A Spectroscopic Study of Nitrogen, Nitrogen/Helium and Fluorobenzenes in a Corona Supersonic Discharge

Jing-Chen Luo

Loyola University Chicago

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A SPECTROSCOPIC STUDY OF NITROGEN, NITROGEN/HELIUM AND
FLUOROBENZENES IN A CORONA SUPersonic DISCHARGE

BY

JING-CHEN LUO

A Dissertation Submitted to the Faculty of the Graduate School
of Loyola University Chicago in Partial Fulfillment of the
Requirements for the Degree of Doctor of Philosophy

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CHAPTER I

INTRODUCTION

Spectroscopy has proven to be a most useful tool in studying the electronic states of molecules [1]. Knowledge in this area is of vital concern to several branches of chemistry, physics, and biology. Among the many spectroscopic techniques, supersonic jets and collimated beams have particularly enhanced knowledge of molecular states since being introduced in the 1970's [2]. However, certain limitations are imposed in the more conventional approaches. For example, when a supersonic jet is probed using laser-induced fluorescence, selection rules limit the investigation to electric-dipole-allowed states. This generally excludes states with spin multiplicity different from the ground state. Since the majority of molecules are of a closed-shell nature in the ground state, jet spectroscopy based solely on radiative excitation has been most informative about singlet states, ground and excited. By comparison, supersonic jets have revealed little about excited states in which the spin multiplicity differs from the ground state.
The work in this thesis has been motivated by interest in molecules which can be excited and cooled in optically forbidden states using a supersonic discharge. The focus lies on the electronic excitation/relaxation processes which can be studied using emission spectroscopy. This thesis reports results of electronic excitation/relaxation experiments with select molecular systems: nitrogen, Nitrogen/Helium, and halogenated aromatics such as hexafluorobenzene radical cation in a corona supersonic discharge.

This thesis is organized as follows. This chapter presents an overview of supersonic expansions and includes a perspective on problems addressed in this work. Chapter II details the apparatus and working procedure of the supersonic discharge experiments. Chapter III presents experimental results and data analysis. A discussion is contained in Chapter VI and conclusions and significance are contained in Chapter V.

A. Overview and Essential Physics of Supersonic Expansions

In the 1970's, supersonic jet techniques became widespread in preparing ultracold molecules for ultraviolet(UV)/visible spectroscopy [2]. Jet techniques make feasible high resolution studies of molecules at very low (translational/rotational) temperatures. In addition, jet
techniques have provided ways to prepare molecular clusters under translationally- and rotationally-cold conditions [2-5]. The conditions for producing the very low temperatures make a supersonic jet quite different from an effusive molecular beam. In a supersonic jet, the size of the hole which the beam emerges greatly exceeds the mean free path of the expanding gas. In an effusive beam experiment, the opposite is true.

In a supersonic expansion, the amount of cooling depends on the pressure drop along the nozzle throat. The cooling derives from the conversion of enthalpy (associated with random motion of gas phase molecules) to directed mass flow. Carrier gases such as argon and helium lack rotational and vibrational degrees of freedom. As a result, monatomics given their low heat capacity makes them ideal carrier gases for seeded polyatomics.

Supersonic speeds are quoted in terms of Mach number $M$, the ratio of mass flow velocity $u$ to the speed of sound $a$:

$$M = \frac{u}{a} \quad (1)$$

Note that $a$ of a gas given by

$$a = (\gamma kT/m)^{1/2} \quad (2)$$
where $\gamma = C_p/C_v$, the ratio of the heat capacities at constant pressure and volume. In a supersonic jet, $M >> 1$. However, $u$ never greatly exceeds the root mean square velocity of the reservoir gas since the amount of enthalpy is finite. As a result, the increase in mass flow velocity upon expansion is finite—even in the case of infinite Mach number where all random energy is converted to kinetic energy. In fact, at infinite Mach number the mass flow velocity of a monatomic gas is only 1.29 times as large as the most probable speed of atoms in an effusive beam [2].

The translational temperature of a supersonic expansion is given by:

$$\frac{T}{T_0} = \left(\frac{P}{P_0}\right)^{\left(\frac{\gamma-1}{\gamma}\right)} = \frac{1}{1+\frac{1}{2\gamma-1}M^2}$$  \hspace{1cm} (3)

where $T_0$, $P_0$ refer to reservoir parameters; $T$, $P$ specify beam conditions several nozzle diameters beyond the expansion point. The Mach number $M$ is a function of the distance downstream from the nozzle:

$$M = A(X/D)^{\gamma-1}$$  \hspace{1cm} (4)

where $A$ is a gas-specific constant, $D$ is the nozzle diameter, and $X$ is the distance from the nozzle.
Note that Equation (4) is based on the assumption that a dense, expanding gas is continuous and subject to hydrodynamic flow. In reality, however, the density of an expanding gas eventually drops to a point where two-body collisions no longer sustain the velocity redistributions required by hydrodynamic flow. As a result, the Mach number and temperature, asymptotically approach terminal values ("freeze"). In the Anderson and Fenn model [6], the terminal Mach number ($M_t$) is given by:

$$M_t = F(\gamma) \left[ \frac{K}{\epsilon} \right]^{-(\gamma-1)/\gamma}$$

where $\epsilon$ is the effectiveness parameter for collisional energy transfer and $K$ is the Knudsen number, the ratio of reservoir mean free path to the aperture diameter [3].

The above equations specify the very low temperatures which can be obtained in a supersonic expansion. For example, for the monatomic gas, argon, with $\epsilon = 0.25$, $\gamma = 5/3$, $F(\gamma) = 2.03$ [3], given the mean free path $6.8 \times 10^{-6}$ cm at 1000 torr [7]. Using the Equation (5) and a nozzle diameter $D = 0.01$ cm, one obtains

$$M_t = F(\gamma) \left[ \frac{K}{\epsilon} \right]^{-(\gamma-1)/\gamma}$$

$$= 2.03 \times \left[ \frac{6.8 \times 10^{-6}}{0.01/0.25} \right]^{-(5/3 - 1)/5/3}$$

$$= 22$$

(6)
Assuming a reservoir temperature $T_0 = 300\text{K}$, one obtains from Equation (3)

$$\frac{T}{T_0} = \frac{1}{1 + \frac{1}{2} (\gamma - 1) M^2}$$

$$= 6 \times 10^{-3}$$

(7)

The important point is that an extraordinarily low terminal temperature $T = 300\text{K} \times 6 \times 10^{-3} = 1.8\text{K}$ can be obtained in a supersonic expansion under rather ordinary conditions.

