The Use of Chirped Pulse Millimeter-Wave Spectroscopy in Chemical Dynamics and Kinetics

by

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ABSTRACT

Chirped-pulse millimeter wave (CPmmW) spectroscopy is a revolutionary technique that has taken advantage of advances in electronics to give high signal to noise broadband rotational spectra in a very short period of time that provides meaningful line intensities. We have implemented this technique in the 58 – 102 GHz range to study the rotational spectra of molecules with two heavy atoms.

Photolysis (at 193 nm) and pyrolysis of vinyl cyanide have produced differing HCN and HNC vibrational population distributions. The photolysis experiment does not sample a collisional regime and the resulting spectra show excited states of HCN and HNC, whereas the pyrolysis experiment, which does sample a collisional regime, results in spectra that are devoid of vibrational satellites. This indicates that the intensities of vibrational satellite transitions sample the photolysis reaction only and not post-photolysis collisional effects. Mono-deuterated vinyl cyanide was photolyzed at 193 nm, in which all HCN/HNC are produced via a four-center mechanism and all DCN/DNC are produced via a three-center mechanism. The HCN and HNC products dominate, demonstrating the greater importance of the three-center mechanism.

CPmmW spectroscopy is also a valuable tool in studying unimolecular and bimolecular reactions. We have studied the unimolecular decomposition of deuterated methyl nitrite which produces DNO products and bimolecular hydrogen abstraction reaction of NO with acetaldehyde resulting in HNO products. These reactions demonstrate the potential use of nitric oxide radical as a gas-phase catalyst to perform cracking of hydrocarbons and sugars.

Thesis Supervisor: Robert W. Field
Title: Haslam and Dewey Professor of Chemistry
Dedication

This thesis is for the pleasure of my spiritual master, His Holiness Radhanath Swami Maharaja, without Whose mercy and guidance I would be lost.
Acknowledgements

I would like to acknowledge many people for their support, guidance and advice over the past few years, making this thesis a reality. First of all, I’d like to thank my advisor Bob Field for his encouragement, kind support and patience as I battled not only with research issues, but with life issues as well. I feel honored to have worked under such a talented and intelligent, yet sincere and humble, advisor.

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Apart from the people associated with MIT, there were many other people in my life who were instrumental in supporting me during my time here:

My mother was physically far away but without her support I don’t think I would have survived the past few years; she was always there for me whether it was to laugh or to cry. I love and appreciate her more than she can know.

I am also very grateful to my temple president, Maha Visnu das, for his support in me pursuing studies at MIT (and of the erratic schedule I had as a result) while at the same time providing me the utmost privilege of performing devotional service for Sri Sri Radha Gopivallabha while living at the ISKCON temple in Boston. I’d also like to thank my spiritual mothers Saranagati devi dasi and Gopa-lila devi dasi, who were always there to give me kind words and advice (and medicine) when I needed them most. And to the entire ISKCON Boston devotee community; if it weren’t for their love and transcendental spirit I’m not sure I would have endured my time here.

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Chapter 1: Introduction to the chirped-pulse millimeter wave technique

1.1 History of rotational spectroscopy techniques

Molecular rotations do not require much energy to excite them and therefore most molecular rotational transitions occur in the microwave and infrared regions of the electromagnetic spectrum [1]. A pure rotation spectrum only occurs for molecules that possess a permanent electric dipole moment. Generally, rotations are about the center of mass of the molecule in order to conserve angular momentum along the rotation axis [1]. Historically, microwave and infrared technologies were created in the 1940s, spurred by World War II efforts to develop microwave oscillators and understand radio frequency (RF) technology [2]. This in turn allowed for the development and evolution of microwave and infrared spectroscopy to study molecular rotations.

The molecular beam, Fabry-Perot, Fourier transform microwave (FTMW) spectrometer by Balle and Flygare in 1979 (Fig. 1.1a) revolutionized microwave spectroscopy and along with modifications to improve resolution and sensitivity, still dominates the field today [3-5]. It performs microwave spectroscopy in the time-domain, providing sensitive detection of the rotational free-induction decay (FID) that follows the microwave pulse (Fig. 1.1b). The use of time-domain spectroscopy increased the frequency resolution by avoiding power broadening or line-shape distortion that was characteristic of the older modulation spectrometers [7]. Also, pulsed molecular beam sources contributed other benefits such as avoiding collisional broadening and providing rotational cooling so that larger molecules could be studied [6]. However, even though this spectrometer is able to operate over a wide range of frequencies (~10 GHz), the cavity must be precisely tuned to resonance at each frequency step and a narrow
frequency region is measured (~500 kHz) before it must be tuned again for the next frequency step. This leads to very long acquisition times and a limitation on many applications due to the possibility of long-term laser frequency drift. This may include a limitation on performing rotational spectroscopy of excited vibrational states [7], which is crucial to providing insight into the mechanisms of fundamental chemical reactions. Information regarding the transition state is embedded in the vibrational and rotational population distributions of the reaction products and can be disentangled by using the well-established transition-state theory (TST) to describe the progression from products to reactants [8-9].

Figure 1.1a The classical Balle-Flygare Fourier transform microwave spectrometer [10]. Diagram shows pulsed nozzle and cavity mirrors which must be mechanically adjusted at each frequency step during the scanning process.
Figure 1.1b The free induction decay of the polarized sample is measured in the time domain (top figure) and then is Fourier-transformed into the frequency domain to give the resulting rotational spectrum (bottom figure) (Figures adopted from reference [10]).

