvolts for pulse sizes of a half Volt. The second gas chosen, methanol, or CH\textsubscript{3}OH, is a colorless liquid with a high vapor pressure and a dipole moment of 1.67 Debye. Several transitions of methanol are visible in the instrument bandwidth, and we present results from the transition near 100.639 GHz. Vapor pulled from a liquid vessel was regulated with a Teflon
Figure 3.1: a) Printed circuit board containing CMOS transmitter and receiver chips and flat mirror of semi-confocal cavity. b) Schematic of breadboard spectrometer.

needle valve to pressures up to 50 mTorr. Despite the larger dipole moment, the larger partition function of 9473.1 reduces the signal strength to a few microvolts for similar pulse magnitudes, however, the pulse width can be significantly narrower.
3.3 Results

A scan of the synthesizer frequency at fixed cavity length for a 25 mm diameter, 25 mm focal length mirror is shown in Fig. 3.2. The cavity length is nominally 25 mm. The mode type and Q-factors are listed for the peaks associated with modes \( q = 14 \) and 15. Figure 3.3 shows the eigenmode simulation result corresponding to the mirror geometry that was measured in the previous figure at a cavity length of 24.5 mm. The calculated eigenfrequencies are listed together with the half-intensity mode volumes.

Figure 3.2: Measured spectrum at fixed mirror position for \( \varnothing 25 \text{ mm}, f = 25 \text{ mm} \). Mode quality factors listed in bold.

Figure 3.4 is a two-dimensional map of the signal amplitude versus cavity length and transmitter frequency for a 50 mm diameter, 50 mm focal length mirror. The plot covers more than 20 half-wavelength nodes and more than one free spectral range. Sections at fixed transmitter frequency and fixed cavity length are projected onto the x- and y-axes, respectively. Across the tested range, there is no mode
Figure 3.3: Numerically calculated eigenmodes corresponding to Figure 2 with $\varnothing 25$ mm, $f = 25$ mm. Primary modes (1 and 3) and secondary modes (2 and 4), which are the types observed in the cavity, are separated by about 6 GHz, which falls within the spectrometer bandwidth of approximately 13 GHz. Half-intensity mode volumes are listed, which can be important when measuring forcibly volatilized samples.

Overlap or crossing. At short to intermediate cavity lengths, the primary mode is most prominent; however, the second- and higher-order modes are also visible. At cavity lengths beyond about 80 mm, only the primary and secondary modes appear.

Mode scans of three different curved mirror geometries are plotted in Figs. 3.5 at five different transmitter frequencies spanning the instrument range: diameter/focal length of 50/50 mm, 25/50 mm, and 25/25 mm. The primary modes peak amplitudes vary somewhat over this wide scan. The 25 mm diameter mirrors have monotonically decreasing peak amplitude with increasing cavity length. The 50/50 mm primary modes are not monotonic but experience some undulation depending on synthesizer frequency. Secondary modes are visible in each mirror geometry and generally have smaller amplitudes than the primary modes although some of the 25 mm diameter
mirror scans have secondary mode amplitudes that approach the primary mode amplitudes. In all cases, the peak amplitudes are relatively constant over most of the instrument range but decrease by a factor of two to five compared to the strongest peaks.

Figure 3.6 shows the primary- and secondary-mode Q-factors for the different mirrors at the bounding frequencies. These data points were obtained by fitting the position scans in the regions immediately surrounding each peak. The 25/50 mm mirror exhibits relatively flat Q-factors for both modes (1000 and 400 at 94 GHz or 2000 and 600 at 104 GHz) across the scan range. The 25/25 mm mirror has a more scattered but also flat Q-factor of about 2500 in the primary and a secondary mode that peaks at approximately 1000 near one focal length. The 50/50 mm mirror has a primary mode Q-factor that increases roughly linearly (log scale considered) to 4000 and 6000 at 94 and 104 GHz, respectively, with increasing cavity volume.
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The secondary mode for the 50/50 mm mirror gives a Q-factor that increases then is constant at around 1000. The thin traces are calculated diffraction Q-factors \((i.e., \, Q_d)\) for the primary modes. For the 25/50 mm case, is comparable to the overall Q-factor over most of the cavity lengths measured. For the 25/25 mm case, approaches the overall Q-factor only at the longest cavity lengths. For the 50/50 mm mirror, \(Q_d\) is significantly greater than the overall Q-factor throughout the test range.

Figure 3.7 is a plot of FWHM versus pulse duration along with traces representing the time-bandwidth product for square and \(sech^2\) envelopes in the time domain. The measured pulses follow the square-pulse uncertainty principle over most of the range and transition toward the \(sech^2\) pulse product at durations less than about 10 ns. Some of the time-domain pulses of different durations are plotted in the inset along with their Fourier Transforms. The time signals show the ratio of on/off amplitudes are on the order of 7 dB in voltage or 14 dB in power. Ideally the off states would have zero amplitude, but there is some leakage in the CMOS switch. This leakage manifests itself in the transformed pulses as a spike at the intermediate frequency, which has been removed from the FFT data. Fits of \(sinc^2\) functions are shown as thin, blue traces. No de-convolution of the mode has been done because the mode is sufficiently wide to observe the oscillations at the fringes.

Measurements of the \(J = 3 \leftarrow 4\) rotational transition in \(N_2O\) and the \(12_3 \leftarrow 13_2\) rotational transition in \(CH_3OH\) are shown in Fig. 3.8 at various pressures. Because we are transforming a small portion of the transmitter pulse along with the free induction decay, the cavity mode appears in the raw data. That baseline has been removed. Depending on the precise timing of the Fourier transform gate relative to
the pulse, the molecular signal can appear as an emission peak or as a dip that looks like a transmission spectrum. With the pulse and timing settings used in the present experiments, the rotational transitions we observed appeared as dips. The FWHM of the gas line is plotted as a function of pressure. The uncertainty is primarily determined by the pressure stability. At pressures above several tens of millitorr, the mean-free-path between collisions becomes comparable to the diameter of the cavity and the signals exhibit pressure broadening of approximately 52 MHz per Torr.

### 3.4 Discussion

The frequency scan in Fig. 3.2 is typical of the modes we have observed at different cavity lengths and with different mirror geometries. After repeating measurements, we found that the high-order modes, which are seen in the baseline between 97 and 102 GHz, can be mitigated with more careful alignment. See, for instance, Figure 3 in reference [68]. The primary and secondary modes \( TEM_{00} \) and \( TEM_{10} \) are clearly visible at 94.265 / 100.467 and 95.761 / 101.965 GHz, respectively. The 10 GHz scan that is plotted is sufficient to determine the free spectral range, which is approximately 6.2 GHz for the 25/25 mm mirror used in this measurement. The mode frequencies measured in Figure 3.2 agree reasonably well with those predicted by the calculation in Figure 3.3, which establishes confidence in the mode volume estimates, which are on the order of 5 mm\(^3\). A benefit of the small mode volumes is that forcibly volatilized samples do not have to fill a large volume to be efficiently measured. Smaller sample requirements are important for in situ measurements where the sample handling and throughput can be constrained.
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Over the 10 GHz band presented in Fig. 3.5, the different mirror types exhibit reasonably constant amplitude across most of the instrument range but roll-off relatively rapidly at the highest frequency. This is consistent with the power output of identical transmitter chips measured by a probe or embedded in waveguide structures and directed into a power meter. Studies are underway to determine the frequency dependences of the cavity coupler structure, which may also limit the bandwidth. Understanding and balancing these system-level trades will ultimately determine the useful bandwidth of the spectrometer.

The fitted Q-factors in Fig. 3.6 vary over the range of cavity lengths. Figure 3.2 showed that some of the peaks (e.g., $TEM_{0-0-15}$) are asymmetric. Some of the variation observed in the measured Q-factors comes from the quality of the fits to these asymmetric peaks. The 50/50 mm mirror exhibits linear Q-factor growth with cavity length as one would expect in the region of low, fixed diffraction loss (see Eq. 3.5). In contrast, the 25mm/50mm mirror shows near constant Q-factor over the test range because of the competing effects of diffraction loss and increasing mode volume at longer cavity lengths.

The diffraction Q-factors in Figure 3.6, which are calculated analytically, yield important information about the efficiency of the Duroid transmitter and receiver couplers. For the 50 mm diameter mirror at a cavity length of 85 mm, Eq. 3.4 predicts a Q-factor $1/Q \approx 1/5000 = 1/Q_r + 1/Q_d + 1/Q_{Tx} + 1/Q_{Rx} = 1/(5 \cdot 10^4) + 1/(2 \cdot 10^4) + 1/Q_{Tx} + 1/Q_{Rx}$. Assuming the coupling losses are the same for the transmitter and receiver, the coupling quality factors are on the order of $1.5 \cdot 10^4$. Mirror geometry and cavity length affect coupling, so this result is only approximate;
however, it agrees with the behavior observed for the smaller 25 mm diameter mirrors for which the overall cavity Q is governed by diffraction losses \(i.e., 1/Q \approx 1/1000 = 1/Q_r + 1/Q_d + 1/Q_{Tx} + 1/Q_{Rx} \approx 1/(5 \cdot 10^4) + 1/(1 \cdot 10^4) + 2/(1.5 \cdot 10^4)\). Since the Q-factors are in the desired range, and the pulses and molecular signals are clearly visible with the instrument, the coupling coefficients are deemed adequate.

Cavity Q-factor tunability is a desirable feature of a resonator [72]. In FTMW experiments, it can allow the generation of a \(\pi/2\) pulse (the time to completely saturate an upper state of a transition) without constraining the pulse bandwidth. The different mirror types in Fig. 6 demonstrate that there is flexibility in the Q-factor over the cavity length span and among the primary/secondary modes. Intentional selection of the cavity parameters yields a discretely variable Q-factor from 500 to 4000 \(i.e., 200 \text{ to } 25\text{ MHz mode bandwidths}\), which can be tailored according to the molecular pumping and bandwidth requirements of a particular application. Moreover, Figure 3.7 shows that the time-bandwidth product is satisfied and that the pulses are approximately square down to about 10 ns. Shorter pulses have a rounded pulse envelop whose time-bandwidth product approaches that of a \(\text{sech}^2\) profile. These short pulses are likely truncated by the mode bandwidth so the pulse shape transition is possibly just a filtering effect.

The time-domain absorption lines in Fig. 3.8 are at the expected frequencies [82]. Although the IF in this version of the instrument was relatively broad (MHz), collisional broadening is still easily observed. The changes in the fitted FWHMs agree with the expected pressure dependence of 5-15 MHz per Torr [66]. The intercept of the pressure broadening curve is partly determined by the offset of the pressure gauge.
used, but it also gives a measure of the transit time broadening, which is roughly 0.3 MHz. The broadening of the features results in reduced peak signal, and reduced contrast with background fluctuations such that ideal pressures for gas sensing are less than 0.1 Torr where the instrumental resolution is time-of-flight limited (about 300-600 kHz depending on mode size, molecular mass and temperature). Even with the relatively broad IF, line positions are accurate to one part in $10^6$.

The Fabry-Perot cavity in our FTmmW spectrometer is 12 to 180 cm$^3$ in volume. The gas detections we have just reported were done with a cavity configured with the 12 cm$^3$ cavity (25/25 mm mirror), which is more than a factor of 200 smaller than the smallest laboratory Fourier-transform spectrometer cavity in Table 3.1 that reported a gas detection [74].

*In situ* measurements of point gas sources are important for planetary and sample return missions. Gas sensing at microwave, millimeter or sub-millimeter wavelengths yields precise determination of molecular and isotopic content based on the frequency dependent absorption of narrow rotational transitions at low pressure. The invention of cavity-based pulsed microwave techniques [55] enabled accurate measurement of molecular structure. These techniques have been improved over the years to detect small quantities of reactive species in discharge plumes [56] and even chiral molecules [57]. In general, rotational spectroscopy is a long-standing field [58] that is experiencing a resurgence as an analytical technique because of some recent technological advances [59–61] that have reduced measurement time and improved sample preparation. The main strength of rotational spectroscopy is the high resolution and accuracy attainable for individual transition frequencies leading to precise identifica-
tion for each polar species including differentiation of isomers and isotopologues.

The Jet Propulsion Laboratory has pursued various kinds of in situ spectrometers in the millimeter (mm) and sub-millimeter (sub-mm) regimes to address the need to characterize the chemical and organic makeup of the solar system [62, 63]. The in situ devices are enabled by multiplier chain sources, which are compact and more efficiently operated than backward wave oscillators or klystrons [64, 65] and are therefore able to streamline requirements for remote deployment. Early targets for an in situ sub-mm absorption spectrometer operating around 300 and 600 GHz were 2 liters, 20 watts, and 10 kilograms [66]. Drouin et al. [67] reported measurements of a plasma mixture made using a 600 GHz instrument that roughly met those goals.

Recently, a first gas detection was reported with a new spectrometer design based on a pulsed Fourier transform millimeter-wave (FTmmW) approach incorporating a Fabry-Perot resonator cavity [68]. The cavity accumulates energy so that very little input power is required to pump rotational transitions. Instrument-level power consumption is on the order of 200 mW. Synthesis, amplification and mixing of the mm-wave radiation are all handled on-chip [69] using custom CMOS electronics. Lock-loop frequencies of the new design are in the range of 92-105 GHz.

\[3.4.1 \text{ Mission Considerations}\]

The laboratory measurements reported are intended to advance the Spec-Chip technology readiness level (TRL) so that it might one day be selected for a mission to space. There are many ways the Spec-Chip spectrometer could be packaged and deployed. At a planetary body with an atmosphere, such as Titan, a vacuum chamber
and sampling orifice would be used to regulate the pressure in the cavity and mitigate collisional broadening. Gases collected from the ambient environment or evolved from collected solid specimens would be flowed into this chamber or prepared in vacuo. The vacuum chamber could be part of a larger sample-handling system as is already done for the Tunable Laser Spectrometer (TLS) on Mars Science Laboratory [83].

Comet surface sample return (CSSR) is a specific mission concept where the new Spec-Chip spectrometer could add significant value, and is one we consider in more detail. A CSSR lander would collect and cache drilled specimens for return to Earth where laboratory testing for the elemental, isotopic, organic, and mineralogical content would be done. The fundamental objective of studying a returned sample would be to learn new information about the origin of the solar system and the early history of water and biogenic elements and compounds [84]. Science questions include [85]

1. What were the initial conditions of the solar system?

2. What inter-stellar matter was incorporated?

3. What were the primordial sources of organics?

4. Are organics synthesized today?

To address these questions, a comet sample mission would measure the abundances of volatile water isotopologues to determine H/D ratio, the abundance of trace organics, and radicals. The volatiles released during collection contain information that would contextualize a cached and returned sample and are a source of preserved material. Therefore, there are proposals to capture and return them. An alternative
approach, which would not involve the risks of hermetic sealing and temperature control during return, is to use a gas spectrometer to characterize the gases as they are volatilized.

The Spec-Chip spectrometer could be placed near drilling operations for this purpose. The spectrometer is small enough that its open cavity could be placed in the line of sight of outgassing products. Volatiles would be sensed by the device without extraneous plumbing. The low power consumption of the Spec-Chip spectrometer, less than 1 W, would have minimal impact on the overall power budget compared to the high-gain transmitter (35 W), drill (13 W), or onboard camera (2-5 W) [86].

CSSR measurements would require specific levels of sensitivity and range for science and contextualization. Sensitivity to HDO is already at ppm levels in a few mTorr of bulk water, resulting in SNR in 1 second of more than 10 for HDO at SMOW isotopic abundances. Based on theoretical detection limits, the ongoing trade space study, and CMOS chip upgrades indicate that one or two orders of magnitude higher sensitivity may be achievable.

Organics with two to four heavy atoms have been identified in mass spectra for the Rosetta mission [87] and might guide targeted spectra. The JPL spectral database [82] contains about half of the 16 molecules used to fit the COSAC mass spectra. Of those, about half have rotational lines in the 92–105 GHz range with adequate line strengths for ppm detection with the currently demonstrated system.

In addition to collecting data during coring operations, the Spec-Chip spectrometer could provide a CSSR mission with valuable data if the sensor is left in place after the mission. Measurements of high outgassing during perihelion would give scientists
species-specific information about loss rates.

3.5 Conclusion

The main strength of millimeter-wave spectroscopy is the specificity with which gases are identified based on the precise frequency of rotational transitions. Pollution monitoring, manufacturing, planetary science and other fields might benefit from in situ millimeter-wave measurements that definitively identify particular chemical species. The new FTmmW spectrometer is compact enough that it could be used as a deployable, in situ instrument. We have demonstrated that the design is able to detect rotational transitions near 100 GHz at meaningful spectral resolution. The results presented here show that the off-axis strip couplers are viable and that a Q-factor of the proper magnitude can be achieved using a very compact cavity. The reduction in size is useful for deployment and also for minimizing the amount of volatilized sample needed for in situ measurements. Reduced sampling requirements are an advantage for sample handling systems that involve drilling, thermal desorption, or laser ablation. Small volumes are also an advantage in laboratory experiments with constrained sample quantity (e.g., pharmaceuticals).
Figure 3.5: Curved mirror scan at various synthesizer frequencies for a) \( \phi 50 \) mm, \( f = 50 \) mm, b) \( \phi 25 \) mm, \( f = 25 \) mm and c) \( \phi 25 \) mm, \( f = 50 \) mm.
Figure 3.6: Quality factors fitted for various mirror types at a) 94 and b) 104 GHz. Inverted triangles, triangles and circles are 50/50, 25/50 and 25/25 mm diameter/focal length mirrors, respectively. Closed symbols are primary modes and open symbols are secondary.
Figure 3.7: FWHM of Fourier Transform of pulses of varying duration. The theoretical FWHM of square and sech$^2$ pulses are also shown.
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Figure 3.8: Pressure broadening of a) nitrous oxide and b) methanol. Fit rotational spectra shown in insets.
Chapter 4

Volatilization and Fragmentation of Alanine by Nanosecond Laser Pulses

4.1 Introduction

Pulsed laser ablation is a method of volatilizing condensed phase samples, in particular solids, and is often used in tandem with analytical methods such as mass spectrometry, rotational spectroscopy, and laser-induced breakdown spectroscopy (LIBS). Depending on the laser parameters, pulsed laser volatilization can comprise vaporization and/or ejection, which are thermal and non-thermal bulk processes, respectively, and are together referred to here as ablation [88]. Compared to other volatilization approaches such as pyrolysis and ion bombardment, laser ablation has several advantages. Unlike pyrolysis laser ablation is: i) spatially resolved by the focused laser beam, ii) practically instantaneous, and iii) can be performed on a wide variety of samples, often without a priori knowledge of melting temperature. Unlike ion bom-
barrdment, lasser ablation can be performed under vacuum or inside a carrier gas and, depending on the pulse energy, generates an arbitrary amount of vapor to match the sensitivity of a particular instrument. Laser pulses have been used recently to volatilize large molecules [89, 90] reportedly without denaturation [91]; however, debate remains over that last point [92], and in general, the analytical chemistry field could benefit from a better understanding of the laser volatilization of condensed-phase molecules.

Until now there have been relatively few investigations about the coupled chemistry and thermodynamics of laser ablation for molecular solids, either organic or inorganic [93, 94]. Such information is, however, important for optimizing the laser ablation process for analytical experiments, i.e., increasing vapor yield and producing a vapor that is chemically representative of the solid. Molecular solids have properties that can affect how they ablate; properties that distinguish them from atomic solids. First, organic molecular solids often have low melting and boiling points, which may affect the phase of the material inside the expanding plume. Second, the intramolecular bonds can break as a result of various processes like photoexcitation, electron impact, or thermally-mediated reactions in the high-temperature, high-pressure plume [88]. These processes, which are collectively called chemical fragmentation, can detrimentally affect analytical measurements by altering the quantity of parent molecules, i.e., the analyte.

In the present study, alanine (C$_3$H$_7$NO$_2$) is chosen as a representative organic molecular solid for several practical reasons. First, it is a medium-sized molecule, so there are enough heavy atoms that we expect to see multiple fragment species.
but not so many heavy atoms that the relationship between those fragments and the parent is indeterminable. Second, compared to much larger molecules, alanine is a size that can be efficiently cooled by collisions in a jet expansion, which is necessary for producing strong emission signal in the microwave measurements that we do. Third, the rotational transitions [95] and molecular beam fragmentation [96–101] of alanine are well studied. Lastly, alanine is an amino-acid and, as a building block of proteins, is of interest in the biology community as an example of a typical molecule that could be studied using laser ablation.

To study the laser volatilization of the alanine molecular solid, we performed three experiments to explore the thermochemical and dynamic aspects of ablation. These experiments include (i) rotational spectroscopy of vaporized alanine and its fragments, (ii) pump-probe shadowgraphs of the shockwave and micro-particle ejection, and (iii) microscopy of nano- and micro-particles ejected from the sample. Laser ablation has been used along with Fourier-transform microwave spectroscopy (FTMW) to characterize the gas-phase structure of molecular solids [102,103], and we use that technique to identify and quantify the ablation products [104]. In typical laser ablation FTMW experiments, a target of solid analyte is irradiated by a laser pulse. The volatilized molecules are supersonically expanded in a vacuum chamber where they are probed by microwave radiation. We detect the rotational transitions of volatilized alanine molecules as well as three fragments: CH$_3$CN, HC$_3$N, and CH$_3$CCH. The fragment detection demonstrates that FTMW spectroscopy can be used to directly detect neutral laser-induced fragmentation of organic compounds. To address the thermo-dynamics of alanine volatilization, two other experiments are performed in addition
to FTWM spectroscopy. Using pump-probe shadowgraphy, we image the expanding plume. At nanosecond timescales, the shadowgraphs show the expulsion of vapor and the shockwave induced in the surrounding gas. Comparing the measured rate of shock propagation from the shadowgraph images with a fluid mechanical simulation allows us to deduce the thermodynamic conditions of the vapor and use that information to perform a kinetic analysis of the alanine fragmentation. At microsecond timescales, the shadowgraphs show the ejection of particles, which are oftentimes undesirable in analytical measurements. In the final experiment, we use a witness plate to collect particles produced by ablation, which we image using scanning electron microscopy (SEM) to deduce their phase. Altogether, the three experiments provide new insight into the nanosecond ablation of a molecular solid. The findings may be generally applied to other similar organic species.