B. Overview and Essential Physics of Supersonic Discharges

Non-radiative excitation is required to access states with spin multiplicity different from the ground state. An electric discharge offers an effective approach based on collisions. Thus far, several research groups have combined electric discharges with supersonic expansions [8-22]. Engelking and co-workers have used supersonic discharges to study molecular free radicals [8-12]. Sharp and Johnson employed supersonic discharges in their low temperature investigation of triplet Rydberg states of nitrogen [13-16].

Some of these studies featured supersonic corona discharges. A unique characteristic of corona discharges is the segregation of different excited species into different regions between the electrodes [18-20]. Positively charged
cations predominate in the region near the cathode known as the negative glow. Neutral molecules and negatively charged anions predominate in the anode region known as the positive column. In cases where molecular anions are unstable, the majority of species in the positive column of a corona discharge are neutral. Of the excited neutral species formed in the positive column, the majority of long lived or metastable species are molecules in optically-spin-forbidden states.

Supersonic discharges are not widespread, compared with jet studies using optical (laser) excitation. Reasons for this lie in the complexity of collisional excitation and relaxation processes involved in an electric discharge. These processes are a focus of this thesis by way of emission spectroscopy of select molecular systems. A better understanding of these excitation/relaxation processes is the goal of this thesis, in order to further the applicability of supersonic discharge techniques.

In this thesis, supersonic discharges of molecular nitrogen in select excited triplet states will be studied. As it turns out, work leading to this thesis included the discovery of a new class of electronically-excited nitrogen clusters with triplet spin multiplicity: \( N_2(C^3\Pi_u, \nu'=0,1) - N_2(X^1\Sigma_g^+) \) and \( N_2(B^3\Pi_g, \nu''=0,1,2,3,4) - N_2(X^1\Sigma_g^+) \). These clusters
are manifest via blue-degraded, blue-shifted sidebands of the second positive (2+) emission from $N_2(C^3Π_u,v')$ in a supersonic discharge.

A collisional relaxation study of nitrogen in a supersonic helium discharge is also contained in this work. The discussion will center on spectra derived from the Penning ionization of nitrogen by metastable (triplet state) helium at selected points of the jet core. The intensity distribution of the first negative group will be used to calculate the $v''$-distribution of $N_2(X^1Σ^+_g,v'')$. This is feasible due to the "vertical" nature of the Penning ionization and the availability of all necessary Franck-Condon factors and Einstein coefficients. The results in this portion of the thesis reveal a propensity rule which governs the vibrational distribution of $N_2(X^1Σ^+_g,v'')$ in a supersonic discharge. The population of the even-numbered $v''$-levels is favored during collisions between $N_2(X^1Σ^+_g,v'')$ and excited species prior to expansion.

Finally, the emission spectroscopy of the radical cations of several fluoroaromatics in a supersonic discharge is considered. An extensive literature surrounds these molecules with doublet spin multiplicity, beginning with the electron gun experiments of Maier and co-workers [23,24]. Cossart-Magos and colleagues obtained higher resolution
spectra of fluorobenzenes using discharge tube in 1979 [25-27]. The electron impact and laser excitation experiments of Miller et al. were extensively analyzed [28-31]. In this work, the fluorescence spectra of $C_6F_6^+$ and $C_6F_5H^+$ molecular ions in a supersonic argon discharge are studied along with the excitation/relaxation information they reveal. The spectra indicate unusual excitation/relaxation phenomena of these aromatic molecules in a supersonic argon discharge. The experiments indicate spectra to derive from collisions between neutral, triplet state $C_6F_6$ and $C_6F_5H$ molecules and metastable argon in the post-nozzle expansion core. These collisions result in unusual electronic-vibrational distributions of the excited aromatic radical cations.
CHAPTER II

EXPERIMENTAL SETUP AND PROCEDURE

A. Experimental Setup

The apparatus used for this work is described in detail in six separate parts: (1) Gas Handling System, (2) Corona Supersonic Discharge Nozzle, (3) Vacuum System, (4) Optical System, (5) High Voltage Power Supply, and (6) Data Acquisition System.

(1) Gas Handling System

The gas handling system is illustrated in Figure 1. The system closely resembles one used by Herschbach and co-workers [3] in their supersonic beam work. For this thesis work, two-stage regulators were used to dispense the contents of the one or more gas cylinders. These regulators maintained a constant pressure at their outlets in all experiments. Fine metering and gate valves were connected in series to the outlets of each regulator. The connections were made using quarter-inch diameter, hard copper tubing in addition to compression fittings. The outlets of both gate valves were
The gas handling system used in the experiments consists of two gas tanks with two stage regulators (REG), two fine metering valves after the regulator (FV), one glass cell (GC) with a teflon valve (TV), one gate valve (GV), and a mechanical pressure gauge (MPG). Copper tube is used for all the connections.
connected to a quarter-inch compression tee using soft copper tubing. The second tee was connected to a glass cell with a teflon valve. This cell was used for introducing the vapor of liquid phase samples to the discharge nozzle. For some experiments, a water bath regulated the temperature (and thus the vapor pressure) of the liquid phase sample. A third tee junction was connected to a 0 - 1000 torr mechanical pressure gauge.

(2) Supersonic Discharge Nozzle

The nozzle used in this work is similar to one described by Kessler and Koglin [32]. Several differences in the dimensions and operating conditions are noted as follows. The cathode assembly (Figure 2) is formed from a 0.6 cm diameter, 21 cm long, stainless steel rod with a machined thirty degree point. This rod was machine-tapped to mount on a threaded high-voltage feedthrough. The rod tap depth and feedthrough thread allowed for length adjustments (22 - 24 cm) of the cathode assembly.

The anode (Figure 3) is formed by a 3.4 cm diameter, 0.6 cm thick ConFlat (Varian) flange. A forty-five degree, conical cavity was machined into the flange. A 100 micron diameter hole passes from the apex of this cavity through the smooth side of the plate. This formed the aperture through
Figure 2: Cathode Assembly of Supersonic Discharge Nozzle (following page).