Pate and co-workers recently pioneered a truly broadband rotational spectroscopy technique in the microwave region: chirped-pulse Fourier-transform microwave (CP-FTMW) spectroscopy (over 10 GHz per pulse in the 7.5-18.5 GHz spectral range) [7]. They achieved this by taking advantage of advances in electronics such as the arbitrary waveform generator (AWG), which creates a “chirped pulse,” a few micro-seconds long phase-reproducible pulse with a linear-in-time frequency sweep. The frequency range of this pulse depends on the number of gigasamples per second (GS/s) of the AWG. The FID emitted by molecules at their transition frequencies is then collected and subsequently digitized by using a high-speed digitizer in a fast digital oscilloscope. Both of these features allow for fast acquisition times covering a broad frequency range in a short period of time. Other major advantages over the traditional Balle-Flygare spectrometer are: (1) FID is averaged until the desired signal to noise is reached; (2)
there are no mechanical parts to scan because of the purely electronic nature of the spectrometer; and (3) the relative intensity of spectral lines becomes meaningful within the spectrum as well as between spectra taken under the same experimental conditions, since the scan over the entire frequency range is covered practically at once.

1.2 The millimeter wave region

For small molecules with large rotational constants (small moments of inertia), the millimeter wave (mm-wave) region (30 – 300 GHz) proves to be very important for making measurements on these molecules [11-13]. Our specific technique, adapted from the CP-FTMW spectrometer established by Brooks Pate, takes advantage of fast electronics to overcome two major issues that have plagued mm-wave spectroscopy: problems with direct generation and detection of mm-waves and absence of truly broadband capabilities. We have developed a CPmmW spectrometer that can operate within 55-102 GHz, encompassing most rotational transitions of molecules containing two heavy atoms.

Classic issues with mm-wave generation come from both the long and short wavelength end of the spectrum. From the long end, microwaves are about 1-3 cm in length, for which electronic oscillators such as magnetrons and other microwave sources are used to work within this region because they require that the wavelength be comparable to the dimensions of the tube [1]. However, for the mm-wave region, this condition is no longer satisfied. From the short end, hot bodies are used to emit infrared radiation and the intensity of the radiation scales with the inverse square of the wavelength [1]. Therefore, the closer one gets to the mm-wave region, the less power there is. And even with the advancements in electronics, transitions must be relatively strong to be observed in a broadband spectrum. The downside of looking at higher frequencies is
that because of the lack of power it will be more difficult to polarize transitions with high dipole moments or small population. One must then surrender to narrowing the bandwidth to increase the degree of polarization [1].

1.3 A truly broadband millimeter wave spectrometer

Advances in broadband millimeter-wave amplifiers, arbitrary waveform generators and heterodyne receivers allow the circumvention of difficulties in the mm-wave region [14]. It is possible because of advancements in amplifiers and active frequency multipliers to up-convert the pulse generated by the AWG into the mm-wave region as well as to down-convert the resulting polarized pulse to allow for easy detection. The schematic of the chirped-pulse millimeter wave (CPmmW) spectrometer designed in the Field lab is shown in Fig. 1.2.
Figure 1.2 Schematic diagram of the CPmmW instrument used for the experiments herein. For a full list of parts, see the Appendix.

All components of the experiment are phase-locked to the same 10 MHz Rubidium frequency standard (i). An 8 Gs/s AWG (iv), operating at the 8.75 GHz rate of an external clock (iii), is used to generate a linearly-chirped pulse, which is up-converted (vi) by mixing with the output of a fixed-frequency 9.375 GHz oscillator (v). The resultant signal is isolated (vii) and amplified (viii). The desired sideband is then selected using a bandpass filter (ix) and actively frequency-multiplied by a factor of 8 (x and xi) to produce a chirped pulse that covers the 55–73 GHz or the 87–102 GHz frequency range with a peak power of 20 mW. The precision attenuator (xii) is introduced for intensity calibration purposes. The mm-wave pulse is coupled into free space using a 24 dBi standard gain horn (xiii) and focused into a molecular beam chamber by a pair of teflon lenses (xiv). After the chirped excitation pulse has polarized the
molecular sample, the FID is collected and down-converted (xviii) by mixing with the output of a Gunn oscillator (xvi). The resultant signal is input to a low-noise amplifier (xix) and averaged in the time domain on an 8 GHz oscilloscope (xx). Figure adopted and modified from Park, et al [14].
Briefly, it operates as follows: An 8 GS/s AWG (Tektronix model AWG7082C) generates customized chirped pulses that are then mixed with a fixed 9.375 GHz phase-locked local oscillator (LO). This resulting frequency is then isolated, amplified, and passed through a band-pass filter to select the sum or difference frequency, respectively. For example, the AWG can generate chirps from 0-4 GHz in theory (the Nyquist frequency is half the sampling rate, which is 8 Gs/s). This frequency is mixed ("up-conversion") with the LO fixed at 9.375 GHz, resulting in two frequency ranges: 5.375 – 9.375 GHz or 9.375 – 13.375 GHz. We can choose either the lower side band or upper side band by using band pass filters (BPFs). We have three BPFs that transmit 6.875 – 9.125 GHz, 8.7 – 10.5 GHz, and 10.9 – 12.7 GHz. These ranges refer to the flatness regions of the BPFs and it is very important that when choosing which BPF to use, any residual microwave power at the carrier frequency of the LO is blocked (therefore we cannot use the second BPF mentioned, but will use the first and third). These ranges are then multiplied by eight in the multiplier chain, at last generating radiation in the mm-wave region. Depending on whether we want to choose lower or upper side bands, the frequency ranges possible are 55 – 73 GHz and 87.2 – 101.6 GHz. We are also limited by the frequency range on our oscilloscope, which is 8 GHz (Tektronix DPO70804C, 25 GS/s Digital Phosphor Oscilloscope). Therefore, we choose a center frequency that will be appropriate for encompassing the transition frequencies we are interested in. The mm-wave frequency is broadcasted from a horn antenna and, with Teflon lenses, is loosely focused in the center of the chamber where it intersects the molecular beam. The CPmmW spectrometer is matched with the pulsed supersonic molecular beam setup via a master 10 MHz clock. Therefore, each shot of the chirped pulse identically polarizes each
beam pulse and all molecular transitions within the chirped pulse's sweep range become polarized. Each of the polarized two-level systems undergoes coherent radiation at their transition frequency, or FID. The FID signal lasts for about 10 µs and is limited by Doppler dephasing. It is then mixed with another LO to a lower frequency ("down-conversion"), amplified with a low-noise amplifier, then recorded in real time by our fast 8 GHz oscilloscope (Tektronix DPO70804C). In this case, the FID is mixed with the 78.76 GHz (9th harmonic of the Miteq 8.75 GHz DLCRO phase-locked oscillator) output of a phase-locked Gunn oscillator. The last step is Fourier-transforming the signal read by the scope into the frequency domain to give the rotational spectrum.