4.2 Methods

4.2.1 Sample Preparation

Powdered DL-alanine (i.e., a mixture of the two handed alanine molecules) from Sigma-Aldrich with 99 percent minimal purity is formed into solid targets. We bind the alanine using copper powder from Sigma-Aldrich with 15-µm diameter neat particles for two reasons: first, it does not contribute organic species that would confound the analysis of the alanine fragmentation (although Cu-containing reaction products are possible), and second, there is a large body of literature documenting the properties, e.g., temperature [105] and electron density [106,107], of copper ablation plumes.
that can be leveraged in our analysis. By varying the proportion of copper in the target, we are able to test samples that are either more metallic or more organic in character; for the copper-dominated samples, the organic alanine molecules are a minor constituent so the plasma properties are presumably governed by the copper. For the shadowgraph and particle collection experiments, we use low-aspect-ratio pellets (6 mm diameter, 3 mm height). The FTMW spectroscopy experiments incorporate a rotation-translation stage that requires the samples to be made as high-aspect-ratio rods: 5 mm diameter, 20 mm height.

4.2.2 Rotational Spectroscopy

Microwave rotational spectroscopy is a high-resolution, high-sensitivity technique used to detect polar molecules, including isotopomers and conformers, based on their unique rotational moments of inertia. In FTMW spectroscopy, the molecules are detected by first populating one or several excited rotational states using a microwave pulse and then detecting the free-induction decay. Compared with mass spectrometry, rotational spectroscopy has the advantage that it does not require ionization, which can complicate the analysis since fragmentation and non-stoichiometric fractionation [108] can occur during the ionization process depending on the bond strengths and dissociation potential of a particular species.

The instrument used in the present study (Fig. 4.1a) has been described in previous papers and consists of two different spectrometers: a chirped-pulse (CP) FTMW spectrometer and a conventional Fabry-Perot cavity spectrometer [78,109]. The CP transceiver and the cavity are arranged perpendicularly with the sample
molecules propagating along the axis of the cavity. The samples are volatilized by focusing the 532 nm output of an Nd:YAG laser on a Cu/alanine target. The temporal width of the laser is approximately 6 ns (full-width half maximum, FWHM) and is operated at a repetition rate of 5 Hz synced to the microwave electronics. Collisions with a high pressure inert carrier gas (Ar) thermalize the ablation products, and the mixture expands adiabatically into the vacuum chamber reaching a rotational temperature of about 4 K in the center of the cavity.

The two spectrometers are used in sequence to first survey the plume composition then quantify the abundance of different species. First, a broadband CP-FTMW spectrum between approximately 7 and 19 GHz is recorded for a 15:85 Cu/alanine target to simultaneously probe all the transitions that arise from alanine and its ablation fragments. The CP-FTMW measurement we report is an average of $18 \times 10^3$ spectra, i.e., $18 \times 10^3$ ablation pulses. Next, the FTMW cavity spectrometer, which spans about 6 to 21 GHz, is used for the quantitative analysis because it is more sensitive than the CP spectrometer and therefore requires less averaging and less ablation of the finite lifetime targets to achieve an acceptable signal-to-noise ratio. The cavity is tuned to an individual transition observed in the CP spectrum to determine its strength at different laser fluences and Cu/alanine molar fractions. The strength of the transition at a specific temperature is proportional to the number density of targeted species [80]. The abundances of alanine and its fragments are determined using OCS as a calibrant: the Ar carrier gas is seeded with a 10 percent dilute mixture of 1 percent OCS in Ne, and the resulting intensities of the OCS transition at 12162.979 MHz and OC$^{34}$S at 11865.662 MHz are measured for this known concen-
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tration. Two kinds of control trials are done to ensure that all the observed lines arise from alanine laser ablation: 

1) in the CP-FTMW experiments, spectra are recorded without the ablation laser and

2) in the cavity experiments, pure copper targets are ablated. In both control tests, no alanine or fragment signals are observed.

4.2.3 Pump-Probe Shadowgraphy

Pump-probe shadowgraph experiments have been utilized by many groups [93, 110, 111] to image the ablation of various materials. Our shadowgraph apparatus incorporates a Nd:YAG pump laser (laser A) and a Ti:sapphire probe laser (laser B) as illustrated in Fig. 4.1b. Pulses from the 1064 nm, 6 ns FWHM pump are focused onto the sample at a fluence of either 10 or 100 J cm\(^{-2}\) to induce ablation. The 800 nm probe pulses, which have a duration of about 100 fs, are focused inside a water cuvette to generate white light that back-illuminates the expanding ablation plume. The image is projected through an objective lens onto a CCD detector. The laser and detector timing is controlled by a set of delay generators to image the plume at different stages of its expansion. The ablation for the shadowgraph experiments is done in a vacuum chamber that is either evacuated to mTorr levels or backfilled with 720 Torr nitrogen; conditions that are relevant for mass spectrometry or FTMW spectroscopy involving a carrier gas, respectively.

The shadowgraphy provides new insight into the conditions during ablation in the FTMW tests; however, there are some caveats that warrant explanation. While 532 nm radiation is used for ablation in the FTMW spectroscopy and particle collection experiments (see next subsection), the difficulty of filtering it from the images

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Figure 4.1: Experimental setups used for a) measuring rotational spectra and b) imaging the ablation plume and collecting ejected micro-particles.

led us to use the 1064 nm fundamental for ablation in the shadowgraph experiments. Based on a previous study of Pd ablation [112], we expect there to be a difference in the yield based on the copper absorptivity for the two wavelengths (about 70 and 8 percent at 532 and 1064 nm, respectively, which we determined for compressed pure alanine and pure copper targets using a spectrophotometer); however, the Pd study also found the electron density and temperature to be comparable. We therefore expect the mechanisms that induce fragmentation to be similar across the studies despite possible differences in the heavy-species density. A second provision involves the shadowgraph post-processing. The shadowgraph images show the position of the
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shockwave fronts and ejected micro-particles in each experiment. Vapor shockfront positions are determined by fitting semicircles to them, and the particle yield is determined by counting the intensity of pixels in the shadowgraphs below a particular threshold and normalizing them by the total number of pixels. The brightnesses of the raw images are adjusted (e.g., in Figure 4.4) to make the plume details clear and uniform. The brightness does not affect interpretation of the data, since it does not change the edge positions of the features. The threshold intensity is set empirically for each image.

A two-phase, fluid mechanical simulation is used to deduce the thermodynamic conditions of the plumes imaged by shadowgraphy. A simulation of pure copper expansion is done as a simplified, non-reactive case that represents the limit where the alanine mole fraction is small, which it is for many of the experiments. Rather than model phase change explicitly, the simulation comprises a layer of vaporized copper that has a parametrically varied initial pressure and temperature. The dimensions of this layer are extracted from optical images of single-shot ablated targets (Fig. 4.7). By varying the position of the focus with a high-numerical aperture objective, we measure ablation depths of about 3 and 5 µm for the 10 and 100 J cm\(^{-2}\) cases, respectively, at 720 Torr. The simulation assumes the supercritical copper layer arises instantaneously then expands freely, that the two fluids are ideal gases, and that the only constituent of the plume to subsequently absorb laser light is the free electrons generated in the high-temperature nitrogen shock. These assumptions are validated by the agreement between the imaged and simulated shock fronts in Fig. 4.4c. Only the copper ablation plume is simulated because of the difficulty of ascribing the si-
multaneous vaporization of the alanine and copper grains given their different optical properties and vaporization rates. The assumption is that the thermodynamics of the Cu/alanine mixtures are of similar order as those for pure copper. The correct initial conditions of the plume are those that yield near-solid density and also reproduce the measured velocity of the shockwave in the bounding nitrogen gas.

The thermodynamic conditions are used as inputs to estimate a lower bound for the rate of alanine decomposition in a two-component kinetic network that contains terms for dissociative electron attachment and unimolecular fragmentation. We consider these two mechanisms, and not electron impact dissociation or heavy species collisions, because they are available in the literature. The dissociative electron attachment cross section \cite{99} and thermal decomposition rate constants \cite{100,101} have been measured in previous experiments. The alanine fragmentation is calculated by the following system of first-order rate equations:

\begin{align}
\frac{dn_p}{dt} &= 2k_en_ex_a^0n_{Cu}^0 + 2k_u^0x_a^0n_{Cu}^0 \\
\frac{dx_a}{dt} &= -k_en_e - k_u x_a.
\end{align}

The density of products \((n_p)\) calculation involves two assumptions: \(i\) that the electron density \((n_e)\) is governed by the expansion of the Cu-dominated plasma and \(ii\) the dissociation creates just two fragments, which do not experience additional fragmentation. For the electron density, we use the time-resolved measurement reported by Gojani \cite{113}. Although he did not report the time-resolved electron density for copper, a similar measurement for zinc was done, and we adopt the zinc electron den-
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This instantaneous electron density at 340 ns is used to deduce the ionization fraction \( I \), and the electron density is then \( n_e = In_{Cu}^{0} \). The electron energy and density are insensitive to fluence [107], so we assume the ionization fraction is the constant throughout the plasma expansion for the 10 and 100 J cm\(^{-2}\) cases. The alanine density changes because of the conversion to fragments but also because of the expansion of the fluid. Instead of coupling the chemistry to the fluid dynamic simulation, we handle the two parts in an approximate way by assuming the local alanine density is a product of the molar fraction determined from kinetics \( (x_a) \) and the fluid-mechanical part predicted for the Cu-dominant expansion \( (x_a^{0}n_{Cu}^{0}) \). The average Cu density \( (n_{Cu}^{0}) \) is determined by a power-law fit to the local Cu density integrated the axis of the plume.

The rate constants in the system of equations are temperature dependent. For the dissociative electron attachment, we assume the electron-temperature equals the plume temperature, which is calculated in the same manner as the Cu density; a power-law fit of the local temperature integrated along the plume axis. The result agrees well with the the time-resolved electron temperature reported by Gojani [113] at 340 ns. That temperature was then used along with the dissociative electron attachment cross section [99] to calculate the rate constant \( (k_e) \) [20]. There are two reports of the unimolar thermal decomposition rate constants for alanine: Sato et al. [100] and Yablokov et al. [101]. The conditions and the measured rate constants are quite different, so we consider them both; extrapolating to the plume temperature.
4.2.4 Particle Imaging

To image ablated particles, a witness plate made from a glass microscope coverslip partially covered by a strip of copper tape is placed about 6 cm away from a pellet made either of pure alanine or pure copper (Fig. 4.1b). After irradiating the pellets with one hundred, 6-ns long 532 nm pulses in sub-mTorr vacuum, the plates are removed from the chamber, coated in 5 nm of gold then imaged using SEM.

4.3 Results and Discussion

The nanosecond ablation plume contains neutral fragments of the alanine analyte as well as neutral fragments. The CP-FTMW spectrum of the ablation products, after removal of the contaminants and electronic artifacts identified by the control trial without ablation, is presented in Figure 4.2. About 30 percent of the transitions observed are assigned to two conformers of alanine (denoted conformers I and IIa [95]) and to three neutral fragments (CH$_3$CN, HC$_3$N, and CH$_3$CCH). As reported elsewhere [95], the IIb, IIIa, and IIIb conformers of alanine are not observed; presumably because their populations are depleted by collisional relaxation in the carrier gas. The remaining observed lines do not correspond to any of the many polar molecules or ions currently compiled in the astrochemical databases [82,115] and thus could be derived from several possible sources: i) uncharacterized fragments or ions of alanine, ii) species derived from additive chemistry, i.e., the bonding of fragments and/or alanine to form new, larger molecules, or iii) molecular clusters involving the carrier gas or Cu-containing species. The identification of these lines is beyond the goals of this
Figure 4.2: CP-FTWM spectrum of 15:85 Cu/alanine pellet showing two alanine conformers and three neutral molecular fragments.

study, but may be of interest for future experiments.

Along with alanine, the CH$_3$CN and HC$_3$N transitions are selected for quantitative analysis because they have a single strong line and multiple confirmed lines, respectively. No further analysis was done on the weak, isolated CH$_3$CCH line. The number of alanine and fragment molecules generated per laser pulse are listed in Table 1 for 50:50, 85:15, and 95:5 Cu/alanine targets with 50 J cm$^{-2}$ fluence. The ratio of volatilized alanine for the 50/50:85/15:95/5 Cu/alanine targets is about 12:2:1 compared with a 10:3:1 for the solid phase. The alanine count is less than or comparable to the number of atoms ablated from pure copper samples based on the nominal damage volume (see 4.7): approximately $10^{14}$ to $10^{15}$ atoms at 10 and 100 J cm$^{-2}$, respectively. Although we focus on the alanine IIa lines because they are stronger, we find a similar $N_I/N_{IIa}$ of 3±2. The relative alanine conformer population $N_I/N_{IIa}$ determined by Blanco et al.8 varied with temperature from about 7 to 4 between
room temperature and 4 K, respectively. The CH$_3$CN count is comparable to alanine and the HC$_3$N is about an order of magnitude lower reflecting differences in the production pathways of the two species.

Table 4.1: number of alanine, CH$_3$CN and HC$_3$N molecules per pulse versus composition (30 mJ pulse, 50 J cm$^{-2}$ fluence)

<table>
<thead>
<tr>
<th>Molecule</th>
<th>50:50 Cu/alanine</th>
<th>85:15 Cu/alanine</th>
<th>95:5 Cu/alanine</th>
</tr>
</thead>
<tbody>
<tr>
<td>alanine IIa</td>
<td>5.9·10$^{14}$</td>
<td>1.1·10$^{14}$</td>
<td>4.8·10$^{13}$</td>
</tr>
<tr>
<td>CH$_3$CN</td>
<td>5.0·10$^{14}$</td>
<td>3.1·10$^{14}$</td>
<td>1.7·10$^{14}$</td>
</tr>
<tr>
<td>HC$_3$N</td>
<td>1.1·10$^{14}$</td>
<td>1.9·10$^{13}$</td>
<td>1.4·10$^{13}$</td>
</tr>
</tbody>
</table>

Scaling the number of alanine molecules by the number of photons in each pulse (Fig. 4.3a), we find that except for the lowest fluence near the ablation threshold, the quantum yield is flat and scales linearly with the amount of alanine in the target from 8·10$^{-3}$ to 1·10$^{-3}$ to 7·10$^{-4}$ per photon for the 50:50, 85:15, and 95:5 targets, respectively. That suggests the mechanism of alanine volatilization is consistent over the 25 to 50 J cm$^{-2}$ range. Above about 25 J cm$^{-2}$, the CHCN and HC$_3$N yields in Figs. 4.3b and 4.3c are also flat with fluence: CH$_3$CN varies from about 1·10$^{-3}$ to 6·10$^{-3}$ molecules per photon while HC$_3$N is slightly less abundant at about 10$^{-4}$ to 10$^{-3}$ molecules per photon. In each of the Fig. 4.3 subfigures, the lowest plotted fluence (9 J cm$^{-2}$) near the threshold of FTMW signal deviates from the otherwise flat traces. The yields at small fluence might be especially sensitive to stochastic variations in the composition, which we are unable to account for in the uncertainty analysis. The mixed Cu and alanine powders sometimes stratify in the pellet press, and local variations in the surface absorptivity could manifest themselves in differ-
ences in the alanine or fragment abundances. At higher fluences, these variations might be overcome as the higher-energy pulse ablate the anomalous surface layer. Nevertheless, the trend of nearly-flat quantum yield above about 20 J cm$^{-2}$ is clear.

Although the large number of unidentified lines in Fig. 4.2 prevents us from thoroughly mapping the alanine fragmentation pathways, we compare our experiment with previous mass spectrometry studies of ions to consider possible formation routes for the neutral CH$_3$CN and HC$_3$N fragments. Molecular beam (MB) experiments [97,116] have found that cleaving of the carboxyl group to form C$_2$H$_6$N$^+$ (mass 44) is the most probable fragmentation event followed by removal of the N-H bonds to form C$_2$H$_4$N$^+$ (mass 42). In our FTMW experiment, neutral CH$_3$CN is the most abundant fragment detected, and it could potentially form by the removal of a proton from the dissociated product C$_2$H$_4$N$^+$. Possible routes to HC$_3$N formation in the laser ablation plumes are less apparent. A search of the UMIST database [30] shows that HC$_3$NH$^+$+$e^-$→HC$_3$N+H [117] and CH$_3$CN+HC$_3$NH$^+$→CH$_3$CNH$^+$+HC$_3$N [118] are two of the most favorable formation mechanisms. The electron and CH$_3$CN reactants are available in the plume, which lends support to these candidate paths; however, HC$_3$NH$^+$, which has lines in the spectrometer bandwidth at 8657.9 and 17316.0 MHz [117], is not detected. It is possible that the HC$_3$NH$^+$ is rapidly scavenged in these reactions and therefore does not have significant signal or does not form because the electron energies in the MB tests [97,116] (below 150 eV) differ from those in the ablation plume; however, it is also possible that this ion is missing because the molecular beam electron impact experiments are a poor analog for laser ablation. Other mechanisms besides electron impact could be responsible for
Figure 4.3: a) Alanine quantum yield versus fluence. The signals are from conformer II and are measured at 10151.76 MHz. b) CH$_3$CN fragment quantum yield versus fluence measured at 18397.8 MHz. c) HC$_3$N fragment quantum yield versus fluence measured at 18196.2 MHz. 95:5, 85:15, and 50:50 mixtures of Cu/alanine are shown. The error bars indicate the uncertainty based on 95-percent-confident fits of the amplitudes of the lines and OCS calibrant gas as well as the uncertainty in the concentration of the calibrant.
fragment production. For example, fragmentation might be driven by molecular collisions or unimolecular decay inside the hot, pressurized vapor plume. To evaluate this possibility, we next study the thermodynamics using shadowgraphy, simulation, and ablation particle imaging.

When a target is heated by a laser pulse, the ablated solid expands outward generating a shockwave that propagates through the bounding gas. The speed of the shockwave increases with the pressure of the ablated material. A smooth copper foil target is chosen to illustrate the features of the laser-induced shockwave at various conditions although similar features are observed for the mixed Cu/alanine targets (see Fig. 4.4). Shadowgraph images of the shockwave are shown in Fig. 4.4 at times just after the peak of the laser pulse. Three different fluence and atmosphere conditions are presented: 100/100, 100/720 and 10 J cm$^{-2}$/720 Torr, which allow us to deduce scaling relationships for the fluence and pressure. The shockwaves for each case have two regions. Near the target, there is a hemispherical shock generated by the outward expanding vapor plume. The hemispherical shock is large for the low-pressure atmosphere since there is less resistance to plume expansion in that case. There is also a cone-shaped shock that appears to grow out of the vapor shock toward the laser source. The cone-shaped shock is known as a laser-supported detonation (LSD) wave and arises due to sustained heating by the nanosecond pulse [119, 120]. In Fig. 4.4c, the simulation of the two-phase expansion shows that the vapor layer produces a shockwave in the 720 Torr N$_2$ that agrees closely with the shadowgraph at the 10 ns instant. The LSD disturbance is reproduced only when plasma absorption is included in the simulation, which suggests that ionization and optical absorption
by the free electrons are coupled processes that focus heat at the leading edge of the shockwave and accelerate propagation there. Depending on the conditions, absorption of laser light at the leading edge, a phenomenon known as plasma shielding [110], may affect the amount of vaporization and fragmentation of the alanine sample.

Figure 4.4: early-stage shadowgraphs of shockwaves induced by vapor expansion for a) 100 / 100, b) 100 / 720 and c) 10 J cm⁻² / 720 Torr cases near the peak of the laser pulse. LSD is laser-supported detonation wave. Part c) shows the speed distribution predicted by the simulation and the kink in the wavefront (i.e., the LSD).

The shockwave evolution is similar for the different copper and alanine targets (see Fig. 4.5). The radii of the largest semi-circles that fit within the bounds of the vapor-shocks imaged in the shadowgraphs are plotted in Fig. 4.6 as a function of
time for an 85:15 Cu/alanine pellet, a Cu pellet, and Cu foil. The shock speeds are extracted by fitting the data to a linear regression and are on the order of 5 to 15 km s\(^{-1}\). For comparison, measurement of the tin ion energy spectrum resulting from picosecond laser ablation [121] at 17 J cm\(^{-2}\) showed that tin ions have a most probable velocity of about 7 km s\(^{-1}\), which is similar to what we observe for our samples with nanosecond pulses at comparable fluence. The foil and Cu pellet have comparable propagation rates which suggests that the microstructure of the pelletized sample does not significantly affect the initial stages of the vaporization process. The shock for the alanine-containing sample has lower propagation speed than the copper foil, which could be a result of dissipation. We find that the shock speed scales with pressure
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according to $P^{-0.31}$ and with pulse energy according to $E^{0.23}$; in good agreement with what we would expect for a spherical point blast: $R(t) \propto P^{-1/5}E^{1/5}$ [122].

