RICE UNIVERSITY

JET-COOLED RADICAL SPECTROSCOPY USING A COLOR CENTER LASER

by

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Jet-cooled radical spectroscopy has been developed for its potential application to high resolution infrared spectroscopic studies of large radicals. In general, radicals containing more than three atoms heavier than hydrogen can not be studied in a room temperature cell using high resolution techniques. For such large species, the infrared spectrum becomes congested and unresolvably complex because of the presence of overlapping rotational lines and vibrational hot bands. By cooling radicals in a supersonic expansion, excited rotational and vibrational levels are depopulated, giving a simplified spectrum.

In this technique, radicals are produced inside a slit supersonic nozzle by 193 or 248 nm excimer laser photolysis of a gas mixture consisting of 1% suitable precursor seeded into 1-11 atm carrier gas (typically helium). To reduce the vibrational temperature of the hot radicals produced upon photolysis, the radicals are thermalized by collisions with the room temperature helium inside the slit thermalization region before expansion. The radicals are then cooled rotationally in the subsequent expansion, and
their transient absorption is probed downstream of the slit orifice by a tunable, computer-controlled color center laser.

The jet-cooled infrared spectroscopy technique was first tested on small radicals with known high resolution spectra. Small radicals such as NH$_2$, OH, and CH$_3$ have been observed in the jet with excellent sensitivity and low rotational temperatures. Rotational temperatures ranging from 13-25K and signal-to-noise ratios of 30-150 have been obtained for these radicals. Additionally, rotational temperatures of 10K have been observed for trans-nitrous acid, a stable species produced upon photolysis of nitric acid in the jet.

Jet-cooled infrared spectroscopic studies of larger radicals were initiated since the technique proved successful in the production, cooling, and detection of small radicals. Spectroscopic searches were made for CH$_2$OH, t-HOCO, CH$_3$NH, C$_2$H$_3$, C$_3$H$_5$, C$_2$H$_5$, and OH-Ar (radical van der Waals complex). Although no new radical species were conclusively observed in the jet photolysis experiments, the initial results of searches for these radicals, including the observation of several stable molecules produced upon photolysis of various precursors, have been described.
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Chemical reactions often proceed through chemical intermediates known as free radicals. Because radicals are open-shelled species with one or more unpaired electrons, they are often highly reactive and exist for very short times. Normally radicals are produced by thermal or photochemical events, and because they are easily formed in the earth's atmosphere or in regions of space, radicals are significant species in our world. Free radicals are important intermediates environmentally because they are present in combustion and pollution processes, and knowledge of their identity and reactions in the gas phase is necessary to model such complicated processes. Radicals are becoming of increasing interest in the preparation of semiconductors, particularly in plasma processing of devices. The reaction kinetics of these transient species is needed to model film growth on substrates. Radicals are also found in the interstellar medium, many having been observed astronomically before their spectroscopic detection in laboratories. The identification of such species is necessary for modelling the chemistry of interstellar clouds.

As illustrated above, the study of radicals is highly important to understanding various gas phase processes. However, the very reactive nature of free radicals imposes some limitations on their observation. Either sensitive detection schemes or transient high concentrations with
consequent fast detection are necessary in order to study them. As a solution to the observational problem, infrared kinetic spectroscopy has been found to be a very powerful tool for the study of transient molecules. Basically, an ultraviolet excimer laser photolyzes a suitable precursor, thereby producing the desired radical, and a tunable, single mode infrared laser then probes its transient absorption. The infrared region is chosen for the probe because of its universality: most molecules exhibit absorptions in the infrared. Thus, many molecular species (transient or otherwise), can be identified and monitored during a given chemical reaction. The narrow linewidth of the tunable, cw infrared probe (< 3 MHz) allows for the Doppler-limited resolution of molecular spectra.

Although infrared kinetic spectroscopy is highly useful for the study of free radicals, the technique is not without its limitations. The main limitation of the method and of high resolution infrared spectroscopy in general is that often molecular species containing more than three atoms heavier than hydrogen can not be studied. For larger species, the spectrum becomes unresolvably congested and very complex and in some cases, the absorptions are too weak for detection. This limitation has been overcome for stable species by incorporating the unique cooling properties of supersonic expansions in spectroscopy. By supersonic expansion the molecules can be cooled to a few K, greatly reducing the number of levels thermally populated and therefore the spectral congestion. The purpose of this research is to explore the possibility of extending supersonic jet sources to spectroscopy of reactive free radicals.
In this work, a supersonic nozzle apparatus was constructed in order to test the possibility of observing jet-cooled radicals using a color center laser as the infrared probe. Chapter two gives background information concerning the applicability of supersonic jets to free radical spectroscopic studies and signal-to-noise requirements, while Chapter three details the construction and testing of the supersonic nozzle apparatus. Chapter five describes apparatus modifications for improvement of sensitivity and other experimental conditions. Chapters four and six are concerned with the initial spectroscopic observation of radicals in the jet and subsequent studies exploring the possibility of extending jet-cooling to larger radicals.
CHAPTER 2
EXPERIMENTAL MOTIVATION

2.1 KINETIC SPECTROSCOPY AND ITS LIMITATIONS

Infrared kinetic spectroscopy has been found to be a highly useful technique for the study of the reaction kinetics and spectroscopy of reactive free radicals\textsuperscript{1,2,3}. In this technique, a suitable precursor is flowed through a room temperature cell with a buffer gas (such as helium or hydrogen), and is photolyzed by an ArF excimer laser, thus producing the desired radicals. The radical transient absorption is then probed by a multipass arrangement of the single mode, computer-controlled color center laser. The resulting signal is detected by an InSb detector, collected by the transient digitizer, and finally stored in the computer. The temporal behavior of the transient species can be monitored, and its high resolution infrared absorption spectrum can be obtained. To study the radical time behavior, the laser is tuned to a particular ro-vibrational transition of the species in question, and its dependence of infrared absorption upon time is then observed. By choosing to save the transient digitizer data collection channel at the time corresponding to the maximum in the transient absorption, the radical spectrum is obtained by scanning the laser frequency over the region of interest.

Many small radicals, such as C\textsubscript{2}H, OH, and NH\textsubscript{2}, have been observed in the room temperature cell using this technique. Infrared kinetic
spectroscopy is well suited for spectroscopic investigations of small radicals, but studies of larger species are limited. The main limitation of kinetic spectroscopy and other high resolution infrared techniques is that molecular species containing more than three heavy atoms cannot be studied in a room temperature cell. For larger molecular species, the rotational levels are more closely spaced, and thus more levels are populated at room temperature in accordance with the Boltzmann distribution law. Consequently, the spectral congestion and complexity is such that analysis is difficult if not impossible because of overlapping rotational lines. Moreover, thermal population of low-lying excited vibrational states results in overlapping vibrational hot bands, providing an additional source for spectral congestion. The resulting congestion and complexity of the spectrum is illustrated by the room temperature infrared spectrum of methanol (a relatively small, closed shell species) shown in Figure 1.

The presence of overlapping hot bands is a particular problem in kinetic spectroscopy because the excimer laser deposits energy in excess of that needed for the breaking of molecular bonds; therefore, higher vibrational states of the newly formed radical species are often populated. Vibrationally excited states of small radicals have been observed with this technique\textsuperscript{4}; such congestion due to vibrational excitation would be intensified for larger radicals. In larger molecular species, the fraction in a particular ro-vibrational state also decreases because more states are populated at room temperature. The lowered column density in a particular state often results in weak or nondetectable spectra. Therefore,
Figure 1

Room temperature spectrum of methanol. a) Doppler-limited normal absorption spectrum. b) Stark modulation spectrum with Stark field parallel to the electric field of the laser. c) Nitric oxide reference gas. d) Reference marker cavity.
the combined effect of overlapping rotational lines, vibrational hot bands, and reduction in detection sensitivity hinders or prevents the high resolution infrared studies of large radicals.

2.2 SUPERSONIC JETS AS A POSSIBLE SOLUTION

Although the observational limitation still exists for large radicals at room temperature, a solution has been found for the elimination of spectral congestion of large stable molecules. Because of the cooling properties of a supersonic expansion, supersonic nozzles have been found to be a useful tool in spectroscopy. The molecules are cooled rotationally to a few K in the expansion, thus greatly reducing spectral congestion since fewer levels are populated. The depopulation of excited rotational and vibrational states into lower states increases detection sensitivity as well. To demonstrate the effectiveness of supersonic cooling, the room temperature and 9K spectra of methanol are compared in Figure 2. The temperature of the 9K methanol spectrum was measured by comparing the relative intensities of the A K 1←0 Q branch components using the known ground-state rotational energy levels (the RQ0 A branch is not shown in this spectrum). These spectra represent a small portion near the band center of the OH stretching fundamental. The 300K spectrum of methanol illustrates that spectral complexity can be a significant problem in normal room temperature spectra. The 9K spectrum is greatly simplified, and lines
Figure 2

Comparison of methanol spectra at room temperature and 9K which illustrates the effectiveness of supersonic jet cooling in spectral simplification.
$T = 300K$

$T = 9K$

Frequency (cm$^{-1}$)

3687.5 3687.0
which were not readily observable in the room temperature spectrum are now easily discerned.

In addition to high resolution infrared studies of stable molecules in the jet\textsuperscript{5,6}, van der Waals complexes formed in the expansion have also been observed by infrared absorption\textsuperscript{7}. The unique properties of the jet allow for the stabilization of van der Waals complexes in a near collisionless environment (any remaining collisions have insufficient energy to break the complex apart\textsuperscript{8}). Supersonic jet-cooling is an established technique for the studies of both stable closed shell molecules and van der Waals complexes; however, it has yet to be successfully tested on radicals.

The goal of this research is to combine infrared kinetic spectroscopy and supersonic cooling techniques in order to observe the spectra of jet-cooled radicals by producing radicals by flash photolysis inside the nozzle of a supersonic jet. The experimental requirements of jet-cooled radical spectroscopy will be more thoroughly discussed in Section 2.5.

2.3 PROPERTIES OF A SUPERSONIC EXPANSION

A brief discussion of expansion properties is necessary in order to understand the effects and estimate the results of cooling radicals in a supersonic jet. Supersonic expansions have been extensively studied and characterized\textsuperscript{9,10,11}. This discussion will be limited to information relevant to spectroscopic studies. A supersonic expansion is formed when gas (typically a monatomic gas, such as helium or argon) in a high pressure
stagnation region is allowed to expand through a pinhole or slit opening into a vacuum chamber. The random thermal motion of the gas particles inside the stagnation region is converted into directed mass flow in the expansion. As the expansion is adiabatic, no heat enters or leaves the gas. The enthalpy of the gas decreases to provide the energy necessary for this ordered flow.

The supersonic jet properties are described by its Mach number \( M \). The Mach number is defined as \( M = \frac{u}{a} \), where \( u \) is the mass flow velocity and \( a \) is the speed of sound in a gas. The speed of sound is equal to \( (\gamma kT/m)^{1/2} \) where \( \gamma \) is the ratio of \( C_p/C_v \) for the expanding gas. For the gas to be supersonic, \( M \) must be > 1. The very high Mach numbers found in supersonic expansions are not due to very high flow velocities, but instead \( M \) increases as the local speed of sound decreases with falling temperature, since \( a \) is \( \propto T^{1/2} \).

In the supersonic expansion, the diameter or width of the nozzle opening is > the mean free path \( \lambda \) of the atoms or molecules, which allows for collisions as the gas exits the orifice and downstream during the expansion. The velocity distribution of the atoms or molecules narrows as the randomness is removed, resulting in translationally cold gas particles. The overall bulk velocity of the gas shifts to a nonzero value since the gas is forced to flow in one direction. If a molecule is seeded into a helium expansion, its velocity will reach that of the bulk gas and its velocity distribution will be the same as the expanding helium. Thus, the seed molecules will have essentially the same translational energy as the helium.
carrier gas, which, depending on the exact nature of the expansion, is typically 1-5K.

Of particular interest here is the cooling of the internal degrees of freedom of the seed (rotation and vibration) in the expansion by collisions of translationally cold helium atoms with the seed molecules. As the translational energy $kT$ is $\approx \Delta E_{\text{rot}}$, the effect of the translationally cold helium collisions will be to cool the rotational excitation of the seed molecules. Typically 1-10 collisions are necessary for rotational cooling, resulting in temperatures ranging from 1-10K. Since $\Delta E_{\text{vib}}$ is $\gg kT$, 100-100,000 collisions are required for vibrational cooling. Thus vibrational temperature becomes decoupled from translational temperature, and, as a result, vibrational temperatures are usually higher than rotational temperatures and are typically 150-200K.

2.4 NOZZLE ORIFICE SELECTION: CIRCULAR VS. SLIT

The most important expansion characteristics for spectroscopic studies are temperature and density. Low rotational temperatures are necessary for reduction in spectral complexity, and molecular concentrations downstream in the probe region of the expansion determine detection sensitivity. Both of these properties are intimately connected with the type of nozzle orifice. The temperature and density properties of two possible nozzle orifices, circular and slit, will be discussed. After the comparison
of the advantages and disadvantages of each orifice, the orifice selection for the jet-cooled radical studies will be justified.

Slit and circular orifices differ most fundamentally in dependence of density upon distance from the orifice. In a slit expansion, the density downstream falls off as \((1/x)\). However, for expansion from a circular orifice, density falls off as \((1/x)^2\). Density and other properties of the expansion are expressed quantitatively by the formulas tabulated by Hagenae\textsuperscript{12} which can be used to describe the properties of both the slit and circular expansions. For example, the density ratio \((n/n_0)\) for expansion from an ideal slit (an infinitely long slit in a zero thickness wall) is given by:

\[
n/n_0 = 0.2(d^*/x)
\]

where \(n\) is the density downstream, \(n_0\) is the density inside the stagnation region, \(d^*\) is the slit width, and \(x\) is the distance downstream from the orifice. Thus, the density \(n_0\) before the slit exit is five times larger than the density \(n\) at the distance one slit width downstream. The corresponding equation for a circular orifice is:

\[
n/n_0 = 0.15(d^*/x)^2
\]

where \(d^*\) is now the diameter of the orifice. The initial density \(n_0\) is almost seven times greater than the density at one nozzle diameter downstream. The density as a function of distance downstream for both a
125 \mu m slit and a 1 mm circular orifice is plotted in Figures 3a and 3b, respectively. Comparison of the density at 10 mm downstream for the two orifices shows that the slit expansion density is greater by almost a factor of 3 than that of the circular expansion.

The expansion can be treated as a reversible adiabatic expansion with the laws of thermodynamics determining the temperature in the expansion. In a reversible adiabatic expansion, $T$ is related to $n$ by:

$$\frac{T}{T_0} = \left(\frac{n}{n_0}\right)^\gamma$$

where $\gamma = (C_p/C_v - 1) = 2/3$ for a monatomic gas such as helium. Thus, for a slit expansion

$$\frac{T}{T_0} = .342(d*/x)^{2/3}$$

At one slit-width distance downstream of the orifice, the temperature $T$ is lower by almost a factor of 3 times than the temperature $T_0$ of the gas inside the stagnation chamber. For a circular expansion, a similar treatment gives

$$\frac{T}{T_0} = .282(d*/x)^{4/3}$$

The plot of the slit and circular expansion temperatures as a function of distance downstream are shown in Figure 3c. As can be seen, temperature falls more rapidly with distance downstream in the circular expansion.
Density and temperature calculations as a function of distance downstream from the nozzle orifice for a 125 μm slit and 1 mm circular orifice. a) Slit expansion density calculations with and without radical reactions. b) Circular expansion density calculations with and without radical reactions. c) Comparison of temperature estimates for both the slit and circular orifice.
[R] cm$^{-3}$

x (mm)

[R]

[R] no reaction

circular

slit
From the comparison of the density and temperature properties of the slit and circular expansions, it can be seen that the slit expansion gives a higher density downstream whereas the circular expansion gives a lower temperature (comparing both properties at 10 mm downstream where the infrared probe would be located). However, the most important point in favor of the slit orifice is its increased effective pathlength in comparison to that of a circular orifice. The shape of the slit orifice also lends itself easily to multipassing by the probe beam. Although the lowest temperature was not obtainable by this orifice selection, the circular expansion temperature was only lower by a factor of almost 2. Since radical density is more important to the success of the jet-cooled radical spectroscopy experiment than the ultimate lowest temperature, a slit nozzle was selected for this research.

2.5 EXTENSION OF JET SOURCES TO THE STUDY OF RADICALS

To obtain the rotationally cold spectrum of a stable molecule, typically 1% of the molecule of interest is seeded into the inert carrier gas, and the mixture is expanded through a slit orifice into a vacuum. The molecular absorption spectrum is probed by an infrared source downstream in the expansion. Thus, the observation of the infrared spectra of stable molecules is straightforward; free radical studies require some modifications of the standard nozzle design.
As discussed in Section 2.3 on supersonic expansion properties, the expansion provides little vibrational cooling. However, vibrational cooling is particularly desirable for radicals produced by photolysis since the excimer deposits energy in excess of that required for bond breaking, resulting in vibrationally hot fragments. When considering collisional energy transfer, the probability of converting internal energy into translational energy is small if the change in internal energy is much larger than the collisional energy. Thus, rather than photolyze the precursor in the middle of the expansion where the collisions have become weak and little vibrational cooling would be expected to occur, a thermalization section was added to the slit nozzle so that vibrationally hot radicals produced by photolysis would thermalize by collision with the room temperature helium. The precursor is photolyzed inside the thermalization region of the slit, using a 1% mixture of a suitable precursor in helium. The radicals undergo $10^5$ collisions at room temperature before exiting the slit orifice. After leaving the orifice, the radicals are cooled rotationally in the subsequent expansion. An infrared laser then probes the transient absorption downstream.

For thermalization and rotational cooling to occur, approximately $10^5$ collisions are required. After the $10^5$ collisions take place, sufficient concentrations of the radicals are necessary at the infrared probe in order to have adequate signal-to-noise. However, because of this large number of collisions, there is increased possibility of radical-radical recombination and radical-precursor reactions, leaving insufficient concentration of the radicals at the infrared probe for adequate signal-to-noise. Calculations of
sensitivity which take into account radical losses due to chemical reaction are described in Section 2.6, and the initial application of jet sources to the spectroscopic study of free radicals is detailed in Chapter 4.

2.6 SENSITIVITY CALCULATIONS

Since the thermalization process requires \( \approx 10^5 \) collisions, radical-radical recombinations and radical-precursor reactions are a source of radical losses in addition to expansion losses. For this experiment to be feasible, it is necessary to have sufficient radical concentration at the probe point downstream of the nozzle orifice. These sensitivity calculations attempt to estimate the density of radicals downstream while accounting for radical losses due to recombination reactions and expansion.

2.6.1 Radical S/N Using Calculated Concentration

To estimate the sensitivity of this experiment, the concentration of radicals has been calculated as a function of distance \( x \) downstream. The feasibility calculations include loss of radicals due to expansion and recombination. In order begin the calculations, an estimate is needed for the initial concentration of radicals. The radicals produced in the thermalization region of the slit have the opportunity to react with the precursor or other radicals; therefore, their concentration at the slit orifice can be determined by chemical kinetics providing the rate constants are
known or can be estimated. The loss of radicals due to collisions in the expansion can then be estimated by numerical integration of the expansion. This numerical calculation of the radical concentration is checked in the absence of reactive collision by comparing the results with Hagena's equations.\textsuperscript{12}

Reaction rates between various radicals and their precursors can vary greatly from case to case. However, radical recombination rates at room temperature are typically $10^{-11}$ cm\(^3\)/s. Therefore, a general radical concentration may be obtained where radical-radical recombinations are a major source of loss. Assuming radical-radical recombinations dominate under conditions where the precursor is extensively photolyzed, the rate of this recombination process can be described using collision theory, where

$$
k_{\text{coll}} = p z_{12} \exp \left( -\frac{E_a}{RT} \right)
$$

with $z_{12} = \frac{Z_{12}}{N_1 N_2}$ and $Z_{12} = N_1 N_2 \pi d^2 \left( \frac{8kT}{\pi \mu} \right)^{1/2}$

$Z_{12}$ is defined as the collision frequency per unit volume for molecular species 1 and 2. $N_1$ and $N_2$ are the number of molecules per unit volume, $p$ is the steric factor for the particular reaction, and $\pi d^2$ is the collision cross-section, in which $d$ is the diameter of the molecules. Substituting $d = 4 \times 10^{-8}$ cm\(^2\), $p = 1$, and $\bar{c} = 1 \times 10^5$ cm/s, $k_{\text{coll}}$ now becomes:

$$
k_{\text{coll}} = 5 \times 10^{-10} \exp \left( -\frac{E_a}{RT} \right)
$$
Since radical recombination reactions have a rate constant of $1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ at room temperature, and a typical negative activation energy for recombination processes is 1.2 kcal/mol, if a temperature of 77K were substituted into this equation, a rate constant of $\approx 1.2 \times 10^{-6} \text{ cm}^3 \text{ s}^{-1}$ would be obtained, which is much greater than the gas kinetic collision number of $2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. Since it is physically impossible for molecules to react faster than their rate of collision, it is necessary to change the form of $k_{\text{coll}}$ such that the rate is limited to gas kinetic at the lower temperatures (100K and less). Using $k_{\text{coll}} = 1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ and working backwards to determine the appropriate rate constant, the rate law now becomes:

$$k = 5 \times 10^{-10} \left(\frac{T}{300}\right)^{1/2} \frac{\exp(600/T)}{362 + \exp(600/T)}$$

where the form of the rate law has been rearranged for ease of substitution of the appropriate values for the temperature.