A major advantage of recording the entire spectrum in one shot and having it synchronized with the molecular beam pulse, is that if the signal to noise (S/N) of a single-shot spectrum is not acceptable, then FID signals from multiple shots can be averaged phase-coherently in the time domain before being Fourier transformed into the frequency domain. In this way, both high-resolution and high S/N can be achieved while uncovering weaker transitions or line characteristics that may not have been apparent in the single-shot spectrum. Also, as was previously noted, another major benefit of single-shot spectroscopy is that the relative line intensities of the transitions become meaningful (within 3%). Because of this, both frequency and intensity data can be used as input into different fit models, an impossible thing to do until chirped pulse spectroscopy.
Chapter 2: HCN/HNC vibrational population distribution in the photolysis reaction

The following work was done in very close collaboration with and guidance from Dr. Kirill Prozument.

2.1 Importance of the four-center mechanism in photolysis of vinyl cyanide

In the photolysis of vinyl cyanide with 193 nm laser radiation, two qualitatively distinct reaction paths were proposed by Derecskei-Kovacs and North via their *ab initio* molecular orbital calculations [15]. The first mechanism passes through a three-center transition state to produce hydrogen cyanide (HCN) and singlet vinylidene, and the second mechanism passes through a four-center transition state to produce hydrogen isocyanide (HNC) and acetylene (Figs. 2.1 a, b, c).

![Figure 2.1a Photodissociation of acrylonitrile molecule via the three-center elimination process, as calculated by high level *ab initio* theory [15]. Hydrogen atom H3 embeds itself between the carbon C2 of the acetylene group and C3 of the cyano- group. The transition state involves formation of two new bonds shown by dashed lines – those between C2, C3, and the “traveling” H3 atom. Therefore, this mechanism is usually called “three-center elimination.” The reaction proceeds from the transition state by](image-url)
eliminating the HCN molecule and the vinylidene radical. In most cases, the latter has been assumed to quickly isomerize to form acetylene (Fig. 2.1c). There is little doubt in the literature that this process is one of the major channels for the photodissociation of the acrylonitrile molecule.

**Figure 2.1b** Dissociation of acrylonitrile molecule via the four-center elimination process, as calculated by high level *ab initio* theory [15]. The cyano-group and the opposite hydrogen atom, H1, approach each other and form three new bonds in the transition state. In the transition state a bond is created between four atoms, C1, C3, H1, and N. Thus this decomposition mechanism is called “four-center elimination.” The resulting products are acetylene and HNC molecules. The reaction is commonly believed to proceed with HNC isomerization to the more stable HCN isomer, as shown in Fig. 1 c).
Figure 2.1c Isomerization of the HNC molecule [15]. The HNC → HCN isomerization is believed to take place subsequent to the four-center elimination step of acrylonitrile photodissociation. This is a fundamental isomerization reaction that proceeds via delocalization of the hydrogen atom during its large amplitude motion around the N-C core. The assumption is that there are collisions with the carrier atoms, which can accommodate the energy released during isomerization.

The authors concluded by their RRKM calculations and the predicted HCN/HNC ratio that the three-center mechanism path should have a yield 124 times greater than that of the four-center one, thereby predicting that the production of HNC will be irrelevant in comparison to that of HCN. This initial proposal was later modified by electronic structure calculations done by Homayoon, et al [16], who recognized that HCN and HNC can both be produced by three or four center mechanisms (Figs. 2.2 a, b). Thus they reduced this ratio to 1.9, still in favor of HCN production, predominantly via a three-center mechanism, and HNC via a four-center mechanism. (All above figures are taken from an ACS PRF research proposal by Dr. Kirill Prozument).
Figure 2.2 These are schematic potential energy diagrams (PEDs) for paths leading to HCN production (panel a) and for paths leading to HNC production (panel b), calculated by Hoyamoon, et al [16]. As both Fig. 2.2 a and b show, HNC and HCN can both be produced from either three or four center mechanisms. Shown are the relative energy values in kcal/mol. Figures are taken directly from reference [16].
To address the reaction mechanism of photolysis of vinyl cyanide (VCN) we carried out a series of CPmmW experiments. The ArF excimer laser (Lambda Physik COMPex) operating at 193 nm with output power of about 30 mJ/pulse was used to photolyze VCN. The resulting CPmmW spectrum of the 87-93 GHz region is shown in Fig 2.3. HCN, and to a lesser extent HNC, are produced in different vibrationally excited states that are comparable in relative population to their respective ground states.
Figure 2.3 Photolysis of vinyl cyanide at 193 nm. Vibrational satellites of HCN and HNC in this millimeter wave spectrum are indicated by the * and + labels, respectively. In a triatomic molecule, the bending vibrations are expected to increase the rotational constant and vice versa with stretches, so lines to the right of the ground state transition are expected to be bending vibrations and lines to the left to be stretching vibrations. The combination vibrations can go either way. The lines assigned to HCN are assigned due to the characteristic hyperfine splitting of HCN [17]. The very intense lines are the precursor lines of vinyl cyanide.
In order to get additional insight into the transition states of the photolysis reaction, we have used isotopically substituted precursor species. In this way, we are able to determine which mechanism is responsible for the observed products. Due to the site-specific labeling, as shown in Fig. 2.4, we can assume that most of the HCN and HNC produced is via the 4-center mechanism while most DCN and DNC produced is via the 3-center mechanism.