The nozzle cathode is formed using a 0.6 cm diameter, 21 cm long, stainless steel rod with a thirty degree point, and threaded high-voltage feedthrough (HVF).
The anode is formed by a diameter $D = 3.4$ cm, $R_1 = 0.6$ cm, $R_2 = 1.0$ cm, $H_1 = 0.6$ cm, and $H_2 = 0.15$ cm ConFlat flange (Varian), with a forty-five degree, conical cavity. A 100 micrometer diameter hole was machined in the middle of the cavity.
Assembled cathode (C), anode (A), body (B), and high-voltage feedthrough (HVF) of the supersonic discharge nozzle used in the experiments of this thesis.
which gas discharges were expanded in all experiments. The assembled discharge nozzle (Figure 4) is mounted on 10 cm flange. Special attention was paid to the cathode length adjustment to ensure proper electrode gap. This gap was usually 1.0 mm to 1.5 mm, depending on the experiment. The anode of the nozzle was mounted on the Conflat Flange using a copper gasket.

(3) Vacuum System

The main chamber of the vacuum system (Figure 5) is 50 cm long and constructed of borosilicate glass. The nozzle inlet was composed of a 65/40 spherical socket. The glass chamber was mounted on the outside of the 9 cm diameter shank of a 23 cm stainless steel flange. The vacuum was maintained in all experiments by a greased (silicone) rubber gasket which filled the small gap between the inner surface of the glass chamber and the outer surface of the stainless steel shank.

The 23 cm stainless steel flange was mounted on a liquid nitrogen cryotrap with nominal air conductance of 1100 liters/second. The cryotrap was mounted on a water cooled baffle with a air conductance of 900 liters/second. The baffle was mounted on an oil diffusion pump with a pumping speed of 800 liters/second. The diffusion pump was water-cooled using the in-house closed-cycle cooling system. A
The vacuum system consists of the primary glass vacuum chamber (home built), one oil diffusion pump (National Research Corporation), ion gauge (Nuclide Co.), two mechanical pumps (Alcaltel), thermocouple gauge (Varian), plus necessary some copper and high vacuum connections.
thermal switch set at 225 °F was mounted on the body of the diffusion pump. The switch was used in-line with the 1190 W, 120 V diffusion pump heater as an interlock to prevent overheating. Two direct-drive mechanical pumps (configured in parallel) with air pumping speed of 3.25 liters/second backed the diffusion pump. A thermocouple gauge was used to monitor the forepressure of the diffusion pump. A Bayard-Alpert ionization gauge was used to monitor pressure in the main chamber.

(4) Optical System

The dispersed emission system (Figure 6) consisted of a Czerny-Turner Monochromator (CVI Laser Digikrom 480). The reciprocal linear dispersion of the monochromator was 1.6 nm/mm with a 1200 g/mm grating. An end-on photomultiplier tube (EMI 9658) with a spectral response range of 300 to 850 nm was used as a detector. The photomultiplier tube was chilled (usually to 250 K) by a water-cooled Peltier refrigerator. Collection optics were mounted in standard cylindrical lens holders. The configuration allows for positioning of the optical axis at different distances from the nozzle.

The monochromator interfaced to a key pad module for manual control. A standard RS-232 C cable connected this
The optical system used in the experiments consists of a 7.5 cm focal length lens (L), a Czerny-Turner Monochromator (MC) (CVI Laser Digikrom 480) with a 1200 g/mm grating and controller (CON), an end-on photomultiplier tube (PMT) (EMI 9658) with a water cooled Peltier refrigerator (PR) (Pacific Instruments), and a homebuilt power supply. The system includes a pre-amplifier (PA), counter (COU), and computer (COM).
module to the serial port of a Zenith PC. This connection allowed for remote PC control of the monochromator.

(5) High Voltage Power Supply

The electronics interfaced to the discharge nozzle are illustrated in Figure 7. An adjustable supply (0 to 15 kV, 1800 W, Voltronics EAM 16-110) was used to initiate and maintain the electric discharges. A 1 KW, 50 kilo-ohm, current limiting resistor bank was used in line between the supply and the nozzle cathode. The voltage-drop across a ten kilo-ohm resistance of the resistor bank was used to measure current through the circuit. A voltage divider provided a 60 mV response per applied kilovolt and drew less than twenty microamps at 12 kV. The body of the discharge valve was held at a common ground potential with respect to the power supply and other components of the apparatus.

(6) Data Acquisition

Data acquisition electronics are illustrated in Figure 8. The anode signal from the photomultiplier tube was directed to preamp (MIT Combo-100). The analogue output of this latter device was monitored during experiments digital storage oscilloscope (Tektronix, 100 MHz). This arrangement allowed for real time observation of the photomultiplier
The high voltage power supply consists of one Voltronics EAM 16-100 adjustable (0-12 kV, 0-1800 W) voltage supply and a resistor bank (25 50 kilo-ohm resistors). A digital volt-meter is used to monitor the voltage.
Figure 8: Schematic for Data Acquisition (following page).

The data acquisition system consists of a pre-amplifier (MIT Combo 100), a digital storage oscilloscope (Tektronix, 100 MHz) used as a monitor, a Dash-8 counter (Metrabyte), 7404 TTL inverter, a time delay module (Evans Electronics), and an interfaced computer (Zenith Data Systems).
signal. The TTL output of the preamp was accumulated and monitored by the computer. In this manner, photon counting was made possible. In all experiments, the counting period was controlled by the computer interfaced to an Evans 4145/4146 time delay module.

B. Samples and Procedure

(1) Gases and Chemicals

All gases used for this thesis work (nitrogen, helium, and argon) were obtained from AIRCO. Each gas was of research grade with minimum purity 99.9995%. All other chemicals (e.g. hexafluorobenzene) were obtained from Aldrich and were used without further purification.

(2) Gas Flow Adjustment

Prior to opening the cylinder valve (Figure 1), the fine metering valve and the gate valve are closed completely. The cylinder valve is then opened completely throughout an experiment. The pressure at the outlet of the a gas cylinder's two-stage regulator is then adjusted to 30 psig (approx. 3 atm absolute). This pressure is maintained for a given experiment. The pressure in the discharge nozzle is adjusted via the fine metering valve (Figure 1). This
pressure was typically < 1 atm for the pure nitrogen, nitrogen/argon and nitrogen/helium experiments; ca. 500 torr for hexafluorobenzene experiments. The mass flow through the fine metering valve remains essentially constant irrespective of whether another source of gas increases the pressure in the discharge nozzle. The mass flow remains essentially constant due to the large pressure gradient between the inlet (>3 atm) and outlet (>1 atm) of the fine metering valve.