Figure 4.6: vapor bulb shock position versus time for 85:15 Cu / alanine pellet, Cu pellet, and Cu foil for various fluence and pressure conditions. The Cu foil shock velocity scales as $P^{-0.31}$ and $E^{0.23}$.

Figure 4.7: Target damage craters for a) copper pellet and b) copper foil made at 100 J cm$^{-2}$ in 720 Torr N$_2$.

The shadowgraphs are compared to a parametrically varied initial temperature and pressure of a thin vaporized copper layer in the fluid-mechanical simulation. For 10 J cm$^{-2}$ fluence, initial conditions for the copper of $1\cdot10^4$ K and 20 GPa yield an initial density and shock propagation velocity that matches the data for the shockwave
in 720 Torr atmosphere. The plume pressure agrees with previous modeling of the initial near-surface stress generated in pure copper samples by femtosecond pulses of identical fluence. For 100 J cm$^{-2}$ fluence, initial conditions of about $5 \cdot 10^4$ K and 60 GPa yield the best agreement with experiment. Although the plume is modeled as a chemically inert ideal gas, the temperature and pressure predicted are corroborated by a more accurate equations of state. Using a rough approximation of the mass of material ablated from the target (see Fig. 4.7) and the known energy of the laser pulse, the energy input per unit ablated mass is $3 \cdot 10^7$ and $6 \cdot 10^7$ J kg$^{-1}$, for the 10 and 100 J cm$^{-2}$ laser fluences, respectively. Compare these values with the internal energy of superfluid copper from a detailed equation of state at the temperature and pressure predicted by the simulation: $5 \cdot 10^6$ and $8 \cdot 10^6$ J kg$^{-1}$, for the 10 and 100 J cm$^{-2}$ laser fluences, respectively. As one would expect, the values calculated from the laser energy and ablated mass are greater than the point values for internal energy since this simple calculation does not factor in heat losses or ionization; however, this simple comparison confirms that the simulation results are accurate to an order-of-magnitude level.

The thermodynamic conditions we calculate are corroborated by an independent test. By measuring the kinetic energy of particles ejected from a laser-irradiated glass, an initial plume pressure on the order of 4 GPa has been deduced in experiments that have similar laser parameters to those in our study. Notwithstanding differences in optical absorptivity of the glass and Cu/alanine targets, the pressure in that previous experiment is on the same order as the one we deduce from simulation. While the lone probe laser in our experiments cannot detect the transit of a single
particle over time, under the assumption that all particles are ejected beginning at time zero, a reasonable first approximation for the earliest particles, we find that the speed of the particles in our study is similar to that for glass ejection (see Fig. 4.8): around 300 m s\(^{-1}\) 100 ns after the ablation pulse.

![Figure 4.8](image)

**Figure 4.8:** position of imaged particles divided by time relative to the peak of the laser pulse for 85:15 Cu/alanine at 100 J cm\(^{-2}\) in 720 Torr N\(_2\).

The temperature and density of the ablation plume extracted from the simulation are used as inputs in a simple kinetic analysis to bound the fragmentation rate. The analysis considers dissociative electron attachment [99] (DEA) based on the electron density of a copper plasma measured by Gonjani [113] and unimolecular dissociation (UD) rates [100, 101] extrapolated to our spatially-averaged plume temperature. While other mechanisms like collision-induced fragmentation could exist, the kinetic analysis in Fig. 4.9 predicts that DEA and UD alone dissociate nearly all the alanine in less than 100 ns; a time-scale over which we expect that the ablation products and bounding gas remain separated. The apparent contradiction between
the kinetics prediction that there should be very little intact alanine in the ablation plume relative to the fragments, and the fact that we observe comparable amounts of the various species in the FTWM spectra has two possible explanations illustrated in Fig. 4.10. First, it could be that the volatilized alanine measured in the FTMW experiments originates from the surface of Cu/alanine ejected particles that are heated inside the ablation plume. The thermal inertia of those particles could delay the vaporization of the solid alanine until a time when the expanding plume has cooled to a temperature favoring gas-phase alanine. Alternatively, it could be that the alanine volatilizes from a melt pool at the surface of the target just below the ablation plume; a cooler region on the divide between the plasma and condensed phases. We considered a third possible source for the intact alanine: fast molecules at the tail of the Boltzmann distribution that speed past the shockfront before they are dissociated; however, at the temperatures for our plume just a small fraction of the alanine, $10^{-4}$ to $10^{-6}$, have sufficient speed to do this and of those, which is not enough to explain the large abundance of intact alanine we observe.

To help evaluate the scenario in which a flux of intact alanine molecules is volatilized from the surface of ejected particles that are heated inside the ablation plume, we have measured the amount of particles at various conditions by analyzing raw shadowgraphs (Fig. 4.11) recorded at delays of many microseconds. The amount of ejected particles, in arbitrary relative units, increases with the magnitude of the shocked loading. In Fig. 4.12a, the fraction of each probe pulse absorbed or scattered by particles is plotted for different delay times for three different alanine-containing targets in 720 Torr $\text{N}_2$ including 50:50, 85:15, and 100:0 Cu/alanine. The shaded
Figure 4.9: Molar fraction of alanine fragmentation product relative to the total organic number density (left axis) and axially-averaged plume temperature (right axis) versus time for 100 J cm$^{-2}$ fluence. The unimolecular decomposition component based on the rates of Sato et al. [100] and Yablokov et al. [101] are both plotted. DEA is the dissociative electron attachment component.

Figure 4.10: schematic of ablation stages with the latest times corresponding to the release of intact alanine vapor.

Uncertainty regions are calculated by increasing or decreasing the threshold intensity for particle detection by thirty percent, which are empirical limits corresponding to either under- or over-counting the number of particles. The onset of particle ejection
in the 50:50 and 85:15 Cu/alanine samples begins after about 1 µs then remains flat for more than 100 µs. Particles have been observed being ejected as late as 300 µs, but in general, the major portion of the ejection is ended by 100 µs. During the steady portion of the ejection, the 50:50, 85:15, and pure copper targets have normalized particle ejections of $0.060^{0.14}_{0.01}, 0.021^{0.15}_{0.001}$ and $1.9 \cdot 10^{-4}$, respectively. The value for the unplotted 95:5 Cu/alanine target is $0.014^{0.011}_{0.001}$. Notwithstanding the scatter in the data, the particle abundance varies with the target alanine content in the same way as the volatilized alanine abundance; especially after accounting for the fact that the calculated particle ejections are based on a two-dimensional projection of the three-dimensional plume. While this similarity would appear to support the argument for a particle-dominated flux of alanine vapor, we do not observe the particle abundance to change linearly with fluence, which, from Fig. 4.3, we know the volatilized alanine does. The normalized particle ejection for the 10 J cm$^{-2}$ case for the 95:5 Cu/alanine target is $0.014^{0.05}_{0.002}$, or about the same as the 100 J cm$^{-2}$ case. Therefore, the delayed vaporization of ejected particles is probably not the source of most of the volatilized alanine.

Instead, we suspect that the pool of fluidized material at the surface of the target is the likely source of the volatilized alanine molecules. Evidence for the fluidize layer comes from shadowgraphs recorded in vacuum (Fig. 4.13). In the absence of a bounding gas to resist the outward expansion of the ablating surface or dissipate energy, the amount of ejected particulate increases by an order of magnitude for the 85:15 Cu/alanine target (Fig. 4.12b). Inspection of the vacuum shadowgraphs clearly shows the expansion and breakup of a fluidized layer, which appears to be
insensitive to the composition of the target. This is in contrast to the ablation imaged in 720 Torr N\textsubscript{2} (Fig. 4.11), which clearly depends on the sample makeup. The reliance on the amount of ejection on the presence of a bounding gas supports the theory of a prolonged fluidized layer at the target surface since the energy dissipated by shocking the bounding gas would tend to differentiate the amount of particles ejected across targets with varying re-solidification rates.

The argument for a fluidized surface layer is corroborated by the particle col-
Figure 4.12: a) mass ejections from pellets made of Cu / alanine mixtures with varying mole fractions in 720 Torr N\textsuperscript{2} and b) from 85:15 Cu / alanine pellets in vacuum. Fluence is 100 J cm\textsuperscript{–2}.

lection experiment. Particles ablated from pure alanine and pure copper samples collected by a witness plate and imaged by SEM are shown in Fig. 4.14 For alanine, two types of particles appear in the SEM images: micron-sized shards about 1 to 5 µm in extent (Fig. 4.14a-i) and sub-micron sized rods ranging from about 75 to 500 nm in length and 10 to 30 nm in diameter (Figs. 4.14a-i and ii). By placing the witness
plate closer to the pellet (about 3 cm), alanine shards as large as 20 µm have been observed. The irregularity of the micro-shards and regularity of the nanorods, is a likely indication of their origin. The shards appear to be fragments of solid that are ejected without phase change, perhaps as a result of the shocked loading induced by the high-pressure ablation plume. Nanoparticles in ablation plumes can form either from a bottom-up process involving nucleation and absorption of vapor or by a top-down process involving the fragmentation of the solid phase or break-up of liquid into droplets [123]. The smoothness and uniform shape of the smaller particles suggests that they are formed by a bottom-up process, such as the stacking or agglomeration of molecular clusters as has been documented for other materials [123].

While alanine ablated particles are solid or perhaps fluid-like clusters, the col-
Figure 4.14: scanning electron micrographs of laser ablated alanine showing i) solid-phase ejection and i and ii) alanine nanorods. b) Cu liquid droplets solidified in different states including i) spherical, ii) bouncing droplets, and iii) flattened expanding wave. Target damage crater for a) copper pellet and b) copper foil.

Selected copper particles appear to be liquid and freeze upon contact with the witness plate (Fig. 4.14b). Depending on the size, initial temperature and impact velocity of the particle, the copper liquid freezes in different shapes. In Fig. 4.14b-i, the copper particle remains spherical, which implies that it had a sufficiently small impact velocity that its surface was not deformed during the freezing period. In contrast, Figs. 4.14b-ii and 4.14b-iii experience significant deformation and appear either as
a bouncing droplet or a flattened, centrifugal wave. Shadowgraphs (Figs. 4.11 and 4.13) show that some very large particles exist in the ablation plume under certain circumstances. Many of the larger particles do not adhere to the witness plate. Indeed, there is a significant difference in the size and shape of particles collected on the copper tape covering the witness plate and the bare glass coverslip (not shown); probably because the two surfaces have different adhesion and conduction properties. The SEM images in Fig. 4.14 are evidence that at least some of the copper ejected is in the liquid state, which constrains the lower limit on the plume temperature at about 2500 K [124]. This is well above the sublimation temperature of alanine (between 400 and 450 K [125]), which means that alanine in contact with the liquid copper particles would tend to be vaporized.

The shadowgraphs and particle imaging experiments support the idea that a pool of fluidized material exists at the target surface long after the initial shockwave has propagated far from the target. A pool of fluidized material in the 95:5 Cu/alanine target at the pressure we calculate for the 10 and 100 J cm$^{-2}$ fluences would liberate a total of $1 \cdot 10^{15}$ and $7 \cdot 10^{15}$ alanine molecules, respectively, during the brief instant when the melt has already cooled to 400 K until the time when it cools to about 230 K, which is roughly the boiling temperature in vacuum [101]. The actual number of vaporized alanine molecules will be less because some of the alanine is already volatilized into the fragmenting plume, because some of it is lost as particles, and because our simple analysis does not account for conduction to the target, which would decrease the time over which the flux is integrated. Nevertheless, the analysis of the vaporizing melt suggests it is a plausible source of the intact neutral alanine; a finding which could
be confirmed by comparing future transient absorption measurements of the ablation plume with our shadowgraphs to determine the precise instance when intact alanine is volatilized.

Together with the imaged particles, the shadowgraphs, fluid and kinetic modeling, and FTMW measurements show that the alanine nanosecond ablation plume is a complex thermodynamic system. Its short lifetime and small spatial extent make a complete characterization of the chemistry and physics difficult; however, the measurements we present are among the most thorough accounts done for any similar organic molecular solid. The existence of neutral molecular fragments, that the intact alanine molecules probably originate from the cooler portions of the ablated material, and the ablation the pelletized solid involves particle ejections that depend on composition and the bounding gas are new findings that should be considered in future implementations of nanosecond ablation in analytical measurements of molecular solids.

4.4 Conclusion

We presented a comprehensive characterization of the aspects nanosecond laser volatilization of solid alanine mixed with copper binder. The rotational spectra of alanine has been analyzed to deduce a quantum yield of about $7 \cdot 10^{-4}$ to $7 \cdot 10^{-3}$ molecules per photon. The yield is roughly proportional to the solid alanine concentration and plateaus with increasing fluence. The ablation plume contains the gaseous molecular fragments CH$_3$CN, HC$_3$N and CH$_3$CCH, and the former two have a quantum yield of about $10^{-4}$ to $10^{-2}$ molecules per photon. The total fragment abundance is linear
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with fluence, which might suggest that they are derived from thermal decomposition of the parent alanine and not by electron impact in the plasma. Comparison of the imaged laser-induced shockwave with numerical simulation suggests the temperature and pressure of the ablation plume are around $1\cdot10^4$ to $5\cdot10^4$ K and 20 to 60 GPa for a 10 to 100 J cm$^{-2}$ fluence, respectively. Laser ablation of the various Cu/alanine pellet mixtures is accompanied by ejections of particles, events which can last more than 100 $\mu$s. Analysis of the particle ejections suggests that most of the flux of the intact neutral alanine originates from the target surface after the first wave of vaporized material has been ejected. These findings may be generally applicable to the nanosecond ablation of other organic molecular solids.
Chapter 5

Detection of Laser Ablated Salt Using Spec-Chip

5.1 Introduction

The Spec-Chip instrument is designed for measuring gas-phase molecules, but the number of applications could be expanded by coupling it to a source that volatilizes condensed-phase species. As a gas-phase detector, there are numerous sites throughout the solar system to which Spec-Chip might be deployed to determine the molecular composition. The instrument can be configured to sample the composition of atmospheres, such as those at Titan, Mars or Venus. In Chapter 3, we briefly considered how the Spec-Chip could be used in a comet sample return mission to measure outgassing species from the regolith. In the present Chapter, we demonstrate that the instrument could also be used to determine the composition of condensed phases that are forcibly volatilized by pulsed laser ablation.
Chapter 5: Detection of Laser Ablated Salt Using Spec-Chip

In the context of *in situ* measurements, forcible volatilization of condensed-phase molecules has been done on multiple previous missions [126–128]. In each case, the approach used is to heat the sample inside a vacuum chamber while monitoring the liberated species using a mass spectrometer. Laser ablation could be an alternative means of liberating the condensed phases, and there would be several advantages to that approach. First, materials can be laser-ablated with high spatial resolution on the order of microns. Certain planetary or geological processes require materials to be probed on the microscale [129], which can be difficult to do when pyrolyzing bulk samples but is easily done by laser ablation. Second, the technique is insensitive to the boiling point of the target making it amenable to studying minerals or salts, which would be difficult to pyrolyze using the limited power budget available on a spacecraft. Finally, the sampling is immediate, which could be advantageous for missions with limited operating lifetime such as surface missions to Venus.

At present, NASA is developing a laser-ablation mass spectrometer for *in situ* deployment [130]. This technique has been applied widely in the laboratory [88, 89] to detect large organic species with good sensitivity. The laser-ablation source and vacuum handling equipment for a deployed mass spectrometer could be coupled to a Spec-Chip cavity to provide complementary capability. Spec-Chip would be able to directly detect neutral molecular species, not just their ions or fragments, which could increase the certainty with which molecular detections are made. Furthermore, if configured properly, rotational spectroscopy is able to distinguish chiral enantiomers [131], which could be an important capability in certain studies of prebiotic scenarios [132].
Chapter 5: Detection of Laser Ablated Salt Using Spec-Chip

For these reasons, developing a laser-ablation-coupled Spec-Chip is an important goal; however, there are two challenges to demonstrating that kind of instrument. First, the ablated molecules are hot. Since the rotational partition function, which is inversely proportional to the signal strength of the free-induction decay, increases with temperature, it is necessary to cool the ablated molecules well below room temperature before their rotational spectra are probed. In the laboratory, two methods have been developed for cooling; both rely on collisions between the hot ablated molecules and cold atoms. The first uses a jet expansion to convert the thermal energy of a carrier gas into translational kinetic energy [133,134]. Since the jet generates a large flux of molecules, it is typically pulsed in sync with the ablation plume to maintain low chamber pressure. The second method for cooling is known as buffer gas cooling and involves ablating into a cell of static cold gas that is heat sunk to a cryocooler [135]. The advantage of that method is that it does not require pulsing since the buffer gas flux into the vacuum cell is relatively slow, which means the measurement can be conducted at high repetition rate. Both methods would be feasible to do in space, but in this study we opt to cool the laser ablation products using a pulsed jet of argon gas.

The second challenge to coupling a laser-ablation source with Spec-Chip is that, as explored in the previous Chapter, the abundance of the volatilized analyte molecules depends on the extent to which molecules are fragmented by, for example, electron-impact ionization, unimolecular dissociation, or photo-fragmentation. To mitigate the complication presented by fragmentation, we choose the alkali-halide salts LiCl, NaCl, and KCl as the target species in this study. These diatomic species
have relatively large ionization/dissociation energies, which should limit fragmenta-
tion. Furthermore, their fragments are limited to two atoms and their ions, which simplifies interpretation of the fragmentation pathways although plume chemistry involving the bonding of those products is possible [136]. The spectroscopy for these salts has been done [137,138], and they have large permanent dipole moments of 7 to 10 Debye, which, for an optimized microwave pulse, leads to large signal [80].

In addition to being a manageable molecular system for studying laser ablation using Spec-Chip, the alkali halide salts are chosen because they have been identified on or around moons of the outer solar system. NaCl has been detected in gas phase around Jupiter’s moon Io using a ground-based millimeter-wave telescope [139] and around Enceladus by the Cassini spacecraft [140]. The NaCl at Io is believed to be volcanically derived. The salt at Enceladus is thought to emanate from the geysers at the south pole and may, in fact, indicate that the subsurface ocean is in contact with rock; conditions reminiscent of hydrothermal vent systems on Earth, which are candidate sites for the origin of terrestrial life. Brown and Hand [141] have hypothesized that NaCl and also KCl should exist on the surface of Europa. The alkalide-halide salts are species of interest in solar-system exploration, and using them as our target species in these Spec-Chip experiments is a first test of the suitability of a laser-ablation-coupled rotational spectrometer for missions that might one-day visit the surface of moons of the outer planets.

In this Chapter, we seek to detect laser-ablated salts using Spec-Chip. In the process, we estimate the volatilization yield. Not all three salts are detected, so we perform complementary measurements to learn more about how the ablation happens.
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5.2 Methods

5.2.1 Rotational Spectroscopy

The setup for measuring the rotational spectra is shown in Fig. 5.1a. It consists of a Spec-Chip system (printed circuit electronics, semi-confocal cavity, and piezomotor translation stage), a laser ablation source (laser, target translation/rotation mechanism, and a pulsed valve nozzle), and a turbo-backed vacuum chamber. To fully expand the gas, we maintain the chamber pressure at approximately 5 µTorr. The control signal for the pulse valve is 500-µs long although we believe the gas pulse is a bit longer than that. The pulse repetition rate is 5 Hz.

![Figure 5.1: Experimental setups used for measuring a) the rotational spectra using Spec-Chip and b) the laser ablation positive ion mass spectra.](image)

A frequency-doubled Nd:YAG laser at 532 nm with 6 ns FWHM pulse duration is used in the present experiments. The pulse energy is adjusted at the beginning of each experiment to maximize signal strength and is on the order of 10 mJ. The pulse valve and laser are synchronized with the millimeter-wave pulse in the Spec-
Chip cavity. A set of delay generators are used to sequence the operations so that the ablation happens inside the carrier gas and that the plume has time to propagate into the Spec-Chip cavity before the mm-wave pulse is transmitted. The optimal duration of the millimeter-wave pulse depends on the dipole moment of the species being measured according to the condition \( t = \frac{\pi \hbar}{|\mu| |E|} \). For the large dipole moments of the salts in this study, pulse durations on the order of 50 ns are bound to be suitable.

5.2.2 Mass Spectrometry

A commercial quadrupole mass spectrometer with a range of about 130 a.m.u. is used to measure the mass spectra of the ablation products in a second setup (Fig. 5.1b). The spectrometer is operated without the ionizing filament to directly detect the positively-charged ablation products. Ablation is done inside a vacuum chamber with the target positioned about 2 cm away from the focusing optics of the quadrupole mass filter. The targets are mounted inside the vacuum chamber at a 45 degree angle with respect to the k-vector of the incoming laser beam so that the ablated material will be ejected into the quadrupole filter. The chamber is pumped to below 6 \( \mu \text{Torr} \) before starting each trial.

The same 532 nm Nd-YAG laser that is used in the Spec-Chip experiment is used in the mass spectrometry tests. The surface roughness and optical reflectance of the targets lead us to select slightly different pulse energies for each particular sample: large enough to see plasma emission from the sample and observe ion signal in the spectra but not so large that electrons from the laser plasma appeared in the baseline
periodically with the mirror/RF scan. The pulse energies that satisfy these conditions are in the range of about 0.1 to 0.3 mJ. The spot size is on the order of 100 µm. The laser pulses (repeated at 10 Hz) and quadrupole filter are not synchronized to one another, but the scanning is slow enough that many laser pulses are applied during the scan over each M/Z. The mass resolution of the experiment is 10 points per M/Z. Noise from shot-to-shot variation and other sources is mitigated by applying a five-data-point smoothing. In addition to the ns experiments, a 100 fs, Ti:sapphire laser operating at 800 nm is tested. The energies of the fs pulses are 0.07 to 0.1 mJ.