Figure 2.4 Shown as the reactant is a d_1 isotopologue of vinyl cyanide. After photolysis of this isotopologue, all HCN and HNC will be necessarily produced by the 4-center mechanism while all DCN and DNC will be from the 3-center mechanism.

Fig. 2.5 shows the CPmmW spectra of photolysis products of normal vinyl cyanide CH_2=CH-CN and its isotopologue CH_2=CD-CN in panels a) and b) respectively. The spectra were recorded under the same conditions; therefore the relative line intensities are meaningful within each spectrum as well as between the two spectra. Interestingly, the two spectra demonstrate very similar vibrational population distributions (VPD) and overall intensities of the lines. If the three-center mechanism is the dominant reaction path, then hardly any HCN would be expected to be produced and DCN and DNC would be the primary reaction products. However, not only was HCN
directly observed in the same vibrational states as in the previous spectra, but the intensities are very comparable between the two spectra; the HCN lines from deuterated vinyl cyanide are about 80% as intense as the HCN lines from normal vinyl cyanide. These results imply that the four-center mechanism is the major path for production of HCN, the three-center one being much less important unless H-D scrambling is considered (see next section on H-D scrambling possibility).

**Figure 2.5** The 193 nm photolysis of vinyl cyanide and its mono-deuterated isotopologue, CH₂=CD-CN, shown in panels a and b, respectively. In panel a, HCN and HNC are produced by both the three and four-center mechanisms. In panel b, due to the isotope substitution at the three-center position, HCN and HNC are exclusively produced via the four-center mechanism, assuming no scrambling effects. Due to the identical
conditions under which the spectra were recorded, the intensities can be directly compared. The parent lines of HCN and HNC in the substituted spectrum are roughly 80% as intense as in panel a, revealing the dominance of the four-center mechanism in both HNC and HCN production.

This conclusion was further supported when the spectrum was taken of the DCN produced from deuterated VCN (Fig. 2.6). Indeed, the ground-state DCN had a relative intensity of 16% that of the vibrational ground state HCN line. According to Fig. 2.4, DCN can only be expected to be created via the three-center mechanism and the lack of DCN product directly supports the four-center over the three-center mechanism, and effectively rules out scrambling. Despite the uncertainty regarding rotational cooling, we do not expect a significant difference in rotational cooling between HCN and DCN. We thus regard the intensities to be comparable under similar conditions.

Figure 2.6 193 nm photolysis of mono-deuterated vinyl cyanide (top). Bottom spectrum is background.
To the best of our knowledge, the only other experiments that have been done to measure the ratio of three-center versus four-center mechanisms was the work done by Wilhelm, et al. They measured, via Fourier transform time-resolved infrared emission spectroscopy, HCN + vinylidene, which they assumed came from a three-center elimination channel versus HNC + acetylene, which they assumed came from a four-center elimination channel [18]. Our experiments show that it is the four-center mechanism that is the dominant one in producing both HCN and HNC in the photolysis reaction of VCN. It would be interesting to explore the geometry of the four-center transition state that results in both HCN and HNC products. Homayoon, et. al were able to also arrive at their predicted ratio of 3.3 by summing over the three-center paths and the four-center paths they derived from their electronic structure calculations. (Fig. 2.2)

2.2 H-D scrambling possibility

There have been reports on the scrambling of H and D atoms in laser-excited molecules [19-21]. The possibility of H-D scrambling in vinyl cyanide prior to its dissociation will be discussed here as this effect could provide an alternative explanation for our results. In the gas phase, H-D scrambling may be initiated, resulting in unimolecular H-D exchange of the intermediates before they fragment into products. However, we do not believe that this effect is relevant in the present study. If it were, we would expect to observe much more DCN and DNC as scrambling of H and D would mean that mono-deuterated vinyl cyanide would make DCN and DNC by the three center mechanism at least one-third of the time if one assumes complete scrambling, but this is not even remotely what is observed. As previously stated, the production of DCN and DNC is about 10% of the total products, not near enough to 33% to suggest significant H-
D exchange. Experiments that have observed scrambling via laser excitation, including 193 nm [20], which provides an excitation energy significantly higher than the energy threshold for breaking of C-H and C-D bonds, the scrambling effect was modeled by one or two 1,2- or 1,3-H/D shifts between near-lying isomers on the potential energy surface. This implies that a special combination of vibrational energy levels is required. Therefore, we can conclude that our results reveal the four-center mechanism to be the dominant pathway for HNC and HCN production in vinyl cyanide.