For a second order reaction, the radical concentration is assumed to be given by:

$$[R] = \frac{[R]_0}{1 + kt[R]_0}$$

However, at longer times $kt[R]_0 >> 1$ so that the radical concentration at time $t$ now becomes:

$$[R] \approx \frac{1}{kt}$$
Using $k = 1 \times 10^{-11}$ cm$^3$ s$^{-1}$ and $t = 5 \mu$sec as the time needed for radicals produced inside the slit thermalization region to arrive at the slit orifice, the radical concentration is calculated to be $\approx 2 \times 10^{16}$ molecules/cm$^3$. Regardless of the initial radical density at the point of photolysis (assuming it is greater than the calculated $2 \times 10^{16}$ molecules/cm$^3$ concentration), it is expected to be no more than $2 \times 10^{16}$ molecules/cm$^3$ 5\(\mu\)sec later at room temperature.

To determine the concentration of radicals in the expansion, the jet properties given by Hagena's formulas for a slit orifice are assumed. These equations are based on the assumption that the slit length is $> x$ (i.e. an infinitely long slit), so experimental radical densities will deviate from calculated densities since the experimental slit length is $\approx x$. Additional assumptions are a thin-walled slit (no thermalization region) and a narrow slit. As discussed in Section 2.4, the radical density downstream of the orifice can be described by:

$$n = 0.2n_0 \left(\frac{x}{d^*}\right)^{-1}$$

At one slit width downstream, the density at this position is 1/5th of the original density inside the stagnation chamber. If it is assumed that little expansion has occurred 125 \(\mu\)m from the slit orifice (125 \(\mu\)m corresponds to the slit width of the nozzle), $n_0$ can then be calculated. Using $n = 2 \times 10^{16}$ molecules/cm$^3$ as the density at one slit width downstream, $n_0$ is determined to be $1 \times 10^{17}$ molecules/cm$^3$. 
Since $n_0$ has been estimated, the radical concentration as a function of distance downstream of the orifice can now be calculated by integrating the equations of volume expansion combined with radical recombination. In Figure 4a, the resulting radical concentration has been plotted as a function of distance. Radical loss due only to expansion (no reaction) and radical loss due to the combination of expansion and recombination reaction are illustrated separately in the two plots. Figure 4a suggests that radical loss by recombination processes is a problem only in the initial expansion, where the density is the greatest. The continued decrease in radical density during the expansion is primarily due to gas expansion. Comparison of the two plots shows that in the probe region the reaction and no reaction radical concentrations should differ by about a factor of two.

Using these estimated radical concentrations, it is now possible to estimate the fractional absorption of the infrared by species in the jet. If the probe point is taken to be 1 cm downstream of the orifice, the radical concentration is $1.1 \times 10^{14}$ molecules/cm$^3$ with a temperature of 7K (the temperature was obtained from Figure 4b, at the probe distance 1 cm downstream). Using the allyl radical as a test case, its absorption can be calculated from the following formula:

$$\Delta I/I = \frac{8\pi^{5/2} |\mu_\alpha|^2 S_{12}^\alpha \exp(-E_1/kT)}{(3uhQ_{int})} \rho_0 L$$
Calculations of slit expansion density and temperature as a function of distance downstream from the nozzle orifice for a 125 μm wide slit. a) Using the calculated radical concentration, decreases in the concentration due to expansion losses only and radical-radical recombinations in addition to expansion losses are plotted separately as a function of x. b) Calculated temperatures for a slit expansion.
a

[R] no reaction
[R] cm$^{-3}$

b

$T$ (K)

$10^1$ $10^2$ $10^3$ $10^4$ $10^5$ $10^6$

x (mm) 0 10 20

$10^1$ $10^2$ $10^3$ $10^4$ $10^5$ $10^6$

x (mm) 0 10 20
where $\mu_\alpha$ is the vibrational transition dipole moment, $S_{12}^\alpha$ is the rotational line strength in the transition between level 1 and 2, $\rho_0$ is the radical concentration, $E_1$ is the rotational energy of the lower level, $u = (2kT/m)^{1/2}$, $Q_{\text{int}}$ is the internal partition function ($Q_{\text{int}} = Q_{\text{vib}}Q_{\text{rot}}$), and $L$ is the slit length. $\Delta I$ is the change in laser power upon absorption, and $I$ is the laser power without absorption (if $I_{\text{tr}} = I_0 \exp(-\sigma n L)$, and $I_{\text{tr}} = I_0 - I_{\text{abs}}$, it can be assumed for small values of $I_{\text{abs}}$ that $\log(I_0 - I_{\text{abs}}) \approx -I_{\text{abs}}$). Assuming the following parameters for allyl radical:

$$\mu_\alpha = 0.05 \text{ debye} = 0.05 \times 10^{-18} \text{ esu/cm}$$

$$S_{12}^\alpha = 1$$

$$E_1 = 0$$

$$Q_{\text{int}} = 66 \text{ (expected for allyl radical at 7K)}$$

$$\rho_0 = 1.1 \times 10^{14} \text{ cm}^{-3}$$

$$u = 5 \times 10^3 \text{ cm/s}$$

$$L = 1 \text{ cm}$$

$\Delta I/I$ is $\approx 6 \times 10^{-3}$ or .6% absorption per pass of the infrared beam. Typically a .01% absorption in cell kinetic spectroscopy gave a S/N ratio of $\approx 1$ if the laser amplitude noise was reduced by use of balanced detectors. Therefore a S/N ratio of $\approx 60$ can be expected for radicals in the jet probed by a single pass of the infrared beam. Because of this low S/N ratio, it
should be necessary to multipass the infrared in order to ensure good sensitivity, particularly for larger radicals.

2.6.2 Radical S/N Using Experimental Concentration

In Section 2.6.1, the percent absorption of allyl radical was estimated using the calculated radical density downstream of the orifice. However, because the transition moment for OH is known accurately, the experimental concentration of OH radicals can be calculated from the observed absorption measured in Section 6.2. The purpose of the following calculations is to compare calculated vs. actual radical concentrations. By introducing the actual OH concentration as an estimate of the allyl radical, a new estimate of the expected S/N for the allyl radical can be obtained. Although the OH concentration will not be exactly the same as that of allyl (one must consider % dissociation of the precursor, rates of radical-radical and radical-precursor reactions inside the thermalization region), it does provide some feeling for the size of the signal which might be expected.

Before calculating the peak absorption cross-section for OH, the dipole transition moment must first be extracted from the Einstein A coefficients of OH, which are tabulated in the work of Nelson et al.\textsuperscript{13} The integrated absorption intensity S(T) is related to Einstein A coefficients in the following equation:
\[
S(T) = \frac{1}{8\pi cv^2} \exp^{-1.4388E''/T} \frac{Q_{VR}}{A_{V''J''}} (2J' + 1)
\]

where \( v = 3568.6 \text{ cm}^{-1}, E'' = 0 \) (rotational energy of the lower level), \( Q_{VR} = 8 \), \( \Delta = 9.6 \text{ Hz} \) for the OH Q(1.5)1± transitions, and \( J' = 1.5 \). Assuming a temperature of 13K, \( S = 5 \times 10^{-19} \text{ cm} \). The peak absorption cross-section \( \sigma_0 \) is related to the integrated intensity \( S \) by:

\[
\sigma_0 = \frac{2S(\ln2)^{1/2}}{\pi^{1/2} (\Delta v)_{\text{FWHM}}}
\]

After substituting in \( (\Delta v)_{\text{FWHM}} = \) the observed linewidth of 200 MHz \((6.67 \times 10^{-3} \text{ cm}^{-1})\), one obtains \( \sigma_0 = 7 \times 10^{-17} \text{ cm}^2 \) for the \( v = 1-0 \) Q(1.5)1± transition of OH at 13K. The concentration of OH radicals can then be calculated from:

\[
\Delta I/I = \sigma_0 n L
\]

For a 7.5% absorption of the infrared light for the OH Q(1.5)1± transition with \( L = 16 \text{ cm} \) (corresponds to 16 passes of the infrared beam probing the 1 cm slit length), \( n \) is calculated to be \( 6.6 \times 10^{13} \text{ molecules/cm}^3 \). A comparison with the calculated density of \( 1.1 \times 10^{14} \text{ molecules/cm}^3 \) from Section 2.6.1 shows that the experimental radical concentration is 40% lower than expected.
The S/N ratio for allyl radical can now be calculated using the radical concentration from the OH calculations. Again assuming a rotational temperature of 7K for allyl radical, the percentage absorption is calculated to be $= 0.3\%$, which would result in a S/N ratio of $\approx 10$ with the current detection and averaging scheme (typically a 1% absorption gave a S/N ratio of 30). Multipassing will be necessary so that an optimum signal-to-noise ratio will be obtained for this larger radical. From the later experimental results discussed in Chapter 5, it was found that S/N typically increased by a factor of 4 with multipassing. With the current multipass arrangement, this would give a S/N ratio of $\approx 40$ for allyl radical.
CHAPTER 3
PULSED SUPERSONIC NOZZLE APPARATUS

3.1 DESIGN OF SUPERSONIC NOZZLE

3.1.1 Smalley Type

In selecting a supersonic nozzle source, several factors were considered. The motivation behind the requirements was to obtain optimal conditions for the production, cooling, and detection of the radicals. Two necessary features were a high gas output pulse and a slit orifice. Also required was a photolysis region inside the nozzle, with nozzle parts being impervious to extensive excimer laser degradation. With these needs in mind, the Smalley nozzle design was chosen, not only for its high gas output per pulse, but for its ease of adaptability to the experimental requirements.

The supersonic nozzle used in this work is an adaptation of the Smalley valve. The inside dimensions and working parts of the nozzle were Smalley designs, while the nozzle body and slit conversion changes were added to meet the current experimental needs. As shown in Figure 5, the nozzle is composed of an aluminum cylinder, with the inner section machined out to allow for a snug fit of all nozzle parts. The parts inside the valve consist of a poppet, poppet foot, poppet bearing, two solenoids, intermediate spacer, spring, adjustable tension rod, and a final spacer and
Diagram of the Smalley type valve with design changes converting the circular orifice to a slit. Typical valve operating conditions were: 20 Hz repetition rate and 40-60V nozzle driver voltage for pulsing the solenoids.
cap. The poppet and solenoid cans are machined out of magnetic silicon steel, the poppet bearing is made of oil impregnated bronze, and the remaining parts are constructed of aluminum or stainless steel. If acids or other corrosive chemicals are to be used, the bearing can be made out of aluminum in order to resist reaction, but oil impregnated bronze is preferable for smooth poppet action.

In order to have the ability to position the nozzle with respect to the infrared laser beam while under vacuum, it proved necessary to completely re-design the valve body. The aluminum cylinder body was machined with an o-ring finish so that the valve could move in and out of the vacuum chamber without breaking vacuum. It was also necessary to re-work the water cooling system and gas inlet for the nozzle. A separate piece containing both water and gas channels bolted onto the main nozzle body, and was made leak-tight by use of o-ring seals. This same piece also contained the 2 mm hole for the circular orifice and the o-ring (Parker size 004) for the poppet foot seal.

The valve is solenoid-actuated, releasing a gas pulse of controllable, variable duration. A current pulse through the top solenoid induces a magnetic field, which attracts the silicon steel poppet upwards, thus breaking the o-ring seal. A spacer between the two solenoids sets the maximum travel of the poppet to about .75 mm. The thickness of the spacer is very important, since the distance from the magnetic field affects the force attracting the poppet. After a variable delay, a current pulse flows through the lower solenoid inducing a magnetic field, which attracts the poppet downwards reseating it onto the o-ring seal. A spring-tension
rod combination is critical to the correct pulsing of the nozzle. A stainless steel spring fits through the center of the top solenoid resting upon the poppet. The adjustable spring tension rod, inserted into the nozzle body through a Cajon fitting for a leak tight seal, screws in through the cap and presses onto the spring. For best nozzle behavior, the tension rod should be set at a level where the exposed poppet with the cooling section off just starts to feel springy to the fingertip. After the nozzle is in operation, further adjustment of the rod is often necessary.

An electronic driver box was constructed according to Smalley group plans to pulse the nozzle solenoids. Using TTL monostable multivibrator chips, the open and close pulses, and the delay between the two pulses can be varied. These TTL pulses are amplified by MOSFETs (metal oxide semiconductor field effect transistors), which are able to carry the high current load (≈ 60A) required by the solenoids. Normally open and close pulses are set around 300-400 μsec, and the delay between pulses is usually varied between 300-700 μsec, depending on how long a gas pulse is desired. The solenoids are connected to the driver box via Ceramaseal beryllium-bronze high voltage connectors and torr-sealed nichrome wire feedthroughs. Inside the nozzle, solenoid leads insulated by spaghetti teflon are then attached to the nichrome feedthroughs using the same type of high voltage connectors.

Since the Smalley nozzle was equipped with a circular orifice, it is necessary to convert this 2 mm hole into a slit. This is accomplished by two pieces, an aluminum "transition" piece and a stainless steel straight slit piece, as shown in Figure 6. In going from a circular to a slit orifice, the
Figure 6

Slit conversion pieces consisting of "transition" and "collimation" sections. The "transition" piece begins with a (.082in)$^2$ square to accommodate the 2 mm circular orifice, and the square widens and flattens to give a slit 1 cm x .017". The final "collimation" piece is a straight slit, 1 cm x .016".
cross-sectional area of the additional pieces is kept constant so that properties of the expansion are not greatly altered. The purpose of the "transition" piece is to change the 2 mm hole into the slit. To do this, the side of the "transition" piece with the (.082in)$^2$ square is bolted onto the main nozzle body such that the 2 mm hole fits inside the square. This square section then narrows and widens, giving a slit 1 cm x .017". To further collimate the expansion, a final slit piece with dimensions 1 cm x .016" is bolted onto the "transition" piece. Since such narrow slits are desired, it was necessary to split the slit pieces into two separate halves so that machining could take place, and then the two halves were bolted together to form the slit. The "transition" piece was machined by milling at an angle, and the two halves for the final slit piece were ground straight across before being bolted together.

In our experience, the main problem with this Smalley type valve is that the solenoids generally last only 2-3 months. These short lifetimes result from the corrosive nature of some precursors perhaps augmented by mechanical vibrations of the solenoid assembly inside the nozzle. As a result of both corrosion and mechanical vibration, the enamel coating of the copper-magnet wire cracks and becomes exposed, leading to shorts to ground with the solenoid can.
3.1.2 Nesbitt Type

In the beginning of this project, two types of supersonic nozzle designs were considered, with the Smalley valve being chosen due to its flexibility and resistance to excimer laser damage. On the other hand, a Nesbitt slit valve\textsuperscript{15} seemed actually preferable because of its straight slit geometry. This valve was not chosen initially because an o-ring seal was directly exposed to the excimer laser, and it was feared that it would be destroyed by UV radiation from the excimer. However, after various experiments with the Smalley type valve, it was judged that this problem might have been overestimated, and the Nesbitt type slit was incorporated into the current valve design in an attempt to improve experimental results.

Let us briefly describe the Nesbitt nozzle. The valve is composed of four main components: the nozzle, nozzle holder, seal assembly, and the solenoid actuator. The nozzle holder, which initially provides the slit geometry, is electric discharge machined to give a knife-edged slot. The slot is sealed by a straight section of o-ring. To pulse the valve, a solenoid actuates the seal assembly, and a leaf spring then returns the seal to a closed position. The final nozzles, which are bolted to the other side of the slot, were initially slits 75-125 \( \mu \text{m} \) wide by 1.25 cm long.

As stated earlier, the main problem anticipated for using the Nesbitt valve for this work was the possible destruction of the sealing o-ring, since it would be directly exposed to excimer radiation in the experiment. This problem was circumvented independently by two design alterations: use of
a viton o-ring seal, which is more highly resistant to UV light, and change of photolysis geometry so that the o-ring is not exposed to the excimer laser. With this problem under control, efforts then concentrated on the inclusion of a Nesbitt type slit into the current valve design.

To convert over to the new slit design, it was found most efficient to redesign the cooling section piece. The design of this piece remained essentially the same as before, except that its center is drilled out so that interchangeable nozzles can be attached. The current cooling section design allows for interchangeable slits of up to 2 cm long. The slit piece was constructed out of stainless steel, with four guiding posts welded in place to prevent free rotation of the poppet foot and a small raised section for the lip. The purpose of this knife-edged lip is to aid in proper sealing of the o-ring, and it was formed after the 1 cm by .016" slot was electric discharge machined. Both the new and the older "pseudo" slit have the same dimensions. To make the o-ring seal, a rectangular poppet foot is constructed with a lengthwise groove so that an 1/8" o-ring would fit in snugly. The o-ring is stretched to fit in the groove, and a drop of glue applied to keep it from sliding. With these design changes, it proved fairly easy to convert the "pseudo" slit into a Nesbitt type slit.

Although the viton o-ring seal withstood excimer laser radiation better than buna rubber, the seal still has problems. After a day of running the nozzle hard, the seal must be replaced because the knife-edge cuts into the o-ring material. As a result of this abuse by the knife-edge coupled with a harsh chemical environment, the o-ring soon becomes brittle and does not seal properly. It is possible that some design flaw in the poppet and its foot
leads to the early destruction of the seal because the spring tension must be adjusted rather tightly in order for the poppet foot o-ring to seal against the knife-edged lip without leaking. The restoring force of the spring plus the magnetic field of the solenoid act together to "plunge" the poppet downward strongly, thus cutting into the o-ring. This seal problem seems to be less severe when the nozzle is pulsed at lower currents; the o-ring then lasts several days.

Since the Nesbitt type slit was constructed midway through the research, it is evaluated in later work. Testing and comparison of this slit with the "pseudo" slit is described in Section 5.3.2, and individual experiments with the new slit are discussed in Chapter 6.

3.2. DESIGN OF NOZZLE VACUUM CHAMBER

In designing the vacuum chamber for the nozzle, two main criteria had to be met: first, the chamber had to fit within the limited space available, and second, it had to easily accommodate the addition of multi-pass optics. With these requirements in mind, a plexiglass box with outside dimensions of 12" by 21" was constructed. The bottom and top of the box were open, with 1/8" o-ring grooves in the middle of both top and bottom surfaces. The walls of the box were 1" thick so that they would not "bow in" as a result of the roughly one ton force experienced upon evacuation. The bottom plate was constructed out of magnetic stainless steel so that optical mounts on magnetic chucks could be firmly positioned. Both the
bottom plate and the 1" thick aluminum top plate contained a small "lip" around the inside perimeter which fitted up against the walls of the plexiglass box. This was to add further rigidity to the walls when the box is put under vacuum. In order to keep the box from moving vertically as a result of o-ring compression, a 1/2" plexiglass lip was added along the bottom of the plexiglass box so that aluminum clamps could be placed every other inch. The box was bolted down onto the laser table while under vacuum so that the o-ring would remain compressed at atmospheric pressure as well. Permanent compression of the o-ring is a necessary measure, since the detectors are mounted onto the side of the box and any slight movement of the box would misalign them. Once the box was pumped down initially and the clamps bolted down, no misalignment problem has been found for subsequent evacuations.

For evacuation of the plexiglass box, it was decided that the largest pumping port possible was needed in order to have maximum pumping capabilities. The pump port on the plexiglass box was 3" in diameter matching the flange on the Rootes blower. Since heavy 3" copper pipe and brass fittings were used to construct the pump line to the blower, it was feared that large flanges bolted directly onto the box would stress and consequently strip the plexiglass threads. To prevent this potential problem, an additional plexiglass flange was fused leak-tight onto the box with methylene chloride so that the pump flange could then be safely bolted onto the box.

The Rootes blower was chosen as the pump for the supersonic nozzle apparatus because of its large throughput at 1 Torr. The blower used in
this experiment is a Leyboldt-Hereaus WA250 having a pumping speed of about 80 l/s at 1 Torr. A Precision rotary pump D-1500 with a pumping speed of 25 l/s backs the Rootes blower and is connected to the blower by 3\" copper pipe. With this pump combination, the throughput is about 80 Tl/s or 100 cc-atm/s at 1 Torr. Since data acquisition in kinetic spectroscopy is limited to 20 Hz, and the nozzle releases about 1 cc-atm per pulse, there is more than sufficient pumping reserve to keep the background pressure inside the box below 1 Torr.