5.2.3 Sample Preparation

The Spec-Chip measurements incorporate a rotating-translating mechanical stage similar to the one used in our previous measurement in Chapter 4. The stage requires the ablation targets to be formed as rods approximately 6 mm in diameter by 20 mm in length. The rods are made by combining approximately 1 g of salt with about 0.1 g of paraffin wax, pestling in a mortar, then compressing the mixture in a mechanical mold. For the mass spectrometry measurements, the targets are formed by mixing salt with about 1 g of vacuum epoxy. For the NaCl target, about 20 mmole of NaCl powder is combined with the epoxy. The amount of salt mixed for the other targets is varied so that the mole count remained constant. The salt/epoxy targets are formed into disks about 1 cm in diameter and 4 mm thick.
5.2.4 Particle Imaging

To image ablated particles, a witness plate made from a glass microscope coverslip partially covered by a strip of copper tape is placed about 6 cm away from a salt disk. After irradiating the target with one hundred, 6-ns long 532 nm pulses in sub-mTorr vacuum, the plates are removed from the chamber, coated in 5 nm of gold then imaged using SEM.

5.3 Results and Discussion

Rotational transitions for ns-ablated NaCl and KCl are detected using Spec-Chip. Figure 5.2 shows the lines for each molecule. The center frequencies are 91169.88 and 92246.50 GHz, respectively. The linewidth is about 200 kHz for both transitions, which we expect is governed by transit time broadening through the small Fabry-Perot cavity and is comparable to the linewidths we have observed in earlier measurements of static gases [62]. The relative intensities of the NaCl:KCl peaks is about 3-to-1, which agrees with the ratio of the low-temperature line strengths documented for these molecules in the astrochemical databases [82,137] and therefore implies that the molecules are volatilized in comparable abundance. We attempted a measurement of LiCl; however, only the minor isotopologue ($^6$Li$^{35}$Cl) has a line within the Spec-Chip bandwidth, and we have been unable to observe it.

The number of ablated salt molecules passing through the cavity is deduced by calibrating with a known flux of a stable molecule. The overlap integral of the standing electromagnetic field and the gas is rather complicated, but because the
field is too weak to saturate the upper-state populations of either CH$_3$CN or the salt, a condition that is validated by the fact that the Rabi cycle is not observed with the Spec-Chip as the amplifier gain is increased, we assume that the extent of the electromagnetic fields responsible for stimulating the FID signal are the same for each gas. That assumption allows us to calculate the cross-section of the gas-field overlap. CH$_3$CN diluted to 0.75 percent in Ne is flowed through the pulse valve with the laser off at a backing pressure of about 760 Torr. We estimate [134] that the area of the expanded plume at the cavity about 10 cm downstream of the nozzle is 1.2 cm$^2$, which is enough to cover the intense portion of the cavity mode (see Chapter 3). Assuming the flux of calibrant is a Heaviside function lasting 500 µs, we estimate about $1.3 \times 10^{15}$ CH$_3$CN molecules pass through the intense region of the cavity per pulse. The timing of the microwave pulse relative to the pulse valve is parametrically varied beginning with a time before the first CH$_3$CN molecules have
Figure 5.3: Line strength for CH$_3$CN ($J = 4 \leftrightarrow 5$ transition) and NaCl ($J = 6 \leftrightarrow 7$) transition versus delay of mm-wave pulse relative to the pulse valve opening. The curve is used to calibrate the total number of salt molecules that pass through the NaCl cavity during each laser pulse.

reached the cavity and ending about a millisecond later once the valve has closed. The $J = 4 \rightarrow 5$ transition of the CH$_3$CN at 91987.09 MHz is measured at each delay step. The same measurement is done for NaCl salt (Fig. 5.3). Integrating the curves over time yields a total signal of about 0.58 and 0.0065 a.u.-s for CH$_3$CN and NaCl, respectively. Neglecting variations within the plume, the low-temperature ratio of the line strengths for the two molecules is about 5 [137]. Combining factors, the total number of NaCl molecules volatilized per pulse is on the order of $3 \times 10^{12}$.

In the solid phase, the NaCl number density is about $2.2 \times 10^{28}$ molecules m$^{-3}$, so the volume of the volatilized material is $1.3 \times 10^{-16}$ m$^3$. For a nominal ablation crater diameter of 100 µm, the depth of the ablation crater created by each laser pulse would be just 17 nm. That is significantly smaller than we expect based on imaging of damage craters for copper in Chapter 4, which were several microns deep.
Therefore, some of the ablated material is not liberated into the gas phase but remains in condensed form as it is ejected.

Instead, a large amount of the material ejected from the target is ejected as micro-particles (Fig. 5.4). The microparticles are cube-shaped, about 200 nm in extent and aggregate in bunches of tens or hundreds. The circular shape of the flattened aggregates on the witness coupon suggests they are spherical before impact. The shape also suggests that the attractive forces between the primary particles are strong since across the range of aggregate sizes, which presumably span a range of high ejection speeds based on the shadowgraphy for Cu/alanine in Chapter 4, there does not appear to be any breakup or splattering. Within the aggregates, there is a continuum of sharp and rounded micro-particles, which, as with the alanine, we interpret to mean that some of the material is liquified by ablation. We hypothesize that evaporation of superheated liquid salt could be a source of the neutral salt molecules in the ablation plume.

Rotational spectroscopy is able to directly detect polar molecules and ions; however, the rotational lines for the ions are not as commonly known, and for low ionization fractions, the abundance can be below the detection limit. Mass spectrometry, however, is quite sensitive to charged particles. The commercial quadrupole spectrometer used here, for example, has a detection limit of about $3 \times 10^4$ charged particles per second.

Nanosecond ablation generates charges in the ablation plume. In Fig. 5.5, the positive ion peaks for each of the salts only appear when the laser is on, which means the ions are generated by ablation. We observe a positive ion peak for the LiCl ns
ablation (at M/Z of 6 to 7) at nearly 200 fA. With NaCl and KCl, the Na\(^+\) and K\(^+\) peaks are observed but are one to two orders of magnitude smaller than the Li\(^+\) peak in the LiCl sample. This difference might be a result of a multi-photon resonance that exists for the LiCl dissociative state and the 532 nm light. We have started to consider the ways the salts could be photo-fragmented by calculating the potential energy surfaces of these diatomics using \textit{ab initio} methods. That is part of ongoing work that is not presented here.

Figure 5.5 also contains mass spectra for the same three salts ablated using fs pulses. In the femtosecond regime, several ion peaks appear. The largest peaks correspond to the alkali metals for each target: \(^6\text{Li}^+\), \(^7\text{Li}^+\), Na\(^+\), \(^{39}\text{K}^+\), and \(^{41}\text{K}^+\). The minor isotopic abundances are in approximately the correct amounts: about 9 and 5 percent for Li\(^+\) and K\(^+\), respectively, compared with 8 and 7 percent for the natural abundances. \(\text{H}_2\text{O}^+\) appears in all of the spectra and is roughly 10 percent
Chapter 5: Detection of Laser Ablated Salt Using Spec-Chip

of that for the alkali ions. Control experiments involving pure epoxy targets do not exhibit the water ion peak, which suggests that water contained in the hygroscopic salts is liberated by the ablation process.

We observe triatomic ion clusters for each of the salt samples: Li$_2$Cl$^+$, Na$_2$Cl$^+$, and K$_2$Cl$^+$ as well as their chlorine isotopes. Na$_2$Cl$^+$ and K$_2$Cl$^+$ were identified by Chupka [142] in 1959 who used an hot plate to volatilize the salt. By analogy to Chupka’s vapor experiments, we presume the ion clusters we see form in the gas phase of the ablation plume rather than being liberated directly from the condensed phase. If that is the case, the molecular ion clusters are indirect evidence of neutral LiCl, NaCl, and KCl vapor existing in the fs ablation plumes; species that we are able to directly detect in the Spec-Chip experiments with ns ablation.

Chupka [142] measured the ratio of $M^+/M_2X^+$ ions as a function of temperature around 700 to 900 K and retrieved constants $A$ and $B$ by fitting to the function

$$\log{M^+/M_2X^+} = C + A(1000/T) - 1.5 \log{1000/T}.$$  

With the caveat that we need to extrapolate the measurements far outside the range of temperatures (nominally 1000 K) used in the Chupka experiments, we can use the fit coefficients to deduce the nominal temperature at which our ion clusters are forming. Substituting our measured ion ratios to the equation, we find two roots. For NaCl, the temperatures that yield the observed temperatures are 240 and $1.6 \times 10^5$ K. For KCl, they are 230 and $2.3 \times 10^5$ K. Because there is no external cooling done on the ablation plume, we conclude that the temperature at which the ion clusters form, a proxy for the plume temperature itself, is quite high. Since we have extrapolated the Chupka fit well outside the range of his experimental data, we conclude simply that the ion clusters
are forming at a temperature significantly above the 1000 K.

Figure 5.5: Mass spectra of laser-ablated LiCl, NaCl, and KCl in epoxy. The thin red and thick blue lines correspond to ns and fs ablation, respectively. For each of the fs spectra, alkali metal ions and ion clusters are detected. For the ns spectra, only the LiCl sample has a detectable alkali ion. In the ns spectra, LiCl has one to two orders of magnitude higher metal ion current than the other two samples.
5.4 Conclusion

The ability of the Spec-Chip spectrometer, based on a miniature Fabry-Perot cavity and CMOS electronics built by the Jet Propulsion Laboratory, to detect solid material forcibly volatilized by ns ablation pulses has been demonstrated. The rotational transitions of two salts, NaCl and KCl, have been measured. These two substances would be species of interest in missions to the surfaces of icy moons like Europa and Enceladus. It is also probable that other ablation products could be measured in future experiments. As with the Cu/alanine experiments in Chapter 4, we find that a significant amount of the ablated material remains in the condensed phase after ablation. The ability to detect laser-ablated molecules could be improved in the future by selecting laser parameters to fully-vaporize the ablated material and maximize the yield of gas-phase species. To that end, particle imaging and rotational spectra of fs pulses and pulses at different wavelengths should be done. Moreover, since some of the ablated material is dissociatively ionized, which reduces the yield of the analyte species, future investigation of the mechanisms and rates of photo- and electron-impact fragmentation should be performed.
Chapter 6

Conclusion

This thesis has reported four studies: the plasma chemistry inside an experimental analog of Titan’s upper atmosphere, measurements of the performance of a miniature Fabry-Perot cavity for \textit{in situ} chemical sensing, quantifying the properties and fragmentation in a nanosecond ablation plume, and, finally, demonstration that a new miniature millimeter-wave detector is capable of detecting laser ablation products.

The positive ion mass spectra and anode current predicted by the numerical model of the Titan Haze Simulation agree with experimental values, which suggests that the electron physics and chemical network adopted in that study are suitable. As with experiment, the model predicts the emergence of reaction products with an increasing number of carbon atoms as more reactive precursor molecules like C$_2$H$_2$ and C$_2$H$_4$ are added to the flow. This behavior is a main feature of the THS experiment that enables the controlled production of the initial stages of the chemistry in a Titan-like environment. Earlier studies had shown that the temperature of the heavy species in the THS experiment were comparable to those in Titan’s upper atmosphere. The
finding that the ionization fraction (nominally $1 \times 10^6$) and mean electron temperature (around 1 eV) are also similar to those at Titan reinforces the idea that the THS experiment is a good analog environment for simulating the chemistry.

Future experiments and iterations of the modeling should focus on constraining the neutral and negative ion chemistry as well as understanding the incipient phases of aerosol formation. The model already contains a number of neutral reactions that could be validated by new experiments. The Team at NASA Ames has plans for a number of interesting ones. The THS apparatus is configured with a cavity ring down spectrometer that could measure the density of neutrals within the channel. A rotational spectrometer, like Spec-Chip is another option for doing that. For the negative ions, the existing Re-TOF-MS can be configured to directly detect the negative ions that form. The chemical network in the model could be augmented to include negative ions, and there already exist compilations of the reactions thought to occur. Negative ion chemistry in Titan's upper atmosphere is significant and was unexpected before the arrival of Casinni [30, 48–50]. It would be interesting to know if it also occurs in the analog environment, especially since PAHs and cyanaromatics, possible building blocks of particles, are electronegative. The mechanisms that convert gases to primary aerosol particles, both at Titan and in the laboratory, are unknown. Some candidate pathways have been proposed for Titan [7–9]. By honing the agreement between the modeled and experimental chemistry of the THS plasma across the ion and neutral species, and by testing many different minor precursor constituents, the THS simulation may be able to determine what species and what reactions are responsible for particle production.
Rotational spectroscopy is a powerful technique for molecular identification. The frequency of transitions for a given molecule represent a unique fingerprint that enable isotopologues and isotopomers to be easily distinguished from one another. Applying the technique to \textit{in situ} measurements in space opens the possibility of definitively identifying and even quantifying new molecules at the surface of a number of sites throughout the solar system. The Jet Propulsion Laboratory’s Spec-Chip device is being developed for that kind of mission and is made possible by a number of new technologies; a new design for a miniature millimeter-wave-coupled Fabry-Perot cavity among them.

The Fabry-Perot cavity has been intentionally designed with a moderate quality factor trading intensity in the electromagnetic signal for bandwidth. We have shown that the resonant modes are well-behaved across the two-dimensional plane of emitter frequency and cavity length. Measured quality factors in the range of 1000 to 6000 depend on the selection of a particular curved mirror dimension and represent a trade space that can be tailored in favor of either discovery potential or sensitivity. The Spec-Chip team has continued to refine the instrument to the point that detections of new gases with the present iteration of the hardware have become routine. There are a large number of applications to which the Spec-Chip platform could be applied. We chose to focus on using Spec-Chip to detect the products of laser ablation because that capability would open a large number of new mission possibilities from spatially-resolved mapping of minerals to the detection of salts precipitated at the surface of icy moons.

Fragmentation in laser ablation is a complicated process that can result from
Chapter 6: Conclusion

the photochemistry, dissociative ionization induced by the impact of free electrons in the plasma, or can be thermally mediated. Using rotational spectroscopy, we have identified several neutral fragments in the plume of Cu/alanine targets ablated by nanosecond pulses: CH$_3$CN, HC$_3$N, and CH$_3$CCH. At the tested intensities, which were slightly above the threshold at which the signal of ablated molecules starts to become visible, the quantum yield of CH$_3$CN and HC$_3$N was between $10^{-4}$ and $10^{-2}$ molecules per photon. Pump-probe imaging of the ablation plume along with numerical simulation of that process suggests that the initial temperature and pressure of the ejected material is on the order of $1\cdot10^4$ to $5\cdot10^4$ K and 20 to 60 GPa for a 10 to 100 J cm$^{-2}$ fluence, respectively. At these conditions, the alanine should be completely fragmented in an amount of time comparable to the lifetime of the expanding shockwave. We hypothesize, therefore, that the intact alanine may originate from the molten surface of the target after it has cooled from its initial state.

To evaluate this possibility, transient absorption measurements of the plume ejection could be done. By monitoring the time-dependence of the intensity of light tuned to the resonance of the observed neutral fragmentation products as it passes through the ablation plume, one can determine when those products first appear. Similarly, probe pulses tuned to an absorption resonance of alanine would be able to distinguish when the alanine is produced: either throughout the ablation event or at late times after cooling. Additionally, it would be interesting to see what affect different laser parameters (e.g. pulse duration and wavelength) have on the neutral fragment distribution.

Having considered the laser ablation of a molecular solid in Chapter 5, the
fragmentation and practical aspects of cooling the ablation plume in a pulsed jet, we
coupled a nanosecond ablation source to the Spec-Chip. The detections of rotational
transitions of two salt molecules, NaCl and KCl, confirm that Spec-Chip can be
used to determine the composition of condensed phases. Using a stable calibrant, we
estimate that about $3 \times 10^{12}$ salt molecules pass through the Spec-Chip cavity per laser
pulse; significantly fewer than we would expect if the ablated material were completely
vaporized. Indeed, Microscopic imaging of a witness coupon placed near the sample
shows that a significant amount of the ablated sample remains in the solid or liquid
phase in the form of micro-particles and aggregates thereof. As with the Cu/alanine
targets studied in Chapter 4, laser ablation can fragment the salt molecules, especially
when ultra-short, high intensity pulses are used. It would be interesting to know if the
high intensity fs pulses also do a more thorough job vaporizing the ablation plume and
to know what is the yield of neutral molecules in that plume. It was not possible to try
fs laser ablation with the Spec-Chip system although doing so would be an interesting
avenue for future work since there have been previous reports of volatilization of large
biomolecules by ultrafast pulses for detection using mass spectrometry. Comparing
the amount of fragmentation across a range of different laser parameters would be an
interesting course of future study.
Appendix A

Chemical Network for Model of Titan

Haze Simulation experiment
Table A.1: Chemical network used in the model of the Titan Haze Simulation experiment. S.R signifies surface rate.