2.3 Analysis of hyperfine splitting in HCN

Bechtel, et al [20] demonstrated how the quadrupole hyperfine structure (hfs) could be used as a sensitive electronic reporter to reveal the degree of bending excitation in HCN ↔ HNC isomerization. In other words, by measuring the hfs, it should be possible to explore how the chemical bond has been transformed when we excite a vibration that is coupled to the isomerization reaction coordinate. In general, the quadrupole effect arises from the non-uniformity of the electronic environment of the nucleus, in which the energy of non-symmetric $I > 1$ nucleus is orientation-dependent. When this nuclear electric quadrupole moment interacts with the non-uniform electric field at that nucleus (specifically, the gradient of the E-field), rotational levels split into several components. The hyperfine splittings were analyzed by fitting the peaks with the Lorentz formula and the table of results is shown in Table 2.1.
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Table 2.1 Details for the hfs of the HCN transitions indicated in Fig. 2.3. For 060 and 080, assignments are tentative, see Fig. 2.7.
The stretches are on the order of about 3000 cm\(^{-1}\) (C-H stretch) and 2000 cm\(^{-1}\) (C-N stretch) while the bends are around 700 cm\(^{-1}\). As Fig. 2.7 shows, the exponential curve fitting the bending modes implies that the bending modes are nearly thermally distributed. If the spectrum reflected a purely thermal population, then we would expect less intensity for higher energy stretches and for bends with higher quanta. However, the assignment of the lines 7 and 8 from Table 2.1 to be the combinations of 02\(^0\)0 (bending vibration) with the two stretches 00\(^0\)1 or 10\(^0\)0, to result in 02\(^1\)1 and 12\(^0\)0, respectively, suggests that this is indicative of a unique detail of the reaction mechanism. The combination bending and stretching levels makes these transitions the most energetic, and yet the rotational transitions are 2-4 times as intense as they are in the pure stretching vibrations.

![193 nm photolysis of VCN, 1.5 cm laser - slit jet distance](image)

**Figure 2.7** An exponential curve has been arbitrarily fitted to the vibrational ground state, 020, and 040 in order to evaluate other assignment possibilities. The tentative 060 assignment does not seem as likely as that for 080 if the bending modes are indeed in a thermal distribution, which appears to be the case.
2.4 Fitting accuracy

Figure 2.8 shows the hyperfine structure of the vibrational ground state of HCN and the resulting multiple-peaks fit. The fittings for less intense lines (Fig. 2.9) seem to be slightly better than those for the most intense lines because of the valley between peaks is not so high and as is apparent in the figure, some shoulders of the most intense peak are left out of the fitting.
**Figure 2.8** The quadrupole hyperfine structure of the HCN vibrational ground state. The fitting underestimates the valleys as well as the shoulders of the individual peaks. This occurs in varying degrees for each peak that has been fitted.
Figure 2.9 The quadrupole hyperfine structure of HCN vibrational excited state (transition no. 10 in Table 2.1). This transition is much weaker than that of the vibrational ground state (see Fig. 2.8) and the fit seems to be much more accurate. It is observed as a general trend that the weaker lines tend to be more accurately fitted than the more intense lines.
2.5 Resolution of the spectra

The resolution of the spectra seems to be in agreement with the +/- 10 kHz from the fit as demonstrated in Figs. 2.10 and 2.11. Fig 2.10 shows the original spectrum zoomed in on line 12 (from Table 2.1) and Fig. 2.11 shows the same line but with the center frequency parameter fixed 10 kHz from the original fit. It is clear that there is a significant difference in the fit agreement between the two spectra.
Figure 2.10 A close up of the original fit of vibrationally excited HCN (the first splitting from peak 12 from Table 1/Fig. 2.3).
Figure 2.11 The same line as in Fig. 2.10, but now the center frequency was fixed 10 kHz away from the original fit at 89.95858 GHz instead of 89.95857. Compared to Fig. 2.10 there is a noticeable difference in the quality of the fit to the observed transition line.

Therefore we conclude our resolution precision is +/- 10 kHz.
Chapter 3: HCN and HNC vibrational population distribution in the pyrolysis reaction

The following work was done in very close collaboration with and guidance from Dr. Kirill Prozument.

3.1 Pyrolysis reactions studied by CPmmW spectroscopy

Pyrolysis is the thermal decomposition of molecules in the absence of oxygen [22]. Characterization of the transient molecules in pyrolysis by spectroscopic methods has important implications for modeling of combustion and atmospheric chemistry. In pyrolysis, the molecules pass through a heated nozzle, (Fig. 3.1) and subsequently undergo supersonic expansion which thereby cools the pyrolysis products so that they may be studied spectroscopically.

Barney Ellison and coworkers is one of the groups which advance understanding of basic chemistry with pyrolysis experiments. They have been studying pyrolysis of nitrites by using a Chen nozzle in conjunction with photo-ionization mass spectrometry and matrix isolation FTIR spectroscopy to disentangle the pyrolysis mechanisms of organic molecules that are significant to biomass decomposition [23-24].

With our implementation of CPmmW spectroscopy, we are in a unique position to look at two-heavy-atom molecules such as formaldehyde, HNO, HCN, HNC, DCN, DNC, C$_2$H, and others. In a cold molecular beam, such molecules have their most intense $J = 0 - 1$ rotational transitions within the range of our spectrometer of 58 – 102 GHz.
Figure 3.1 This is a schematic diagram of the widely used pyrolysis nozzle designed by Chen et al [25-26]. The tube is 4 cm long and 1 mm inner diameter, made of silicon carbide, SiC (Saint-Gobain Ceramics, Hexoloy SE). Figure by Dr. Donald David, University of Colorado.