(3) Discharge Initiation

The discharge is initiated by adjusting the rheostat of the high voltage power supply until a voltage drop is read across the resistor bank. This drop indicates flow of current through the circuit. The potential for the onset of the discharge was typically 1.5 kV and continuous discharges were able to be sustained using potentials as low as 1.0 kV. The intensity of the discharge emission would ordinarily cease fluctuation within a 10 minute warm-up period.

(4) Spectral Data Collection

The primary collection optic (Figure 6) used in the experiments was a 40 mm diameter, 75 mm focal length lens. For a typical experiment, this lens was placed ca. 20 cm from the jet axis along the vacuum chamber. The entrance slits of
the monochromator were placed ca. 12 cm from the lens. The large distance separating the jet axis and lens minimized image aberrations. Collection of spectra was computer controlled. All spectra were stored on floppy disks in both random access and sequential format.
CHAPTER III

RESULTS AND ANALYSIS

A. Pure Nitrogen Supersonic Discharge Experiments

1. Rotational Distribution of 2+ Emission

Pure N\textsubscript{2} discharges were struck and maintained using potentials of ca. 1 kilovolt and nozzle pressures of ca. 700 torr. The discharges became electrically and optically stable following twenty minute warm-up periods. The current was normally 20 milliamps and varied only a few percent over the stable operating range. Pure N\textsubscript{2} supersonic discharges were visibly bright and yellow-orange in color. The emitting portion extended more than thirty cm when using nozzle pressure 700 torr.

Emission spectra were composed of well-known band systems: N\textsubscript{2} C\textsuperscript{3}\Pi\textsubscript{u} \rightarrow B\textsuperscript{3}\Pi\textsubscript{g}, N\textsubscript{2} B\textsuperscript{3}\Pi\textsubscript{g} \rightarrow A\textsuperscript{3}\Sigma\textsuperscript{+}, and N\textsubscript{2} \textsuperscript{+} B\textsuperscript{2}\Sigma\textsuperscript{+} \rightarrow X\textsuperscript{2}\Sigma\textsuperscript{+}. Historically, these systems have been referred to as the second positive (2+), first positive (1+), and first negative (1-) groups, respectively [33]. In a pure nitrogen discharge, the 2+ emission is the most intense of the three.
Figure 9: Emission Spectrum of Second Positive Group of Pure Nitrogen Supersonic Discharge. (following page).

Near-ultraviolet emission spectrum integrated from discharge core 3 cm from the nozzle. In recording this spectrum, the forepressure was 700 torr and the nozzle voltage was 1 kV. The vibrational sequences of the second positive group \( \text{N}_2 \ C^3 \Pi_u \rightarrow B^3 \Pi_g \) are labeled. Other bands are due to emission of the first negative group.
Figure 10: Spectrum of First Negative Group and Second Positive Group of Supersonic Nitrogen Discharge (following page).

Near-UV/visible emission spectrum integrated from discharge core 3 cm from the nozzle. The forepressure was 700 torr and the nozzle voltage was 1 kV. The first negative ($N_2 \text{B}^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$) and second positive sequences are labeled.
Figure 11: Emission Spectrum of First Positive Group of Supersonic Nitrogen Discharge (following page).

Visible emission spectrum integrated from discharge core 3 cm from the nozzle. The forepressure was 700 torr and the nozzle voltage was 1 kV. Vibrational sequences of the first positive sequences ($N_2 B^3Π_g \rightarrow A^3Σ_u^+$) are labeled.
Relative Intensity

Wavelength (Å)

ΔV = 3

ΔV = 4

ΔV = 2

5650.0 6800.0 7950.0
Representative spectra for the above three systems are contained in Figures 9-11. Note that throughout this work, emission associated with other band systems of nitrogen (both neutral monomer and ion) were not observed. Also, the nozzle components degraded very little with extensive use since sputtering was not significant. As a result, emission from nozzle components (iron, chromium, copper, carbon) did not contaminate spectra. The relative intensity of 1- emission due to \( N_2^+ (B^2 \Sigma_u^+) \) scaled sharply with the nozzle voltage. No emission was ever observed from atomic nitrogen.

Emission due to \( N_2 (C^3 \Pi_u) \) (radiative lifetime < 100 nsec \[33]] could be observed at distances > 30 cm from the nozzle. This indicated that metastable species undergoing electronic relaxation were key components of expanded supersonic discharge. The rotational and vibrational distributions of the \( N_2 C^3 \Pi_u \rightarrow B^3 \Pi_g \) emission spectra were invariant to changes in the nozzle voltage and reservoir pressure. A key parameter, however, was the point along the expansion axis from which the \( N_2 C^3 \Pi_u \rightarrow B^3 \Pi_g \) emission was collected. Figure 12, illustrates rotational profiles of the \( N_2 C^3 \Pi_u, v' = 0 \rightarrow B^3 \Pi_g, v'' = 2 \) emission. These spectra were collected by imaging points within the jet core which were 0.1 and 12 cm from the discharge source.

Detailed comparison was made between rotational profiles
Figure 12: Rotational Profiles of Second Positive group (N₂ C(v' = 0) --> B(v'' = 2)) of emission of Supersonic Nitrogen Discharge (following page).

Top: Normalized N₂ C³Π_u, v' = 0 --> B³Π_g, v'' = 2 emission collected from supersonic discharge core 0.1 cm from nozzle. Bottom: Normalized N₂ C³Π_u, v' = 0 --> B³Π_g, v'' = 2 emission collected from supersonic discharge core 12 cm from nozzle.
of the $N_2 C^3Π_u \rightarrow B^3Π_g$ emission which were experimentally-recorded, and ones computed using the spectroscopic constants of $N_2(C^3Π_u)$ and $N_2(B^3Π_g)$ [33], formulae given in Herzberg [34], and the resolution (0.8 Å) of the experiments. The object was to identify the rotational population distribution of emitting $N_2(C^3Π_u)$. An experimentally-recorded profile was compared with several thousand computed profiles via least-squares analysis in the search for the best matches. It is important to note that profiles obtained by experiment could never be matched in any satisfactory way with $N_2 C^3Π_u \rightarrow B^3Π_g$ emission computed at a single rotational temperature.