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<td>(e + H_2 \rightarrow e + 2H)</td>
<td>(f(\bar{e}))</td>
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<td>$e + N_2(A) \rightarrow 2e + N_2(A)^+$</td>
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<td>$e + N_2(B) \rightarrow 2e + N_2(A)^+$</td>
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<td>47</td>
<td>$e + N_2(B') \rightarrow e + N_2(X)$</td>
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<td>$e + N_2(C) \rightarrow e + N_2(X)$</td>
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<td>e+N₂(E) → e+N₂(X)</td>
<td>(f(\bar{\epsilon}))</td>
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<td>e+N₂(W) → e+N₂(X)</td>
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<td>51</td>
<td>e+N₂(X) → 2e+N(S) + N⁺</td>
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<td>52</td>
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<td>54</td>
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<td>55</td>
<td>e+N₂(X) → e+2N(S)</td>
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<td>56</td>
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<td>e+N₂(X) → e+N₂(B)</td>
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<td>e+N₂(X) → e+N₂(E)</td>
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<td>e+N₂(X)→e+N₂(X)</td>
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<td>e+N₂(X)→e+N₂(a)</td>
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<td>e+N₂(X)→e+N₂(a'')</td>
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<td>e+N₂(X)→e+N₂ w₁</td>
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<td>e+N₂(X)⁺→2N(S)</td>
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<td>68</td>
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<td>69</td>
<td>e+N₂(X)⁺→e+N₂(B)⁺</td>
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<td>70</td>
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<td>86</td>
<td>$2N_2(X) + N^+ \rightarrow N_2(X) + N_3^+$</td>
<td>$1.8 \times 10^{-29} [\text{cm}^6/\text{s}]$</td>
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<td>87</td>
<td>$C + HC_3N \rightarrow H + C_4N$</td>
<td>$1 \times 10^{-10} [\text{cm}^3/\text{s}]$</td>
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<td>$C_4H_2 + C_2H_5^+ \rightarrow C_2H_4 + C_4H_3^+$</td>
<td>$3.0 \times 10^{-9} [\text{cm}^3/\text{s}]$</td>
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<td>89</td>
<td>$C_4H_2 + C_4H_3^+ \rightarrow C_2H_6 + C_6H_3^+$</td>
<td>$7.4 \times 10^{-10} [\text{cm}^3/\text{s}]$</td>
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<td>$C_4H_2 + C_5H_5^+ \rightarrow C_2H_2 + C_7H_5^+$</td>
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<td>91</td>
<td>$C_4H_2 + HCNH^+ \rightarrow HCN + C_4H_3^+$</td>
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<td>$C_6H_2 + C_2H_5^+ \rightarrow C_2H_4 + C_6H_3^+$</td>
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<td>$C_6H_2 + C_4H_3^+ \rightarrow C_2H_2 + C_8H_3^+$</td>
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<td>CH+CH₄→C₂H₄+H</td>
<td>((1.06 \times 10^{-10} \text{[cm}^3/\text{s}]) \cdot (T/1\text{[K]})^{-1.04} \exp[-36.1\text{[K]}/T])</td>
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<td>98</td>
<td>CH+N⁺→H+CN⁺</td>
<td>((6.6 \times 10^{-10} \text{[cm}^3/\text{s}]) \cdot [0.62 + 1.59(300\text{[K]}/T)^{0.5}])</td>
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<td>99</td>
<td>CH₂+CH₂→C₂H₄</td>
<td>(1.7 \times 10^{-13}\text{[cm}^3/\text{s}])</td>
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<td>100</td>
<td>CH₂+CH₄→CH₃+CH₃</td>
<td>((2.14 \times 10^{-11} \text{[cm}^3/\text{s}]) \cdot (T/1\text{[K]})^{0.5})</td>
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<td>101</td>
<td>CH₂+C⁺→C+CH₂⁺</td>
<td>((6.7 \times 10^{-10} \text{[cm}^3/\text{s}]) \cdot [0.62 + 0.67(300\text{[K]}/T)^{0.5}])</td>
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<td>CH₂+H₂→CH₃+H</td>
<td>((3.34 \times 10^{-11} \text{[cm}^3/\text{s}]) \cdot (T/1\text{[K]})^{0.5})</td>
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<td>103</td>
<td>CH₃NH+C₂H₆⁺→C₂H₄+CH₂NH₂⁺</td>
<td>(3.0 \times 10^{-9}\text{[cm}^3/\text{s}])</td>
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<td>104</td>
<td>CH₂NH+HCNH⁺→HCN+CH₂NH₂⁺</td>
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<td>CH₃+CH₂→C₂H₄+H</td>
<td>(7 \times 10^{-11}\text{[cm}^3/\text{s}])</td>
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<td>106</td>
<td>CH₂+CH₃→C₂H₅+H</td>
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<td>CH₃+CH₃→C₂H₆</td>
<td>((4 \times 10^{-10} \text{[cm}^3/\text{s}]) \cdot (T/1\text{[K]})^{-0.4})</td>
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<td>108</td>
<td>CH₃CN+CH₃⁺→C₂H₅CNH⁺</td>
<td>(9.0 \times 10^{-11}\text{[cm}^3/\text{s}])</td>
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<td>109</td>
<td>CH$_3$CN + C$_2$H$_5^+$ \to C$_2$H$_4$ + CH$_3$CNH$^+$</td>
<td>$3.8 \times 10^{-9}$[cm$^3$/s]</td>
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<td>CH$_3$CN + HCNH$^+$ \to HCN + CH$_3$CNH$^+$</td>
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<td>CH$_3$NH$_2$ + N$_2$(X)$^+$ \to N$_2$(X) + H + CH$_2$NH$_2^+$</td>
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<td>CH$_4$ + CH$_2^+$ \to H$_2$ + C$_2$H$_4^+$</td>
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<td>117</td>
<td>CH$_4$ + CH$_3$ \to C$_2$H$_5$ + H$_2$</td>
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<td>CH$_4$ + CH$_3^+$ \to H$_2$ + C$_2$H$_5^+$</td>
<td>$1.1 \times 10^{-9}$[cm$^3$/s]</td>
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<td>119</td>
<td>( \text{CH}_4 + \text{CH}_4^+ \rightarrow \text{CH}_3 + \text{CH}_5^+ )</td>
<td>( 1.1 \times 10^{-9} \text{[cm}^3/\text{s}] )</td>
<td>[25]</td>
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<tr>
<td>120</td>
<td>( \text{CH}_4 + \text{C}_2\text{H}_2^+ \rightarrow \text{H}_2 + \text{C}_3\text{H}_4^+ )</td>
<td>( 1.87 \times 10^{-10} \text{[cm}^3/\text{s}] )</td>
<td>[149]</td>
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<tr>
<td>121</td>
<td>( \text{CH}_4 + \text{C}_2\text{H}_3^+ \rightarrow \text{H}_2 + \text{C}_3\text{H}_5^+ )</td>
<td>( 1.9 \times 10^{-10} \text{[cm}^3/\text{s}] )</td>
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<tr>
<td>122</td>
<td>( \text{CH}_4 + \text{C}_2\text{H}^+ \rightarrow \text{H}_2 + \text{clC}_3\text{H}_3^+ )</td>
<td>( 1.87 \times 10^{-10} \text{[cm}^3/\text{s}] )</td>
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<td>123</td>
<td>( \text{CH}_4 + \text{C}_2\text{H}^+ \rightarrow \text{H}_2 + \text{lC}_3\text{H}_3^+ )</td>
<td>( 1.87 \times 10^{-10} \text{[cm}^3/\text{s}] )</td>
<td>[149]</td>
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<tr>
<td>124</td>
<td>( \text{CH}_4 + \text{H} \rightarrow \text{H}_2 + \text{CH}_3 )</td>
<td>( (2.2 \times 10^{-20} \text{[cm}^3/\text{s}]) \cdot \exp[-4045[K]/T] )</td>
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<tr>
<td>125</td>
<td>( \text{CH}_4 + \text{HCN}^+ \rightarrow \text{CH}_3 + \text{HCNH}^+ )</td>
<td>( 1.1 \times 10^{-9} \text{[cm}^3/\text{s}] )</td>
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<tr>
<td>126</td>
<td>( \text{CH}_4 + \text{N}_2(X)^+ \rightarrow \text{N}_2(X) + \text{H} + \text{CH}_3^+ )</td>
<td>( 1.3 \times 10^{-9} \text{[cm}^3/\text{s}] )</td>
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<td>127</td>
<td>( \text{CH}_4 + \text{N}_2^+ \rightarrow \text{N}_2(X) + \text{CH}_5^+ )</td>
<td>( 8.9 \times 10^{-10} \text{[cm}^3/\text{s}] )</td>
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<td>128</td>
<td>( \text{CH}_4 + \text{N}^+ \rightarrow \text{H}_2 + \text{HCNH}^+ )</td>
<td>( 4.1 \times 10^{-10} \text{[cm}^3/\text{s}] )</td>
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<td>129</td>
<td>( \text{CN} + \text{CH}_3\text{CN} \rightarrow \text{C}_2\text{N}_2 + \text{CH}_3 )</td>
<td>( (6.46 \times 10^{-11} \text{[cm}^3/\text{s}]) \cdot \exp[-1190[K]/T] )</td>
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<td>130</td>
<td>( \text{CN} + \text{C}_2\text{H}_2 \rightarrow \text{HC}_3\text{N} + \text{H} )</td>
<td>( (2.71 \times 10^{-9} \text{[cm}^3/\text{s}]) \cdot (T/1[K])^{-0.52} \exp[-20[K]/T] )</td>
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<td>131</td>
<td>CN+HCN→C₂N₂+H</td>
<td>((4.3 \times 10^{-13}[\text{cm}^3/\text{s}]) \cdot (T/1[\text{K}])^{1.71} \exp \left[-770[\text{K}]/T\right])</td>
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<td>132</td>
<td>CN+HC₃N→C₄N₂+H</td>
<td>((1.7 \times 10^{-11}[\text{cm}^3/\text{s}]) \cdot (T/300[\text{K}])^{-0.67})</td>
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<td>C₂H+C⁺→H+C⁺⁺</td>
<td>((1.7 \times 10^{-11}[\text{cm}^3/\text{s}]) \cdot [0.62 + 0.64(300[\text{K}]/T)^{0.5}])</td>
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<td>134</td>
<td>C₂H₂+C₄H₂⁺→C₆H₄⁺⁺</td>
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<td>135</td>
<td>C₂H₂+CH₃⁺→H₂+clC₃H₃⁺⁺</td>
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<td>136</td>
<td>C₂H₂+CH₃⁺→H₂+ClC₃H₃⁺⁺</td>
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<td>137</td>
<td>C₂H₂+CH₅⁺→CH₄+C₂H₃⁺⁺</td>
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<td>C₂H₂+CH⁺→H+ClC₂H₂⁺⁺</td>
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<td>C₂H₂+CN→H+HC₃N</td>
<td>((2.7 \times 10^{-10}[\text{cm}^3/\text{s}]) \cdot (T/300[\text{K}])^{-0.52} \exp \left[-20[\text{K}]/T\right])</td>
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<td>C₂H₂+C₂H₂⁺→H+C₄H₃⁺⁺</td>
<td>(9.52 \times 10^{-10}[\text{cm}^3/\text{s}])</td>
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<td>141</td>
<td>C₂H₂+C₂H₂⁺→H₂+C₄H₂⁺⁺</td>
<td>(4.5 \times 10^{-10}[\text{cm}^3/\text{s}])</td>
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<tr>
<td>142</td>
<td>C₂H₂+CH₄⁺⁺→CH₃+ClC₃H₃⁺⁺</td>
<td>(6.5 \times 10^{-10}[\text{cm}^3/\text{s}])</td>
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<td>$\text{C}_2\text{H}_2 + \text{C}_2\text{H}_4^+ \rightarrow \text{CH}_3 + \text{I}_3\text{H}_3^+$</td>
<td>$6.5 \times 10^{-10}[\text{cm}^3/\text{s}]$</td>
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<td>144</td>
<td>$\text{C}_2\text{H}_2 + \text{C}_2\text{H}_4^+ \rightarrow \text{H} + \text{C}_4\text{H}_5^+$</td>
<td>$1.93 \times 10^{-10}[\text{cm}^3/\text{s}]$</td>
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<td>145</td>
<td>$\text{C}_2\text{H}_2 + \text{C}_2\text{H}_5^+ \rightarrow \text{CH}_4 + \text{IC}_3\text{H}_3^+$</td>
<td>$6.8 \times 10^{-11}[\text{cm}^3/\text{s}]$</td>
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<td>$6.8 \times 10^{-11}[\text{cm}^3/\text{s}]$</td>
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<td>147</td>
<td>$\text{C}_2\text{H}_2 + \text{C}_2\text{N}_2^+ \rightarrow \text{H} + \text{C}_4\text{N}_2\text{H}^+$</td>
<td>$7.0 \times 10^{-11}[\text{cm}^3/\text{s}]$</td>
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<td>$3.0 \times 10^{-11}[\text{cm}^3/\text{s}]$</td>
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<td>$3.8 \times 10^{-10}[\text{cm}^3/\text{s}]$</td>
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<td>$\text{C}_2\text{H}_2 + \text{C}_4\text{H}_3^+ \rightarrow \text{C}_6\text{H}_5^+$</td>
<td>$2.2 \times 10^{-10}[\text{cm}^3/\text{s}]$</td>
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<td>$\text{C}_2\text{H}_3 + \text{C}_2\text{H}_4^+ \rightarrow \text{H}_2 + \text{C}_4\text{H}_5^+$</td>
<td>$(5.2 \times 10^{-10}[\text{cm}^3/\text{s}]) \cdot (T/300[\text{K}])^{-0.5}$</td>
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<td>153</td>
<td>$\text{C}_2\text{H}_3\text{CN} + \text{C}_2\text{H}_5^+ \rightarrow$</td>
<td>$3.0 \times 10^{-9}[\text{cm}^3/\text{s}]$</td>
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<td></td>
<td>$\text{C}_2\text{H}_4 + \text{C}_2\text{H}_3\text{CNH}^+$</td>
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<td>154</td>
<td>$\text{C}_2\text{H}_3\text{CN}+\text{HCNH}^+ \rightarrow$</td>
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<td></td>
<td>$\text{HCN}+\text{C}_2\text{H}_3\text{CNH}^+$</td>
<td>$4.5 \times 10^{-9}[\text{cm}^3/\text{s}]$</td>
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<td>155</td>
<td>$\text{C}_2\text{H}_4+\text{CH}_5^+ \rightarrow \text{CH}_4+\text{C}_2\text{H}_5^+$</td>
<td>$1.5 \times 10^{-9}[\text{cm}^3/\text{s}]$</td>
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<td>$\text{C}_2\text{H}_4+\text{C}_2\text{H}_2^+ \rightarrow \text{H}+\text{C}_4\text{H}_5^+$</td>
<td>$3.04 \times 10^{-10}[\text{cm}^3/\text{s}]$</td>
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<td>158</td>
<td>$\text{C}_2\text{H}_4+\text{C}_2\text{H}_4^+ \rightarrow \text{H}+\text{C}_4\text{H}_7^+$</td>
<td>$7.47 \times 10^{-11}[\text{cm}^3/\text{s}]$</td>
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<td>$\text{C}_2\text{H}_4+\text{C}_2\text{H}_5^+ \rightarrow \text{CH}_4+\text{C}_3\text{H}_5^+$</td>
<td>$3.6 \times 10^{-10}[\text{cm}^3/\text{s}]$</td>
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<td>$\text{C}_2\text{H}_4+\text{C}_2\text{H}_2^+ \rightarrow \text{H}+\text{H}_2+\text{C}_4\text{H}_2^+$</td>
<td>$2.91 \times 10^{-10}[\text{cm}^3/\text{s}]$</td>
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<td>161</td>
<td>$\text{C}_2\text{H}_4+\text{C}_2\text{H}^+ \rightarrow \text{H}_2+\text{C}_4\text{H}_3^+$</td>
<td>$1.42 \times 10^{-9}[\text{cm}^3/\text{s}]$</td>
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<td>$\text{C}_2\text{H}_4+\text{C}_3\text{H}_5^+ \rightarrow \text{C}_5\text{H}_9^+$</td>
<td>$5.10 \times 10^{-11}[\text{cm}^3/\text{s}]$</td>
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<td>163</td>
<td>$\text{C}_2\text{H}_4+\text{C}_3\text{H}_5^+ \rightarrow \text{H}_2+\text{C}_5\text{H}_7^+$</td>
<td>$1.19 \times 10^{-10}[\text{cm}^3/\text{s}]$</td>
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<td>164</td>
<td>$\text{C}_2\text{H}_4+\text{C}_4\text{H}_3^+ \rightarrow \text{H}_2+\text{C}_6\text{H}_5^+$</td>
<td>$1.2 \times 10^{-10}[\text{cm}^3/\text{s}]$</td>
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<td>165</td>
<td>$\text{C}_2\text{H}_4+\text{C}_4\text{H}_3^+ \rightarrow \text{H}_2+\text{C}_6\text{H}_7^+$</td>
<td>$6.3 \times 10^{-11}[\text{cm}^3/\text{s}]$</td>
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<td>166</td>
<td>C(_2)H(_4)+HC(_3)NH(^+)→H+C(_4)H(_5)NH(^+)</td>
<td>1.3 × 10(^{-9}) [cm(^3)/s]</td>
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<tr>
<td>167</td>
<td>C(_2)H(_4)+lC(_3)H(_3)^+→C(_5)H(_7)^+</td>
<td>5.5 × 10(^{-10}) [cm(^3)/s]</td>
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<tr>
<td>168</td>
<td>C(_2)H(_4)+lC(_3)H(_3)^+→H(_2)+C(_5)H(_5)^+</td>
<td>5.5 × 10(^{-10}) [cm(^3)/s]</td>
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<td>169</td>
<td>C(_2)H(_5)+H→CH(_3)+CH(_3)</td>
<td>(7.95 × 10(^{-11}) [cm(^3)/s]) · exp [−127[K]/T]</td>
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<td>170</td>
<td>C(_2)H(_5)+H→C(_2)H(_6)</td>
<td>6 × 10(^{-11}) [cm(^3)/s]</td>
<td>[24]</td>
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<tr>
<td>171</td>
<td>C(_2)H(_5)CN+C(_2)H(_5)^+→C(_2)H(_4)+C(_2)H(_5)CNH(^+)</td>
<td>3.0 × 10(^{-9}) [cm(^3)/s]</td>
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<tr>
<td>172</td>
<td>C(_2)H(_5)CN+HCNH(^+)→HCN+C(_2)H(_5)CNH(^+)</td>
<td>3.0 × 10(^{-9}) [cm(^3)/s]</td>
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<td>173</td>
<td>C(_2)H(_6)+CH(_3)→C(_2)H(_5)+CH(_4)</td>
<td>(2.5 × 10(^{-31}) [cm(^3)/s]) · (T/1[K])(^6) exp [−3750[K]/T]</td>
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<td>174</td>
<td>C(_2)H(_6)+H→C(_2)H(_5)+H(_2)</td>
<td>(2.5 × 10(^{-15}) [cm(^3)/s]) · (T/1[K])(^6) exp [−3730[K]/T]</td>
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<td>175</td>
<td>C(_2)H(_6)+H(_2)^+→H(_2)+C(_2)H(_6)^+</td>
<td>2.94 × 10(^{-10}) [cm(^3)/s]</td>
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<td>$\text{C}_3\text{H}_4 + \text{C}_3\text{H}_4^+ \rightarrow \text{C}_2\text{H}_2 + \text{C}_4\text{H}_6^+$</td>
<td>$2.2 \times 10^{-11}[\text{cm}^3/\text{s}]$</td>
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<td>$\text{C}_4\text{H}_5\text{N} + \text{C}_2\text{H}_5^+ \rightarrow$</td>
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<td>$\text{C}_4\text{H}_3\text{N} + \text{HCNH}^+ \rightarrow$</td>
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<td>$\text{HCN} + \text{C}_4\text{H}_3\text{NH}^+$</td>
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<td>$1 \times 10^{-10}[\text{cm}^3/\text{s}]$</td>
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<td>$\text{C}_6\text{H}_6 + \text{C}_2\text{H}_5^+ \rightarrow \text{C}_2\text{H}_4 + \text{C}_6\text{H}_7^+$</td>
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<td>$\text{C}_6\text{H}_6 + \text{HCNH}^+ \rightarrow \text{HCN} + \text{C}_6\text{H}_7^+$</td>
<td>$3.0 \times 10^{-9}[\text{cm}^3/\text{s}]$</td>
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<td>$\text{C}_7\text{H}_4 + \text{C}_2\text{H}_5^+ \rightarrow \text{C}_2\text{H}_4 + \text{C}_7\text{H}_5^+$</td>
<td>$3.0 \times 10^{-9}[\text{cm}^3/\text{s}]$</td>
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<td>$\text{C}_7\text{H}_4 + \text{HCNH}^+ \rightarrow \text{HCN} + \text{C}_7\text{H}_5^+$</td>
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<td>$4.96 \times 10^{-10} \text{[cm}^3/\text{s]}$</td>
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<td>$\text{HCN} + \text{CN}^+ \rightarrow \text{H} + \text{C}_2\text{N}_2^+$</td>
<td>$3.15 \times 10^{-10} \text{[cm}^3/\text{s]}$</td>
<td>[149]</td>
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<tr>
<td>191</td>
<td>$\text{HCN} + \text{C}_2\text{H} \rightarrow \text{HC}_3\text{N} + \text{H}$</td>
<td>$(5.3 \times 10^{-12} \text{[cm}^3/\text{s}] \cdot \exp[-770\text{[K]}/T]$</td>
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<tr>
<td>192</td>
<td>$\text{HCN} + \text{C}_2\text{H}_5^+ \rightarrow \text{C}_2\text{H}_4 + \text{HCNH}^+$</td>
<td>$2.7 \times 10^{-9} \text{[cm}^3/\text{s]}$</td>
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<tr>
<td>193</td>
<td>$\text{HCN} + \text{C}_3\text{H}_5^+ \rightarrow \text{C}_4\text{H}_5\text{NH}^+$</td>
<td>$5.0 \times 10^{-11} \text{[cm}^3/\text{s]}$</td>
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<tr>
<td>194</td>
<td>$\text{HCN} + \text{N}_2(\text{X})^+ \rightarrow \text{N}_2(\text{X}) + \text{HCN}^+$</td>
<td>$1.0 \times 10^{-9} \text{[cm}^3/\text{s]}$</td>
<td>[149]</td>
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<tr>
<td>195</td>
<td>$\text{HCN} + \text{IC}_3\text{H}_3^+ \rightarrow \text{C}_4\text{H}_3\text{NH}^+$</td>
<td>$4.8 \times 10^{-10} \text{[cm}^3/\text{s]}$</td>
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<td>196</td>
<td>$\text{HCNH} + \text{H} \rightarrow \text{HCN} + \text{H}_2$</td>
<td>$(2.9 \times 10^{-11} \text{[cm}^3/\text{s}] \cdot (T/\text{1[K]})^{0.5}$</td>
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<td>197</td>
<td>$\text{HC}_3\text{N} + \text{C}_2\text{H}_2^+ \rightarrow \text{C}_5\text{H}_3\text{N}^+$</td>
<td>$(2 \times 10^{-12} \text{[cm}^3/\text{s}] \cdot (T/\text{300[K]})^{-0.25}$</td>
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<td>198</td>
<td>$\text{HC}_3\text{N} + \text{C}_2\text{H}_5^+ \rightarrow \text{C}_2\text{H}_4 + \text{HC}_3\text{NH}^+$</td>
<td>$3.6 \times 10^{-9} \text{[cm}^3/\text{s}]$</td>
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<td>199</td>
<td>$\text{HC}_3\text{N} + \text{HCNH}^+ \rightarrow \text{HCN} + \text{HC}_3\text{NH}^+$</td>
<td>$3.4 \times 10^{-9} \text{[cm}^3/\text{s}]$</td>
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<td>200</td>
<td>$\text{H}_2 + \text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_6 + \text{H}$</td>
<td>$(4.1 \times 10^{-15} \text{[cm}^3/\text{s}]) \cdot (T/300[\text{K}])^{3.6} \exp [-4240[\text{K}]/T]$</td>
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<td>201</td>
<td>$\text{H}_2 + \text{C}^+ \rightarrow \text{CH}_2^+$</td>
<td>$(2.0 \times 10^{-16} \text{[cm}^3/\text{s}]) \cdot (T/300[\text{K}])^{-1.3} \exp [-23[\text{K}]/T]$</td>
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<td>202</td>
<td>$\text{H}_2 + \text{N}_2(X)^+ \rightarrow \text{H} + \text{N}_2\text{H}^+$</td>
<td>$2.0 \times 10^{-9} \text{[cm}^3/\text{s}]$</td>
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<td>203</td>
<td>$\text{N(S)} + \text{CH}_2 \rightarrow \text{CN} + 2\text{H}$</td>
<td>$1.6 \times 10^{-11} \text{[cm}^3/\text{s}]$</td>
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<td>204</td>
<td>$\text{N(S)} + \text{CH}_2 \rightarrow \text{CN} + \text{H}_2$</td>
<td>$1.6 \times 10^{-11} \text{[cm}^3/\text{s}]$</td>
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<td>205</td>
<td>$\text{N(S)} + \text{CH}_2 \rightarrow \text{HCN} + \text{H}$</td>
<td>$(5 \times 10^{-11} \text{[cm}^3/\text{s}]) \cdot \exp [-250[\text{K}]/T]$</td>
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<td>$\text{N(S)} + \text{CH}_3 \rightarrow \text{HCN} + \text{H}_2$</td>
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<td>207</td>
<td>$\text{N(S)} + \text{C}_2\text{H}_2^+ \rightarrow \text{HCN} + \text{CH}^+$</td>
<td>$2.5 \times 10^{-11} \text{[cm}^3/\text{s}]$</td>
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<td>208</td>
<td>$\text{N(S)} + \text{C}_3\text{H}_4^+ \rightarrow \text{H}_2 + \text{HC}_3\text{NH}^+$</td>
<td>$1.00 \times 10^{-10} \text{[cm}^3/\text{s}]$</td>
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<td>209</td>
<td>$\text{N(S)} + \text{HCNH} \rightarrow \text{HCN} + \text{NH}$</td>
<td>$6.7 \times 10^{-11} \text{[cm}^3/\text{s}]$</td>
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<td>210</td>
<td>N(S)+NH→N₂(X)+H</td>
<td>$(8.6 \times 10^{-12}[\text{cm}^3/\text{s}]) \cdot (T/1[\text{K}])^{0.5}$</td>
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<tr>
<td>211</td>
<td>N(S)+N₂(X)+N₂(X)⁺→N₂(X)+N₃⁺</td>
<td>$(0.9 \times 10^{-29}[\text{cm}^6/\text{s}]) \cdot \exp [400[\text{K}]/T]$</td>
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<td>212</td>
<td>N(S)+N₂(X)⁺→N₂(X)+N⁺</td>
<td>$(7.2 \times 10^{-13}[\text{cm}^3/\text{s}]) \cdot \exp [T/300[\text{K}]]$</td>
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<tr>
<td>213</td>
<td>N(S)+N₃⁺→N₂(X)+N₂(X)⁺</td>
<td>$6.6 \times 10^{-11}[\text{cm}^3/\text{s}]$</td>
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<tr>
<td>214</td>
<td>NH+H→N(S)+H₂</td>
<td>$(1.7 \times 10^{-12}[\text{cm}^3/\text{s}]) \cdot (T/1[\text{K}])^{0.68} \exp [-950[\text{K}]/T]$</td>
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<td>215</td>
<td>NH₃+CH₃⁺→H₂+CH₂NH₂⁺</td>
<td>$1.5 \times 10^{-9}[\text{cm}^3/\text{s}]$</td>
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<tr>
<td>216</td>
<td>NH₃+C₂H₅⁺→C₂H₄+NH₄⁺</td>
<td>$2.1 \times 10^{-9}[\text{cm}^3/\text{s}]$</td>
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<tr>
<td>217</td>
<td>NH₃+HCNH⁺→HCN+NH₄⁺</td>
<td>$2.3 \times 10^{-9}[\text{cm}^3/\text{s}]$</td>
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<td>218</td>
<td>N₂(A)+CH₄→N₂(X)+CH₄</td>
<td>$3.2 \times 10^{-15}[\text{cm}^3/\text{s}]$</td>
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<tr>
<td>219</td>
<td>N₂(A)+H→N₂(X)+H</td>
<td>$2.1 \times 10^{-10}[\text{cm}^3/\text{s}]$</td>
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<td>220</td>
<td>N₂(A)+H₂→N₂(X)+2H</td>
<td>$2.4 \times 10^{-15}[\text{cm}^3/\text{s}]$</td>
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<tr>
<td>221</td>
<td>N₂(A)+N(S)→N₂(X)+N(S)</td>
<td>$5 \times 10^{-11}[\text{cm}^3/\text{s}]$</td>
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<td>222</td>
<td>$N_2(A) + N_2(X) \rightarrow 2N_2(X)$</td>
<td>$3 \times 10^{-16} [\text{cm}^3/\text{s}]$</td>
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<tr>
<td>223</td>
<td>$N_2(A) + N_2(a') \rightarrow N_2(X) + e + N_2(X)^+$</td>
<td>$1.5 \times 10^{-11} [\text{cm}^3/\text{s}]$</td>
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<td>224</td>
<td>$N_2(A) + N_2(a') \rightarrow e + N_4^+$</td>
<td>$1.5 \times 10^{-11} [\text{cm}^3/\text{s}]$</td>
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<td>225</td>
<td>$N_2(B) \rightarrow N_2(A)$</td>
<td>$6.25 \times 10^4 [1/\text{s}]$</td>
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<td>226</td>
<td>$N_2(B) + \text{CH}_4 \rightarrow N_2(A) + \text{CH}_4$</td>
<td>$2.85 \times 10^{-10} [\text{cm}^3/\text{s}]$</td>
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<tr>
<td>227</td>
<td>$N_2(B) + \text{CH}_4 \rightarrow N_2(X) + \text{CH}_4$</td>
<td>$1.5 \times 10^{-11} [\text{cm}^3/\text{s}]$</td>
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<td>228</td>
<td>$N_2(B) + \text{H}_2 \rightarrow N_2(A) + \text{H}_2$</td>
<td>$2.4 \times 10^{-11} [\text{cm}^3/\text{s}]$</td>
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<tr>
<td>229</td>
<td>$N_2(B) + N_2(X) \rightarrow 2N_2(X)$</td>
<td>$3 \times 10^{-11} [\text{cm}^3/\text{s}]$</td>
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<tr>
<td>230</td>
<td>$N_2(C) \rightarrow N_2(B)$</td>
<td>$13.9 \times 10^6 [1/\text{s}]$</td>
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<td>231</td>
<td>$N_2(C) + N_2(X) \rightarrow N_2(a') + N_2(X)$</td>
<td>$1.0 \times 10^{-11} [\text{cm}^3/\text{s}]$</td>
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<tr>
<td>232</td>
<td>$N_2(X) + N_2(A)^+ \rightarrow N(S) + N_3^+$</td>
<td>$5.5 \times 10^{-11} [\text{cm}^3/\text{s}]$</td>
<td>[151]</td>
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<tr>
<td>233</td>
<td>$N_2(X) + N_2(B)^+ \rightarrow N(S) + N_3^+$</td>
<td>$5.5 \times 10^{-11} [\text{cm}^3/\text{s}]$</td>
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<tr>
<td>234</td>
<td>$N_2(X) + N_4^+ \rightarrow 2N_2(X) + N_2(X)^+$</td>
<td>$(2.1 \times 10^{-16}[\text{cm}^3/\text{s}]) \cdot \exp[T/121[\text{K}]]$</td>
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<tr>
<td>235</td>
<td>$N_2(a) \rightarrow N_2(X)$</td>
<td>$1.8 \times 10^4[1/\text{s}]$</td>
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<tr>
<td>236</td>
<td>$N_2(a) \rightarrow N_2(a')$</td>
<td>$1.91 \times 10^2[1/\text{s}]$</td>
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<tr>
<td>237</td>
<td>$N_2(a) + \text{CH}_4 \rightarrow N_2(X) + \text{CH}_4$</td>
<td>$5.2 \times 10^{-10}[\text{cm}^3/\text{s}]$</td>
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<tr>
<td>238</td>
<td>$N_2(a) + N_2(X) \rightarrow N_2(a') + N_2(X)$</td>
<td>$2.0 \times 10^{-11}[\text{cm}^3/\text{s}]$</td>
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<tr>
<td>239</td>
<td>$N_2(a') + \text{CH}_4 \rightarrow N_2(X) + \text{CH}_4$</td>
<td>$3 \times 10^{-10}[\text{cm}^3/\text{s}]$</td>
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<tr>
<td>240</td>
<td>$N_2(a') + H \rightarrow N_2(X) + H$</td>
<td>$2.1 \times 10^{-10}[\text{cm}^3/\text{s}]$</td>
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<tr>
<td>241</td>
<td>$N_2(a') + H_2 \rightarrow N_2(X) + 2H$</td>
<td>$2.6 \times 10^{-11}[\text{cm}^3/\text{s}]$</td>
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<td>242</td>
<td>$N_2(a') + N_2(X) \rightarrow N_2(B) + N_2(X)$</td>
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<td>243</td>
<td>$N_2(a') + N_2(a') \rightarrow N_2(X) + e + N_2(X)^+$</td>
<td>$1.0 \times 10^{-11}[\text{cm}^3/\text{s}]$</td>
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<tr>
<td>244</td>
<td>$N_2\text{H}_4 + C_2\text{H}_5^+ \rightarrow C_2\text{H}_4 + N_2\text{H}_5^+$</td>
<td>$3.0 \times 10^{-9}[\text{cm}^3/\text{s}]$</td>
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<tr>
<td>245</td>
<td>$N_2\text{H}_4 + \text{HCNH}^+ \rightarrow \text{HCN} + N_2\text{H}_5^+$</td>
<td>$3.0 \times 10^{-9}[\text{cm}^3/\text{s}]$</td>
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<td>246</td>
<td>e+N$_2$(X)$^+$→2N(S)</td>
<td>$(4.8 \times 10^{-7}[\text{cm}^3/\text{s}] \cdot (300[\text{K}]/T_e)^{0.5}$</td>
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<tr>
<td>247</td>
<td>e+N$_4^+$→2N$_2$(X)</td>
<td>$(2.0 \times 10^{-6}[\text{cm}^3/\text{s}] \cdot (300[\text{K}]/T_e)^{0.5}$</td>
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<td>248</td>
<td>e+C$_4$H$_7^+$→CH$_4$+clC$_3$H$_3$</td>
<td>$(1.95 \times 10^{-7}[\text{cm}^3/\text{s}] \cdot (300[\text{K}]/T)^{0.5}$</td>
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<td>249</td>
<td>e+C$_6$H$_7^+$→H+C$_6$H$_6$</td>
<td>$(5 \times 10^{-7}[\text{cm}^3/\text{s}] \cdot (300[\text{K}]/T)^{0.5}$</td>
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<td>250</td>
<td>C$_4$H$_2^+$→C$_4$H$_2$</td>
<td>S.R.</td>
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<td>C$_5$H$_2$N$^+$→C$_5$H$_2$N</td>
<td>S.R.</td>
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<td>CH$_2$NH$_2^+$→CH$_2$NH$_2$</td>
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<td>CH$_2^+$→CH$_2$</td>
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<td>CH$_3$CNH$^+$→CH$_3$CNH</td>
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<td>CH$_3^+$→CH$_3$</td>
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<td>258</td>
<td>CH$_4^+$→CH$_4$</td>
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<td>CH$_5^+$ → CH$_5$</td>
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<td>260</td>
<td>CH$^+$ → CH</td>
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<td>261</td>
<td>CN$^+$ → CN</td>
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<td>C$_2$H$_3^+$ → C$_2$H$_2$</td>
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<td>C$_2$H$_5$CNH$^+$ → C$_2$H$_5$CNH</td>
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<td>C$_2$H$_5^+$ → C$_2$H$_5$</td>
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<td>268</td>
<td>C$_2$H$_6^+$ → C$_2$H$_6$</td>
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<td>269</td>
<td>C$_2$H$^+$ → C$_2$H</td>
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<td>C$_2$N$_2^+$ → C$_2$N$_2$</td>
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<td>C₃H₅⁺ → C₃H₅</td>
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<td>C₃⁺ → C₃</td>
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<td>C₄H₃NH⁺ → C₄H₃NH</td>
<td>S.R.</td>
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<td>C₄H₃⁺ → C₄H₃</td>
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<td>277</td>
<td>C₄H₅NH⁺ → C₄H₅NH</td>
<td>S.R.</td>
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<tr>
<td>278</td>
<td>C₄H₅⁺ → C₄H₅</td>
<td>S.R.</td>
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<tr>
<td>279</td>
<td>C₄H₆⁺ → C₄H₆</td>
<td>S.R.</td>
<td>N/A</td>
</tr>
<tr>
<td>280</td>
<td>C₄H₇⁺ → C₄H₇</td>
<td>S.R.</td>
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<td>281</td>
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<td>S.R.</td>
<td>N/A</td>
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<tr>
<td>282</td>
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<td>S.R.</td>
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<td>283</td>
<td>$\text{C}_5\text{H}_3\text{N}^+ \rightarrow \text{C}_5\text{H}_3\text{N}$</td>
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<td>S.R.</td>
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<td>285</td>
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<td>286</td>
<td>$\text{C}_5\text{H}_9^+ \rightarrow \text{C}_5\text{H}_9$</td>
<td>S.R.</td>
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<td>$\text{C}_6\text{H}_4^+ \rightarrow \text{C}_6\text{H}_4$</td>
<td>S.R.</td>
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<td>289</td>
<td>$\text{C}_6\text{H}_5^+ \rightarrow \text{C}_6\text{H}_5$</td>
<td>S.R.</td>
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<td>290</td>
<td>$\text{C}_6\text{H}_7^+ \rightarrow \text{C}_6\text{H}_7$</td>
<td>S.R.</td>
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<td>$\text{C}_7\text{H}_5^+ \rightarrow \text{C}_7\text{H}_5$</td>
<td>S.R.</td>
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<td>$\text{C}_7\text{H}_9^+ \rightarrow \text{C}_7\text{H}_9$</td>
<td>S.R.</td>
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<td>293</td>
<td>$\text{C}_8\text{H}_3^+ \rightarrow \text{C}_8\text{H}_3$</td>
<td>S.R.</td>
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<td>HCN(^+) \rightarrow HCN</td>
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<tr>
<td>306</td>
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<td>N/A</td>
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<td>N/A</td>
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<tr>
<td>312</td>
<td>( \text{N}^+ \rightarrow \text{N(S)} )</td>
<td>S.R.</td>
<td>N/A</td>
</tr>
<tr>
<td>313</td>
<td>( \text{ClC}_3\text{H}_3^+ \rightarrow \text{ClC}_3\text{H}_3 )</td>
<td>S.R.</td>
<td>N/A</td>
</tr>
<tr>
<td>314</td>
<td>( \text{lC}_3\text{H}_3^+ \rightarrow \text{lC}_3\text{H}_3 )</td>
<td>S.R.</td>
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Appendix B