3.2 Comparison of the intensities of vibrational satellite transitions in photolysis vs. pyrolysis

HCN and HNC were produced by pyrolysis of vinyl cyanide (Fig. 3.2). In contrast to the CPmmW photolysis spectrum of vinyl cyanide, we do not detect any vibrational satellites for HCN or HNC. The 000 line of HCN is very intense and there are no satellite transitions with a signal-to-noise ratio within a factor of 20 weaker than the vibrational ground state transition, whereas the intensities of the satellite lines in the photolysis spectrum were comparable to that of the 000 line within a factor of three in intensity.
When a molecule breaks, there is a change in geometry for the fragments, and these fragment molecules can be left vibrating in states that indicate the geometry changes that occur as the molecule traverses the fragmentation transition state. Thus we hope to gain insight into the pyrolysis mechanism by observation of the relative intensities of the vibrational satellites. For example, formaldehyde was observed in an out-of-plane bending vibrational level, which we initially believed was indicative of the fragmentation mechanism. However, when pure formaldehyde was put through the hot pyrolysis nozzle, a similar vibrational population distribution was observed, which therefore revealed that the population in the out of plane bending vibration is determined primarily by the collisional cooling (or lack thereof for this particular mode) during the supersonic expansion from the nozzle.
Figure 3.2 Pyrolysis of vinyl cyanide (1% in argon). This spectrum does not show any vibrational satellites of HCN in contrast to the photolysis spectrum of vinyl cyanide under the same conditions (Fig.2.3).
The difference between the pyrolysis and photolysis experiments described here that affects the vibrational population distribution of products is that pyrolysis reactions occur in the hot tube prior to expansion. In photolysis, the expansion from the slit jet occurs first and afterwards the photofragmentation reaction occurs, thereby allowing the probing laser to not sample the most important effects of post-reaction collisional cooling. Since we are only able to sample populations in low-J levels, we require some collisions to rotationally cool the product molecules but we want to minimize vibrational relaxation. To explore this further, these photolysis experiments could be repeated in an axial jet. The slit jet is designed to be a 1-dimensional expansion in which the number density of the gas decreases as 1/d, where d is the distance from the slit [27-28] whereas in the axial jet the number density follows the 1/d² law [29]. It is difficult to place the laser precisely within the collisional region in an axial jet expansion to obtain rotational cooling because the collisional region is limited to a length of only a few nozzle diameters, i.e. a few millimeters.

3.3 Cooling in an adiabatic expansion: comparing the experimental results of pyrolysis vs. photolysis

Buffer gas is adiabatically expanded, which means that there is no exchange of energy between the buffer gas molecules and the surroundings. To illustrate, consider a container of gas molecules. The molecules collide in the container to equilibrate at a certain temperature. When this gas mixture is contained, molecules collide, fly away from each other, bounce off the wall, then return and exchange energy with other molecules, thereby continually exchanging energy by heating up and cooling down via these collisions. But in an expansion, the “wall” is always getting further away, so there is less chance for the molecules to return and re-heat colder molecules via collision. The molecules are gone for good.
Behind the nozzle, the molecules start out having \(3/2 \, kT\) of translational energy. As the gas expands from the nozzle, all collisions are converted into forward motion (Boltzmann velocity distribution) as the beam speeds up and consequently unidirectional binary collisions provide extensive cooling of the translational degrees of freedom [30]. This cooling happens since while still in collisional region, faster molecules catch up and collide with slower atoms in front, resulting in all the fast atoms getting slower and vice versa. So what was a Boltzmann velocity distribution in the beginning is now much cooler. The rotational degrees of freedom are likewise cooled by rare gas molecules since the kinetic energy of the argon atoms approximately match the rotational energy level spacing (typical B constants are a few cm\(^{-1}\)).

With the slit jet it is much easier to locate the photolysis laser beam within the extended collisional region of the expansion in order to achieve sufficient rotational cooling without subsequent vibrational cooling. Therefore the pyrolysis measurement, where no vibrational satellite transitions are observed, may be telling us that collisional cooling, which is severe in the pyrolysis jet, is not responsible for the vibrational satellites in the photolysis spectrum. In other words, in the pyrolysis jet, collisional cooling completely relaxes both stretching and bending modes in HCN, effectively depopulating all vibrationally excited states of HCN. This is in contrast to our observations for molecules such as formaldehyde and OCS, which are resistant to complete vibrational cooling. For example, in formaldehyde, mode 4 is resistant to vibrational cooling but other modes are not [to be published]. But the fact that we detect the vibrational satellites in the photolysis spectrum implies that collisional cooling of vibrational populations is minimal. Thus, we can be assured that we are in a low collisional regime. This is important to note because then we can assume that the intensities of vibrational satellite transitions sample the photolysis reaction only and not post-photolysis collisional effects.
3.4 Relative abundance of HCN and HNC pyrolysis products