Spectra could be matched more satisfactorily using a weighted combination of two or more spectra, each computed at a different rotational temperature. Spectra could be simulated equally well or better using a random walk algorithm involving the population $P(J)$ distributed over the $J$-levels of $N_2(C^3Π_u)$. In such a procedure, a $P(J)$ is modified incrementally in a walk guided by the experimentally-recorded spectrum. For each step, two different $J$-levels are chosen randomly from the set \{0,1,2,...,J_{max}\}. A small fraction (< 0.05) of population in one of these $J$-levels is then transferred to the other to yield a trial $P'(J)$. Such a step is accepted if the $N_2 C^3Π_u \rightarrow B^3Π_g$ emission computed from $P'(J)$ is a better match with the experimentally-recorded spectrum, compared with results derived from $P(J)$. The step
is rejected otherwise, the old $P(J)$ is retained, and another trial $P'(J)$ is formulated. The program is run optimally in alternating coarse- and fine-tune modes. In the former mode, the population exchanges take place between any two randomly chosen levels from the set $\{0,1,2,\ldots,J_{\text{max}}\}$. In the fine-tuning mode, the population exchanges involve randomly chosen $J,J'$-levels whereby $|J - J'| \leq 2$.

The choice of obtaining best-match $P(J)$ via a sum of Boltzmann distributions, or via the random walk method was usually a mixed one. In former approach, it is assumed that temperatures characterize the rotational populations. The random walk procedure assumes nothing about $P(J)$, although it deals with a large number of parameters. The results of both methods were corroborative. Also, the results of the random walk analysis were independent of the number of $J$-levels considered beyond $J_{\text{max}} > 45$. The best-match $P(J)$ obtained from random walk analysis were insensitive to changes in the seed distribution.

Figure 13 illustrates experimental and simulated results of the $N_2$ $C^3\Pi_u, v'=0 \rightarrow B^3\Pi_g, v''=2$ emission. Figure 14 illustrates best-match $P(J)$ derived from spectra collected from different points along the expansion axis. All best-match $P(J)$ were observed to be at least bimodal. The results indicate maxima near $J^* \approx 5, 18, \text{ and } 32$ for $P(J)$ derived from
Figure 13. Experimental and Simulated Rotational Profiles of Second Positive Group ($N_2\; C(v'=0) \rightarrow B(v''=2)$) (following page)

Top: Normalized $N_2\; C^3\Pi_u, v'=0 \rightarrow B^3\Pi_g, v''=2$ emission collected from supersonic discharge core 0.1 cm from nozzle. Bottom: Normalized spectrum simulated from the best-match $P(J)$ obtained from random walk analysis.
Figure 14: Best-Match Rotational Population Distribution $P(J)$ as function of distance along the supersonic jet core (following page)

Best-match $P(J)$ obtained from random walk analysis of the $N_2$ $C^3\Pi_u, v''=0 \rightarrow B^3\Pi_g, v'=2$ emission. Inset quantities refer to the distance (cm) from the expansion aperture at which the spectrum used to compute $P(J)$ was collected.
spectra collected at 0.1 cm from the expansion point. These maxima suggest of Boltzmann distributions with $T \approx 2hcB(J^* + 1/2)^2/k_B \approx 160, 1800, \text{ and } 5500 \text{ K}$. Best-match $P(J)$ derived from spectra collected $\geq 6$ cm from the aperture suggest maxima near $J^* \approx 3$ and 17. These indicate rotational temperatures near 65 and 1600 K. The best-match $P(J)$ was nearly the same for spectra collected $\geq 6$ cm from aperture. Best-match $P(J)$ with a maximum near $J^* \approx 5$ were observed in only from spectra collected at points $< 4$ cm. $P(J)$ with a maximum near $J^* \approx 3$ were observed in spectra collected at axis points $\geq 4$ cm. $P(J)$ with maxima near $J^* \approx 17$ were observed in spectra collected at points as far as 12 cm from the expansion aperture.

2. Appearance of Sidebands of 2+ Emission

The appearance of new spectral bands was discovered in experiments which varied the nozzle electrode gap. These variations changed the coupling between the discharge excitation and the supersonic expansion. When excitation was focused further from the expansion point, spectra revealed sidebands of the $2+ N_2 \ C^3\Pi_u \longrightarrow B^3\Pi_g$ emission. These sidebands were observed by employing electrode-aperture gaps of 1.5 - 1.7 mm using pure nitrogen. These same sidebands were observed using electrode-aperture gaps as low as 1.3 mm using fifty-fifty mixtures of nitrogen/helium and
nitrogen/argon.

Figure 15 illustrates emission spectrum with the sidebands indicated by arrows. This particular spectrum derived from a fifty-fifty mixture of nitrogen/helium excited and cooled in a supersonic discharge. The spectrum was collected from the light emitted from the jet core (nozzle pressure ~1000 torr, electrode-aperture gap 1.7 mm) at 1 cm from the expansion point. The spectrum includes the \( \Delta v = +1, 0, -1, -2, -3 \) sequences of the \( 2^+ N_2 C^3 \Pi_u \rightarrow B^3 \Pi_g \) emission. The sidebands are blue-shifted with respect to emission from \( N_2(C^3 \Pi_u, v'=0,1) \) and are blue-degraded. Figure 16, illustrates the \( 0 - 0 \) spectral region recorded under electrode-aperture gap conditions appropriate to generating the sidebands.

The sidebands derive neither from any previously-characterized spectroscopic systems of nitrogen nor electronic systems calculated on the basis of previously-reported constants [33]. There appeared no connection between the sidebands and possible impurity species of the electric discharges. Instead, the sidebands were sensitive to the electrode-aperture gap, and thus the coupling of the discharge excitation to the supersonic expansion.

Table I lists the observable transition energies and
Figure 15: Emission Spectrum of Supersonic Discharge with sidebands of the Second Positive Group (following page).

This spectrum derived from a fifty-fifty mixture of nitrogen/helium. Sidebands to the blue of the emission from $\text{N}_2(\text{C}^3\Pi_u, v'=0,1)$ are indicated. The nozzle forepressure was 700 torr and the potential was at 1 kV.
Figure 16: Spectrum of 0 - 0 Band and Cluster Sideband of the Second Positive Group (following page).