Rotation of Molecules

The theory of molecular rotations is explained in this Appendix. The formulation that follows is based on the general quantum mechanical texts [152, 153] as well as [154]. We begin by introducing the concept of the rotation operator as a means to determining the rotational state and describing properties that constrain the transitions between those states. We then describe the solutions for those states in three-dimensional space (wave functions).

B.1 Translation and Rotation Operators and Angular Momentum

B.1.1 Translation

The development of the rotation operator presented by [153] relies heavily on the translation operator, so let us begin by developing translations and discussing their
Appendix B: Rotation of Molecules

properties. The translation operator obeys the property

\[ T(\vec{a}) |\vec{r}\rangle = |\vec{r} + \vec{a}\rangle. \]  

(B.1)

In one dimension, an infinitesimal translation goes as

\[ T(dx) = 1 - \frac{i}{\hbar} p_x dx, \]  

(B.2)

where \( p_x \) is the generator of translation and also the momentum operator. Applying this infinitesimal translation \( N \) times leads to

\[ T(a) = \lim_{N \to \infty} \left[ 1 - \frac{i}{\hbar} p_x \left( \frac{a}{N} \right) \right]^N. \]  

A Taylor expansion can be used to show that this expression is identical to \( e^{-ip_xa/\hbar} \), so

\[ T(\hat{a}x) = e^{-ip_xa_x/\hbar} = 1 - \frac{ip_xa_x}{\hbar} - \frac{p_x^2a_x^2}{2\hbar^2} + \cdots \]  

(B.3a)

\[ T(\hat{a}y) = e^{-ip_ya_y/\hbar} = 1 - \frac{ip_ya_y}{\hbar} - \frac{p_y^2a_y^2}{2\hbar^2} + \cdots \]  

(B.3b)

\[ T(\hat{a}z) = e^{-ip_za_z/\hbar} = 1 - \frac{ip_za_z}{\hbar} - \frac{p_z^2a_z^2}{2\hbar^2} + \cdots \]  

(B.3c)

Classically, it is easy to show that translations commute with one another, meaning the order of two successive translations does not affect the final position. Using the translation operator with up to second-order terms, one can show that \( p_x p_y - p_y p_x = 0 \), or \( [p_x, p_y] = 0 \), where the brackets represent commutation. As a result,

\[ T(\vec{a}) = e^{-ip_xa_x/\hbar} e^{-ip_ya_y/\hbar} e^{-ip_za_z/\hbar} = e^{-\vec{p} \cdot \vec{a}/\hbar}. \]  

Translations do not, however, commute with the position operator, which is defined as \( \hat{a} |\vec{r}\rangle = a |\vec{r}\rangle \). For example, to first order,

\[ [\hat{x}, \hat{T}(a_x)] = \hat{x} \left[ 1 - \frac{i\hat{p}_xa_x}{\hbar} \right] - \left[ 1 - \frac{i\hat{p}_xa_x}{\hbar} \right] \hat{x} = -\frac{ia_x}{\hbar} (\hat{x}\hat{p}_x - \hat{p}_x\hat{x}) = -\frac{ia_x}{\hbar} [\hat{x}, \hat{p}_x]. \]  

(B.4)
Applying the operator in Eq. B.4 to a state yields

\[
\hat{x}, \hat{T}(a_x \hat{i}) |\psi\rangle = \left( -\frac{ia_x}{\hbar} \right) (\hat{x}\hat{p}_x - \hat{p}_x \hat{x}) |\psi\rangle. \tag{B.5}
\]

The identity operator, \(\int |x\rangle \langle x| dx = 1\), can be inserted in Eq. B.5 to yield

\[
\hat{x}, \hat{T}(a_x \hat{i}) \int |x\rangle \langle x| |\psi\rangle = \left( -\frac{ia_x}{\hbar} \right) (\hat{x}\hat{p}_x - \hat{p}_x \hat{x}) |\psi\rangle =
\]

\[
\hat{x} \int dx |x + a_x\rangle \langle x | \psi\rangle - \hat{T}(a_x \hat{i}) \int dx |x\rangle \langle x | \psi\rangle =
\]

\[
\hat{x} \int dx (x + a_x) |x + a_x\rangle \langle x | \psi\rangle - \hat{T}(a_x \hat{i}) \int dx |x + a_x\rangle \langle x | \psi\rangle =
\]

\[
a_x \int dx |x + a_x\rangle \langle x | \psi\rangle = \delta_x \int dx |x\rangle \langle x | \psi\rangle = \delta_x |\psi\rangle.
\]

The last two equalities follow for small \(a_x\) for which \(a_x \to \delta x\). Substituting this result into Eq. B.5 gives

\[
\hat{x}, \hat{T}(\delta_x \hat{i}) = a_x = \frac{ia_x}{\hbar} [\hat{x}, \hat{p}_x]. \tag{B.7}
\]

Therefore,

\[
[\hat{x}, \hat{p}_x] = i\hbar. \tag{B.8}
\]

If, however, the position and momentum operator axes are different, the operators do commute. For example,

\[
\hat{y}, \hat{T}(a_x \hat{i}) = 0, \tag{B.9}
\]
which implies $[\hat{y}, \hat{p}_x] = 0$. In general,

$$[\hat{x}_i, \hat{p}_j] = i\hbar \delta_{ij}. \quad (B.10)$$

## B.1.2 Form of the Momentum Operator

Next, we can use the translation operator to derive the form of the momentum operator. To do this, we first apply the translation operator to the state, $|\psi\rangle$.

$$\hat{T}(\delta x) |\psi\rangle = \hat{T}(\delta x) \int dx |x\rangle \langle x| \psi\rangle = \int dx |x + \delta x\rangle \langle x| \psi\rangle. \quad (B.11)$$

Substituting $x' = x - \delta x$ yields

$$\hat{T}(\delta x) |\psi\rangle = \int dx' |x'\rangle \langle x' - \delta x| \psi\rangle = \int dx' |x'\rangle \psi(x' - \delta x), \quad (B.12)$$

where $\psi(x' - \delta x) \approx \psi(x') - \delta x \frac{\partial}{\partial x} \psi(x') = \langle x'| \psi\rangle - \delta x \frac{\partial}{\partial x} \langle x'| \psi\rangle$, so Eq. B.12 becomes

$$\hat{T}(\delta x) |\psi\rangle = \int dx' |x'\rangle \left( \langle x'| \psi\rangle - \delta x \frac{\partial}{\partial x} \langle x'| \psi\rangle \right) =$$

$$|\psi\rangle - \delta x \int dx' |x'\rangle \frac{\partial}{\partial x} \langle x'| \psi\rangle = \left( 1 - \frac{i}{\hbar} \hat{p}_x \delta x \right) |\psi\rangle, \quad (B.13)$$

with the last equality following from Eq. B.2. As a result,

$$\hat{p}_x |\psi\rangle = \frac{\hbar}{i} \int dx' |x'\rangle \frac{\partial}{\partial x} \langle x'| \psi\rangle. \quad (B.14)$$

Taking the inner product with the position vector yields
Appendix B: Rotation of Molecules

\[ \langle x | \hat{p}_x | \psi \rangle = \frac{\hbar}{i} \int dx' \langle x | x' \rangle \frac{\partial}{\partial x} \langle x | \psi \rangle = \frac{\hbar}{i} \int dx' \delta (x - x') \frac{\partial}{\partial x} \langle x' | \psi \rangle = \frac{\hbar}{i} \frac{\partial}{\partial x} \langle x | \psi \rangle \cdot \hat{p}_x \rightarrow \frac{\hbar}{i} \frac{\partial}{\partial x} . \]  
(B.15)

By analogy, one can show that

\[ \langle \vec{r} | \hat{p} | \psi \rangle = \frac{\hbar}{i} = \nabla \langle \vec{r} | \psi \rangle \cdot \hat{p} \rightarrow \frac{\hbar}{i} \nabla . \]  
(B.16)

This detailed development of the linear momentum operator is analogous to that for angular momentum.