The pyrolysis spectrum (Fig. 3.2) reflects a distribution of HCN and HNC products resulting from a pyrolysis reaction at $T_{\text{nozzle}} = 1873 \pm 100$ K. The energy difference between HCN and HNC vibrational ground states was calculated to be $\sim 5400 \text{ cm}^{-1}$ [31]. The integrated areas of HCN and HNC transitions in our pyrolysis spectrum, taking the splitting of HCN into account are 0.0991 and 0.00293 (in arbitrary units), giving a ratio of $[\text{HCN}]/[\text{HNC}] = 33.8$. The areas are themselves proportional to the square of their dipole moments, which are 2.94 D for HCN and 3.05 D for HNC. Thus, $[\text{HCN}] = A_1/2.94^2$ and $[\text{HNC}] = A_2/3.05^2$. Let us assume that the areas themselves are each proportional to the Boltzmann distribution $\exp[-E_e/kT]$, such that $A_1/A_2 = (3.05/2.94)^2 \exp[5400 \text{ cm}^{-1} / (0.695 \text{ cm}^{-1}/K)]$, where $T_{\text{eff}}$ is some effective temperature. Calculation to determine the $T_{\text{eff}}$ follows below:

$$
\frac{A_1}{A_2} = \frac{0.0991}{0.00293} = 33.8 = \frac{(3.05/2.94)^2 \frac{E_2-E_1}{kT} = 1.076 \times e^{5400 \text{ cm}^{-1} / \text{0.695 cm}^{-1}/K}}{1.076 \times e^{7769.78 \text{ K}/T}}
$$

$$
\ln \frac{33.8}{1.076} = 3.45 = \frac{7769.78 \text{ K}}{T}
$$

Thus $T_{\text{eff}} = 2252.1$ K for the HCN and HNC products of the photolysis reaction, which is 379 K higher than the temperature measured by the optical pyrometer of $T_{\text{nozzle}} = 1600 \pm 100$ C, or 1873 ($\pm 100$) K. One may expect some cooling of HNC molecules in the supersonic expansion, which would result in HCN and HNC populations distributed with $T_{\text{eff}} < T_{\text{nozzle}}$. One can argue that the HCN population is frozen in the $\sim 11 \text{500 cm}^{-1}$ HNC potential well [25] at the very beginning of the supersonic expansion, and the expected distribution is the one with $T_{\text{eff}} \approx T_{\text{nozzle}}$. We observe that the $[\text{HCN}]/[\text{HNC}]$ ratio is slightly less than it would be expected if the HCN and HNC states were thermally equilibrated at $T_{\text{nozzle}} = 1873$ K pyrolysis nozzle and about an order
of magnitude greater than it was in the photolysis measurements described in this work. The results are suggesting that either thermal decomposition is proceeding differently via the transition states, or that a significant amount of HNC is converted to HCN in the hot pyrolysis tube. More pyrolysis experiments, at different temperatures, are desirable. We hope in the future to explore the pyrolysis studies of the system to gain more insight.

3.5 Vibrational cooling vs. rotational cooling and connection to jet type

A common generalization made about cooling in a supersonic jet is that vibrations cool about 1000 times more slowly than rotations [29]. However, such cooling effects cannot be taken for granted and there are many additional complex factors that have to be taken into account, such as the degree of coupling between vibrations and rotations. It is a good question about why some molecules vibrationally cool and others do not. For example, the similarity in geometry of HCN and OCS might make one at first assume that they would behave the same way with respect to vibrational cooling, but we see that whereas OSC is resistant to vibrational cooling, HCN is not. More detailed and complete studies of vinyl cyanide photolysis need to be done in the future to check for populations in other vibrational levels and elucidate more information.
Chapter 4: HNO as a product of thermal decomposition of organic nitrite molecules

What follows is a preliminary discussion of a project that deserves more work. The following work was done in very close collaboration with and guidance from Dr. Kirill Prozument.

4.1 Thermal decomposition of ethyl nitrite

Thermal decomposition of ethyl nitrite is known to proceed through the cleavage of the relatively weak \( (E_a = 42 \text{ kcal/mol}) \) O–NO bond:

\[
\text{CH}_3\text{CH}_2\text{ONO} \rightarrow [\text{CH}_3\text{CH}_2\text{O}] + \text{NO} \\
[\text{CH}_3\text{CH}_2\text{O}] \rightarrow \text{CH}_3\text{CHO} + \text{H} \quad (1) \\
[\text{CH}_3\text{CH}_2\text{O}] \rightarrow \text{CH}_2\text{CO} + \cdot\text{CH}_3 \quad (2)
\]

Both acetaldehyde and formaldehyde as produced by paths (1) and (2), respectively, can be detected by our CPmmW spectrometer. The analysis of the formaldehyde vibrational population distribution (VPD) via path (2) will be discussed in a future publication by Dr. Kirill Prozument et al. Also it was an accidental finding by K. Prozument that H atoms may play an important role in bimolecular pyrolysis reactions in addition to unimolecular decomposition, e.g. the proposed mechanism for acetaldehyde to formaldehyde:
Proposed Mechanism:

\[
\begin{align*}
\text{H}_3\text{C}-\text{CH} & \rightarrow \text{H}_3\text{C}-\text{CH}_2 \\
\text{H}_3\text{C}-\text{CH} & \rightarrow \text{H}_3\text{C}-\text{C}^\cdot + \cdot\text{H} \\
\text{H}_3\text{C}-\text{CH} & \rightarrow \text{H}_2\text{C}^\cdot + \cdot\text{CH}_3
\end{align*}
\]

Figure 4.1 Proposed mechanism for acetaldehyde to formaldehyde making use of the hydrogen radical as a reactant.

4.2 Nitric oxide radical abstracts deuterium and hydrogen via unimolecular and bimolecular reactions

Most of the kinetic data is known for ethyl nitrite but for simplicity sake we have conducted our experiments primarily using methyl nitrite. From the above observed reactions and the proposed role played by the hydrogen radical, it is possible to think that H-atom chemistry and possibly other radicals could be of importance in the pyrolysis of biomass (plant-derived materials, e.g. cellulose). In the experiments described in this section we studied the reaction of NO radical with acetaldehyde. HNO molecule was detected, confirming the hydrogen abstraction reaction by NO radical in a hot pyrolysis reactor. We also qualitatively compared the rate of that bimolecular reaction with the rate of unimolecular reaction in methyl nitrite.