In order to position the nozzle while under vacuum, a flange was designed so that the valve could be fairly easily moved in x, y, and z directions. The nozzle body slides through the center of the positioning flange and is mounted onto the side of the plexiglass box. This assembly is held in place by positioning screws fitting into sliding grooves. The inside of the positioning flange, which holds the valve body, has two separate o-ring grooves so that a dynamic seal can be made. This seal works well for moving the nozzle further in the box, but the opposite movement is somewhat more difficult. Since moving against the vacuum turned out to be a problem, often the box is opened to atmospheric pressure in order to set the nozzle position in this direction.
3.3 NOZZLE CHARACTERIZATION

3.3.1 H$_2$O

The goals of the initial nozzle tests were to characterize the properties of the Smalley type valve, commonly referred to in our lab as the "pseudo" slit. The most important goal was to first observe an infrared absorption; once a signal was observed, all other tests would then be possible. It was desirable to test the nozzle using a stable molecule with a known infrared spectrum; therefore, water, a fairly innocuous substance, was chosen. The nozzle properties to be explored were: S/N ratios and percentage absorption, linewidth, and rotational temperature. Other characteristics to be investigated were the rotational temperature as a function of distance from the slit and perpendicular vs. parallel probing of the slit.

The experimental set-up for the H$_2$O studies is shown in Figure 7. A single pass of a tunable, computer-controlled color center laser$^{16}$ probes the infrared absorption of water. A single Infrared Associates InSb detector then detects the change in absorption, and this current is converted into a voltage using a Judson preamplifier. The signal is then amplified using a homebuilt, x10 - x100 amplifier with a variable dc offset. After amplification, the signal is collected by a LeCroy model 2256AS transient digitizer and is then read into the LSI 11/23 computer. The transient digitizer is triggered by the valve pulse and requires a 50 $\Omega$, +5V TTL trigger input.
Experimental set-up for initial testing of the nozzle with H$_2$O. The H$_2$O pulse from the nozzle is probed by the color center laser, and the absorption signal is then detected by an Infrared Associates InSb detector. The resulting current from the detector is converted into a voltage with the Judson preamplifier, and the signal is then amplified before collection by the transient digitizer and storage into the DEC 11/23 computer. 

W = CaF$_2$ window  
L = plano-convex CaF$_2$ lens (f=10 cm)
In normal valve operation, the open and close pulses are 300 μsec in width, with the delay between pulses ranging from 300-700 μsec. The DC voltage from the electronic driver box is typically turned up to 40V. With this set of valve conditions and a helium backing pressure of 4-8 atm, pressure inside the vacuum chamber ranges from 30 to 100 mTorr with the Rootes blower operating. For the water absorption experiments, the optimal signal was found to be produced by passing helium through a pipe filled with water-soaked glass wool. The 4" long, 1/4" pipe is stuffed with glass wool which is then saturated with H2O. Excess water is blown out with compressed air in order to avoid flooding the nozzle. Helium pressure behind the nozzle is 50-100 psig. Because of these high backing pressures, it is necessary to place the water source far from the nozzle; otherwise, water is pushed up into the nozzle body, creating solenoid shorts.

The first tests of the valve concentrated on observing a H2O pulse absorption. Probing .5 cm downstream of the nozzle, the \( v_3 \ 0_{00} \leftarrow 1_{01} \) H2O line at 3732.1354 cm\(^{-1}\) was observed with a preamplified signal on the oscilloscope of 60 mV. As the chopped infrared beam was 300 mV, the corresponding absorption of the infrared for this water line was 20%. In comparison with the reference cell water lines, the same lines from the slit valve were approximately 1/3 the width of the room temperature lines. As shown in Figure 8, the FWHM of the 0_{00} \leftarrow 1_{01} line of water is 230 MHz wide. Although the peak width was narrower than the room temperature lines, it was not as narrow as expected. The step size of the laser was then decreased to see if the line width would become narrower, and the
The lower trace is a frequency scan over the \( v_3 \) 000 \( \leftarrow \) 101 transition of jet-cooled H\(_2\)O at 3732.1354 cm\(^{-1}\), illustrating linewidth narrowing in a supersonic expansion. The FWHM is \( \approx 230 \) MHz wide with 20 MHz laser steps and decreases to 170 MHz with 5 MHz laser steps. The upper trace is H\(_2\)O obtained from the room temperature reference cell. Note that the width of the reference cell 000 \( \leftarrow \) 101 line is \( \approx 3 \) times wider at FWHM than the jet-cooled line.
linewidth decreased to 170 MHz. The laser was scanned over a ground state line originating from J=2, but the transition was not observed. It appeared that these higher J levels were being cooled away in the jet, since only lines arising from the 1_{01} and 0_{00} levels were seen.

The main question before testing was whether or not the "pseudo" slit would indeed act as a slit source. One possibility was that the gas would not fill the entire slit and would remain centered through the slit as if it were a circular expansion. To test this idea, the valve was rotated 90° such that the slit was perpendicular to the infrared beam. The nozzle would then be moved up and down in order to check for complete filling of the slit. First probing through the center of the slit, the 0_{00} \leftarrow 1_{01} water line was again observed, and the signal as viewed on the scope was approximately five times weaker than the signal observed from the parallel slit position. Various slit regions were probed, including 1 mm above the slit, the edge of the slit, and 1/4 of the way down from the top. Understandably, the H_{2}O signal was weaker 1 mm above the slit. The signal at the edge of the slit was not quite as strong as at 1/4 cm from the top or in the middle, but there was little difference between the 1/4 cm from the top or the middle positions. As illustrated in Figure 9, these results confirmed that the "pseudo" slit was acting as a slit orifice in the sense that the gas was filling the slit area.

The frequency scan over the 0_{00} \leftarrow 1_{01} line revealed a mysterious doubling of the peak, as shown in Figure 10. In this figure, the two components are observed when the infrared beam probes the shock boundaries at the top and bottom of the expansion. The linewidth and
Probing perpendicularly the different regions of the "pseudo" slit expansion by scanning the laser frequency over H₂O absorptions. The $v_3\ 0_{00} \leftarrow 1_{01}$ transition of H₂O is being monitored at 1 mm above the slit edge, the slit edge, .25 cm below the slit edge, and the slit center. The H₂O absorptions are plotted on the same scale. The .25 cm below the slit edge absorption is much larger than that of the slit center, presumably because of H₂O clustering at the central position.
1 mm above slit edge

slit edge

.25 cm below slit edge

slit center
Doppler shifting of the $v_3 \ 0_{00} \leftarrow 1_{01}$ line of H$_2$O when the expansion is probed perpendicularly. The dip in the center of the absorption is most likely due to the formation of (H$_2$O)$_n$ clusters in the colder central part of the expansion.
\[ \nu_3 \ 0_{00} \leftarrow 1_{01} \]

Frequency (cm\(^{-1}\))

3732.14
lineshape are expected to be determined by the Doppler effect. In Figure 11, the relationship between the direction of propagation of the probe laser beam and the velocities in the jet is depicted. As a result of the range of molecular velocities along the direction of the probe beam, a wide linewidth is expected and calculations reveal that the expected lineshape should be flat-topped. Therefore, the decrease in infrared absorption in the middle of the peak is a curious feature of this frequency scan. At the center frequency, the infrared is probing the middle of the jet, the coldest, densest region of the expansion. Presumably the cold water molecules are clustering out in the form of \((\text{H}_2\text{O})_n\), thus leading to the decrease in absorption.

The rotational temperature of water was calculated as a function of distance from the infrared probe. To do this, the absorption intensities of the \(1_{11} \leftarrow 0_{00}\) and \(2_{20} \leftarrow 1_{11}\) \(\text{H}_2\text{O}\) transitions were monitored at 4 and 6 mm downstream from the slit exit, and then the rotational temperature was calculated by comparing the relative intensities of the two transitions using the following equation:

\[
I_1/I_2 = (S_1/S_2)\exp[-(E_1-E_2)/kT]
\]

By rearranging the equation, the temperature can be calculated from:

\[
T = \frac{(E_2-E_1)}{k \ln \left( \frac{I_1S_2}{I_2S_1} \right)}
\]

Here \(T\) is the temperature (K); \(E_2, S_2, I_2\) are the energy, rotational line
Diagram of the infrared probe interacting with molecular velocities in the perpendicular slit position. The molecules in the center of the expansion have no perpendicular velocity component, thus giving no Doppler shift, whereas molecules in the two shock boundaries have perpendicular velocity components to interact with the probe beam.
Infrared probe

Nozzle
strength, and relative intensity of the upper level, respectively; and 
\( E_1, S_1, I_1 \) are the same variables for the lower level. Substituting in the 
appropriate values, the rotational temperature at 4 mm was calculated to be 
23K, whereas the temperature at 6 mm downstream decreased to 16K.

3.3.2 \( \text{C}_2\text{H}_2 \)

Since the \( \text{H}_2\text{O} \) temperature in the jet was measured to be \( \approx 20\text{K} \), 
nozzle testing was continued with \( \text{C}_2\text{H}_2 \), a heavier molecule with more 
closely spaced rotational levels, in order to determine if the apparent high 
temperature is the result of decoupling of rotational and translational 
temperature arising because the rotational spacings in \( \text{H}_2\text{O} \) are much larger 
than the collisional energies downstream in the jet. If this is the case, 
lower rotational temperatures should be obtained with a molecule having 
much smaller rotational spacings. In searching for the lowest temperature 
achievable, precursor flow rates were varied, and the corresponding 
temperatures calculated in an attempt to determine the best seed ratios. 
The effect of the carrier gas on the linewidth was also investigated, using 
helium and argon as the backing gas. The valve was further characterized 
by removing the final slit plate and probing perpendicular and parallel to 
the infrared beam. Knowledge of these various properties served to 
increase understanding of the "pseudo" slit expansion and to add to the 
body of information concerning valve operational conditions.
The experimental set-up is similar to that used in the H$_2$O studies, however, several changes have been made. In the C$_2$H$_2$ studies and in all further work, a balanced detector scheme was used in order to reduce low frequency pump laser noise and to some degree, high frequency noise. Before the detector current enters the preamplifier, the detectors leads are wired such that one detector has a "positive" signal lead while the other has a "negative" one. With the currents of the two detectors thus opposed to one another, the two detector signals subtract. The noise is greatly reduced if the detector signals are made equal but of opposite amplitude. This balancing of the detector amplitudes is accomplished by attenuating the "signal" detector infrared light such that it matches the intensity of light on the "reference" detector.

The balanced detector apparatus is shown in Figure 12. In order to split the infrared to the two detectors, a 3° wedged ZnSe beamsplitter is used. Approximately 30% of the infrared is reflected off the ZnSe, which then is focussed into the reference detector using a 10 cm CaF$_2$ lens. The remaining 70% of the infrared goes to the nozzle chamber, where a single-pass mirror arrangement sends it in front of the nozzle and then to the signal detector, where it is first attenuated by a MgF$_2$ polarizer and then focussed onto the detector using another 10 cm CaF$_2$ lens. As illustrated in Figure 13, the subtracted signal from the two detectors goes to either a Judson or Infrared Associates preamplifier, is further amplified using a homebuilt x1-x10 amplifier with DC bias, and is then collected by the transient digitizer and stored in the computer.
Balanced detector scheme for C$_2$H$_2$ jet studies. 30% of the infrared beam goes to the reference detector with the remaining 70% going to the supersonic nozzle apparatus. B = 3° wedged ZnSe beamsplitter  L = plano-convex CaF$_2$ lens (f=10 cm)  L1 = plano-convex CaF$_2$ lens (f=100 cm)  W = CaF$_2$ window  P = MgF$_2$ polarizer
Rootes Blower

Det

L

P

Nozzle

Inlet Gas

W

IR beam
(Color Center laser)
Diagram of the electronic circuitry used in the balanced detector method. The subtracted signal from the reference and signal detectors is preamplified and converted into a voltage by either the Judson or Infrared Associates preamplifier. The signal is then further amplified before collection by the transient digitizer and storage into the computer.
The first work with C$_2$H$_2$ were studies of temperature vs. flow rate of C$_2$H$_2$ (or % seed of C$_2$H$_2$). The flow meter arrangement is shown in Figure 14. With the C$_2$H$_2$ tests, the total backing pressure available to the nozzle experiment was limited by the maximum allowed regulated pressure of the C$_2$H$_2$ cylinder, which was approximately 30 psig. For the flow rate experiments, the nozzle backing pressure was typically 1.5 atm, with the C$_2$H$_2$ flow rate varying from 5-50 ($\approx$ 3–30 cm$^3$/min) on the 150 mm scale of the Matheson 610A meter and the He flow remaining around 70/130 ($\approx$ 480 cm$^3$/min) on the 602 meter. The valve was located approximately 7 mm away from the infrared beam, and the pressure inside the vacuum chamber was 200 mTorr when the nozzle driver voltage was set to 40V. The rotational temperature was calculated by comparing the peak intensities of the v$_3$ R(0) and R(2) lines, which have the same nuclear spin symmetry$^{18}$. As the percentage precursor seed was increased, the rotational temperature appeared to decrease. This result seems contradictory to properties of supersonic expansions, because as the precursor is increased, the heat capacity of the system decreases, and higher rotational temperatures result. The apparently erroneous result could be due to experimental errors, such as gases not thoroughly mixed or saturation of amplified signal which would cut off peak intensities.

The rotational temperatures as a function of the probe distance downstream of the nozzle were explored as well. In these studies, the flow rate remained fairly constant with a nozzle backing pressure of 1.5 atm. The nozzle was placed 1, 11, and 15 mm upstream of the infrared beam. The temperatures corresponding to these distances were 7, 8, and 4K,
The flow meter arrangement for seeding $C_2H_2$ into the helium carrier gas. Typical backing pressures behind the acetylene and helium flow meters was 30 psig, which corresponds to the upper limit of the acetylene pressure regulator. $F = \text{flow meter}$  $N = \text{needle valve for fine pressure control}$  $S = \text{shut-off valve}$
respectively. The rotational temperature should decrease with increasing distance from the orifice as long as collisions continue downstream. Once energy is no longer exchanged between the precursor and the translationally cold carrier gas, the rotational temperature of the seed molecules reaches a plateau.

The final slit of the "pseudo" slit assembly was removed in order to determine its effectiveness. The nozzle was parallel to the infrared beam, at a distance 7 mm away. In a frequency scan over the R(0) line of acetylene, the linewidth was 550 MHz, definitely wider than linewidths obtained with the final slit. Apparently the final slit is necessary to collimate further the velocities of the gas particles, because the flaring geometry of the transition piece produces a spread of molecular velocities. The valve was rotated 90° so that filling of the transition slit piece could be checked as well. The detector signal on the scope remained essentially the same as the nozzle was moved down the slit. Even at this point in the slit assembly, it appears that the gas is completely filling the slit.

Additional studies were performed with C₂H₂, in which argon replaced helium as a carrier gas in order to determine the effect upon peak linewidth. The entire "pseudo" slit assembly was used and the nozzle was placed approximately 10 mm away from the laser probe. In comparison with the 190 MHz linewidths of C₂H₂ in helium, the corresponding peaks in argon were narrower, having a linewidth of 110 MHz as shown in Figure 15. The reason for this difference in broadening can be illustrated in the following equation:
Figure 15

Frequency scans of acetylene in the jet using helium and argon as the carrier gas. (a) R(0) ro-vibrational transition of acetylene with helium carrier gas, giving a linewidth of 190 MHz. (b) With argon carrier gas, the R(2) transition of acetylene was observed having a narrower linewidth of 110 MHz.
\[ \Delta v = \frac{v}{c} \left( \frac{2kT\ln 2}{m} \right)^{1/2} \]

The HWHM linewidth is proportional to \( m^{-1/2} \) and as the mass of the gas increases, the linewidth decreases. However, the Doppler-broadened linewidth equation does not fully explain the observed linewidth in the slit expansion, since wider linewidths are obtained than those expected.
CHAPTER 4
TEST CASE NH₂

4.1 EXPERIMENTAL SET-UP

The objective of this research was to explore the possibility of observing free radicals in a supersonic expansion. In order to determine the feasibility of this experiment, the radical NH₂ was used as a test case. NH₂ seemed an ideal choice since it is easily produced upon UV photolysis of ammonia, the precursor has a high vapor pressure, it does not react with ammonia, and its infrared spectrum is known.

The experimental set-up for the photolysis experiments was similar to that described in Section 3.3.2, with the addition of a UV grade CaF₂ window for allowing the excimer beam inside the vacuum chamber. For the initial experiments, the Smalley type valve with the "pseudo" slit was used. The valve was normally pulsed at a 20 Hz repetition rate, releasing a gas pulse of .1 to .5 cm³ atm with a duration of 300 to 700 μsec. The percentage of ammonia precursor seeded into the carrier gas varied from 2-7%, with a total backing pressure of 3-4 atm. The nozzle driver was normally set at the lower range of its operating voltage, 40V. When the delay between open and close pulses was set to give the optimum NH₃ signal, typical pressures in the vacuum chamber ranged from 200 to 300 mTorr.
As shown in Figure 16, the excimer is aimed directly into the nozzle. The unfocussed excimer is fired in the middle of the gas pulse, thus producing the desired radical species inside the throat of the slit. The hot radicals are then vibrationally and rotationally thermalized with the room temperature helium inside the slit. Upon exit from the orifice, the radicals experience rotational cooling in the expansion. The transient absorption of the radicals is probed 3-10 mm downstream from the orifice by a single pass of the color center laser. The transient signal is detected using the balanced detector scheme described in Section 3.3.2. The amplified signal is collected by the transient digitizer and then transmitted to the computer. The transient digitizer can be triggered by either the valve pulse or the excimer laser.

For simplicity, the final detection and amplification set-up will be described, since the electronics scheme underwent a few changes before the optimum and most convenient system was developed. For the excimer laser photolysis experiments, the fast Infrared Associates preamplifier was used in conjunction with the balanced detectors. The resulting signal is then further amplified with an ac-coupled x10 or x30 homebuilt amplifier. The ac-coupled amplifier eliminated the need to continually adjust the DC offset for the transient digitizer. The overall response time of the detection system has been determined as approximately 4 μsec by observing the decay of the emission signal from the red F₂ laser line. The timing circuitry for the valve, excimer laser, and transient digitizer is depicted in Figure 17. The valve is triggered on the rising edge of a 5V pulse from a one-shot, and this same pulse is variably delayed for the excimer firing. The
Experimental set-up for the NH$_3$ photolysis studies. The apparatus is essentially the same as in Figure 12, with the addition of an UV grade CaF$_2$ window for the excimer laser and slight changes in the detection circuitry. The Infrared Associates preamplifier was used with the balanced detectors, and the resulting signal was amplified by an ac-coupled x10 or x30 amplifier before collection by the transient digitizer. W = CaF$_2$ window L = plano-convex CaF$_2$ lens (f=10 cm)  P = MgF$_2$ polarizer
Figure 17

The timing circuitry for the jet experiment relating nozzle, excimer, and transient digitizer trigger pulses. The excimer laser external trigger requires a 10V, 50Ω input, and the transient digitizer is triggered by a 5V, 50Ω, 100 ns wide pulse.
Valve trigger
(≈ 40 ms duration)

Excimer trigger
(1 ms duration)

TD Stop trigger
(.1μs duration)

\[ T_d = 0.2 - 2 \text{ msec} \]
excimer laser and transient digitizer are triggered concurrently by this delayed pulse. The excimer external trigger requires a 10V, 50 Ω input whereas the transient digitizer is triggered by a 5V, 50 Ω input, 100 ns pulse. Pulses longer than 100 ns cause erratic triggering problems because the transient digitizer sometimes triggers off the falling edge of the +5V pulse. Shortening the pulse avoids erratic triggering of the transient digitizer; triggering off the rising or falling edge of a 100 ns pulse makes little difference in the μsec timescale experiment.

The method of mixing the precursor with the carrier gas is similar to the flow meter arrangement shown in Figure 14. The same backing pressure behind the metering valves is required to be greater than the downstream pressure for both the helium and precursor cylinders, or else there would be no flow of that component. Because the ammonia regulator has an upper limit of 40 psig, this put an upper limit to the stagnant pressure behind the nozzle. Therefore, experiments with higher than 3-4 atm. backing pressure were not performed in the NH₂ studies. Typical flow rates for ammonia are ≈ 6 cm³/min, which correspond to 15 on the 150 mm scale of the 610A flow meter. The helium flow rate is normally around 300 cm³/min, corresponding to glass ball reading of 110 on the 602 flow meter. These particular flow readings give a seeding ratio of 2 ± 1%, but higher ratios of up to 7% NH₃ were used as well.