B.1.3 The Momentum and Hamiltonian Operators

The linear momentum operator is used to establish the Hamiltonian for translations.

For a two-body system,

\[ \hat{H} = \frac{\hat{p}_1^2}{2m_1} + \frac{\hat{p}_2^2}{2m_2} + V (|\vec{r}_1 - \vec{r}_2|) , \]  
(B.17)

where \( \hat{p}_i^2 = \hat{p}_{ix}^2 + \hat{p}_{iy}^2 + \hat{p}_{iz}^2 \). The position basis state is \( |\vec{r}_1, \vec{r}_2\rangle = |r_1\rangle_1 \otimes |r_2\rangle_2 \).

Equation B.17 can be rewritten as

\[ \hat{H} = \frac{\hat{p}^2}{2M} + \frac{\hat{p}^2}{2\mu} + V (|\vec{r}|) , \]  
(B.18)

where

\[ \hat{P} = \hat{p}_1 + \hat{p}_2 \]  
(B.19a)

\[ \hat{p} = \frac{m_2 \hat{p}_1 + m_1 \hat{p}_2}{m_1 + m_2} \]  
(B.19b)
Appendix B: Rotation of Molecules

\[ M = m_1 + m_2 \]  (B.19c)

\[ \mu = \frac{m_1 + m_2}{m_1 m_2}, \]  (B.19d)

and \( V (|\hat{r}|) \) is the potential energy. In center-of-mass coordinates, \( \hat{P} = 0 \), so

\[ \hat{H} = \frac{\hat{p}^2}{2\mu} + V (|\hat{r}|). \]  (B.20)

Consider, for a moment, classical analogies to the component operators in the Hamiltonian Eq. B.20. They depend only on the lengths of the vectors: \( \hat{p}^2 = \hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2 \) and

\[ |\hat{r}| = (\hat{x}^2 + \hat{y}^2 + \hat{z}^2)^{1/2}, \] and therefore do not vary as the two-body system rotates.

This clue about the rotational invariance of the translating two-body Hamiltonian suggests that energy will be conserved in the rotating system. To prove that, we next develop the rotation operator and use it to define the orbital angular momentum of the rigid, two-atom molecule.

**B.1.4 Rotation of a Two-body System**

Consider the rotation of the position state about the \( z \)-axis:

\[ \hat{R} \left( d\phi \hat{k} \right) |x, y, z\rangle = |x - yd\phi, y + xd\phi, z\rangle. \]  (B.21)

We define the operation that achieves this rotation as

\[ \hat{R} \left( d\phi \hat{k} \right) = 1 - \frac{i}{\hbar} \hat{L}_z d\phi. \]  (B.22)

This operation can be written in terms of the momentum operator as
Appendix B: Rotation of Molecules

\[ |x - yd\phi\rangle = \left( 1 - \frac{i}{\hbar} \hat{p}_x (-yd\phi) \right) |x\rangle \]  \hspace{1cm} (B.23a)

\[ |y + xd\phi\rangle = \left( 1 - \frac{i}{\hbar} \hat{p}_y (xd\phi) \right) |y\rangle , \]  \hspace{1cm} (B.23b)

so

\[ |x - yd\phi, y + xd\phi, z\rangle = \left( 1 - \frac{i}{\hbar} \hat{p}_x (-yd\phi) \right) \left( 1 - \frac{i}{\hbar} \hat{p}_y (xd\phi) \right) |x, y, z\rangle . \]  \hspace{1cm} (B.24)

To first order, Eq. B.24 simplifies to

\[ |x - yd\phi, y + xd\phi, z\rangle = \left( 1 - \frac{i}{\hbar} (\hat{x}\hat{p}_y - \hat{y}\hat{p}_x) d\phi \right) |x, y, z\rangle . \]  \hspace{1cm} (B.25)

Comparing Eqs. B.25 with B.22, one can see that the momentum operator is given by

\[ \hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x \]  \hspace{1cm} (B.26a)

\[ \hat{L}_y = \hat{z}\hat{p}_x - \hat{y}\hat{p}_z \]  \hspace{1cm} (B.26b)

\[ \hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y , \]  \hspace{1cm} (B.26c)

where we have also written the analogous relations for \( \hat{L}_y \) and \( \hat{L}_x \). To show that the Hamiltonian is rotationally invariant, we will need to show that \( [\hat{L}, \hat{H}] = [\hat{L}, \frac{\hat{p}^2}{2\mu} - \frac{e^2}{r}] = 0 \). To do that, consider each term beginning with \( \hat{L}_z \) and \( \hat{p}_x \).

\[ [\hat{L}_z, \hat{p}_x] = [\hat{x}\hat{p}_y - \hat{y}\hat{p}_x, \hat{p}_x] = [\hat{x}\hat{p}_y, \hat{p}_x] = [\hat{x}, \hat{p}_x] \hat{p}_y = i\hbar \hat{p}_y , \]  \hspace{1cm} (B.27)
where the second equality follows because \([\hat{p}_x, \hat{p}_y] = 0\), the third equality follows because \([\hat{p}_x, \hat{p}_y] = 0\) [152], and the last equality follows from Eq. B.8. Similarly, \([\hat{L}_z, \hat{p}_y] = -i\hbar \hat{p}_x\). The \(\hat{L}_z\) and \(\hat{p}_z\) terms yield

\[
\left[ \hat{L}_z, \hat{p}_z \right] = \left[ \hat{x}\hat{p}_y - \hat{y}\hat{p}_x, \hat{p}_z \right] = 0
\]  
(B.28)

since \([\hat{p}_y, \hat{p}_z] = 0\) and \([\hat{p}_x, \hat{p}_z] = 0\). With these relations, and some straightforward algebraic manipulations, we find that

\[
\left[ \hat{L}_z, \hat{p}^2 \right] = \left[ \hat{L}_z, \hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2 \right] = 0.
\]  
(B.29)

Likewise,

\[
\left[ \hat{L}_y, \hat{p}^2 \right] = 0.
\]  
(B.30)

\[
\left[ \hat{L}_y, \hat{p}^2 \right] = 0.
\]  
(B.31)

**B.1.5 Angular Momentum Properties**

Position and momentum commute only for \(i = j\):

\[
[\hat{x}_i, \hat{p}_j] = i\hbar \delta_{ij}
\]  
(B.32)

where \(\delta_{ij}\) is the Kronecker delta. Two additional relations that are useful are

\[
[\hat{x}_i, \hat{x}_j] = 0
\]  
(B.33)
\[ [\hat{p}_i, \hat{p}_j] = 0. \]  \hfill (B.34)

In quantum mechanics, physical observables are associated with operators. The operator for a particular observable, \( \hat{A} \), can be obtained by beginning with a symmetrized classical expression based on a function \( A (\vec{r}, \vec{p}, t) \) and replacing that function with an operator \( A (t) = \hat{A} (\vec{r}, \vec{p}, t) \), where the script denotes an operator. Classically, angular momentum is given by

\[
\vec{L} = \vec{r} \times \vec{p} = (yp_z - zp_y) \hat{i} + (zp_x - xp_z) \hat{j} + (xp_y - yp_x) \hat{k}. \tag{B.35}
\]

The symmetry requirement comes from the fact that classically, position and momentum commute, i.e., \([\vec{r}, \vec{p}] = 0\), but the position and momentum operators do not, i.e., \([\hat{r}, \hat{p}] \neq 0\) because \( \hat{r} \cdot \hat{p} = \hat{x} \hat{p}_x + \hat{y} \hat{p}_y + \hat{z} \hat{p}_z \neq \hat{p} \cdot \hat{r} = \hat{p}_x \hat{x} + \hat{p}_y \hat{y} + \hat{p}_z \hat{z} \). In the case of angular momentum, eq. B.32 shows that \([\hat{y}, \hat{p}_z] = 0\) and \([\hat{z}, \hat{p}_y] = 0\), so we can write directly

\[
\hat{L}_x = \hat{y} \hat{p}_z - \hat{z} \hat{p}_y \tag{B.36}
\]

\[
\hat{L}_y = \hat{z} \hat{p}_x - \hat{x} \hat{p}_z \tag{B.37}
\]

\[
\hat{L}_z = \hat{x} \hat{p}_y - \hat{y} \hat{p}_x \tag{B.38}
\]

or generally

\[
\hat{L} = \vec{r} \times \vec{p}. \tag{B.39}
\]
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With eqs. B.36 to B.38, we get the orbital angular momentum commutation relations.

For $\hat{L}_x$ and $\hat{L}_y$,

$$\left[ \hat{L}_x, \hat{L}_y \right] = \left[ \hat{y}\hat{\hat{p}}_z - \hat{z}\hat{\hat{p}}_y, \hat{\hat{p}}_x - \hat{x}\hat{\hat{p}}_z \right] = \left[ \hat{y}\hat{\hat{p}}_z, \hat{\hat{p}}_x \right] + \left[ \hat{z}\hat{\hat{p}}_y, \hat{x}\hat{\hat{p}}_z \right] = \left[ \hat{y}\hat{\hat{p}}_z, \hat{z}\hat{\hat{p}}_x \right] + \left[ \hat{x}\hat{\hat{p}}_y, \hat{\hat{p}}_z \right] = i\hbar \hat{L}_z$$

(B.40)

where the second equality follows because $\left[ \hat{y}\hat{\hat{p}}_z, \hat{z}\hat{\hat{p}}_x \right] = 0$ and $\left[ \hat{z}\hat{\hat{p}}_y, \hat{x}\hat{\hat{p}}_z \right] = 0$. By similar exercises,

$$\left[ \hat{L}_y, \hat{L}_z \right] = i\hbar \hat{L}_x$$

(B.41)

$$\left[ \hat{L}_z, \hat{L}_x \right] = i\hbar \hat{L}_y$$

(B.42)

and $\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$ is the square of the total orbital angular momentum. If we want to include the spin with the orbital angular momentum, the total angular momentum, $\hat{J}$, obeys the following similar relationships:

$$\left[ \hat{J}_x, \hat{J}_y \right] = i\hbar \hat{J}_z$$

(B.43)

$$\left[ \hat{J}_y, \hat{J}_z \right] = i\hbar \hat{J}_x$$

(B.44)

$$\left[ \hat{J}_z, \hat{J}_x \right] = i\hbar \hat{J}_y$$

(B.45)

$$\hat{J}^2 = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2.$$  

(B.46)

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Henceforth, I will call the total angular momentum operator simply the angular momentum operator.

B.1.6 Properties of the Angular Momentum Operator

We can show that the square modulus of the angular momentum commutes with the angular momentum. It is true that \( \hat{J} = \hat{J}_x + \hat{J}_y + \hat{J}_z \). Also,

\[
\begin{align*}
\left[ \hat{J}^2, \hat{J}_x \right] &= \left[ \hat{J}^2, \hat{J}_y \right] + \left[ \hat{J}^2, \hat{J}_z \right] = \\
(\hat{J}_y \hat{J}_y \hat{J}_x - \hat{J}_x \hat{J}_y \hat{J}_y) + (\hat{J}_z \hat{J}_z \hat{J}_x - \hat{J}_x \hat{J}_z \hat{J}_z) &= \\
(\hat{J}_y \hat{J}_y \hat{J}_x - \hat{J}_x \hat{J}_y \hat{J}_y) + (\hat{J}_y \hat{J}_y \hat{J}_x - \hat{J}_x \hat{J}_y \hat{J}_y) + \\
(\hat{J}_z \hat{J}_z \hat{J}_x - \hat{J}_x \hat{J}_z \hat{J}_z) &= (\hat{J}_z \hat{J}_z \hat{J}_x - \hat{J}_x \hat{J}_z \hat{J}_z) = \\
\hat{J}_y \left[ \hat{J}_y, \hat{J}_x \right] + \left[ \hat{J}_y, \hat{J}_x \right] \hat{J}_x + \hat{J}_z \left[ \hat{J}_z, \hat{J}_x \right] + \left[ \hat{J}_z, \hat{J}_x \right] \hat{J}_z = \\
-\hbar \hat{J}_y \hat{J}_x - \hbar \hat{J}_z \hat{J}_y + \hbar \hat{J}_z \hat{J}_x + \hbar \hat{J}_y \hat{J}_z = 0.
\end{align*}
\]

(B.47)

In the the same way,

\[
\left[ \hat{J}^2, \hat{J}_y \right] = 0
\]

(B.48)

\[
\left[ \hat{J}^2, \hat{J}_z \right] = 0.
\]

(B.49)

Since \( \left[ \hat{J}^2, \hat{J} \right] = \left[ \hat{J}^2, \hat{J}_x \right] + \left[ \hat{J}^2, \hat{J}_y \right] + \left[ \hat{J}^2, \hat{J}_z \right] \), combining eqs. B.47-B.49 gives:

\[
\left[ \hat{J}^2, \hat{J} \right] = 0.
\]

(B.50)
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Next, I will define the raising and lowering operators, which are combinations of the \( \hat{J} \) components that are useful for solving the the rigid rotor eigenvalue problem. The operators are

\[
\hat{J}_+ = \hat{J}_x + i\hat{J}_y \quad \text{(B.51)}
\]

\[
\hat{J}_- = \hat{J}_x - i\hat{J}_y. \quad \text{(B.52)}
\]

Additionally, there are a series of commutation relations involving these operators that are useful in the manipulations that follow.

\[
\left[ \hat{J}_z, \hat{J}_+ \right] = \hbar \hat{J}_+ \quad \text{(B.53)}
\]

\[
\left[ \hat{J}_z, \hat{J}_- \right] = -\hbar \hat{J}_- \quad \text{(B.54)}
\]

\[
\left[ \hat{J}_+, \hat{J}_- \right] = 2\hbar \hat{J}_z \quad \text{(B.55)}
\]

\[
\left[ \hat{J}^2, \hat{J}_+ \right] = \left[ \hat{J}^2, \hat{J}_- \right] = 0 \quad \text{(B.56)}
\]

\[
\hat{J}_+ \hat{J}_- = \hat{J}_x^2 + \hat{J}_y^2 + \hbar \hat{J}_z = \hat{J}^2 - \hat{J}_z^2 + \hbar \hat{J}_z \quad \text{(B.57)}
\]

\[
\hat{J}_- \hat{J}_+ = \hat{J}_x^2 + \hat{J}_y^2 - \hbar \hat{J}_z = \hat{J}^2 - \hat{J}_z^2 - \hbar \hat{J}_z \quad \text{(B.58)}
\]
The component $\hat{J}_i$ commutes with itself, which makes $\hat{J}_i^2$ Hermitian. $\hat{J}^2$ is the sum of Hermitian operators and is therefore Hermitian itself, which means that $\langle \psi | \hat{J}^2 | \psi \rangle$.

Therefore, in the equation,

\[
\langle \psi | \hat{J}^2 | \psi \rangle = \langle \psi | \hat{J}_x^2 | \psi \rangle + \langle \psi | \hat{J}_y^2 | \psi \rangle + \langle \psi | \hat{J}_z^2 | \psi \rangle = \lambda h^2 \langle \psi | \psi \rangle
\]

so that the eigenvalues of $\hat{J}^2$ must be non-negative. It simplifies the manipulations that follow to write the eigenvalues of $\hat{J}^2$ as $\lambda = j (j + 1) h^2$ with $j \geq 0$. The $h^2$ factor gives the eigenvalue the correct units. The quantum number $j$ is unique because $j^2 + j - \lambda = 0$ only has one positive root, the quantum number is unique. Since $\hat{J}$ commutes with one component of $\hat{J}$ but not all of them, we choose one arbitrary axis, $\hat{J}_z$ to ascribe simultaneous eigenstates. The eigenvalue of $\hat{J}_z$ is $m h$. The simultaneous eigenstates of $\hat{J}^2$ and $\hat{J}_z$ are labeled according to their quantum numbers and a third index, $k$, that differentiates between degeneracies, i.e., $j (j + 1) h^2 = m h$. The simultaneous eigenvalue problems for angular momentum are then
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\[ \hat{J}^2 |k, j, m\rangle = j (j + 1) \hbar^2 |k, j, m\rangle \quad \text{(B.62)} \]

\[ \hat{J}_z |k, j, m\rangle = m \hbar |k, j, m\rangle . \quad \text{(B.63)} \]

To obtain the spectrum of \( \hat{J} \) and \( \hat{J}_z \), consider the following three lemmas.

**B.1.7 Lemma 1**

Consider the vectors \( J_+ |k, j, m\rangle \) and \( J_- |k, j, m\rangle \). Because \( J_+ = J_+^\dagger \),

\[ |J_+ |k, j, m\rangle|^2 = \langle k, j, m | J_- J_+ |k, j, m\rangle \geq 0 \quad \text{(B.64)} \]

and

\[ |J_- |k, j, m\rangle|^2 = \langle k, j, k | J_+ J_- |k, j, m\rangle \geq 0. \quad \text{(B.65)} \]

Using B.58, one obtains

\[ |J_+ |k, j, m\rangle|^2 = \langle k, j, k | \hat{J}^2 - J_z^2 - \hbar J_z |k, j, m\rangle = \left[ j (j + 1) \hbar^2 - m^2 \hbar^2 - m \hbar^2 \right] \langle k, j, m |k, j, m\rangle \geq 0 \quad \text{(B.66)} \]

and

\[ |J_- |k, j, m\rangle|^2 = j (j + 1) \hbar^2 - m^2 \hbar^2 + m \hbar^2 \geq 0. \quad \text{(B.67)} \]

These equations yield a system.
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\[ j (j + 1) - m (m + 1) = (j - m) (j + m + 1) \geq 0. \]  \hfill (B.68)

\[ j (j + 1) - m (m - 1) = (j - m + 1) (j + m) \geq 0, \]  \hfill (B.69)

respectively, so

\[ - (j + 1) \leq m \leq j \]  \hfill (B.70)

\[ - j \leq m \leq j + 1. \]  \hfill (B.71)

**B.1.8 Lemma 2**

Consider the cases of Eq. B.70. If \( m = j \), then

\[ J_+ |k, j, j\rangle = 0 \]  \hfill (B.72)

and if \( m < j \), then \( J_+ |k, j, m\rangle \) is a simultaneous eigenfunction of \( |\hat{J}|^2 \) and \( J_z \) with eigenvalues \( j (j + 1) \hbar^2 \). To prove Eq. B.79, begin with Eq. B.68. Substituting for \( m \) gives \( j (j + 1) - j (j + 1) = 0 \). To prove that \( |\hat{J}|^2 \) and \( J_z \) are simultaneous eigenvalues for \( m < j \), apply Eq. B.56 to yield

\[ |\hat{J}|^2 J_+ |k, j, m\rangle = J_+ |\hat{J}|^2 |k, j, m\rangle = j (j + 1) \hbar^2 J_+ |k, j, m\rangle. \]  \hfill (B.73)

The two outer equalities show that \( J_+ |k, j, m\rangle \) is an eigenvalue of \( |\hat{J}|^2 \). Furthermore, Eq. B.53 is used to show that
\begin{equation}
J_z J_+ |k, j, m\rangle = J_+ J_z |k, j, m\rangle + h J_+ |k, j, m\rangle = \tag{B.74}
m h J_+ |k, j, m\rangle + h J_+ |k, j, m\rangle = (m + 1) h J_+ |k, j, m\rangle.
\end{equation}

Comparing the outer equalities, noticed that \( J_+ |k, j, m\rangle \) is also an eigenvalue of \( J_z \) with eigenvalue \((m + 1) h\).

\section*{B.1.9 Lemma 3}

Let us next consider the cases of Eq. B.71. If \( m = -j \), then

\begin{equation}
J_+ |k, j, m\rangle = J_- |k, j, -j\rangle = 0 \tag{B.75}
\end{equation}

since the projection \( J_z \) cannot go beyond \( \hat{J}_z \). Equation B.75 can be proven as follows. From Lemma 1, it is known that \(|J_- |k, j, m\rangle|^2 = \hbar^2 [j (j + 1) - m (m - 1)]\), which is zero if \( m = -j \). Therefore, \( J_- |k, j, -j\rangle = 0 \). Applying \( J_+ \) to Eq. B.75 along with Eq. B.69 yields

\begin{equation}
J_+ J_- |k, j, -j\rangle = \hbar^2 (j - j) (j + j + 1) |k, j, m\rangle = 0. \tag{B.76}
\end{equation}

If \( m > -j \), then \( J_- |k, j, m\rangle \) is a simultaneous eigenvector of \( \hat{J}_z^2 \) and \( \hat{J}_z \) with eigenvalues \( j (j + 1) \hbar^2 \) and \( (m - 1) \hbar \). This can be proven using the fact that, from Eq. B.69, \(|J_- |k, j, m\rangle|^2 > 0 \). By Eq. B.56, we know that

\begin{equation}
\hat{J}_z^2 J_- |k, j, m\rangle = J_- \hat{J}_z^2 |k, j, m\rangle = j (j + 1) \hbar^2 J_- |k, j, m\rangle. \tag{B.77}
\end{equation}

Comparing the left- and right-most equalities, \( J_- |k, j, m\rangle \) is an eigenvector of \( \hat{J}_z^2 \) with an eigenvalue \( j (j + 1) \hbar^2 \). Similarly, by Eq. B.54,
Comparing the outermost equalities, \( J_\perp |k, j, m\rangle \) is an even vector of \( J_z \) with eigenvalue \((m - 1) \hbar\).