Region of the 0 - 0 band of \( N_2 \; C^3\Pi_u \longrightarrow B^3\Pi_g \) emission. This spectrum derived from a forty-sixty mixture of nitrogen/argon expanded as a supersonic discharge. The sideband is assigned to emission \( N_2(C^3\Pi_u, v' = 0) - N_2(X^1 \Pi_g) \longrightarrow N_2(B^3\Pi_g, v'' = 0) - N_2(X^1 \Pi_g) \).
Table I Caption

Observed transition energies and shifts of the sidebands relative to the nearest-neighbor, $2+ N_2 C^3Π_u \rightarrow B^3Π_g$ emission bands. Uncertainties are ca. ± 3 cm$^{-1}$. These sidebands are attributed to transitions involving excited nitrogen clusters.
### Table I

<table>
<thead>
<tr>
<th>$v'$</th>
<th>$v''$</th>
<th>$v$ sideband&lt;sup&gt;a&lt;/sup&gt;</th>
<th>blue shift&lt;sup&gt;b&lt;/sup&gt;</th>
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</tr>
<tr>
<td>0</td>
<td>2</td>
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</tr>
<tr>
<td>1</td>
<td>4</td>
<td>25213</td>
<td>125</td>
</tr>
</tbody>
</table>

<sup>a</sup>Values given in wavenumbers (cm<sup>-1</sup>).

<sup>b</sup>Difference between observed sideband transition energy and $\nu_{v',v''}$ of $2+ \text{N}_2 \ C^3\Pi_u \rightarrow B^3\Pi_g$ emission system.
shifts of the sidebands relative to the nearest-neighbor bands of the $2+ N_2 \text{C}^3\Pi_u \rightarrow \text{B}^3\Pi_g$ emission. These sidebands are assigned to transitions involving neutral, excited nitrogen clusters

$$N_2(\text{C}^3\Pi_u, v'=0,1) - N_2(X^1\Sigma_g^+) \rightarrow N_2(\text{B}^3\Pi_g, v''=0,1,2\ldots) - N_2(X^1\Sigma_g^+) + \text{photon.}$$

The distances (>5 cm) over which the sidebands can be observed in the jet flow indicate an important role of metastable nitrogen clusters which are parent to $N_2(\text{C}^3\Pi_u, v'=0,1) - N_2(X^1\Sigma_g^+)$. These parent clusters nucleate near the supersonic expansion source and relax electronically to yield $N_2(\text{C}^3\Pi_u, v'=0,1) - N_2(X^1\Sigma_g^+)$. 

B. Nitrogen-Helium Supersonic Discharge Experiments

In experiments using helium seeded with nitrogen, electric discharges were struck and maintained using potentials of 120 V and nozzle pressures of 700 torr. 1-emission spectra were studied as the $N_2$/He ratio was varied over the range of $2 \times 10^{-5} - 6 \times 10^{-3}$. In these experiments, the nozzle current was 12 milliamps and varied only a few percent over the stable operating range. As in the pure-nitrogen experiments, the emitting portion of the expansions extended several centimeters.
Spectra were composed by 1-group transitions

\[ N_2^+(B^2\Sigma_u^+,v') \rightarrow N_2^+(X^2\Sigma_g^+,v'') + \text{photon}. \]

As illustrated in Figure 17, the intensity distribution depended on the nitrogen/helium mixing ratio. Emission from higher-lying \( v' \)-levels was enhanced at the higher diatomic/monatomic ratios. Also, the discharge-expansion coupling could be adjusted so as to accentuate the profile of Figure 17D. The results were spectra such as illustrated in Figure 18. In the latter case, the emitting \( N_2^+(B^2\Sigma_u^+,v') \) population is concentrated (as in 17D) in the even-numbered vibrational levels. Regardless of discharge/expansion conditions, all spectra demonstrated rotational (r) temperatures near 250 K. These were considerably higher than r-temperatures (50 K) obtainable from supersonic cooling under the conditions employed.

The radiative lifetime of \( N_2^+(B^2\Sigma_u^+,v') \) (50 nsec [33]), the jet emitting length (> 5 cm), the nitrogen mole fractions (0.00002 - 0.006), radiative intensity, and r-temperatures indicated collisions in the post-nozzle gas flow to underlie the spectra. All factors pointed to Penning ionization of \( N_2(X^1\Sigma_g^+,v'') \) by metastable helium

\[ N_2(X^1\Sigma_g^+,v'') + \text{He}^* \rightarrow N_2^+(B^2\Sigma_u^+,v') + \text{He} + \text{e}^- \]
Figure 17. Emission Spectra of First Negative Group of Supersonic Nitrogen/Helium Discharges (following page).

Portions of 1- emission featuring the $\Delta v = +2$ sequence. These spectra were integrated from the supersonic discharge core 0.5 cm from nozzle. Nitrogen mole fractions in these experiments are given as follows: (A) 0.00002, (B) 0.0005, (C) 0.002, (D) 0.004, and (E) 0.006.
Figure 18. Emission Spectrum of Nitrogen/Helium Supersonic Discharge Using Coupling Conditions which enhance the distribution features of 17d.

Portion of 1- emission featuring the $\Delta v = +2$ sequence obtained by changing the discharge-expansion coupling. This coupling is controlled by the inner electrode-aperture gap of the nozzle. This spectrum was integrated from light emitted by the expansion core ca. 0.5 cm from nozzle. The nitrogen mole fraction was ca. 0.005.
as responsible for $N_2^+(B^2Σ_u^+,v')$ in the expansion core. This was consistent with the low voltages employed in the nozzle throat, and collision rates of $10^5 - 10^3$ sec$^{-1}$ along the expansion axis 0.5 - 5 cm beyond the aperture. In expanded discharges, distributions of $N_2(X^1Σ_g^+,v'')$ were frozen after a certain number of collisions at the nozzle throat. These distributions were interrogated downstream as a result of the infrequent collisions between $He^*$ and $N_2(X^1Σ_g^+,v'')$. That Penning ionization did not retain low r-temperatures in the emitting products is due to the $N_2(X^1Σ_g^+,v'')$-$He^*$ transition state lifetime and geometry [35,36].

The literature reports different sets of Einstein and Franck-Condon coefficients appropriate to the 1- emission. At least two different sets of Franck-Condon coefficients relating $N_2(X^1Σ_g^+,v'')$ and $N_2^+(B^2Σ_u^+,v')$ populations are available [37,38]. The analysis for this thesis used Einstein and Franck-Condon coefficients supplied by Piper [39]. These coefficients enabled determination of $N_2^+(B^2Σ_u^+,v')$ populations ($v'$) from the spectra, and $N_2(X^1Σ_g^+,v'')$ populations ($v''$) which were precursor to $N_2^+(B^2Σ_u^+,v')$ in the expansion core.