Depending on the information required, the color center laser can be operated such that either temporal or spectral information of a given species can be obtained. Normally the laser is scanned over the frequency region of interest in order to locate the absorption. Once the laser is
centered on this absorption, a time scan is performed. Using the positions in time of either the maximum depletion of the precursor or the peak transient absorption from the time scan, transient digitizer points are set so that a spectrum can be collected while changing the laser frequency. In addition to the noise reduction of the balanced detectors scheme, the signal-to-noise ratio is further enhanced by subtracting points before the excimer flash and at the maximum signal. This subtraction aids in the reduction of any amplitude fluctuations that are incompletely eliminated by the balanced detectors.

4.2 NH$_3$ PHOTOLYSIS

As mentioned above, NH$_2$ seemed an almost ideal first choice for jet-cooled radical studies. Another point not previously mentioned is the fact that the precursor ro-vibrational spectrum is also known, and this is used to simplify setting photolysis conditions as will be explained shortly. The transient absorption of 2% NH$_3$ seeded in helium is shown in Figure 18. This signal was obtained by monitoring the time behavior of NH$_3$ molecules in the $v_1 1_0 ← 0_0$ state probed 3 mm downstream from the orifice by the color center laser. The dip near the middle of the pulse corresponds to a decrease in infrared absorption due to unfocussed 193 nm ArF photolysis of NH$_3$. The position of the excimer delay within the gas pulse is placed by observing the signal on an oscilloscope. This delay setting remains centered in the gas pulse unless flow conditions are changed
Transient absorption of NH$_3$ $v_1 \ 1_0 \leftarrow 0_0$ observed in the supersonic expansion. The infrared probe is $\approx 3$ mm from the slit orifice. 2% NH$_3$ is seeded into helium, with a backing pressure $\approx 3.7$ atm. The sharp decrease in absorption in the middle of the pulse is due to NH$_3$ photolysis by $\approx 100$ mJ unfocussed ArF. The NH$_3$ peak absorption is $\approx 5\%$ of the infrared beam, and the precursor depletion is about 40% of the total NH$_3$ absorption.
NH₃ Pulse

$\nu_1 \rightarrow \rightarrow 0_0$

Time (µsec)
greatly. The peak absorption of NH$_3$ in Figure 18 is approximately 5% of the infrared beam, and the depletion of the precursor corresponds to almost 40% of the total NH$_3$ signal.

### 4.3 TIME BEHAVIOR OF NH$_2$

Figure 19a shows the expanded NH$_3$ depletion signal as viewed immediately after the excimer flash with the transient digitizer set for 50 µsec full scale. The infrared absorptions displayed in figure 19b and figure 19c are the NH$_2$ $v_1 \ 2_{20} \rightarrow 1_{11}, 5/2 \rightarrow 3/2$ and $1_{11} \rightarrow 0_{00}, 3/2 \rightarrow 1/2$ ro-vibrational lines, respectively. The peak of the ground rotational NH$_2$ absorption appears approximately 1 µsec after the maximum of the NH$_3$ depletion. The peak absorption of the excited rotational level of NH$_2$ reaches a maximum about .5 µsec earlier than the absorption of the ground state level.

In Figures 19b and 19c, an upward spike can be seen. This was unrelated to infrared laser probe wavelength or precursor used and appears to be due to infrared luminescence from the excimer laser. The detector response in relation to the near delta function excimer flash results in a sharply rising spike. The true detector response of 4 µsec is reflected in the onset of the NH$_3$ depletion signal. The signal shape arises from the convolution of an exponential decay with a step function. There are several possible reasons for not observing the excimer spike in the NH$_3$ depletion: the spike signal is in the same direction as the depletion signal,
Comparison of time behavior of the expanded NH₃ depletion and the NH₂ absorption signals with the same conditions as in Figure 18. (a) Depletion in infrared absorption of transient NH₃. The maximum depletion point corresponds to the time expected for the gas to travel from inside the slit to the infrared probe. (b) NH₂ transient infrared absorption $v_1 2_{20} \leftarrow 1_{11}, 5/2 \leftarrow 3/2$ under the same conditions as (a). (c) NH₂ transient infrared absorption $v_1 1_{11} \leftarrow 0_{00}, 3/2 \leftarrow 1/2$. The peak signal corresponds to $\approx 1\%$ absorption of the infrared. The peak absorption occurs about 1 μsec later than the NH₃ depletion and 0.5 μsec later than in (b) due to better cooling of NH₂ formed in the back of the slit.
the depletion is much larger than the spike, and the depletion occurs within several nanoseconds of the spike whereas the NH$_2$ absorption signals are delayed several μsec.

Upon firing of the excimer, the NH$_3$ absorption should show an immediate depletion. However, due to the detector response of 4 μsec, the NH$_3$ depletion is more gradual and looks like the signal expected for a step function shape. This signal shape arises from the convolution of an exponential decay to a new level. Although the depletion agrees with the predicted shape, it is not certain that the observed onset time of the decrease of NH$_3$ completely matches the detector response. If a final expected beam velocity of 1.7 x 10$^5$ cm/s is used in calculations, the observed maximum depletion in time corresponds to gas photolyzed about 1 mm inside the final slit.

The maximum in the $1_{11} \leftarrow 0_{00}$ NH$_2$ signal is correlated with NH$_3$ photolyzed about 3 mm inside the slit. The NH$_2$ produced upon photolysis is rotationally "hot"; collisions relax it into the state being probed. NH$_2$ formed further inside the nozzle will experience more collisions and be more cooled before reaching the infrared beam. Therefore, it is reasonable that the peak of the $2_{20} \leftarrow 1_{11}$ transition occurs before the $1_{11} \leftarrow 0_{00}$ maximum, because the $1_{11}, 3/2$ level will lose population to the $0_{00}$ level upon further cooling.
4.4 TEMPERATURE MEASUREMENT

In order to investigate the rotational temperatures obtainable under the photolysis conditions, the dependence of the signal on seeding ratio and probe distance was explored. By frequency scans over several NH$_2$ transitions, rotational temperatures were obtained from comparisons of the relative intensities of transitions arising from ground and excited rotational states. Figure 20 shows such a frequency scan which includes both the ground state line $v_1 \ 1_{11} \leftarrow 0_{00}, \ 3/2 \leftarrow 1/2$ and an excited rotational state $v_1 \ 2_{20} \leftarrow 2_{11}, \ 3/2 \leftarrow 3/2$. For the purpose of calculating rotational temperature, $v_1 \ 1_{11} \leftarrow 0_{00}, \ 3/2 \leftarrow 1/2$ and $v_1 \ 2_{20} \leftarrow 1_{11}, \ 5/2 \leftarrow 3/2$ (not shown in this figure) transitions were compared. For 2% NH$_3$ in helium, several comparisons using both the peak absorption values of time and frequency scans gave a temperature of 25 ± 5K.

Figure 20 illustrates the temperature dependence of the expansion upon the seeding ratio of precursor. Figure 20a shows a frequency scan with 7% NH$_3$ in helium in which the excited rotational state $v_1 \ 2_{20} \leftarrow 2_{11}, \ 3/2 \leftarrow 3/2$ is clearly observable. This rotational level is 83.741 cm$^{-1}$ above $0_{00}$, and comparison of the relative intensities of the two lines of Figure 20a resulted in a temperature of about 80K. When the NH$_3$ dilution was decreased to 2%, this line was too weak to be discerned in Figure 20b, since the temperature is now 25K. Rotational temperature decreases as the NH$_3$ is diluted with helium. This effect is not surprising since a higher seeding ratio results in the decreased $\gamma = (C_p/C_v)$ of the gas mixture. With a
Figure 20

Frequency scan containing two NH$_2$ v$_1$ transitions, $1_{11} \leftarrow 0_{00}$, 3/2 $\leftarrow$ 1/2 and $2_{20} \leftarrow 2_{11}$, 3/2 $\leftarrow$ 3/2. (a) 7% NH$_3$ seeded in helium. The measured rotational temperature for this % seed is about 80K. (b) 2% NH$_3$ in helium. The rotational temperature for this seeding is about 25K, using the NH$_2$ $2_{20} \leftarrow 1_{11}$, 5/2 $\leftarrow$ 3/2 transition from another scan for temperature determination. Scans (a) and (b) are plotted on the same scale.
**NH$_2$**

a

$2_2^0 \leftarrow 2_{11}, 3/2 \leftarrow 3/2$

$1_{11} \leftarrow 0_{00}, 3/2 \leftarrow 1/2$

b

7% NH$_3$ in He
T=80K

2% NH$_3$ in He
T=25K

---

**Frequency (cm$^{-1}$)**
greater percentage of NH₃, the density of potential UV absorbers increases as well, resulting in greater energy deposition in the gas. Thus a gas mixture containing a larger percentage of NH₃ is at a higher temperature before expansion and is cooled less effectively by supersonic expansion.

Many temperature measurements were made on NH₂ with this arrangement, and as the lowest temperature observed was 25K, the possibility of rotational and translational temperature divergence was explored. Because the rotational constants of NH₂ are large, it seems plausible that weak collisions with cold helium would be ineffective in relaxing NH₂. Therefore, the possibility of rotational and translational temperature divergence was explored. The NH₂ temperature was measured at distances 3 and 10 mm downstream of the nozzle. Using 2% NH₃ in helium and comparing the v₁ l₁₁ ← 0₀₀, 3/2 ← 1/2 and 2_2₀ ← 1₁₁, 5/2 ← 3/2 relative intensities gave a temperature of 25K at both distances. This result suggests that the rotational and translational temperatures are in fact diverging.

4.5 DISCUSSION

The basic purpose of this experiment was to explore the possibility of observing free radicals in a jet. These results show that radicals can be created, cooled, and detected by direct infrared absorption in a supersonic expansion. Free radicals are not only observable in the jet, but they can be seen at signal-to-noise sufficient for spectroscopic studies. A 1%
absorption on the $v_1 1_{11} \leftarrow 0_{00}, 3/2 \leftarrow 1/2$ transition of NH$_2$ gave a S/N ratio of about 30. Although lower temperatures of 10K or lower are desired for studies of larger radicals, a temperature of 25K is an encouraging starting point, since improvements can be hoped for from efforts to reduce the temperature. Overall, the prospects of applying this technique to the spectroscopic study of larger radicals are excellent.

NH$_2$ falls a little short of the test radical ideal because of its widely spaced rotational levels which set a limit on the lowest attainable temperature in the jet. In a comparison study with H$_2$O, temperature measurements using the same pair of rotational transitions as in the NH$_2$ experiments gave a similar temperature of 20K. Both NH$_2$ and H$_2$O differ from the 5K temperature obtained for acetylene; it is possible that the rotational and translational temperatures are diverging such that rotational excitation is "frozen in" for these species.

When the internal energy gaps are larger than the energy of collisions, collisions are not efficient in converting internal energy into translation. As an example, the lowest excited rotational level of NH$_2$ having the same nuclear spin symmetry as the ground $0_{00}, 1/2$ level is the $1_{11}, 3/2$ level, which is 31.775 cm$^{-1}$ higher. For translational temperatures less than 45.7K (the temperature equivalent of 31.8 cm$^{-1}$), the rotational temperature is expected to be decoupled from the translational temperature. Unfortunately, there is no convenient way to measure the translational temperature in these experiments, but the translational temperature should decrease with increasing distance from the slit orifice. As mentioned earlier, the NH$_2$ rotational temperature was observed to be
the same at 3 and 10 mm from the nozzle, thus indicating that the temperature was independent of the distance downstream. Therefore, it seems possible that rotational excitation is "frozen in" for this light radical, which would explain the high temperatures. Because larger radicals with more closely spaced rotational levels would experience divergence between the rotational and translational energies at lower temperatures than that of NH$_2$, lower rotational temperatures should be obtainable for these species.

Although the "freezing in" of rotational excitation seems a plausible explanation for the higher rotational temperatures observed for NH$_2$ and H$_2$O, there is another possibility. The cooling of the rotational energies takes place in the expansion, where initially there are many collisions with the translationally cold helium atoms. If part of this expansion process were to occur early in the nozzle, i.e. inside the slit sections or at the poppet, it is possible that the gas is already cold (≈100K) at the point of photolysis. As the temperature jump imparted by the photolysis will be the same for gas at 100K and 300K, there would be less expansion available to remove this photolysis heating in the early expansion case. Since it was feared that possible early expansion was limiting the temperature, this early expansion idea is investigated by comparison with an improved nozzle design, as discussed in Chapter 5.

Another potential problem is heating of the gas stream by the photolysis or heating of the nozzle by the photolysis laser. As we shall see this does appear to be a problem with NH$_2$. With higher backing pressures, the heat capacity of the gas is increased, but the photolysis energy deposition remains the same. Thus, the expansion starts from a
lower temperature due to the thermalization process with increased carrier heat capacity, and consequently lower temperatures might be obtained in the expansion. Also, higher backing pressures continue cooling collisions further downstream, and should therefore result in a lower temperature. With our current pumping system, more intense pulses are possible, and future experiments using backing pressures of 10 atm or more are described in Chapters 5 and 6.

Several experimental improvements have been suggested in order to reduce the rotational temperature, but changes can be made to increase signal-to-noise as well. In these initial experiments, the effective absorption pathlength is 1 cm, the length of the slit. The pathlength can be increased by using a longer slit and multipassing the infrared beam. The S/N ratios should improve by a factor of 20 by implementing these refinements. Improved signal-to-noise using a 2 cm slit and a multipass White cell are detailed in Chapter 5.
5.1 MULTIPASS WHITE CELL

Originally, the slit nozzle was chosen over the pinhole orifice for its longer pathlength. An additional advantage is that the slit geometry lends itself quite well to multipassing, which is needed for increased detection sensitivity. In the selection of the multipass system, an important criterion was that the multiple infrared beams be aligned with the direction of the slit. As was demonstrated in Chapter 3, the linewidths with the laser beam propagating along the slit direction is much smaller than when it propagates perpendicular to the slit direction. Since narrow linewidths of around 100-200 MHz were observed with the laser propagating along the slit, a calculation was made determining the angle from a central perpendicular of the direction of propagation corresponding to this linewidth.

Assuming the velocity of molecules in the jet is $1.4 \times 10^5$ cm/s, the Doppler shift for moving off parallelism with the nozzle face but still parallel to the slit is given by:

$$
\Delta v = \frac{(v/c)v}{c} = \frac{(v/c) \cos \theta v}{c}
$$

$$
\cos \theta = \frac{(c/v) (\Delta v/v)}{c}
$$

$$
\cos \theta = \frac{(3 \times 10^{10} \text{ cm/s} / 1.4 \times 10^5 \text{ cm/s})}{3600 \text{ cm}^{-1} \times \Delta v}
$$
For $\Delta v = 60$ MHz or equivalently $2 \times 10^{-3}$ cm$^{-1}$, $\theta = 83.2^\circ$. The angle of the infrared beam can be up to $7^\circ$ off the perpendicular axis, and maintain a shift of 60 MHz, thus giving a minimum linewidth of 120 MHz.

The White cell arrangement is shown in Figure 21. It consists of two $f = 20$ cm plano-concave gold-coated mirrors separated by their radius of curvature, i.e. the two mirrors are 40 cm apart. Two 1" pyrex mirror substrates were individually cut before coating to produce a notched and two "D" pieces. The notch mirror was cut out to leave a .5" center section. For mode-matching into the White cell, the infrared beam is focussed at the notched mirror. D-mirrors are kinematically mounted on the side of the plexiglass vacuum chamber. After a number of infrared passes, the signal beam is attenuated by the polarizer and focussed onto the detector as in the single-pass experimental set-up. The signal and reference detectors are balanced by the polarizer as in the balanced detector scheme described in Chapter 4, using the same electronic circuitry.

A comparison of signal-to-noise of the single pass and multipass set-up is shown in the frequency scans of Figure 22, which use methanol seeded in helium. The experimental conditions for the single and multipass arrangements were similar (high pressure helium mixing cylinder regulating the backing pressure behind the nozzle to 2-2.5 atm). As seen in Figure 22b, the S/N ratio for the single-pass methanol scan is about 8 for the $QR_0(0)$ A absorption, whereas in Figure 22a, the S/N ratio for the multipass with 12 passes of the infrared beam is $\approx 72$. For this spectrum, the signal-to-noise improvement is 25% lower than expected. Signal-to-noise has also been compared for NH$_2$ between single and multipass. A
Figure 21

Addition of the multipass White cell to the supersonic nozzle apparatus. The infrared beam was normally passed through the supersonic expansion 16-20 times. $W = \text{CaF}_2$ window $M = \text{White cell mirrors}$ $P = \text{MgF}_2$ polarizer $L = \text{plano-convex lens (f=10 cm)}$ $L_2 = \text{plano-convex lens (f=10 cm)}$
Comparison of jet-cooled methanol spectra using single pass and multipass infrared beam. 12 passes of the infrared beam gives a S/N ratio of 72 for (a) whereas a single pass of the infrared results in a S/N ratio of 8 for (b).
Frequency (cm$^{-1}$)
S/N ratio of 30 was observed for the single-pass experiments; the ratio increased to 140 with the White cell. In this case, the expected S/N ratio for 16 passes of the infrared beam would be \( \approx 480 \), but instead the result is a factor of 3 too low. The 30x amplifier saturated for amplified signals of \( .5 \text{ V} \), so it is possible that the peak of the NH\(_2\) signal was cut off, resulting in a decreased S/N ratio.

5.2 COMPARISON OF PHOTOLYSIS GEOMETRIES

In order to determine if firing the excimer directly into the nozzle was limiting the lowest ultimate temperature because of nozzle heating, the photolysis geometry was changed to investigate this possibility. Since it was deemed still desirable to fire the excimer inside the thermalization region, the final slit piece is replaced with a glass slit, which also serves as a window for the excimer beam. In this alternate photolysis arrangement, the excimer laser is directed at 90° such that the beam is perpendicular to the plane of the slit and no longer fires directly inside the nozzle. To make this possible, a hole was cut in the aluminum lid of the vacuum chamber for the placement of the excimer CaF\(_2\) window, and an UV mirror was mounted to reflect the excimer inside the chamber. The glass slit is composed of two Dynasil VUV grade fused silica 1.25" x 5 mm pieces with the slit width determined by aluminum shims sandwiched between them. With this assembly, the width of the glass slit piece is the same as with the previous final slit section, and the width and length of the glass slit can be
varied by use of appropriate shims. The glass slit was attached originally

to the 2 cm transition slit piece by Torr seal; a later version used an

aluminum mount for this purpose. The new photolysis geometry

arrangement is diagrammed in Figure 23.

The excimer could be focussed in the middle of the glass slit, or
depending on the experimental conditions desired, the focus was either
moved down the slit or removed entirely. The new photolysis set-up was
first evaluated with NH₂, using a 1% mix of NH₃ in argon. The rotational
temperature obtained by intensity comparisons of the ro-vibrational
transitions \( v_1 \rightarrow 0_00, 3/2 \leftarrow 1/2 \) and \( 220 \leftarrow 1_11, 5/2 \leftarrow 3/2 \) was 13K. This result seems to contradict the suggestion previously put forward of
rotational and translational divergence, and further complicating evidence
will be discussed in Section 5.3.2.

The spectrum of a heavier molecule, t-nitrous acid, was explored with
the 90° photolysis set-up. t-HONO was produced by photolysis of nitric
acid seeded into 8 atm of helium. Previous production of t-HONO from
photolysis inside the nozzle yielded a rotational temperature of 25-35K,
which is high for a large molecule. The same photolysis was again
performed by focussing the excimer beam in the center of the glass slit,
and temperatures obtained for this test were 10K. The new spectrum of t-
HONO, shown in Figure 24, clearly appears colder in the comparison
between the 25-35K and 10K spectra.

From these studies, it can be concluded that the change in photolysis
geometry reduces the rotational temperature. Apparently firing straight
into the throat of the nozzle heats the nozzle itself, consequently warming
Figure 23

New 90° photolysis geometry in which the excimer beam (focussed or unfocussed) is directed perpendicularly to the dynasil glass slit such that photolysis occurs in the thermalization region of the slit. This geometry has the advantage in that no metal nozzle parts are heated and temperatures of species produced by photolysis are colder.
Multiple reflection cell for infrared beam

Excimer beam

Dynasil glass slit plates

Nozzle body
Comparison of t-nitrous acid spectra observed in the supersonic expansion by photolysis of .5-.7% fuming HNO$_3$ seeded into either argon or helium. (a) The excimer was shooting directly into the bore of the 2 cm "pseudo" slit, giving a rotational temperature of 25-35K. (b) When the excimer was directed perpendicularly into the dynasil glass slit, a lower rotational temperature of 10K was obtained.

Figure 24
$v_1$ t-HONO

Frequency (cm$^{-1}$)
the gases in the thermalization region. With the expansion beginning initially from a higher temperature, the lowest temperature attained is higher. Thus, the glass slit is a positive step towards rotational temperature reduction; an additional evaluation of its capabilities will be presented in Chapter 6.