In order to distinguish between the bimolecular and unimolecular reactions, we synthesized fully deuterated methyl nitrite, CD\textsubscript{3}ONO. The unimolecular pyrolysis of CD\textsubscript{3}ONO can result in DNO product, which could be confirmation of the below reactions scheme:
CD$_3$ – O – N = O → CD$_2$O + DNO

DNO has rotational transitions (from the vibrational ground state) at 73084.5745 and 73085.4600 MHz. The chirp is made to cover 73084 – 73086 MHz, or when backtracking from the up-conversion (divide by 8 and subtract 10.7 GHz): from 1564.25 – 1564.50 MHz. Therefore we were looking for lines on the oscilloscope (after down-conversion: 84.385 GHz (9th harmonic of the Gunn oscillator) – transition frequency) at 11.299 and 11.300 GHz. Fig. 4.2 shows the observed transition line that appears to be two unresolved peaks at the above-mentioned frequencies.
Figure 4.2 CPmmW spectrum of DNO upon pyrolysis of the mixture 3% acetaldehyde and 5.5% deuterated methyl nitrite. Spectrum was taken at long FID duration for higher resolution (2.0 μs/division). The peaks did not completely resolve, but it appears that both transitions at 11.299 and 11.300 GHz are present in the spectrum. Absolute stagnation pressure in the pyrolysis nozzle was 3.5 bars and pyrolysis temperature was 800 °C.
The bimolecular reaction of NO radical with H atoms of acetaldehyde would result in HNO molecules in the chamber. We therefore searched for HNO under the same conditions.

HNO has a ground state transition with quadrupole hyperfine splitting at 81477.49 MHz, and referring to the above up-conversion and down-conversion discussion, we made a single-frequency chirp at 515.31 MHz (81.47749 GHz/8 – 10.7 GHz) and looked for the transition on our oscilloscope at 2.9075 GHz (84.385 GHz – 81.47749 GHz). Figure 4.3 shows the CPmmW spectrum of HNO.
Figure 4.3 CPmmW spectrum of HNO at short FID or lower resolution (400 ns/division). The spectrum is only indicative of H atoms that were already present in the chamber, but still we clearly see a peak at 2.908 GHz that corresponds to the 3 degenerate ground-state rotational transitions at 81477.49 GHz. Absolute stagnation pressure in the pyrolysis nozzle was 3.5 bars and temperature was 800°C.
Comparing the DNO and HNO signals in Figs. 4.2 and 4.3, respectively, we can conclude that the unimolecular decomposition of methyl nitrite with DNO products and bimolecular hydrogen abstraction reaction of NO with acetaldehyde resulting in HNO product will result in a similar yield of DNO and HNO. More quantitative studies and modeling will be required to obtain the rates of the reactions.

In general, to thermally crack molecules such as H₂, acetaldehyde, or methanol, just to name a few examples, very high temperatures and pressures are required and results in a mixture of products containing a high proportion of alkene products [32]. Modern fluid catalytic cracking uses a solid catalyst [33]. These cracking experiments by nitric oxide radical demonstrate that •NO can be used as a gas-phase catalyst to perform the cracking at much lower temperatures and with higher efficiency than thermal cracking.

Concluding this section, the key features of CPmmW spectroscopy, which are the ability to detect a broad spectral range simultaneously, high sensitivity and meaningful relative intensities, were used to detect multiple pyrolysis products. In this work we have demonstrated the use of CPmmW spectroscopy for studying unimolecular and bimolecular reactions.
Appendix: Parts list of CPmmW spectrometer

i. 10 MHz Rubidium frequency standard (Stanford Research Systems FS725)
ii. 90 MHz phase-locked crystal oscillator (Miteq PLD-10-90-15P)
iii. 8.75 GHz DLCRO phase-locked oscillator (Miteq DLCRO-010-08750-3-15P)
iv. 8 GS/s arbitrary waveform generator (Tektronix AWG7082C)
v. 9.375 GHz DLCRO (dual loop phase-locked coaxial resonator oscillator) (Miteq DLCRO-010-09375-3-15P)
vi. Triple-balanced mixer (Macom MY51C)
vi. 8-16 GHz circulator (Hitachi R3113110)
viii. 6-18 GHz Amplifier (ALC Microwave ALS03-0283, 20 dB gain)
ix. a. 6.875–9.125 GHz bandpass filter (Spectrum Microwave 311-307389-001)
   b. 10.9 – 12.7 GHz bandpass filter (Spectrum Microwave C11800-1951-1355)
x. Active frequency quadrupler (Phase One SX50-416)
xii. Active frequency doubler (Millitech AMC-12-110546)
xii. Direct Reading Precision Attenuator (Cernex CDA 12609009)
xiii. WR10 gain horn, 24 dBi gain mid-band (TRG 861W/387)
xiv. Teflon circular lenses, 30 cm and 40 cm focal length at 80 GHz (custom)
xv. Gunn phase lock module (LX Microwave model 800A)
xvi. W-Band Gunn oscillator (J. E. Carlstrom Co.)
xvii. W-Band subharmonic downconverter (Pacific Millimeter Products)
xviii. E-Band balanced mixer (Ducommun Technologies FDB-12-01)
xix. Low-noise amplifier (Miteq AMF-7D00101800-24-10P, 55 dB gain)
xx. 8 GHz fast digital storage oscilloscope (Tektronix DPO70804C, 25 GS/s)
References