In the analysis, $v''$ and $v'$ are related by a linear transformation

$$v' = Q v''$$
where $Q$ is a matrix composed of $X^1\Sigma_g^+ \leftrightarrow B^2\Sigma_u^+$ Franck-Condon coefficients [38]. In principle, $V''$ can be obtained directly from the quantity $Q^{-1}v'$. In practice, however, the inversion/multiplication procedure is extremely sensitive to truncation, round-off, and experimental uncertainty. Often the quantity $Q^{-1}v'$ yields negative values (physically impossible!) for various components of $V''$.

A least-squares strategy proved more successful. It was assumed that only levels $v'' = 0, 1, \ldots 4$ of $N_2(X^1\Sigma_g^+, v'')$ were populated in the discharge. This was reasonable given ambient gas temperatures of $< 1000$ K inside the nozzle throat. A five-parameter, least-squares-fitting routine then identified the $V''$ most consistent with the data. In this routine, a trial $V''$ is multiplied by $Q$ to yield a trial $v'$. The latter is then compared with $v'$ determined from the 1- spectra. Several non-trivial assumptions are at work in this analysis. However, the approach yielded good correlations between experimentally observed $v'$ and best-fit $QV''$ (Figure 19).

Results (Table II) indicated the $N_2(X^1\Sigma_g^+, v'')$ populations to be highly non-Boltzmann. Also, collisions in the supersonic discharges biased the lower-lying populations of nitrogen heavily in favor of the even-numbered $v''$-levels.
Figure 19: Experimental Value and Best-fit $QV''$ of the Quantities of $\ln(N_{v'}/N_{v'=0})$ (following page).

Representative $v'$-populations of $N_2^+(B^2\Sigma_u^+,v')$. Symbols refer to quantities $\ln(N_{v'}/N_{v'=0})$ determined directly from $1-$ spectra. Letters refer to conditions under which the spectra of Figure 17 were recorded. Uncertainties of the analysis are less than the symbol widths. Symbols for $\ln(N_{v'}/N_{v'=0})$ computed on the basis of best-fit $QV''$ overlap with those allied with $1-$ spectra. For presentation purposes, splines (solid lines) have been constructed and illustrated regarding $\ln(N_{v'}/N_{v'=0})$ determined from best-fit $QV''$. 
Table II Caption

Components of $V''$ determined by least squares analysis. The product $QV''$ is that which best-matches $V'$ determined experimentally from 1- spectra. Letters refer to conditions under which spectra of Figure 2 were recorded.
<table>
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<tr>
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<td>0.1364</td>
</tr>
<tr>
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</table>
C. Fluorobenzene-Argon Supersonic Discharge Experiments

In these experiments, continuous supersonic discharges of argon seeded with either C$_6$F$_6$ or C$_6$F$_5$H were struck and maintained using potentials of 120 V and nozzle pressures of ca. 500 torr. With proper seeding conditions, the emitting portion of the supersonic jets extended several cm. Spectra collected from C$_6$F$_6}$/Ar, C$_6$F$_5$H/Ar and C$_6$F$_3$H$_3$/Ar discharges were composed by the transitions

\[
\text{C}_6\text{F}_6^+(B^2A_{2u}) \longrightarrow \text{C}_6\text{F}_6^+(X^2E_{1g}) + \text{photon}
\]

\[
\text{C}_6\text{F}_5\text{H}^+(B^2B_2) \longrightarrow \text{C}_6\text{F}_5\text{H}^+(X^2X_2) + \text{photon}.
\]

\[
\text{C}_6\text{F}_3\text{H}_3^+(B^2A''_2) \longrightarrow \text{C}_6\text{F}_3\text{H}_3^+(X^2E''_2) + \text{photon}
\]

As illustrated in Figures 20, 21 and 22, the spectra demonstrated much electronic-vibrational structure, much of which has been characterized and assigned by previous researchers [27]. The degree of congestion, however, is less than that of spectra recorded from the more conventional discharge experiments. This is due to the cooling of the supersonic expansions. This cooling makes possible the assignment of electronic-vibrational bands which are obscure and/or diffuse in experiments using conventional discharges.
Figure 20. Emission Spectrum of Hexafluorobenzene Radical Cation $\text{C}_6\text{F}_6^+$ in Supersonic Argon Discharge (following page).

$\text{C}_6\text{F}_6^+$ $\text{B}^2\text{A}_2u \rightarrow \text{X}^2\text{E}_1g$ emission band system. Spectrum was collected from the supersonic discharge core 0.5 cm from the nozzle aperture. Assignment notation is that used by Cossart-Magos and co-workers in reference 27.
Figure 21. Spectrum of Pentafluorobenzene Radical Cation \( \text{C}_6\text{F}_5\text{H}^+ \) in Supersonic Argon Discharge (following page).

\( \text{C}_6\text{F}_5\text{H}^+ \rightarrow \text{B}^2\text{B}_2 \rightarrow \text{X}^2\text{A}_2 \) emission band system. Spectrum was collected from the supersonic discharge core 0.5 cm from the nozzle aperture. Assignment notation is that used by Cossart-Magos and co-workers in reference 27. The argon atomic lines have been subtracted from the spectrum.
Relative Intensity

$6a_0^1$, $9a_0^1$, $1_0^1 6a_1^0$, $6a_0^1 1_1^0$, $9a_0^1 6a_1^0$, $9a_1^0$, $6a_1^0$

4240.0 Å 4332.5 Å 4425.0 Å
Figure 22. Emission Spectrum of 1,3,5 Tri-fluorobenzene Radical Cation $\text{C}_6\text{F}_3\text{H}_3^+$ in supersonic argon discharge (following page).