5.3 SLIT DESIGN CHANGES

5.3.1 Longer "Pseudo" Slit

In addition to multipassing the infrared beam, a longer slit was also constructed in order to increase signal-to-noise. The new slit was 2 cm long by .008" wide, giving the same cross-sectional area as the 1 cm slit. The construction of this 2 cm slit was essentially the same as that of the previous 1 cm "pseudo" slit, with the design differing only in the final dimensions. The 2 cm transition slit piece was followed by either a 5 mm or 10 mm thick slit extension piece. Since it had been observed that the final slit section of the original "pseudo" slit greatly aided in the reduction of Doppler shifting, the 10 mm slit piece was tested with the new slit to see if further reduction in linewidths was possible.

Initial tests of the 2 cm slit were performed without the multi-pass set-up. With nearly the same seeding ratio of ammonia in helium, the NH$_3$ signal for the 1 cm and 2 cm slits was compared. The signal without amplification was 100 mV for both slits; however, the laser power had dropped by $\approx 30\%$ at the time of the 2 cm version test. Moreover, for the
2 cm slit, the %NH₃ was higher by around 1%, which could also attribute to the discrepancy since the best cooling and consequently maximum signal would not be obtained.

The 2 cm slit was also tested with methanol spectroscopic studies, and using argon as the carrier gas, linewidths of 200 MHz were obtained. Normally linewidths in argon were 110-150 MHz for C₂H₂. When both slit plates were added, giving a total straight slit section of 1.5 cm, the signal-to-noise was very poor and the linewidth was still 230 MHz.

Later tests involving the 2 cm slit with 1 cm wide final slit piece and the 1 cm slit with 5 mm wide final slit section gave similar S/N ratios. For the studies of t-nitrous acid with the addition of the White cell, a S/N of 5 was obtained for both slits. The linewidth obtained for t-HONO using the 2 cm slit with 1 cm wide collimation slit was 180 MHz. With the 2 cm slit, the probe beam was 1.5 cm downstream whereas the 1 cm slit was located 2 cm from the infrared. When the 2 cm slit with the 5 mm extension piece was tested at the same probe distance, the S/N of the same t-nitrous acid line increased to 8. Thus, an increase by nearly a factor of two was observed between the 2 cm and 1 cm slit.

From these tests, the new slit appears to be some improvement over the 1 cm slit. The t-HONO tests demonstrated that almost a factor of two could be gained in signal-to-noise by using the 2 cm slit with the 5 mm final slit piece. The earlier tests with NH₃ are not regarded as valid since the precursor seed differed by about 1%; moreover, the color center laser power had decreased at the time the 2 cm slit measurement was made. However, the increased collimation region of the 2 cm slit with 5 and 10
mm wide extension pieces seemed to have no effect on the linewidth, and use of both extension pieces to give a 1.5 cm collimation slit gave a very poor S/N ratio for the methanol spectrum.

5.3.2 Nesbitt Type Slit

The Nesbitt type slit has been previously described in Section 3.1.2. This slit design was developed in an attempt to reduce absorption linewidths and rotational temperature for species observed in the expansion. Several comparison tests of the Nesbitt type slit were performed, using methanol, NH$_2$, and NO as the species probed. OH was also tested with the new nozzle, however those studies will be presented in Section 6.2.1.

To test the nozzle without photolysis, part of the methanol spectrum was re-scanned for comparison. As shown in Figure 25b, the methanol spectrum is much weaker and appears colder. It is possible that the weak signal limits observation of higher rotational transitions. Clusters in the form (CH$_3$OH)$_n$ may also be the reason for weak methanol absorptions. The backing pressure of 3 atm was not changed to see if the methanol absorptions would become stronger. For both frequency scans involving the two different slits, the seeding ratio of methanol in helium was initially 0.5%, and the multipass White cell was used as well.

Following unfocussed excimer photolysis of 1% NH$_3$ in helium, the NH$_2$ temperature was $26 \pm 5$ K with the Nesbitt type slit, which was within
Methanol spectra obtained in the 2 cm "pseudo" and 1 cm Nesbitt type slit expansions by multipass infrared probing. For both experiments, a .5% seed mixture was made by adding 100 ml of methanol to a small gas cylinder and pressurizing it to 23 atm with helium. (a) 9K methanol spectrum observed in the "pseudo" slit expansion. (b) Weaker and possibly colder methanol spectrum obtained in the Nesbitt type slit expansion.
Frequency (cm\(^{-1}\))
experimental error of the previously observed NH$_2$ rotational temperature of the "pseudo" slit. In this experiment, the glass slit was bolted onto the new slit so that the excimer laser could be fired from above and photolyze the precursor somewhere in the center of the glass pieces. When the excimer laser was focused in the middle of the glass slit, a rotational temperature of $23 \pm 5$K was obtained for NH$_2$. These temperature results appear to support the idea of rotational and translational temperature divergence, since heating of the nozzle body itself is not possible when the excimer fires into the glass slit. However, the temperature results of the Nesbitt type valve with the glass slit seem to contradict an earlier "pseudo" slit rotational temperature, since 13K was obtained by firing inside the glass slit. Unlike the methanol spectrum, good signal-to-noise of $\approx 140$ was observed for the $v_1 l_{11} \leftrightarrow 0_{00}, 1.5 \leftrightarrow .5$ transition of NH$_2$, as shown in Figure 26. The linewidth for the $v_1 l_{11} \leftrightarrow 0_{00}, .5 \leftrightarrow .5$ transition of NH$_2$ was 240 MHz, which was a little higher than the 180-200 MHz linewidths observed with the "pseudo" slit.

Since the NH$_2$ temperature was higher due to possible rotational energy divergence, it was desirable to measure the rotational temperature of a larger radical produced upon photolysis. For this purpose, NO$_2$ was chosen as a precursor for NO, and a 1% mix of NO$_2$ in helium was made. The Nesbitt type slit and the 2 cm "pseudo" slit, each with individual window slit attachments, were compared consecutively to determine temperature characteristics. With the new slit, the NO rotational temperature using the $v = 2-0 R_1(.5)$ and $R_1(1.5)$ transitions$^{22}$ was 13K, whereas the temperature for the 2 cm "pseudo" slit was 11K for the same
Observation of NH$_2$ v$_1$ ro-vibrational transitions in the expansion of the Nesbitt type slit with dynasil glass slit. The 90° photolysis geometry was used to photolyze the 1% NH$_3$ in helium mixture inside the thermalization region of the glass slit. A rotational temperature of 26K was obtained. S/N ratio was 140 for the v$_1$ 1$\rightarrow$ 0$_{00}$, 3/2 $\rightarrow$ 1/2 transition of NH$_2$. This transition linewidth appears fatter due to a laser scanning problem. The FWHM linewidth of the NH$_2$ v$_1$ 1$\rightarrow$ 0$_{00}$, 1/2 $\rightarrow$ 1/2 transition was 240 MHz.
$1_{11} \leftarrow 0_{00}, 1.5 \leftarrow .5$

$1_{11} \leftarrow 0_{00}, .5 \leftarrow .5$

Frequency (cm$^{-1}$)
Considering experimental error, the rotational temperatures obtained in the "pseudo" slit and Nesbitt type slit expansions are essentially the same.

Overall, these results show that the Nesbitt type slit and "pseudo" slit are behaving comparably; it is somewhat of a disappointment that better linewidths and signal-to-noise were not achieved with the new slit design. Nesbitt observes 50 MHz linewidths with argon as a carrier gas, and these values are limited by the probe laser linewidth. The discrepancy may be partially accounted for by recognizing that Nesbitt's 75 μm wide, 2 cm long slit comes closer to the infinitely long slit, thin width ideal upon which slit nozzle properties and calculations are based upon.

5.4 NOISE MEASUREMENTS

During the course of the jet-cooled spectroscopy experiments, noise levels were measured to see if improvements could be made in the existing detection set-up. The normal detection scheme consists of balanced Infrared Associates detectors used in conjunction with the fast Infrared Associates preamplifier. When observing the detector signal on the scope, it is found that the high frequency noise remains essentially the same with the laser on the detector or blocked. This high frequency noise is on the order of 1 mV, which is equivalent to a .05% absorption of the infrared assuming 2 V chopped laser power. It appears that the limiting noise in this experiment is that from the detector. This observation contradicts
earlier kinetic spectroscopy work in which signal noise was a factor of 2 or 3 greater than detector noise, even after balancing the detectors.\textsuperscript{24}

Noise levels were further investigated in time and frequency scans in which signals for laser on and off were compared. In the single-shot, 50 $\mu$sec time scans of Figure 27, it can be seen that the high frequency noise does not differ when the laser is blocked or on the detector. Modulation of the laser output is obvious when the dither is applied to the intra-cavity etalon. In the frequency scans, the averaged signal appears noisier when the laser is on, as illustrated in Figure 28. The reason for this increased noise may be due to averages taken on different slopes of the laser output; the balanced detector scheme considerably reduces low frequency noise from the krypton ion pump laser, but additional noise is possibly introduced by the dithering of the laser output.

At this point, an explanation for the noise results is unclear. The detector-limited noise is a mysterious problem, in light of previous kinetic spectroscopy results. One possibility is that the apparent detector-limited noise may be related to the preamplifier. Further testing of the detectors and detection electronics is necessary in order to understand and correct the problem.
Figure 27

Comparison of noise levels for color center laser blocked and on the detector using single-shot, 50 μsec time scans. a) Noise level with detector blocked, valve and excimer laser are not running. b) Laser on detector with valve, excimer laser, and etalon dither not in operation. c) Laser on detector with etalon dither on, valve and excimer laser not operating. There is little difference in the magnitude of the signals for laser blocked or on the detector.
Figure 28

Frequency scans comparing noise levels for color center laser blocked and on the detector.  

a) Noise level for laser blocked, valve and excimer laser not operating.  
b) The noise increases when the laser is scanned with infrared light on the detector. The valve and excimer laser are not running.  
c) Noise level for laser on, valve and excimer laser running. It is difficult to determine whether operation of the valve increases the noise level in c).
6.1 INTRODUCTION

The jet-cooled infrared kinetic spectroscopy technique was found to be successful in the production, cooling, and detection of small free radicals in the jet. Since small radicals could be observed with sufficient signal-to-noise for spectroscopic studies, the next step in this research was to extend the jet-cooling technique to the study of larger radicals. Extension of this method to the observation of larger species required improvements in sensitivity described in the last chapter. For the following experiments, the experimental set-up was essentially the same as described in Chapter 4, with the addition of the multipass infrared beam arrangement. Since temperatures of <10K were desired for large radicals, different slits were tested, and the photolysis geometry was changed in an attempt to lower the temperature. The results of these two changes will be discussed in the individual experiments.

In the following spectroscopic studies, a wide range of potential radical precursors were investigated which required various means of precursor mixing and flexibility in the gas handling system. The selection of a suitable precursor was often nontrivial, as several properties had to be considered. An important and often limiting factor was the vapor pressure of the precursor, since at least 20 Torr was necessary for sufficient
concentration in the carrier gas. The high resolution infrared spectrum of many of the precursors was unknown, which created difficulties in setting the excimer firing to the middle of the pulse. Ordinarily the precursor fluoresced when the excimer was fired into the pulse, so the excimer delay could be set visually by observing the fluorescence as the excimer firing was varied over the gas pulse.

Another problem was that some of the most promising precursors are quite toxic, and methods of mixing could lead to possible exposure in the lab. Additionally, the photochemistry of many precursors was unknown or questionable, thus the production of the desired radical was not always ensured. Often the UV absorption cross-sections at 193 nm could not be located in the literature.

Although jet-cooled infrared spectroscopy was a proven technique for the observation of small radicals, initially it seemed more reasonable to search for radicals containing 2 or 3 heavy atoms as opposed to the really large radicals for which the method is intended. Most of the potential radicals in this chapter have been observed either in matrix isolation or in high resolution techniques such as laser-induced fluorescence. Observation of larger radicals is the goal of this section; however, several small radicals were detected throughout the course of the studies. Since the UV photolysis products of many of the precursors was unknown, this uncertainty about whether radical production is efficient added to the exploratory nature of these experiments.
6.2 OH RADICAL

The ultimate goal in the OH radical experiments was to observe the spectrum of the OH-Ar van der Waals complex, but before starting those efforts, it was necessary to maximize OH production. Hydroxylamine (NH₂OH) was first tested as a possible precursor to OH. The sample was synthesized and the crystals were placed inside a mixing cylinder while N₂ was passed over it in order to minimize decomposition since hydroxylamine readily decomposes to NH₃ and H₂O upon contact with air. The cylinder was then pressurized with argon to 23 atm. Neither OH from NH₂OH 193 nm photolysis nor the hydroxylamine transition were observed. Hydroxylamine was believed to have decomposed either due to moisture in the air upon transfer or catalysis on the metal surface inside the cylinder.

The next precursor for OH radicals to be tested was fuming nitric acid, and although it is corrosive, its photochemistry at 193 nm is known to produce OH radicals in large quantities (UV cross-section is 2 x 10⁻¹⁷ cm² molecule⁻¹). The optimum set-up for seeding the precursor into the carrier gas consisted of ~4 ft. long U-tube constructed out of 1/2" stainless steel tubing. The ends of the tubing were bent upwards such that the region containing the ~10 ml of fuming nitric acid was about 2 ft. long. Varying pressures of helium or argon were passed over the nitric acid, and this mixture was allowed to further equilibrate in 6-8 feet of 1/8" stainless steel tubing before reaching the nozzle. Since corrosion inside the nozzle
reduced or eliminated the OH signal, it was necessary to remove all brass pieces (the cap and the poppet bushing) and replace them with aluminum parts.

In these experiments, the nozzle was typically 5-15 mm from the infrared probe, and with the addition of the White cell, the width of the probe region extended to a little over 1 cm. The valve driver was turned up to 60V, thus producing more intense gas pulses, and the pressure in the vacuum chamber was ≈ 200 mTorr. Both the 1 cm and 2 cm "pseudo" slits were used, with the 2 cm version giving a larger signal by a factor of two. The excimer was fired directly into the throat of the nozzle, and for the lower backing pressures, it was found that an unfocussed beam gave the best OH signal. Firing straight into the nozzle created a heating problem of the gas inside the nozzle, however. As shown in Figure 29a, at lower backing pressures of carrier gas the hot nitric acid molecules are not cooled sufficiently, thus leading to a complicated spectrum in the region of interest. In Figure 29b, as the backing pressure is raised to 11 atm, the heat capacity of the gas increases, and the hot nitric acid rotational levels disappear. Also, because of the increased heat capacity of the gas, it was possible to focus mildly into the slit and produce more OH radicals while maintaining the rotational cooling. Typical unamplified OH signals were 50 mV for the v = 1-0 R(1.5)2± transitions, giving a 2.5% peak absorption with 2V chopped laser beam.
Observation of OH Q(1.5)1± transitions in the jet upon photolysis of fuming HNO₃ seeded into argon. The infrared probe is 1.5 cm downstream of the nozzle orifice. (a) The pressure behind the nozzle is .7 atm. The OH transitions are observed clearly, but there is spectral congestion due to hot nitric acid absorptions. (b) When the backing pressure is increased to 11 atm, the hot rotational lines of HNO₃ are cooled away, leaving the OH ground state lines and possibly a t-HONO line.
a

HNO₃

b

OH Q(1.5)1±

Frequency (cm⁻¹)

3569.55  3568.95  3568.35
6.2.1 The Search for OH-Ar·

In order to understand intermolecular and intramolecular forces in the gas phase, a variety of closed shell van der Waals complexes have been studied. The OH-Ar complex is novel in that it is an open shell species, and therefore the presence of the unpaired electron adds a new variable to studies in gas phase van der Waals bonding. In previous laser induced fluorescence studies, the electronic spectra of OH-Ar van der Waals complexes were observed. From these OH-Ar studies, it has not been conclusively determined whether the ground state structure is linear or bent. However, in two separate studies, the ground state rotational constant was determined to be $0.104 \pm 0.003 \text{ cm}^{-1}$ or $0.100 \pm 0.002 \text{ cm}^{-1}$. The OH stretching fundamental of the complex is expected to be shifted $0.6 \pm 0.1 \text{ cm}^{-1}$ toward lower energy from the OH fundamental at $3569.64 \text{ cm}^{-1}$.

Since it had been determined that the origin of the OH-Ar complex was red-shifted by $0.6 \text{ cm}^{-1}$ from the uncomplexed OH, spectroscopic searches were centered in this region around $3569 \text{ cm}^{-1}$. Survey scans were made with backing pressures of argon varying from 7-11 atm, as it was necessary to employ high gas pressures in order to cool the rotationally hot nitric acid precursor such that spectral interference is eliminated. The Q(1.5)1± ground state lines of free OH are in the vicinity of the predicted OH-Ar band origin; thus, the Q(1.5)1± OH signal could be conveniently maximized immediately before scanning for OH-Ar to ensure optimum conditions. Typical unamplified signals for the Q(1.5)1± OH
transitions were 150 mV, giving 7.5% absorption of the ≈ 2V chopped laser beam. The best S/N ratio obtained under these experimental conditions was ≈ 75, as shown in Figure 30.

In the search for OH-Ar, a "mystery" line appeared having a different time behavior than that of the OH transitions. As shown in Figure 31, the "mystery" line absorption maximum was delayed from that of OH. This line was thought to be the Q branch of OH-Ar with P and R branches too weak for observation, but further work proved that idea incorrect. While scanning around 3590 cm⁻¹, an unknown band was discovered with transitions having similar delayed time behavior as that of the "mystery" line. The new band rotational structure was indicative of a polyatomic, asymmetric rotor, and the line positions matched with that of t-nitrous acid.³² The delayed time behavior of t-HONO suggested that it was formed further inside the slit section upon photolysis of HNO₃. Further scans covering the region between 3558 - 3580 cm⁻¹ revealed only OH, HNO₃, and possible t-HONO lines.

Observation of the ν₁ band of t-HONO was important because it, as has been previously described, provides a good probe of temperature. The 30K temperature observed for t-HONO is too high for observing OH-Ar. Temperatures of <10K are necessary to ensure the observation of OH-Ar. At this point in the experiment, it seemed that expansion temperatures and signal-to-noise were preventing the observation of OH-Ar, so work on this species was temporarily delayed until construction of the new nozzle was completed.
Figure 30

OH Q(1.5)1± transitions with a S/N ratio of ≈ 75. The OH is produced by shooting the excimer straight into the "pseudo" slit and photolyzing fuming HNO₃ seeded into 11 atm helium. The additional lines are most likely HNO₃ and t-HONO absorptions.
11 atm Ar/HNO₃

S/N approx. 75
Time behavior comparison of OH and t-HONO produced in the jet by photolysis of fuming nitric acid seeded into argon. The edge of the multipass infrared probe was $\approx 1.5$ cm from the nozzle orifice. (a) The maximum in the OH absorption occurs around 21 $\mu$sec whereas in (b) the t-HONO absorption maximum occurs $\approx 4$ $\mu$sec later, suggesting that t-HONO is produced further inside the slit.

**Figure 31**
The Nesbitt type slit, described in section 3.1.2, was to provide lower rotational temperatures since early expansion would be less of a problem than with the "pseudo" slit. When the new nozzle was initially tested, no OH signal in argon was observed. Switching over to helium carrier gas, a weak OH signal was detected (150 mV with 30x amplifier, ≈ 2V chopped laser, .25% absorption) under extreme conditions, the valve pulse open wide and 1 Torr pressure in the vacuum chamber. It was possible under these conditions that OH was produced by photolysis of the background gas. t-HONO was also observed with the new slit under extreme conditions i.e., focussed excimer beam, valve pulse wide open, 1 Torr in vacuum chamber, and photolysis 5 mm downstream of the nozzle. Again, photolysis of the background gas may be the source of t-HONO. If that were the case, it is expected that the spectrum would be rotationally hotter than that of t-HONO observed in the jet. Unfortunately, it is not possible to compare the mode-hop scan of t-HONO obtained under these conditions with the high resolution 30K spectrum, since line intensities are most likely incorrect for the lower resolution scan. Several permutations of the experimental set-up were then tested in an effort to observe OH in helium using the new slit under normal valve operating conditions. The excimer was fired straight into the bore of the Nesbitt type slit with or without the dynasil slit plates attached, and the photolysis geometry was changed such that the excimer fired from above, either inside or without the glass slit. In all four cases, no OH signal in helium was seen.

In the event conditions were inherently wrong in the HNO₃ photolysis experiments, the 2 cm "pseudo" slit with the torr-sealed glass plates was
switched with the Nesbitt type slit, and OH was seen immediately from the perpendicular photolysis of the precursor. When photolyzing outside the glass slit, the photolysis region producing the maximum signal (2% absorption) was located ≈ 3 mm downstream of the orifice and ≈1 mm from the edge of the infrared probe beam region. The helium backing pressure was ≈ 8 atm. It is questionable whether or not OH experiences sufficient collisions at this point during the expansion. The collision frequency can be estimated by $(2)^{1/2} n \sigma v$, where $n$ is the gas density downstream of the orifice at 3 mm calculated by the Hagen-Poiseuille formulas, $\sigma = \pi d^2$, and $v$ is the local mean velocity at 25K. Before the OH reaches the infrared probe 1 mm away, it is estimated to experience 20 collisions, which is probably an insufficient number of collisions to cool OH rotationally. When the unfocussed excimer beam was placed inside the dynasil plates, the $Q(1.5)_{1±}$ OH signal was observed with .5% peak absorption, with the edge of the infrared probe region 3 mm from the slit orifice.