Next, we use the results of B.1.7 through B.1.9 to obtain the possible values of \( j \) and \( m \), i.e., the spectrum. From Section B.1.7, \(-j \leq m \leq j\). Therefore, there must be a non-negative integer, \( p \), such that

\[
-j \leq m - p < -j + 1.
\]  \hspace{1cm} (B.79)

If we apply \( J_\perp \) recursively \( p \) times, we obtain the sequence

\[
|k, j, m\rangle, J_\perp |k, j, m\rangle, \ldots, J_\perp^p |k, j, m\rangle.
\]  \hspace{1cm} (B.80)

Each of the \( J_\perp^n |k, j, m\rangle \) vectors, where \( n = 0, 1 \ldots, p \), must be non-null, simultaneous eigenvectors of \( \hat{J}^2 \) and \( \hat{J}_z \) by Lemma 3 with eigenvalues \( j(j + 1) \hbar^2 \) and \((m - n) \hbar\). This means that the eigenvalue of \( J_\perp^p |k, j, m\rangle \) is \((m - p) \hbar\). Assume, for a moment, that \( m - p > -j \). Per Eq. B.79., this is possible. From Lemma 3, that means that \( j(j + 1) \hbar^2 \) and \((m - p - 1) \hbar\) are eigenvalues of \( J_\perp J_\perp^p |k, j, m\rangle \); however, this would contradict Lemma 1 because, as already specified, \( m - p - 1 < -j \) by Eq. B.79. The only way to simultaneously satisfy Eq. B.79 and perform the operation \( J_\perp J_\perp^p \) is if

\[
m - p = -j,
\]  \hspace{1cm} (B.81)
so that $J^p_+ |k, j, m\rangle = -j \hbar |k, j, m\rangle$, which makes the eigenvector of $J_- J^p_+ |k, j, m\rangle$ zero. Similarly, using Lemma 2, one can show that there exists an integer, $q$, such that

$$m + q = j. \quad (B.82)$$

that limits the sequence of vectors

$$|k, j, m\rangle, J_+ |k, j, m\rangle, \ldots, J^q_+ |k, j, m\rangle \quad (B.83)$$

so that Lemma 1 is not violated. Together, Eqs. B.82 and B.83 imply that

$$p + q = 2j \quad (B.84)$$

where, again, $p$ and $q$ are integers. That means that $j$ may take on half-integer values, \textit{i.e.},

$$j = 0, 1/2, 1, \ldots, j' \quad (B.85)$$

and there are $2j + 1$ values of $m$

$$m = -j, -j + 1, \ldots, j - 1, j \quad (B.86)$$

with $m$ integral if $j$ is integral and $m$ half-integral if $j$ is half-integral.
Appendix B: Rotation of Molecules

B.2 Spatial Solutions to the Angular Momentum Eigenvalue Problem

Section B.1 considered the properties of the rotation operator and the constraints on the transitions between energy levels that fall out of it. Next, let us consider how the rotation operator determines the spatial distribution of the wavefunctions for a rigid rotor. Writing the momentum explicitly, Eqs. B.36 – B.38 are

\[
L_x = \frac{\hbar}{i} \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \tag{B.87a}
\]

\[
L_y = \frac{\hbar}{i} \left( z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \tag{B.87b}
\]

\[
L_z = \frac{\hbar}{i} \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \tag{B.87c}
\]

where one can write \( x = r \sin \theta \cos \phi \), \( y = r \sin \theta \sin \phi \), and \( z = r \cos \theta \). Changing variables in Eq. B.87 yields

\[
L_x = i \hbar \left( \sin \phi \frac{\partial}{\partial \theta} + \frac{\cos \phi}{\tan \theta} \frac{\partial}{\partial \phi} \right) \tag{B.88a}
\]

\[
L_y = i \hbar \left( -\cos \phi \frac{\partial}{\partial \theta} + \frac{\sin \phi}{\tan \theta} \frac{\partial}{\partial \phi} \right) \tag{B.88b}
\]

\[
L_z = \frac{\hbar}{i} \frac{\partial}{\partial \phi}. \tag{B.88c}
\]

Combining these equations, one can show that

\[
\hat{L}^2 = -\hbar^2 \left( \frac{\partial^2}{\partial \theta^2} + \frac{1}{\tan \theta} \frac{\partial}{\partial \theta} + \frac{1}{\sin \theta^2} \frac{\partial^2}{\partial \phi^2} \right) \tag{B.89}
\]
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\[ L_+ = \hbar e^{i\phi} \left( \frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \phi} \right) \]  
(B.90)

\[ L_- = \hbar e^{i\phi} \left( -\frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \phi} \right) . \]  
(B.91)

The eigenvalue problems for \( \hat{L}^2 \) and \( L_z \) can be written using these operators. Notice there is no \( r \)-dependence in either case, so one can solve only for the part of the wavefunction that depends on \( \theta \) and \( \phi \), which is denoted \( Y_{l}^{m}(\theta, \phi) \):

\[ \hat{L}^2 Y_{l}^{m}(\theta, \phi) = l (l + 1) \hbar^2 Y_{l}^{m}(\theta, \phi) \]  
(B.92)

\[ L_z Y_{l}^{m}(\theta, \phi) = m \hbar Y_{l}^{m}(\theta, \phi) . \]  
(B.93)

Substituting Eq. B.88, Eq. B.93 becomes

\[ \frac{\hbar}{i} \frac{\partial}{\partial \phi} Y_{l}^{m}(\theta, \phi) = m \hbar Y_{l}^{m}(\theta, \phi) = m \hbar F_{l}^{m}(\theta) e^{im\phi} \]  
(B.94)

where the last equality can be seen immediately since the derivative is only with respect to \( \phi \). The state must be continuous, even for \( \phi = 0 \) and \( 2\pi \), which implies that

\[ Y_{l}^{m}(\theta, \phi = 0) = Y_{l}^{m}(\theta, \phi = 2\pi) . \]  
(B.95)

Condition B.95 means that \( e^0 = 1 = e^{2m\pi} \). Therefore, \( m \) must be an integer, which further constrains Eqs. B.85 and B.86. Orbital angular momentum has integer quantum numbers.
Appendix B: Rotation of Molecules

For an integer $l \geq 0$,

$$L_+ Y_{l}^m (\theta, \phi) = \hbar \phi \left( \frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \phi} \right) F_{l}^{m} (\theta) e^{i\phi} = 0$$

(B.96)

or, after some simplification,

$$e^{i(l+1)\phi} \left( \frac{\partial}{\partial \theta} - l \cot \theta \right) F_{l}^{m} (\theta) = 0,$$

which means that

$$\frac{d}{d\theta} - l \cot \theta \right) F_{l}^{m} (\theta) = 0.$$  

(B.98)

Equation B.98 can be solved by the method of integrating factor:

$$F_{l}^{m} (\theta) = c_l \sin \theta^l,$$

(B.99)

so that

$$Y_{l}^m (\theta, \phi) = c_l \sin \theta^l e^{i\phi}.$$

(B.100)

The solutions $Y_{l}^{l-1}, \ldots, Y_{l}^{m}, \ldots, Y_{l}^{-l}$ are had by recursively applying $L_-$. From Eq. 6.C-50 in [152], which states

$$L_{\pm} Y_{l}^{m} (\theta, \phi) = \hbar \sqrt{l(l + 1) - m(m \pm 1)} F_{l}^{m \pm 1} (\theta, \phi),$$

(B.101)

and the definitions B.90 and B.91, we arrive at the recurrence relations

$$e^{i\phi} \left( \frac{\partial}{\partial \theta} - m \cot \theta \right) F_{l}^{m} (\theta) = \sqrt{l(l + 1) - m(m + 1)} F_{l}^{m+1} (\theta)$$

(B.102)
\[ e^{i\phi} \left( -\frac{\partial}{\partial \theta} - m \cot \theta \right) F_l^m(\theta) = \sqrt{l(l+1) - m(m-1)} F_l^{m-1}(\theta). \] 

(B.103)

### B.2.1 Proof of Eq. B.101

Equation B.101 can be proved in the following way:

\[ L^m_l(\theta, \phi) = h\sqrt{l(l+1) - m(m+1)}Y_l^{m+1}(\theta, \phi) = \]

\[ h\sqrt{(l \pm m)(l \pm m + 1)}Y_l^{m+1}(\theta, \phi). \]

(B.104)

Consider two eigenvectors that depend on \( l \) and \( m \), \textit{i.e.}, \( l(l+1) \hbar \) and \( m\hbar \), and another quantum number, \( k \). Applying the operators to raise then lower or lower then raise yields

\[ \langle k_2, l, m| L_- L_\pm |k_1, l, m\rangle = \langle k_2, l, m| \hat{L}^2 L_z^2 \mp \hbar L_z |k_1, l, m\rangle = \]

\[ [l(l+1) - m(m \pm 1)] \hbar^2 \langle k_2, l, m|k_1, l, m\rangle. \]

The product is zero if \( k_2 \neq k_1 \), or, if \( k_1 = k_2 \), then

\[ \langle k, l, m| L_- L_\pm |k, l, m\rangle = |L_\pm |k, l, m\rangle|^2 = [l(l+1) - m(m \pm 1)] \hbar^2. \]

(B.105)

One can show that \( L_\pm |k, l, m\rangle \propto |k, l, m+1\rangle \), so it must be that \( L_\pm |k, l, m\rangle = \sqrt{[l(l+1) - m(m \pm 1)] \hbar^2} |k, l, m \pm 1\rangle. \)
B.2.2 Orthonormality

After solving Eqs. B.92 and B.93, one can form the state: \( \psi_{lm}(r, \theta, \phi) = f(r) Y_l^m(\theta, \phi) \). \( \psi_{lm}(r, \theta, \phi) \) needs to be normalized, a condition that can be imposed by separately normalizing \( f \) and \( Y_l^m \), i.e.,

\[
\int_0^{2\pi} d\phi \int_0^\pi \sin \theta r^2 |f(r)|^2 d\theta = 1. \tag{B.108}
\]

Normalizing Eq. B.107 yields the coefficients \( c_l \), which, for the moment, we write also using the index \( m \): \( c_{l,m} \). We may write any function as an infinite series using \( Y_l^m(\theta, \phi) \) as a basis set:

\[
f(\theta, \phi) = \sum_{l=-\infty}^{\infty} \sum_{m=-l}^{l} c_{l,m} Y_l^m(\theta, \phi) \tag{B.109}
\]

where

\[
c_{l,m} = \int_0^{2\pi} d\phi \int_0^\pi \sin \theta r^2 |f(r)|^2 d\theta Y_l^m(\theta, \phi) f(\theta, \phi) \tag{B.110}
\]

Given that \( Y_l^i(\pi - \theta, \pi + \phi) = c_{l,i} (\sin \theta)^i e^{i\phi} \), \( c_{l,i} \) can be obtained from the normalization condition.

\[
\int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta \left| Y_l^i(\theta, \phi) \right|^2 = |c_{l,i}|^2 \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta (\sin \theta)^{2l} = 1 \tag{B.111}
\]

A change of variable and integration by parts gives
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\[ |c_{l,l}| = \sqrt{\frac{1}{2\pi} \frac{2l+1}{(2l+1)!} (l!)^2} = \frac{1}{2l!} \sqrt{\frac{(2l+1)!}{4\pi}} \]  

(B.112)

The phase of \(c_{l,l}\) is arbitrary. For \(Y_l^0(\theta, \phi)\) to be real and positive for \(\theta = 0\), then choose

\[ c_{l,l} = \frac{(-1)^l}{2^l!} \frac{(2l+1)!}{4\pi} \]  

(B.113)

To obtain \(Y_l^m(\theta, \phi)\), apply \(L_-\) repeatedly \(l - m\) times,

\[ (L_-)^{l-m} Y_l^l(\theta, \phi) = h^{l-m} \sqrt{(l+l)(l-l+1) \cdots (l-m)(l+m+1)} Y_l^m(\theta, \phi). \]  

(B.114)

Rearranging gives

\[ Y_l^m(\theta, \phi) = \sqrt{\frac{(l+m)!}{2l!(l-m)!}} \left( \frac{L_-}{h} \right)^{l-m} c_{l,l}(\sin \theta)^l e^{il\phi}, \]  

(B.115)

where the relation for \(Y_l^l = c_{l,l}(\sin \theta)^l e^{il\phi}\) has been inserted. The operation

\[ (L_-)^{l-m} \left[ e^{il\phi} (\sin \theta)^l \right] = (h)^{l-m} e^{il\phi} (\sin \theta)^{-m} \frac{d^{l-m}}{d(\cos \theta)^{-l-m}} \left[ (\sin \theta)^l (\sin \theta)^l \right]. \]  

(B.116)

Combining Eqs. B.115 and B.116 yields

\[ Y_l^m(\theta, \phi) = \frac{(-1)^l}{2^l!} \frac{2l+1}{4\pi (l-m)!} e^{il\phi} (\sin \phi)^{-m} \frac{d^{l-m}}{d(\cos \theta)^{-l-m}} (\sin \theta)^{2l}. \]  

(B.117)

Having obtained a form of \(Y_l^m(\theta, \phi)\), let us next prove a recursive property needed for the complete solution. Recall from Eq. B.94 that the \(\theta\) and \(\phi\) part of \(Y_l^m(\theta, \phi)\) can be separated as in


\[ L_\pm \left( e^{im\phi} F (\theta) \right) = \hbar e^{\pm i\phi} \left[ \pm \frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \phi} \right] \left( e^{im\phi} F (\theta) \right) = \]
\[ \mp \hbar e^{i(m \pm 1)} (\sin \theta)^{1 \pm m} \frac{d}{d \cos \theta} \left[ (\sin \theta)^{\mp m} F (\theta) \right] \]  

(B.118)

or, if the operator is applied \( p \) times,

\[ (L_\pm)^p \left( e^{im\phi} F (\theta) \right) = (\mp \hbar)^p e^{i(m \pm p)} (\sin \theta)^{p \pm m} \frac{d^p}{d (\cos \theta)^p} \left[ (\sin \theta)^{\mp m} F (\theta) \right] . \]  

(B.119)

To prove relation B.120, assume it is true for \( p - 1 \):

\[ (L_\pm)^{p-1} \left[ e^{im\phi} F (\theta) \right] = (\mp \hbar)^{p-1} e^{i(m \pm 1)} (\sin \theta)^{p-1 \pm m} \frac{d^{p-1}}{d (\cos \theta)^{p-1}} \left[ (\sin \theta)^{\mp m} F (\theta) \right] . \]  

(B.120)

Next, apply \( L_\pm \) to both sides. The easiest way to do this is to recall that, in Eq. B.118, \( m \) is any integer and \( F (\theta) \) is any function of \( \theta \). Therefore, we can substitute \( m \rightarrow m \pm p \mp 1 \) and \( F (\theta) \rightarrow \hbar^{p-1} (\sin \theta)^{p-1 \pm m} \frac{d^{p-1}}{d (\cos \theta)^{p-1}} \left[ (\sin \theta)^{\mp m} F (\theta) \right] \). After a few lines of manipulation, one arrives at Eq. B.120, which proves the relationship.

**B.2.3 Properties of Spherical Harmonics**

To achieve a reflection through the origin, the following substitutions are made,

\[ r \rightarrow r \quad \text{(B.121a)} \]

\[ \theta \rightarrow \pi - \theta \quad \text{(B.121b)} \]

\[ \phi \rightarrow \pi + \phi , \quad \text{(B.121c)} \]
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which imply that

\[
\sin \theta \rightarrow \sin (\pi - \theta) = \sin \theta \\
\cos \theta \rightarrow \cos (\pi - \theta) = -\cos \theta \\
e^{im\phi} \rightarrow e^{i(m+\pi)\phi} = (-1)^m e^{im\phi},
\]

\[
\frac{\partial}{\partial \theta} \rightarrow -\frac{\partial}{\partial \theta} \\
\frac{\partial}{\partial \phi} \rightarrow \frac{\partial}{\partial \phi}
\]

These substitutions mean that

\[
Y_{l}^{l} (\theta, \phi) \rightarrow Y_{l}^{l} (\pi - \theta, \pi + \phi) = (-1)^l Y_{l}^{l} (\theta, \phi)
\]

\[
L_\pm \rightarrow \hbar (-1)^l e^{\pm i\phi} \left( \mp \frac{\partial}{\partial \theta} - i \cot \theta \frac{\partial}{\partial \phi} \right) = L_\pm.
\]

Equation B.124 means that \(L_+\) and \(L_-\) are even operators, or that their action on \(-\hat{r}\) is the same as that on \(\hat{r}\). When \(\hat{L}_-\) is applied to \(Y_{l}^{l} (\theta, \phi)\), it yields

\[
Y_{l}^{m} (\pi - \theta, \pi + \phi) = (-1)^l Y_{l}^{m} (\theta, \phi).
\]

If \(l\) is even, the spherical harmonic is even. If \(l\) is odd, the spherical harmonic is odd.

B.2.4 Classical Interpretation

Consider the classical picture illustrated in Fig. B.1. Let \(|\hat{O}L| = \hbar \sqrt{l(l+1)}\) and \(|\hat{O}H| = m\hbar\), so \(|\hat{O}J| = \sqrt{|\hat{O}J|^2 - |\hat{O}H|^2} = \hbar \sqrt{l(l+1) - m^2}\).
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Figure B.1: Classical picture for a rotating dipole.

\[ |\vec{O}I| = \hbar \sqrt{l(l + 1)} - m^2 \cos \phi \]  \hspace{1cm} (B.126a)

\[ |\vec{O}K| = \hbar \sqrt{l(l + 1)} - m^2 \sin \phi \]  \hspace{1cm} (B.126b)

\[ |\vec{O}H| = \hbar \sqrt{l(l + 1)} \cos \theta = mh. \]  \hspace{1cm} (B.126c)

Integrating $|\vec{O}I|$ and $|\vec{O}K|$ over $\phi$ from 0 to $2\pi$, one finds

\[ \int_{0}^{2\pi} |\vec{O}I| \sin \phi \, d\phi \bigg|_{0}^{2\pi} = 0 \]  \hspace{1cm} (B.127)

\[ \int_{0}^{2\pi} |\vec{O}K| \cos \phi \, d\phi \bigg|_{0}^{2\pi} = 0. \]  \hspace{1cm} (B.128)

Moreover,

\[ \langle |\vec{O}I|^2 \rangle = \frac{1}{2\pi} \int_{0}^{2\pi} |\vec{O}I|^2 \, d\phi = \frac{1}{2\pi} \hbar^2 \left[ l(l + 1) - m^2 \right] \int_{0}^{2\pi} \cos^2 \phi \, d\phi = \frac{\hbar^2}{2} \left[ l(l + 1) - m^2 \right]. \]  \hspace{1cm} (B.129)
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The result to the right of the last equality is the same as what one would find quantum-mechanically for \( \langle L_x \rangle \). Similarly, \( \left| \langle \vec{O} \vec{K} \rangle \right|^2 = \frac{\hbar^2}{2} \left[ l (l + 1) - m^2 \right] \), which is the same as what one would obtain quantum-mechanically for \( \langle L_y \rangle \). From these projections, one can see that there is correspondence between the classical and quantum-mechanical pictures.

B.2.5 Diatomic Linear Molecule

The wave function of a stationary rotational state only depends on the angles \( \theta \) and \( \phi \). Consider the center-of-mass frame, where the distance of atoms 1 and 2 from the origin are \( r_1 \) and \( r_2 \), respectively. Defining \( r_e = r_1 + r_2 \),

\[
I = \frac{m_1 m_2}{m_1 + m_2} r_e^2, \tag{B.130}
\]

where \( I \) is the moment of inertia of the molecule. The angular momentum is, classically,

\[
|\vec{L}| = m_1 r_1 \omega_R + m_2 r_2 \omega_R = I \omega_R = \mu r_e^2 \omega_R, \tag{B.131}
\]

and the kinetic energy of rotation is

\[
|\vec{H}| = \frac{1}{2} I \omega_R^2 = \frac{|\vec{L}|^2}{2I}. \tag{B.132}
\]

Ignoring vibrations so that \( r_e \) is fixed, the quantum state of our rotor is \( \psi (\theta, \phi) \), no depending on \( r \). It is subject to the normalization

\[
\int_0^{2\pi} \int_0^{\pi} \sin \theta d\theta |\psi (\theta, \phi)|^2 = 1. \tag{B.133}
\]
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$|\psi (\theta, \phi)|^2$ is the probability of finding the axis of rotation pointing into the solid angle $d\Omega$. From the classical equation B.132, one can conjecture that

$$\hat{H} = \frac{\hat{L}^2}{2\mu r_e^2}, \quad (B.134)$$

and from [152] 6.D.6a, it is known that

$$\hat{H} |\psi\rangle = -\frac{\hbar^2}{2\mu r_e^2} \left[ \frac{\partial^2}{\partial \theta^2} + \frac{1}{\tan \theta} \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] |\psi (\theta, \phi)\rangle. \quad (B.135)$$

From Eq. [154],

$$\hat{H} |l, m\rangle = \frac{l(l+1)\hbar^2}{2\mu r_e^2} |l, m\rangle = Bhl (l+1) |l, m\rangle, \quad (B.136)$$

where $B = \hbar/(4\pi I)$. The eigenvalues of $\hat{H}$ are therefore $Bhl (l+1)$. Since the Hamiltonian is the energy operator, the difference between eigenvalues of adjacent rotational quantum numbers gives the energy of the diatomic rotational transitions, i.e.,

$$\tilde{\omega} = E_l - E_{l-1} = 2Bhl. \quad (B.137)$$
Bibliography


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Bibliography