Since OH had been observed with the "pseudo" slit, the Nesbitt type slit was tested again for OH with no success. Something unusual was occurring with the new slit for the production or detection of OH radicals because all other radicals observed in the "pseudo" slit were also seen in the Nesbitt type slit. A possibility is that the new slit provided a stronger expansion in which a greater number of collisions afforded the OH radicals more opportunities for reaction with the precursor. In future experiments, this idea could be checked by centering the color center laser on a ground state absorption of H$_2$O, which would be present in the unphotolyzed 90%
nitric acid, and monitoring the change in intensity (if any) upon photolysis of the precursor, since OH should react to give \( \text{H}_2\text{O} \). Changes in \( \text{H}_2\text{O} \) absorption intensity due to heating of the gas should be minimal if the photolysis occurred inside the thermalization region and a high backing pressure was used in the nozzle. Clustering of the carrier gas with the OH radicals is not a likely explanation of the failure to observe OH since helium was used in the Nesbitt slit tests.

OH was not observed in the 2 cm "pseudo" slit perpendicular photolysis of nitric acid seeded in argon. With 8 atm argon backing pressure, no OH was observed when the excimer fired inside the dynasill slit extension; however, an OH signal was detected when the photolysis occurred outside the glass slit. When the backing pressure was dropped to 1.7 atm, an OH signal was observed inside and outside the glass slit, with the signal size outside the slit \( \approx 8 \) times larger. The use of argon in the 2 cm "pseudo" slit experiments complicates results somewhat, as the polarizability and stickiness of the carrier gas introduces variable argon clustering with the seed gas. Since firing the excimer into the glass slit extension allowed more thermalization of the OH radicals and consequently lower internal temperatures before expansion, it is possible that extensive clustering occurred during the expansion, thus resulting in loss of OH signal. Photolysis outside the nozzle in the expansion region allows the hot OH radicals to experience some rotational cooling with less time for clustering with argon. The alternative explanation of chemical reaction with the precursor seems a less likely explanation for the complete disappearance of OH, since similar photolysis experiments inside the glass
slit using helium as the carrier gas yielded a strong OH signal. However, it should be remembered that in previous experiments in which the excimer was fired directly into the 2 cm "pseudo" slit, OH signals were still observed in the argon expansion. A possibility is that Ar(HNO₃)ₙ clusters in the early part of the expansion were photolyzed, giving a stronger uncomplexed OH signal. Alternatively, since higher internal temperatures were observed for species produced by direct photolysis into the slit due to heating of the nozzle, perhaps condensation was not as extensive since the expansion was starting from higher temperatures.

Under a variety of experimental conditions, scans over the predicted OH-Ar band origin region revealed no absorptions of the OH-Ar species. Since OH was not observed with the Nesbitt type slit, no searches for OH-Ar were attempted using it. Previous experiments in which the excimer fired directly into the 1 or 2 cm "pseudo" slits with argon backing pressures ranging from 1-11 atm produced no OH-Ar as well. When nitric acid seeded into 10 atm of argon was photolyzed inside the glass slit of the 2 cm "pseudo" slit, again no OH-Ar was observed. In the event that larger (OH)Arₙ clusters were being formed with 100% argon, carrier gas mixtures containing 1 and 5% argon in helium with 3 or 7 atm backing pressure behind the nozzle were tested to see if dimer production would be increased. OH-Ar was not detected with the argon/helium carrier gas mixtures as well.

Searches were also made for vibrationally excited OH using the perpendicular photolysis geometry in conjunction with the 2 cm "pseudo" slit. With 100 psig backing pressure of helium, photolysis inside the
dynasil glass slit produced no v= 2-1 OH. However, when the photolysis occurred downstream of the expansion, the 2-1 R(1.5)1± OH was observed with an amplified signal of 50 mV (no chopped laser power measurement for this region, but it is estimated to be between 1.1-1.5V, which gives .1-.15% absorption). It appears that photolyzed species inside the glass slit piece experience some vibrational thermalization with the room temperature helium gas before the expansion occurs, although reactions of the vibrationally hot OH with the precursor could be responsible for the lack of signal.

The last test with HNO₃ photolysis was an attempt to lower t-HONO rotational temperature by photolyzing inside the glass slit of the 2 cm "pseudo" slit. This experiment has been described in section 5.2, but to reiterate briefly, the new rotational temperature for t-HONO was approximately 20K lower than previously obtained. It should also be mentioned that c-HONO, the other possible isomer, was not observed in the photolysis while scanning over its band origin region at 3430 cm⁻¹. The t-HONO results are encouraging in that a large molecular species produced upon excimer photolysis can be cooled to low rotational temperatures around 10K in a supersonic expansion.

Although low rotational temperatures are necessary for optimum OH-Ar signal, the limiting factor in these experiments appears to be the signal-to-noise ratio. The maximum S/N ratio for OH was ≈ 100, and since dimer formation is estimated to be about 1% of the monomer, a S/N of 1 (or less since the OH-Ar partition function is large) would be expected for OH-Ar.
Therefore, at this point, spectroscopic studies of OH-Ar have ceased until signal-to-noise has been improved.

6.3 CH$_3$ RADICAL

The $v_3$ $\ell_1 \leftarrow 0_0$ transition of the methyl radical$^{33}$ was first observed while photolyzing CH$_3$NH$_2$ at 193 nm. The search for CH$_3$ was initiated in order to further understand methylamine photolysis (see section 6.5.1 for complete background and details). In this experiment, the perpendicular photolysis geometry was used in conjunction with the 2 cm "pseudo" slit with dynasil slit extension pieces. The unfocussed excimer was fired into the glass slit piece, photolyzing a 3-6% mixture of methylamine in helium. With 3 atm backing pressure, the $\ell_1 \leftarrow 0_0$ line at 3174.2935 cm$^{-1}$ was observed with a S/N ratio of 4.

In later experiments, methyl production was optimized in order to set good photolysis conditions before searching for unknown radicals. Again, the photolysis geometry was the same as with the methylamine photolysis. Methyl ethyl ketone was photolyzed to give methyl and possibly ethyl radicals. A 400 mV CH$_3$ signal (with 30x amp) was observed when $\approx$ 50 ml of methyl ethyl ketone was placed in the mixing cylinder, pressurized to 330 psig with helium, and regulated to give 2.7 atm backing pressure. The same size signal was also seen with $\approx$ 20 ml of the precursor in the U-tube using 11 atm of He backing pressure. Absorption was .6% for the $\ell_1 \leftarrow 0_0$ transition of methyl for the methyl ethyl ketone precursor. When the
precursor CH$_3$I was placed in the U-tube, a 1.5V signal with the 30x amp was observed on the same transition of CH$_3$, giving $\approx 4\%$ absorption for the $1_1 \leftarrow 0_0$ transition. This factor of $\approx 6$ increase required an unfocussed excimer beam and photolysis just outside the glass slit extension. Acetone photolysis at 193 nm also produced CH$_3$, with a 40 mV unamplified signal on the same $v_3 1_1 \leftarrow 0_0$ transition ($\approx 1.4\%$ absorption, assuming 2.8V chopped laser power which was typically the power for the newly reprocessed laser in this region).

The methyl radical signal was also tested with the 1 cm Nesbitt type slit. In this situation, the excimer was firing straight into the throat of the slit. With acetone as the precursor, the $v_3 1_1 \leftarrow 0_0$ transition of CH$_3$ was observed with a signal of 300 mV using the 30x amplifier. Although this signal was a factor of 4 less than previously observed for acetone photolysis, part of the difference may be a slight decrease in color center laser power, since the Nesbitt type slit measurement was taken two days later. Another factor of 2 could be attributed to decrease in infrared pathlength since the 1 cm Nesbitt type slit was used rather than the 2 cm "pseudo" slit. Considering these conditions, the photolysis of acetone produced comparable CH$_3$ signals in the Nesbitt type slit and the "pseudo" slit.
6.4 BROMINE ATOM

The bromine atom observations were initiated to determine if a desired precursor photolysis was occurring. A 1% C₂H₃Br mixture in 23 atm of helium which was regulated to 3 atm was photolyzed by firing the excimer straight into the 1 cm "pseudo" slit. A 200 mV signal (amplified x30) was observed for the 2 ← 3 component of the \(^2\text{P}_{1/2} ← ^2\text{P}_{3/2}\) Br atom transition\(^{34}\), giving .3% absorption of the 2V chopped laser power. The observed transitions of Br due to this photolysis are shown in Figure 32. No cooling is gained in the bromine atom spectrum, but its observation does determine the effective column density in the probed region since the cross-section is known.

Since the peak absorption cross-section (\(\sigma_0\)) and the % absorption of the infrared power are known for the 2 ← 3 transition of Br, the column density can be calculated. The value of the peak absorption cross-section is determined at the peak of the Doppler-limited line. Since the Doppler broadened line is proportional to \(T^{1/2}\), the peak value from the jet photolysis experiments should be corrected because the peak intensity value drops with increased temperature. The formula for the Doppler-limited absorption cross-section is:

\[
\sigma = \frac{8\pi^{5/2} |\mu_\alpha|^2 S^{\alpha}_{12} \exp(-E_1/kT)}{(3uhQ_{\text{int}}) \exp[-(v - v_0)^2\lambda^2/u^2]}
\]
Bromine atom transitions observed in the jet upon photolysis of 1% mixture of vinyl bromide in helium. The Br atom experiences no cooling in the jet, however this frequency scan illustrates the sensitivity of the jet-cooled radical technique.
where $\lambda$ is the wavelength at the center of the line, $(v - v_0)$ is HWHM of the observed line, and $u$ is the most probable velocity $(2kT/m)^{1/2}$. For the peak absorption cross-section, $v = v_0$ and the formula becomes:

$$
\sigma_0 = \frac{8\pi^{5/2} |\mu_\alpha|^2 S_{12}^\alpha \exp(-E_1/kT)}{(3u\hbar Q_{int})}
$$

Parameters $\mu_\alpha$, $S$, $E_1$, and $Q_{int}$ have been previously described in Section 2.6.1. $\sigma_0$ has been determined from the peak value of the Doppler broadened line at 300K, but the peak value used in these calculations takes into account the observed Br linewidth. In the jet photolysis experiments, the Br observed linewidth (HWHM) is 225 MHz; however, the Doppler broadened linewidth at 300K is calculated as 76 MHz, using the formula $\Delta v_{1/2} = u/\lambda (\ln 2)^{1/2}$. The column density is then calculated using:

$$
CD = \frac{(\Delta I/I)}{\sigma_0} x \frac{\Delta v_{300K}}{\Delta v_{obs}}
$$

Using $\Delta I/I = 0.003$, $\sigma_0 = 5.2 \times 10^{-18}$ cm$^2$, and the above linewidths, the column density $= 1.9 \times 10^{14}$ cm$^{-2}$. To obtain the Br atom concentration, the column density is divided by the pathlength (16 cm in this case), and the number of Br atoms is $1.2 \times 10^{13}$ atoms/cm$^3$.

Bromobenzene and allyl bromide were also photolyzed with similar although weaker signals. Since the vapor pressure of bromobenzene is low ($< 20$ Torr at room temperature), a closed loop heating system was used to
increase the precursor temperature to 55°C, and subsequent photolysis with a mild focus produced an amplified signal of 100 mV on the Br 2 ← 3 transition. The Br atom concentration can be calculated assuming the observed absorption linewidth from the vinyl bromide photolysis. In this case, the concentration of Br atoms is 6.7 x 10^{12} molecules/cm^3. Assuming the primary dissociation products of bromobenzene are phenyl radical and Br atoms, the concentration of Br atoms is equal to the concentration of phenyl radicals.

6.5 DESCRIPTION OF SEARCHES FOR SEVERAL NEW RADICALS

6.5.1 CH₃NH Radical

The amidogen methyl radical has not been observed in infrared spectroscopic studies, but evidence of its existence has been suggested by analysis of photochemical products of methylamine and its deuterated analogs. From mass spectrometric analysis of the products resulting from the 194-244 nm photolysis of methylamine in a cell, the following primary dissociation processes were proposed:

1) CH₃NH₂ + hv = H + CH₃NH  75%
2) = H + CH₂NH₂  7.5%
3) = CH₃ + NH₂
With the primary dissociation yield close to unity, reaction 1 should account for about 75% of the primary process while the production of reaction 2 is estimated to be 10% of 1. The remaining channels then account for ≈ 18% of the primary dissociation processes.

In 147 nm photolysis studies of methylamines, Magenheimer et al. also observed that H atom formation was the primary dissociation process, but the hydrogen was preferentially lost from the carbon rather than the nitrogen atom. In this experiment, CH3NH2 and CD3NH2 were photolyzed in the presence and absence of scavengers C2D4 or C2H4. Their results provided relative quantum yields and additional primary dissociation pathways as shown below:

5) CD3NH2 + hv = CD3NH + H .21
6) = CD2NH2 + D .47
7) = CD3N + H2 .05
8) = CDNH2 + D2 .05
9) = CD2NH + HD .09
10) = CD3 + NH2 .13

In these primary dissociation pathways at 147 nm, two additional products are included, CDNH2 and CD2NH.
In the jet experiments, the methylamine precursor was photolyzed by perpendicularly directing the focussed or unfocussed excimer beam into the glass extension of the 2 cm "pseudo" slit. Initially, spectral searches in the jet and the room temperature reference cell were conducted for the precursor because observation of the methylamine gas pulse in the jet would aid in determining the percentage of photolysis due to the excimer firing. Only extremely weak lines, if any, were observed, since it was difficult to distinguish the questionable peaks from noise. The lack of sensitivity was not too surprising as the methylamine $v_1$ NH$_2$ symmetric stretch at 3360 cm$^{-1}$ is very weak.$^{37}$

Using a 1-5% mixture of CH$_3$NH$_2$ in helium with a nozzle backing pressure of 1-3 atm, survey scans centered around 3250 cm$^{-1}$ were performed. NH$_2$ lines were observed as well as some weak lines of an unknown species. It was found that the weak lines increased in intensity as the seeding ratio increased. Next, a pure expansion of methylamine was tested, and some broad absorptions and the same unknown rotational lines appeared. These lines were observed in both focussed and unfocussed excimer laser photolysis. Comparison with the HCN spectrum confirmed the observation in the jet of the $(v_3, v_2^1 + v_3 - v_2^1)$ dyad of HCN.$^{38}$ With incomplete coverage of the P branch region of the $v_3$ fundamental, J values up to 23 were observed in the pure expansion of methylamine.

The conversion of methylamine to hydrogen cyanide upon 193 nm excimer laser photolysis has been observed by Nishi et al.$^{39}$ After 3600 shots of the 50-100 mJ per pulse laser, mass analysis revealed that 70% of the methylamine in a static cell had been converted to HCN. If equations 1-
4 are considered, there is no direct channel for formation of HCN using 193 nm photolysis. However, vibrationally and electronically excited methylenimine, a possible intermediate at 147 nm photolysis as shown in equation 9, is known to dissociate into HCN + H₂.⁴⁰ According to the authors, there is some speculation that small fragments produced upon the photolysis may react with methylamine to give methylenimine, which could then dissociate into HCN. In addition to these indirect HCN sources, HCN might be produced by multiphoton fragmentation. Nishi et al. were unable to decide conclusively which mechanism is producing HCN; hence it is difficult to deduce the source of HCN in the jet experiments. With 193 nm photolysis, it seems unlikely that direct formation of methylenimine is taking place. However, searches can be made for methylenimine as it is fairly stable, although it might not be observed if it had nearly converted to HCN. From the comparison of the time behavior of HCN and NH₂ produced from methylamine photolysis with 3 atm nozzle backing pressure, it appears that the maximum signal is arising from the same point inside the nozzle, as shown in Figure 33. From our data, neither radical reactions nor multiphoton processes can be eliminated as means of HCN production in the jet. Further studies in the room temperature flowing gas cell, which would provide temporal information for the methylamine photolysis products, may reveal more about what is taking place.

NH₂ signals were normally optimized to achieve maximum photolysis conditions before switching over to the study of methylamine photolysis. The comparison of NH₂ signals obtained from photolysis of both precursors indicates the extent of CH₃NH₂ dissociation. First, a 3% NH₃ in
Time behavior comparison of HCN and NH$_2$ produced by ArF photolysis of methylamine inside the glass slit of the 2 cm "pseudo" slit. The absorptions of the two species have been plotted on the same scale for ease of comparison. The noise spike at the beginning of the time scans is due to excimer pick-up and ringing of the amplifier circuitry. (a) $v_1 \, 1_{11} \leftrightarrow 0_{00}$, $3/2 \leftrightarrow 1/2$ transition of NH$_2$. (b) $v_3$ P(20) transition of HCN. Note that both species have absorption maximums at nearly the same point in time ($\approx 15 \, \mu\text{sec}$).
He mix was photolyzed using the unfocussed excimer beam to give a 600 mV NH$_2$ signal (amplified x30). After pumping on the mixing cylinder containing the previous NH$_3$ mixture for almost an hour to ensure that NH$_3$ is removed as completely as is practical from the system, 6-7% CH$_3$NH$_2$ was seeded into helium using the same cylinder. The NH$_2$ signal obtained from the methylamine photolysis was 450 mV (also amplified x30). Since the amount of dissociation of the precursor and the infrared absorption cross-section for NH$_2$ is unknown, it is not possible to make a quantitative statement concerning the percentage of methylamine dissociation into this channel; however, the large NH$_2$ signal suggests CH$_3$ as the other photolysis product. To investigate this, the infrared laser was scanned in the region of the CH$_3$ v$_3$ band during methylamine photolysis, and indeed the $1_1 \leftarrow 0_0$ and $2_2 \leftarrow 1_1$ transitions of CH$_3$ were observed.

With the observation of CH$_3$, it appears that the photolysis of methylamine is to some significant degree going through the supposedly minor channel 3. Since the infrared absorption cross-section ($\sigma_{ir}$) is not known, it is not possible at this stage to calculate the concentration of CH$_3$ produced. Knowledge of the CH$_3$ concentration would then aid in determining the branching ratio into this particular channel. However, it was feared that dissociation of methylamine into NH$_2$ and CH$_3$ accounted for a large percentage of the precursor photolysis; therefore, studies on this system were halted.

The work of Nishi et al. in a flowing gas cell demonstrates that the use of a high power excimer laser as the photolysis source results in different dissociation processes than those observed in the flashlamp
Two-photon absorption by methylamine becomes important with the excimer source. Absorption of two photons at 193 nm (equivalent to 12.8 eV) produces very high excitation even above the ionization potential of methylamine (8.97 eV). Indeed, Nishi et al. observed the fluorescence spectra of NH, CN, CH, and NH₂. They found evidence for the intermediate production of either CH₃NH or CH₂NH₂ by the results of mass analysis of the methylamine photolysis products after 450 excimer shots. An ion signal at m/e = 30 was observed and attributed to species of the formula CH₄N. This observation does not distinguish between CH₃NH and CH₂NH₂. The percentage of CH₃NH and CH₂NH₂ is relatively high at 16.1% when compared to other products, but it decreases to 6.2% after 3600 laser shots.

Although amidogen methyl radical was not observed in methylamine photolysis in the jet, it can not be concluded that the radical is not being produced. As mentioned earlier, the v₁ CH₃NH₂ symmetric stretch is very weak and was never observed with the color center laser spectrometer, so it is conceivable that the NH stretch of CH₂NH is too weak to detect as well. It would be better to monitor the CH₃ asymmetric stretches since they are quite strong. Unfortunately the CH₃ stretches of methylamine are located at 2960-85 cm⁻¹, which is at the lower lasing limit of the color center laser.
6.5.2 \( \text{CH}_2\text{OH} \) Radical

The vibrational spectrum of \( \text{CH}_2\text{OH} \) has been observed in an argon matrix after the products of mixing \( \text{CH}_3\text{OH} \) with hot argon atoms or \( \text{F} \) atoms produced in a discharge were frozen at 14K.\(^42\) The \( \text{OH} \) stretch of \( \text{CH}_2\text{OH} \) was observed in the matrix at 3650 \( \text{cm}^{-1} \) and was classified as of medium strength. To observe this radical in the jet by excimer laser photolysis, some other scheme for hydroxy methyl production is necessary. Since acetone photolyzes at 193 nm to give \( 2\text{CH}_3 \) radicals and \( \text{CO} \), it was postulated that the photolysis of acetol might occur in a similar fashion, producing the desired \( \text{CH}_2\text{OH} \) radicals in this manner:

\[
\text{CH}_3\text{COCH}_2\text{OH} \rightarrow \text{CH}_3 + \text{CO} + \text{CH}_2\text{OH}
\]

A static fill of acetol was photolyzed in the gas cell of the diode laser apparatus, and the production of \( \text{CO} \) was observed. No temporal information on the \( \text{CO} \) absorption was obtained, so it is not known how quickly the \( \text{CO} \) is produced. The rate of \( \text{CO} \) production in acetol photolysis is important because photolysis studies of acetone indicate that an acetyl radical is formed initially, which then dissociates into \( \text{CO} \) and \( \text{CH}_3 \).\(^43\) Since the acetol precursor is 1,2-propanediol, there should be no acetone impurities present in the acetol precursor to give the \( \text{CO} \) signal.

The major drawback with acetol as a precursor was its low vapor pressure (\( \approx 10 \) Torr). Before searching for the acetol spectrum in the jet,
the acetol vapor was placed in the reference cell of the supersonic nozzle apparatus, and a normal absorption spectrum was recorded using lock-in detection. Many overlapping lines were observed to be concentrated at 3506 cm\(^{-1}\), so the search for cold acetol was centered around this region. The purpose of observing acetol in the jet was to ensure that a sufficient percentage of precursor was seeded into the carrier gas. When less than 1 atm of helium was passed through acetol in a glass bubbler, no acetol lines were observed in the expansion.

In spite of this failure to observe acetol in the jet, searches for the CH\(_2\)OH radical began around 3650 cm\(^{-1}\). A mixing cylinder was used as the bubbler in order to have higher backing pressures of helium available. The excimer was focussed mildly into the slit by a 2 m cylindrical lens, and the region 3680-3620 cm\(^{-1}\) was scanned without success. In case acetol was photolyzing to give OH, the laser was scanned over the R(1.5)2± OH transition at 3663.73 cm\(^{-1}\); OH was not observed. In later acetol photolysis attempts, the excimer was softly focussed into the nozzle by a 30 cm cylindrical lens (note: the 30 cm lens, of course, produces a stronger focus than the 2 m lens, but the photolysis region was not at the focus). Approximately 15 ml of acetol was placed in the U-tube while 3 atm of helium flowed through, giving a .5% mixture of precursor. With this arrangement, H\(_2\)O, OH, and an unknown line were observed. The OH and mystery line only appeared at later time channels, and the OH signal was a weak 100 mV absorption with 30x amplification. The source of OH could have been the photolysis of water which absorbs very weakly at 193 nm, since a major impurity in the acetol was water (≈10%).
In further investigations, the acetol precursor was heated by hot tap water in an effort to increase the vapor pressure. Gas lines leading up to the nozzle and the nozzle body were heated to prevent condensation. Before precursor placement in the U-tube, molecular sieve was added to the acetol sample to absorb water, and the acetol was then pumped on to further remove water. Without the focussing lens, only H$_2$O and no OH was observed, but when the soft focus was added, the H$_2$O line became stronger and the OH lines appeared. With only 3 atm backing pressure and the excimer firing straight into the slit, heating of the nozzle or gas stream was most likely occurring to give hot H$_2$O.

Since no CH$_2$OH radicals were observed, it was concluded that the vapor pressure of acetol was too low or that photolysis of the precursor was not creating the correct product. Another possible means of CH$_2$OH production is through abstraction of a methyl hydrogen from methanol to give the desired radical. In particular, chlorine atom abstraction is known to preferentially remove the H from the methyl group. A gas mixture containing CH$_3$OH and CCl$_2$F$_2$ was photolyzed at 193 nm inside the nozzle in order to produce the Cl atoms for the abstraction. Although this reaction was not extensively studied, in the initial investigations no signals which could arise from CH$_2$OH were observed.
6.5.3 HOCO Radical

The hydroxylformyl radical has been postulated to be the intermediate in the reaction of OH + CO\textsuperscript{45} to give ultimately CO\textsubscript{2} + H and in the corresponding reverse reaction of CO\textsubscript{2} + H to produce OH + CO. The vibrational spectrum of trans-HOCO has been observed in matrix isolation when formic acid was codeposited at 14K with excited argon atoms or fluorine atoms produced in a discharge. A peak observed in the matrix at 3608 cm\textsuperscript{-1} was attributed to t-HOCO, although a combination band of CO\textsubscript{2} which absorbs at 3609 cm\textsuperscript{-1} in the gas phase could be responsible for this absorption. Further evidence seems to verify the peak as belonging to t-HOCO since the rate of disappearance of this peak upon photolysis matched that of other t-HOCO peaks. Also, experiments with carbon-13 enriched formic acid showed no shift in the peak position, contrary to what would be expected for carbon-13 CO\textsubscript{2}\textsuperscript{46}.

A suitable precursor was necessary to produce the desired HOCO radicals in the jet. The photochemistry of trifluoroacetic acid vapor had been explored by Mearns and Back at wavelengths between 200 and 220 nm, and the photolysis results seemed to suggest HOCO as a possible product.\textsuperscript{47} In this experiment, various pressures of trifluoroacetic acid vapor were photolyzed in a closed cell using a mercury lamp as the photolysis source with the temperature of the cell varied from 90-190\textdegree\textsubscript{C}. The primary photolysis pathways were determined to be:
Steps 2 and 3 accounted for no more than 27% and 7% respectively of the total primary processes at 165°C.

There is evidence in the work of Mearns and Back for the presence of free hydroxylformyl radical. When isobutane or 1-butene were added to the cell, the distribution of final products was altered, suggesting reactions with an intermediate. As further evidence for HOCO radical, formic acid was detected in the products upon addition of isobutane. In the photolysis of the pure acid, it was proposed that the HOCO radicals combine and disproportionate in the following manner:

4) $2\text{COOH} \rightarrow (\text{COOH})_2$
5) $\rightarrow \text{CO}_2 + \text{HCOOH}$
6) $\rightarrow 2\text{CO}_2 + \text{H}_2$
7) $\rightarrow \text{CO}_2 + \text{CO} + \text{H}_2\text{O}$

From the photolysis products of the pure acid and the reaction with isobutane and 1-butene, a mechanism fitting the experimental results suggested that pathway 5, the disproportionation of HOCO radicals, was possibly the major reaction channel for the hydroxylformyl radicals.
In the jet photolysis attempts at producing t-HOCO radicals, ≈ 10-20 ml of trifluoroacetic acid was placed in the U-tube, with 4.4 atm of helium backing pressure. Upon firing the excimer straight into the 1 cm "pseudo" slit, unknown rotational lines were observed when the excimer beam was tightly focussed. These lines were matched with ro-vibrational transitions of the v3 + 2v2 combination band of CO2, and were only observed when the excimer was tightly focussed. In addition to P(2), P(4), and P(6) ro-vibrational transitions of CO2, rotationally hot water lines were observed as well; a portion of the spectrum is shown in Figure 34. The water was most likely present as an impurity in the precursor, and the tightly focussed excimer served to heat the gas stream resulting in thermal population higher states. Color center laser mode-hop scans surveying the region from 3630-3570 cm⁻¹ revealed no t-HOCO transitions nor were OH transitions detected. It is possible that a minor dissociation pathway is favored under these photolysis conditions, but without further studies it is difficult to determine if CO2 is a primary dissociation product (reaction 2) or a result of t-HOCO radical recombination reactions (reactions 6 or 7). The necessity of a tightly focussed excimer beam in order to produce CO2 seems to suggest multiphoton fragmentation of the precursor. However, spectral searches for formic acid could be undertaken in order to determine if disproportionation processes were the source of CO2 production.
Frequency scan showing the photolysis products of 1% trifluoroacetic acid seeded into helium. The backing pressure behind the nozzle was 4.4 atm, and the ArF excimer beam was shooting directly into the 1 cm "pseudo" slit. P(4) and P(6) lines of the $v_3 + 2v_2$ combination band of CO$_2$ were observed, along with a rotationally hot water line $6_06 \leftarrow 7_07$. Comparison of the water reference cell gas (upper trace) with the lower trace shows that the $6_{16} \leftarrow 7_{17}$ H$_2$O transition does not appear.
$\text{H}_2\text{O}$

$\text{CO}_2 \nu_3 + 2\nu_2$

Frequency (cm$^{-1}$)
6.5.4 Vinyl Radical

Vibrational absorptions of vinyl radical were first suggested by Jacox and Olson\textsuperscript{49} in a study of acetylene codeposited with a beam of excited argon atoms in an argon matrix. Although the study was primarily undertaken to observe the C_2H radical, two unknown absorptions at 900 and 926 cm\textsuperscript{-1} were proposed to originate from the C_2H_3 radical. Since that work, vinyl radical and its isotopomers have been more extensively investigated by FTIR matrix isolation studies in which photolysis products of an acetylene/HI mixture or ethylene were trapped in an argon matrix.\textsuperscript{50} The observation by Shepherd et al. of the 900 cm\textsuperscript{-1} band and its behavior upon isotopic substitution, plus the ab initio calculations by Dupuis and Wendoloski,\textsuperscript{51} suggested that this absorption was the v_7 band of C_2H_3 radical (CH_2 out of plane bend plus CH out of plane bend). Kanamori et al. have observed the high resolution spectrum of vinyl radical by diode laser kinetic spectroscopy.\textsuperscript{52} They observed a c-type band at \( \approx 895 \) cm\textsuperscript{-1}, which is the same band Shepherd et al. observed at 900 cm\textsuperscript{-1}. Unfortunately Shepherd et al. were unable to observe the CH or CH_2 asymmetric and symmetric stretches due to interfering strong bands of ethylene and acetylene around 3192 and 3116 cm\textsuperscript{-1}. The \( \alpha \)CH fundamental stretch of vinyl radical has been predicted to lie at 3165 cm\textsuperscript{-1} by the ab initio calculations.\textsuperscript{51}

For the vinyl radical search in the jet, the excimer was fired directly into the 1 cm "pseudo" slit, thus photolyzing the 1% mixture of vinyl bromide in helium. Since vinyl bromide has a high vapor pressure at room
temperature, the 1% gas mixture was made by adding the precursor to the mixing cylinder and pressurizing the cylinder with 23 atm of helium. Bromine atom was observed around 3685 cm\(^{-1}\) from the initial photolysis tests at 193 nm with vinyl bromide precursor. Survey scans were performed around 3250 cm\(^{-1}\) for \(\text{C}_2\text{H}_3\), and with 8 atm backing pressure behind the nozzle, many unknown rotational lines appeared. Upon comparison with acetylene in the reference gas cell, it was found that ground state acetylene along with the \(v_2 + v_3 - v_2\) vibrationally excited state of acetylene were being formed in the jet by the photolysis of vinyl bromide. These acetylene lines appeared when the excimer laser was focussed or unfocussed, as shown in Figure 35, although the spectrum arising from the unfocussed excimer photolysis was simpler presumably due to a lower rotational temperature. In survey scans covering the region 3165-3300 cm\(^{-1}\), only acetylene in ground and excited vibrational states was observed from the photolysis of vinyl bromide. If vinyl radical is being produced, the lines would be difficult to distinguish due to the spectral interference by acetylene.

The observation of acetylene in the 193 nm photolysis of vinyl bromide is not too surprising since the photolysis is known to produce both acetylene and vinyl radical. In the study of Slagle et al.\(^5\), the 193 nm photolysis of vinyl bromide was investigated in order to determine photolysis products. The experiments were performed at 599K with a flowing gas mixture containing .003% vinyl bromide with helium to give a total pressure of 3.6 Torr. The main products detected by photoionization
Vinyl bromide photolysis results in the jet. A 1% vinyl bromide in helium mixture is photolyzed straight into the 1 cm "pseudo" slit with 8 atm helium pressure behind the nozzle. Acetylene was observed as a photolysis product when the excimer was focussed or unfocussed. (a) The room temperature acetylene spectrum is shown for comparison. (b) Focussed photolysis of vinyl bromide showing ground and vibrationally excited lines of acetylene. (c) Unfocussed photolysis of vinyl bromide with much fewer lines, presumably due to a colder rotational temperature because of less heating of the nozzle. vibrationally excited lines of the \( v_2 + v_3 - v_2 \) acetylene band still appear, however.
$C_2H_2 \quad \blacksquare \, v_2 + v_4^1 + v_5^1 \quad \bullet \, v_2 + v_3 - v_2$

**Frequency (cm$^{-1}$)**

- **a**
- **b**
- **c**

- **R(5)**
- **R(3)**
mass spectrometry were C₂H₃, C₂H₂, Br, and HBr. They concluded that the photolysis followed two routes:

1) C₂H₃Br + 193 nm → C₂H₃ + Br
2) → C₂H₂ + HBr

Another 193 nm photolysis study of vinyl bromide by Wodtke et al. determined that the branching ratio of the Br/HBr elimination pathways was 1.28 ± .05, with Br atom production then accounting for little more than half of the total signal.⁵⁴

Since the absorption cross-section of Br atom is known, the concentration of Br atoms in the probe region can be determined, and the concentration of vinyl radicals can then be estimated using the branching ratio above. The Br atom concentration was calculated in Section 6.3 to be 1.2 x 10¹³ atoms/cm³. Since 56% of the vinyl bromide dissociation produces vinyl radical, ≈ 6.7 x 10¹² molecules/cm³ would be the number of vinyl radicals expected from this photolysis assuming that the Br atom concentration is not increased because of HBr photolysis. Using the concentration of vinyl radicals, the % absorption of the infrared can be estimated. ΔI/I is defined as:

\[ \Delta I/I = \frac{8\pi^{5/2} |\mu_\alpha|^2 S_{12}^\alpha \exp(-E_1/kT)}{(3uhQ_{int})^{3/2}} \rho_0 L \]
Estimating $\mu_\alpha = 0.05-1 \times 10^{-18}$ esu/cm, and using $S = 1$, $E_1 = 0$, $u = 7.8 \times 10^3$ cm/s, $Q_{\text{int}} = 23$ at 10 K, and $L = 1$ cm, $\Delta I/I = 0.07-2\%$ absorption (see Section 2.6.1 for description of parameters). Since the vibrational transition dipole moment is not known for vinyl radical, this % absorption is only an estimate. With our current multipass scheme, an improvement in signal-to-noise by a factor of 4 can be expected. A S/N ratio of $\approx 10^{-240}$ can be expected with multipassing. Higher concentrations of vinyl radical and improved sensitivity are necessary to ensure observation of this species.

6.5.5 Allyl Radical

The allyl radical has been observed spectroscopically in an argon matrix by infrared, ultraviolet, and ESR techniques. The radicals were produced by flash pyrolysis of allyl iodide, 1,5-hexadiene, diallyl oxalate, or allyl disulfide. The various allyl CH stretches have been observed at 3107, 3051, 3040, and 3019 cm$^{-1}$, with intensities ranging from weak to medium.\textsuperscript{56}

In the jet flash photolysis experiments, both allyl bromide and 1,5-hexadiene were tested as possible precursors for allyl radical. Bromine atom had previously been observed in the jet upon excimer laser photolysis at 193 nm of allyl bromide. In the gas phase studies of Shimo et al., laser photolysis at 193 nm of numerous 1-alkenes, including 1,5-hexadiene, yielded allyl radical.\textsuperscript{57} For our experiments, the liquid precursor was
placed in the U-tube, with approximately 8-14 atm of helium backing pressure. The 193 nm excimer beam was fired straight into the 1 cm "pseudo" slit. In both allyl bromide and 1,5-hexadiene photolysis experiments, broad absorptions were observed around 3120-3060 cm\(^{-1}\) completely obscuring the spectral region of interest. For 1,5-hexadiene, the broad absorption band occurred with and without photolysis, indicating that the precursor was responsible for the absorption. Use of the excimer appeared only to blue-shift the frequency of the maximum in the broad absorption. In retrospect, it is possible that these broad absorptions were due to water absorptions in the unevacuated reference arm of the apparatus. Because of the extensive broad absorptions, further allyl radical studies were halted.

6.5.6 Ethyl Radical

The infrared spectrum of \(\text{CH}_3\text{CH}_2\) radical was first observed by Pacansky et al. by trapping the photolysis products of dipropionyl peroxide in an argon matrix.\(^58\) Later detailed experimental and theoretical studies by Pacansky and Dupuis provided assignments for the infrared absorptions of ethyl.\(^59\) The \(\text{CH}_2\) asymmetric and symmetric stretches were assigned to 3112 and 3033 cm\(^{-1}\), respectively, and the bending mode of the methylene group was located at 540 cm\(^{-1}\). Trevor Sears has observed this bending mode in high resolution studies using a diode laser spectrometer.\(^60\) It should be noted from the matrix isolation work that the bending mode of
ethyl is \( \approx 3 \) times more intense than either of the methylene group stretches.

Since the photolysis precursor in the matrix isolation studies was dipropionyl peroxide, a solid with a low vapor pressure, other potential ethyl radical precursors for the jet experiments were necessary. Because the 193 nm photolysis of acetone was known to produce CO plus CH\(_3\) radicals,\(^{61}\) it was postulated that an analogous precursor, methyl ethyl ketone, would produce CO, CH\(_3\), and CH\(_3\)CH\(_2\) molecular species. Following this photolysis pattern, another possible precursor was diethyl ketone; aqueous solutions of diethyl ketone are known to produce ethyl radicals upon photolysis.\(^{62}\) In addition to the ketone precursors, halogenated alkyls are also possible ethyl radical sources. The gas phase 254 nm photolysis of ethyl bromide has been studied, and the process is known to result primarily in CH\(_3\)CH\(_2\) radicals and bromine atoms, with a quantum yield of one for this dissociation pathway.\(^{63}\) The UV spectrum of the corresponding alkyl iodide, ethyl iodide, displayed absorption maximums at \( \approx 255 \) and 203 nm, thus indicating probable photolysis at the available excimer wavelengths. The excimer laser photolysis of these four precursors was then investigated using the ArF and KrF lines at 193 nm and 248 nm, respectively.

In the initial attempts at ethyl radical observation, the excimer beam was directed into the glass slit extension of the 2 cm "pseudo" slit, thereby photolyzing the precursor inside the thermalization region of the slit. Since all four precursors are liquid at room temperature, the U-tube was used almost exclusively to seed the precursor vapor into the carrier gas.
because of its flexibility in varying the backing pressures. When methyl ethyl ketone was placed in the U-tube, giving a 1% mixture with 11 atm of helium backing pressure, unfocussed ArF 193 nm photolysis produced a 400 mV signal of the $1_1 \leftarrow 0_0$ transition of CH$_3$. After optimization of the CH$_3$ radical signal, survey scans over the region 3140-3100 cm$^{-1}$ were performed for ethyl radical, revealing no CH$_3$CH$_2$ absorptions. A .4% mixture of diethyl ketone with 6 atm backing pressure of helium was then tried as a potential precursor, and scans with either unfocussed or softly focussed excimer beam over 3135-3095 cm$^{-1}$ produced no absorptions as well.

Since negative photolysis results were obtained for the ketone precursors, the alkyl halides were then explored as potential sources for ethyl radical. 193 nm photolysis of 19% ethyl bromide seeded in 2.7 atm backing pressure of helium produced no CH$_3$CH$_2$ radicals. Before experimenting with ethyl iodide, methyl iodide was first tested to determine the relative yield of CH$_3$ radicals as compared to the methyl ethyl ketone photolysis. Photolysis of the methyl iodide produced a 1.5 V CH$_3$ signal, approximately six times larger than the 250 mV signal obtained the preceding day from methyl ethyl ketone. An unfocussed excimer beam inside the glass slit extension gave the largest signal; however, a focussed beam also produced a good signal when the photolysis occurred immediately outside the glass slit orifice.

With the establishment of larger CH$_3$ radical production upon photolysis of methyl iodide at 193 nm, studies then progressed to ethyl iodide photolysis in the hopes of producing ethyl radical. When ethyl
iodide was photolyzed with a tightly focussed excimer beam, many lines were observed at both 11 (1% seed ratio) and 2 (7% seed ratio) atm backing pressures. At 2 atm backing pressure, the unknown signal from focussed photolysis was 300 mV with the x30 amplifier, and lines were observed in the region 3105-3143 cm\(^{-1}\). As a comparison test, a 3% mixture of ethylene in helium was expanded in the jet with 2 atm backing pressure, and after scanning the color center laser over a distinctive region of the unknown spectrum at 3123 cm\(^{-1}\), it was found that the unknown lines matched that of ethylene, as shown in Figure 36.

Ethyl iodide photolysis was then explored at 248 nm in order to determine if the dissociation channel producing ethyl radical might be favored at this wavelength. With 2 atm backing pressure of helium and a tightly focussed excimer beam, two lines were observed in the 3123 cm\(^{-1}\) region. Comparison of the two lines with the cold ethylene spectrum showed that these lines were indeed ethylene. Further comparison with focussed 193 nm results inside the glass slit with 2 atm backing pressure displayed that the 248 nm ethylene spectrum was much simpler. Increased backing pressure of 8 atm and a softer excimer focus resulted in no lines at 3123 cm\(^{-1}\). However, at this point the dynasil glass slit extension was well sooted, which could attribute to the weakened or nonexistent signal. When methyl ethyl ketone was photolyzed next, the soot in the glass slit was removed, presumably due to oxidation by the photolysis products of the precursor. Both methyl ethyl ketone and ethyl bromide photolysis under 8 atm helium and soft focussing conditions produced no absorptions of ethylene around 3123 cm\(^{-1}\).
Comparison of ethyl iodide photolysis products in the jet with expansion of a 3% mixture of ethylene seeded into helium. The nozzle backing pressure was 2 atm for both experiments. (a) ArF excimer photolysis of ethyl iodide within the glass slit. Most lines match the cold ethylene spectrum, with the remaining lines matching the room temperature spectrum of ethylene. (b) Ethylene expanded in the jet with no photolysis.
To temporarily circumvent the glass slit sooting problem, the photolysis experiments then continued by firing the excimer straight into the 1 cm "pseudo" slit. When focussing the 248 nm excimer radiation into the slit containing ethyl iodide seeded into 8 atm helium, a large signal was observed, saturating the x30 amplifier. Basically, in this photolysis set-up, strong ethylene absorptions were observed with tightly focussed excimer while weak ethylene signals were seen for unfocussed photolysis of ethyl iodide seeded into both 8 and 14 atm of helium. 248 nm focussed photolysis of methyl ethyl ketone seeded into 11 atm helium resulted in ≈ 1 V x30 amplified signal of ethylene.

The methyl ethyl ketone photolysis was then repeated using the same experimental conditions as above with the exception of the use of an unfocussed 193 nm excimer beam. In order to directly compare the photolysis data with the ethylene spectrum, ≈ 20 Torr of ethylene was placed in the reference gas cell. After maximizing the ethylene signal with the focussing lens, the lens was then removed for further ethyl radical searches. Some ethylene lines were observed, but weak lines not matching the ethylene were detected as well, as shown in Figure 37. When the precursor and photolysis wavelength were changed to ethyl iodide and 248 nm, again lines appeared which did not match with the ethylene transitions, as displayed in Figure 38. The presence of these unknown lines suggests the possibility of ethyl radical production, although some vibrationally excited band of ethylene could be responsible for the absorptions.

A thorough comparison of the previous results (focussed 193 nm excimer inside the glass slit, 2 and 11 atm backing pressure; focussed 248
Comparison of methyl ethyl ketone photolysis at 193 nm with the room temperature ethylene spectrum (a). (b) To photolyze methyl ethyl ketone, the unfocussed excimer was shooting directly inside the slit, with 11 atm backing pressure behind the nozzle. Transitions were observed in the jet which did not match the room temperature ethylene spectrum.
a

b

Frequency (cm$^{-1}$)

3129.0  3128.6
KrF excimer photolysis of ethyl iodide compared with the room temperature ethylene spectrum (a). (b) The unfocussed excimer fired straight inside the slit photolyzing the ethyl iodide, with 11 atm backing pressure behind the nozzle. Several unknown (possibly ethyl radical) and ethylene lines were observed in the expansion. The lines matching the ethylene spectrum are marked.

Figure 38
nm excimer directly into the slit; 193 and 248 nm unfocussed excimer directly into the slit) with the ethylene reference gas spectrum confirmed that nearly all lines observed were ethylene, with the questionable lines most probably obscured by overlapping transitions. However, as stated earlier, there were some unknown lines observed around 3129 cm$^{-1}$ which appeared in the unfocussed 248 nm photolysis of ethyl iodide seeded into 11 atm of helium inside the throat of the 1 cm "pseudo" slit. In Figure 39, comparison of this data with the 193 nm focussed photolysis inside the glass slit with 2 atm backing pressure showed that the latter spectrum was less complex and possibly only one transition matched in both spectra. Figure 40 shows that some of the unknown lines also matched the 193 nm unfocussed photolysis of methyl ethyl ketone, also aiming directly inside the slit. At this point, it is difficult to come to a definite conclusion concerning the unknown lines since the temperatures of the two spectra are not known. However, it would seem reasonable that the temperature obtained with 11 atm backing pressure, unfocussed photolysis straight into the slit would be comparable or colder than the temperature for 2 atm backing pressure, focussed photolysis inside the glass slit. This general observation suggests the possibility of ethyl radical as the source of unknown lines. Further comparison with jet-cooled pure ethylene, focussed 193 nm photolysis inside the glass slit with 11 atm backing pressure, and 248 nm focussed photolysis directly into the slit is needed in order to eliminate the possibility of either cold ethylene not observable at room temperature or vibrationally excited ethylene.
Ethyl iodide photolysis under different conditions compared with room temperature ethylene spectrum (a). (c) Ethyl iodide was photolyzed inside the glass slit by a focused 193 nm excimer beam. The backing pressure was 2 atm. The lines in this spectrum match up with the room temperature ethylene and is less congested than spectrum (b). (b) Ethyl iodide was photolyzed inside the throat of the 1 cm "pseudo" slit by an unfocused 248 nm excimer beam. The backing pressure was 11 atm. This is the same spectrum as Figure 38b, but is contracted for comparison with (c). There are many more lines in (b), even with this high backing pressure.
Comparison of unfocussed 248 nm photolysis of ethyl iodide and 193 nm photolysis of methyl ethyl ketone shows that some of the unknown transitions match. The backing pressure is 11 atm and the excimer is firing straight into the 1 cm "pseudo" slit for both photolysis experiments. (a) The ethylene room temperature spectrum is shown to distinguish between ethylene and possible ethyl lines observed in the photolysis experiments. (b) Spectrum obtained by ethyl iodide photolysis. (c) Spectrum obtained by methyl ethyl ketone photolysis. Ethylene lines observed in b) and c) are marked.
After reviewing the methyl ethyl ketone and ethyl iodide photolysis results, a trend becomes evident. Using the perpendicular photolysis geometry in which the excimer photolyzes inside the glass slit, the unfocussed 193 nm photolysis of either precursor resulted in no ethylene or unknown lines. When ethyl iodide was photolyzed with a focussed excimer beam (varying from medium to tight focus), strong ethylene lines did appear. It does not seem likely that a different rotational temperature is responsible for the lack of ethylene lines in the unfocussed case because the jet-cooled spectrum line positions of 3% C₂H₄ in helium closely matched that of the focussed excimer photolysis of ethyl iodide. Although there was some difference in line intensities due to the variance in rotational temperatures, it was clearly obvious that the lines matched in the unphotolyzed ethylene and the photolyzed ethyl iodide spectra.

A puzzling observation still remains: basically, ethylene was not observed for unfocussed photolysis inside the glass slit, yet it suddenly appeared strongly for focussed photolysis. Furthermore, ethyl radical was not detected in the unfocussed photolysis experiments inside the glass slit. The results of the initial tests of methyl iodide using the same experimental arrangement may help to explain the ethyl iodide photolysis. When methyl iodide was photolyzed, the best signal was obtained for unfocussed photolysis inside the thermalization region of the glass slit. A focussed excimer beam only gave a good signal when the photolysis occurred immediately outside of the glass slit orifice. This seems to suggest that for focussed photolysis inside the slit either the CH₃ radicals experienced further fragmentation due to multiphoton absorption or recombination
with other methyl radicals due to a greater dissociation of the precursor. If multiphoton fragmentation was the source of decreased CH$_3$ signal inside the glass slit, it would seem that a smaller signal would be obtained outside the orifice as well. Recombination reactions seem to explain the observations inside the glass slit since the thermalization region provides $\approx 10^5$ collisions for cooling, which would also give greater opportunities for reaction. By comparison of the methyl iodide photolysis results, reactions and multiphoton processes might explain the ethyl iodide photolysis observations.

In order to investigate the nonexistent ethyl radical signal and the ethylene production, elucidation of the possible ethyl iodide dissociation and ethyl radical reaction pathways is necessary. Considering first the ethyl iodide photolysis, there are many pathways yielding ethylene. Disproportionation, HX elimination, abstraction, and multiphoton fragmentation processes are all potential sources of ethylene, as illustrated below:

1) $2\text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_4 + \text{C}_2\text{H}_6$

2) $\text{C}_2\text{H}_5\text{I} + \text{hv} \rightarrow \text{C}_2\text{H}_4 + \text{HI}$

3) $\text{C}_2\text{H}_5 + \text{I} \rightarrow \text{C}_2\text{H}_4 + \text{HI}$

4) $\text{C}_2\text{H}_5\text{I} + \text{hv} \rightarrow \text{C}_2\text{H}_5 + \text{I} + \text{hv} \rightarrow \text{C}_2\text{H}_4 + \text{H}$
These dissociation and reaction channels along with their possibility of contributing to ethylene formation in the ethyl iodide photolysis experiments will be discussed.

Disproportionation of ethyl radicals to give ethylene and ethane could be checked by scanning over the ethane absorptions around $2985 \text{ cm}^{-1}$ while focussing the excimer beam inside the glass slit. Observation of ethane would explain the production of ethylene under focussed photolysis conditions. In addition to disproportionation, there are other possible reactions involving ethyl radical which would lead to loss of signal:

5) $2\text{C}_2\text{H}_5 \rightarrow \text{C}_4\text{H}_{10}$

6) $\text{C}_2\text{H}_5 + \text{C}_2\text{H}_5\text{I} \rightarrow \text{C}_2\text{H}_6 + \text{C}_2\text{H}_4\text{I}$

Radical-radical recombinations and reactions with the precursor could then contribute to the lack of ethyl radical signal, provided that these reactions were fast. Spectral searches for butane ($2968 \text{ cm}^{-1}$) and ethane using unfocussed photolysis inside the glass slit are necessary to determine the fate of the ethyl radical, assuming its formation from photolysis of ethyl iodide at 193 nm.

By analogy to the 254 nm gas phase photolysis results of bromoethane, in which the quantum yield of ethyl radicals was unity, it would not seem that immediate HI elimination from ethyl iodide would be responsible for the presence of ethylene. However, spectral searches for HI would be necessary to completely eliminate that possibility. Since neither the HI fundamental or overtone frequencies are accessible in the color center
lasing region, it would be necessary to photolyze deuterated ethyl iodide and search for the overtone of DI. Additionally, if HI was observed, it would be difficult to distinguish between HI elimination and I abstraction in the jet since time behavior of species produced upon photolysis is lost as the gas pulse travels from inside the slit to the infrared probe. Also, the iodine abstraction channel could be a likely possibility only if a large percentage of precursor was being photolyzed. For less efficient photolysis, the ethyl radicals would have a greater probability of colliding (and potentially reacting) with the precursor rather than the iodine atoms.

Because the appearance of ethylene lines correlates with increased fluence of the excimer beam, it seems likely that two-photon events are resulting in ethylene production for focussed photolysis in the glass slit. Studies of the UV spectrum of ethyl radical indicate that the species has an absorption at \( \approx 200 \text{ nm} \).\textsuperscript{64} Also, if a greater percentage of precursor were dissociated, radical-radical reactions may play an important role in ethylene formation. The other disproportionation species, ethane, would have to be observed as well to confirm this pathway for ethylene production.

Because the photofragmentation processes of ketones differs from that of the alkyl halides, alternate reactions or events would be necessary to form ethylene. The proposed methyl ethyl ketone photolysis pathways are based on the photofragmentation process of acetone at 193 nm\textsuperscript{61} and a variety of ketone photolysis experiments at wavelengths 215-235 nm.\textsuperscript{65} The UV absorption cross section of acetone at 193 nm is large (2 x 10\textsuperscript{-18} cm\textsuperscript{2} molecule\textsuperscript{-1}), and the dominant fragmentation with a quantum yield of
.96 gives two methyl radicals and CO as photolysis products. The photofragmentation process is thought to be a two-step mechanism in which methyl and acetyl radicals are initially formed, subsequently followed by unimolecular decomposition of the acetyl group into CO plus methyl radical. Laser multiphoton ionization studies further substantiate this two-step process. Acetyl and methyl radicals are produced initially upon absorption of 193 nm photons, and subsequently the acetyl species are ionized due to the high fluence of the laser, eventually decomposing to give methyl radical and CO.

Since the dominant photofragmentation process of acetone at 193 nm yields two methyl radicals and CO, a similar dissociation pattern can be envisioned for methyl ethyl ketone. As methyl ethyl ketone is an unsymmetric ketone, it seems likely that either an ethyl or methyl radical could be produced initially with the second radical species forming later upon the decomposition of acetyl or propionyl radical. Assuming a similar photofragmentation as that of acetone, the possible primary dissociation products of methyl ethyl ketone are illustrated below by

\[
\begin{align*}
7) \ \text{CH}_3\text{COCH}_2\text{CH}_3 + \text{hv} & \rightarrow \text{CH}_3 + \text{COCH}_2\text{CH}_3 \\
8) & \rightarrow \text{CH}_2\text{CH}_3 + \text{COCH}_3
\end{align*}
\]

where the propionyl group decomposes to give ethyl radical and CO, and the acetyl group decomposes to produce methyl radical and CO. Methyl radical has been observed for the above photolysis, but assuming there are
two dissociation pathways, the branching ratio for pathway 7 is unknown since no other radical species were observed.

As mentioned earlier, the ethyl radical was not observed for unfocussed photolysis of methyl ethyl ketone inside the glass slit. The acetyl radical produced from the photolysis of acetone has been postulated to have a substantial lifetime. If channel 7 was the primary dissociation pathway, with decreased laser fluence (such as unfocussed excimer beam) where one photon events dominate, the propionyl radical may exist past the infrared probe region. The time required for the precursor and photolysis species to reach the infrared beam was typically 7-10 µsec. A propionyl lifetime greater than 10 µsec would prevent observation of the ethyl radical.

The appearance of ethylene in the methyl ethyl ketone photolysis has yet to be explained. Because of the ketone molecular structure, the pathways yielding ethylene are more limited for methyl ethyl ketone photolysis than for ethyl iodide. Possible sources of ethylene production are multiphoton fragmentation (9) and two disproportionation reactions (10,11), as shown in the following processes:

9) \( \text{COCH}_2\text{CH}_3 + \text{hv} \rightarrow \text{CO} + \text{H} + \text{CH}_2\text{CH}_2 \)

10) \( 2\text{CH}_2\text{CH}_3 \rightarrow \text{CH}_2\text{CH}_2 + \text{CH}_3\text{CH}_3 \)

11) \( \text{CH}_2\text{CH}_3 + \text{CH}_3 \rightarrow \text{CH}_2\text{CH}_2 + \text{CH}_4 \)

In order to determine which process was responsible for ethylene formation, spectral searches are necessary for ethane and methane. Also, a
radical scavenger such as NO2 could be added to see if OH were formed by reaction with H atoms, which would suggest dissociation pathway (9) as the likely source of ethylene.

It should be stressed that ethylene was only observed for focussed 248 nm and unfocussed 193 nm photolysis of methyl ethyl ketone in which the excimer laser was firing straight into the bore of the 1 cm "pseudo" slit. Ethylene was not observed for focussed 248 nm photolysis occurring inside the 2 cm glass slit, but absence of the signal could possibly be attributed to soot present in the glass slit blocking the incoming excimer beam. Thus, a direct comparison with ethyl iodide results can not be made for excimer photolysis directed inside the thermalization region of the glass slit. However, some comparison may be made for methyl ethyl ketone and ethyl iodide photolysis straight into the 1 cm "pseudo" slit. Basically, ethylene was observed for focussed and unfocussed photolysis in the throat of the slit, in direct contrast to the glass slit photolysis results. For both precursors, the ethylene signal was much stronger for the focussed photolysis, and this observation could be due to multiphoton absorption or dominating recombination reactions brought about by near complete dissociation of the precursor.

The primary goal of the methyl ethyl ketone and ethyl iodide photolysis studies was to observe the spectrum of ethyl radical. Although efforts were sidetracked by the presence of the ethylene spectrum, the unfocussed photolysis results of both precursors inside the bore of the 1 cm slit do offer some hope of attaining that goal, since unknown lines were observed in addition to the weak ethylene lines. A thorough search for
other molecular species is needed in order to completely understand the jet results, since ethylene still appears in unfocussed photolysis (where presumably one photon events dominate) when the excimer is fired into the bore of the slit.

In addition to the jet work, photolysis of methyl ethyl ketone and ethyl iodide has been tested in the flowing gas White cell. The principal reason for transferring over to the White cell was that time behavior of radical species could be monitored. It was hoped that observation of ethylene and its rate of appearance would give some insight into the dissociation processes of the precursors. Methyl radical has been observed from the photolysis of methyl ethyl ketone, acetone, and methyl iodide with good sensitivity. Searches for ethyl radical and ethylene were unrewarded; however, a problem with the apparatus may have been responsible for the lack of signal. Further work with the flowing gas cell would be helpful in understanding the photolysis results of the jet.
7.1 JET-COOLED RADICAL RESEARCH HIGHLIGHTS

Jet-cooled infrared spectroscopy is an effective tool for the production, cooling, and detection of small free radicals. NH$_2$, OH, CH$_3$, and Br radical species were observed in the jet with good sensitivity. Typically, a 1% absorption of the infrared light results in a S/N ratio of 30. Additionally, low rotational temperatures (10-25K) are obtained for molecular species produced by photolysis.

The exploratory nature of this technique is evident throughout the course of the searches for larger radicals. These experiments increased knowledge of the various precursor photochemical products, but understanding of the results is far from complete. In the attempts to produce and detect large radicals, several closed shell molecules were observed by accident. HCN, t-HONO, CO$_2$, C$_2$H$_2$, and C$_2$H$_4$ were all detected with good to excellent sensitivity. Although larger radicals were not conclusively observed, an important result of these studies is that rotational temperatures of 10K can be obtained, assuming mild photolysis inside the glass slit and high nozzle backing pressures are used. Low temperatures of 10K or less are necessary to ensure observation of larger species.
7.2 SENSITIVITY IMPROVEMENTS

The most effective design improvements were the addition of the multipass White cell and the incorporation of the glass slit into the nozzle design. A factor of 4 increase in signal-to-noise was gained with multipass infrared probing of the jet. Photolysis of the precursor inside the glass slit resulted in lower rotational temperatures of the photolysis products, since the problem with the excimer laser heating the nozzle and subsequent warming of the gas stream was eliminated. A rotational temperature of 25K was measured for NH$_2$ when the excimer fired directly into the throat of the stainless steel slit, whereas a lower temperature of 13K was obtained when NH$_2$ was produced inside the glass slit.

Although the S/N ratios for small radicals and photolysis temperature results are quite satisfactory, further improvements of the signal-to-noise are desired for larger radicals and radical van der Waals complexes. As noted above, a typical S/N ratio for a 1% absorption of the infrared is 30. In the room temperature kinetic cell, a .01% absorption resulted in a S/N ratio of 1. Comparison of the jet and room temperature cell signal-to-noise results reveals that the jet S/N appears to be ~ a factor of 3 lower for the same fractional absorption. Additionally, the multipass White cell has not yet given the expected factor of 10-20 increase in sensitivity. Possible improvements in sensitivity would involve changes in the detection circuitry and optimization of the multipass arrangement. For example, matched detectors having greater sensitivity and a faster response time may
be found to replace the detectors currently in use. The absorption pathlength can be increased by adjusting the White cell to give further infrared passes, provided there is proper mode-matching and alignment of the infrared beam such that beam spots do not overlap on the mirror.

7.3 FUTURE STUDIES

The excellent temperature and sensitivity results of jet-cooled spectroscopy of small radicals appear promising for the extension of this technique to the study of larger radicals; however, further understanding of photochemical, radical recombination, and reaction processes is necessary in order to understand and hopefully increase large radical production. In our studies, there seems to be two photolysis patterns: a stable species is formed which appears almost unrelatedly different from the precursor or the precursor loses two atoms to give a stable molecule having multiple bonds. In both these cases, the mechanism for the stable molecule production is unclear. Multiphoton fragmentation, radical-radical disproportionation, and radical-precursor reactions are all possible sources of stable species produced upon photolysis. For many of the precursors, additional studies in the room temperature kinetic spectroscopy cell would be helpful in understanding the formation processes of the stable molecules. Since gas cell kinetic spectroscopy permits temporal study of the photolysis products, information on the rates and products of radical-precursor and radical-radical reactions can be obtained.
For further radical studies, two systems seem most suitable: OH-Ar van der Waals complex and ethyl radical. The OH-Ar studies were halted because of insufficient sensitivity. With a more sensitive detection scheme (i.e. increased passes of the infrared beam, better detectors and detection electronics), the possibility of observing OH-Ar may be increased. Studies of known, closed shell van der Waals complexes should be undertaken to ensure that the current nozzle produces such complexes. In the previous ethyl radical studies, the observation of the unknown lines observed in the photolysis of methyl ethyl ketone and ethyl iodide needs further investigation.


60. T. Sears (unpublished work)