$\text{C}_6\text{F}_3\text{H}_3^+ \quad \text{B}^2\text{A}'' \rightarrow \text{X}^2\text{E}''$ emission band system. Spectrum was collected from the supersonic discharge core 0.5 cm from the nozzle aperture. Assignment notation is that used by Cossart-Magos and co-workers in reference 27. The argon atomic lines have been subtracted from the spectrum.
Tentative assignments are labeled in the figures using Wilson notation for the vibrations. It is seen the most active transitions are allied with vibrational modes 2 and 18 of the ground and excited states. However, several distinct sequence bands are also revealed in the spectra.
A. Pure Nitrogen Supersonic Discharge Experiments

1. Discussion of Rotational Distribution of 2+ Emission

If one considers nitrogen as an ideal gas which can absorb all discharge power prior to the expansion, well-known formulae allow the nozzle throat temperature $T_0$, terminal translational temperature $T_t$, and collision frequency $z$ along the jet axis to be estimated. These quantities are important to interpreting the emission (Chapter III) in order to yield information about electronic excitation and relaxation.

Typical values for the nozzle reservoir (pressure at 1000 torr) density, flow rate, discharge power, and aperture diameter are given, respectively, by $5 \times 10^{19}$ molecules/cm$^3$ ($n_0$), $5 \times 10^{20}$ molecules/sec, 50 watts, and 0.01 cm (D). If energy $\approx 1 \times 10^{-12}$ ergs received by each N$_2$ molecule is distributed statistically, a pre-expansion temperature $T_0 \approx 2E/7k_b \approx 2100$ K characterizes the different degrees of freedom. Here the translational (t), rotational (r), and
vibrational (v) degrees of freedom account for the diatomic heat capacity.

The terminal Mach number $M_t$ is then given by Equation (5) of chapter I:

$$M_t = F(\gamma) \left[ \frac{K}{\epsilon} \right]^{-1/\gamma}$$

When assuming vibrational cooling to be minimal, $\gamma = 7/5$ [3]. This is reasonable given the high pre-expansion temperature and the vibrational level spacing (2000 cm$^{-1}$) of nitrogen. $F(\gamma) = 2.48$ while $\epsilon \approx 0.5$ for diatomics [3]. These quantities and the cross section of N$_2$ ($\sigma = 43$ Å$^2$) yield a value of $M_t \approx 32$. $T_t$ is then estimated as

$$T_t \approx T_0 \left[ 1 + (0.5) (\gamma - 1) M_t^2 \right]^{-1}$$

$$\approx 10 \text{ K}$$

The collision rate $z$ at distance $x$ from the expansion source is given in the kinetic theory of gases as

$$z(T,x) = \sigma \left( \frac{8k_BT}{\pi\mu} \right)^{1/2} n(x)$$
where \( n(x) \) is the density along the jet axis and \( \mu \) is the reduced mass for colliding nitrogen molecules. For the region of "free" molecular flow, \( n(x) \) is given by

\[
n(x) = n_0 (x_r/x)^2
\]  

(4)

where

\[
x_r = D \left[ (0.5) (\gamma - 1) A(\gamma)^2 \right]^{-1/2(\gamma - 1)}
\]  

(5)

From reference [3], \( A \) is found to equal 3.65 when \( \gamma = 7/5 \). Using the experimental apparatus value of \( D \) (Chapter II, 0.01 cm), one obtains a value of \( 2.9 \times 10^{-3} \) cm for \( x_r \). The above values of \( \sigma \) and \( T_t \) yield \( 1.6 \times 10^6 - 6 \times 10^2 \) sec\(^{-1} \) for the collision rate along the jet axis 0.1 - 5 cm beyond the aperture; 100 sec\(^{-1} \) at 12 cm.

The number of collisions experienced by a nitrogen molecule traveling in a given region beyond the supersonic discharge nozzle can be estimated following certain approximations. If enthalpy \( (7/2)k_B T_0 \) per molecule is converted to directed mass flow during the expansion, the terminal velocity \( v_t \) is estimated as

\[
v_t \approx \left( 7k_B T_0 / m \right)^{1/2}
\]  

(6)
A value of 2100 for $T_0$ places $v_t$ near $2.1 \times 10^5$ cm/sec. The incremental number of core collisions $dZ$ experienced by $N_2$ moving along length element $dx$ is then

$$dZ \approx \sigma (8k_BT/\pi \mu)^{1/2} \left[ n(x)/v_t \right] dx \quad (7)$$

In Equation (7), it is assumed that the expansion travels at velocity nearly equal to $v_t$. This is reasonable for the flow region beyond a few nozzle diameters. It follows that the total number of collisions over a region bounded by $x_1$ and $x_2$ is

$$Z \approx \sigma (8k_BT/\pi \mu)^{1/2} n_0 \left[ x_r^2 / v_t \right] \int_{x_1}^{x_2} dx \cdot x^2$$

$$= \sigma (8k_BT/\pi \mu)^{1/2} n_0 [x_r^2/v_t] \{1/x_1 - 1/x_2\} \quad (8)$$

Using integration limits of 0.1 cm and 5 cm and $n(x=0)$, $Z \approx 0.7$ collisions based on the cross section $N_2$. In the region bounded by 5 cm and 12 cm, $Z \approx 0.08$ collisions.

While specific to $N_2$, the above calculations are relevant to within an order-of-magnitude for many molecules which can be studied using the supersonic discharge technique. The calculations point out that the pre-expansion temperatures are much greater than those of more conventional ($T_0 \approx 300$ K)
jet studies. However, extensive translational and rotational cooling can be realized several nozzle diameters beyond the aperture.

The electronic relaxation principles are then given as follows. For any excited metastables of nitrogen ($N_2^*$) in the supersonic discharge, low t- and r-temperatures will be the rule. Further, such low temperatures will hold for any nitrogen species $N_2''$ derived beyond the nozzle from a radiative process

$$N_2^* \xrightarrow{} N_2'' + \text{photon.}$$

Since the above is subject to strict angular momentum constraints ($\Delta J = 0, +1, -1$), the t- and r-distributions of $N_2^*$ and $N_2''$ will almost mirror each other.

The calculations also show that post-nozzle collision frequencies can exceed the radiative rates of metastables, especially within a few cm of the expansion point. As a result, electronic relaxation of any forms of metastable nitrogen by collision

$$N_2^* + N_2 \xrightarrow{} N_2'' + N_2$$

competes effectively with radiative relaxation at points close
to the aperture. Unlike radiative relaxation, however, electronic relaxation by collision will not retain low r-temperatures in the product species. This is due to the exchange of torque in the collider transition state. This type of electronic relaxation is characterized by r-temperatures in product N$_2^*$ which exceed T$_t$. The r-temperatures will depend critically on the N$_2^*$$\rightarrow$N$_2^*$ energy gap, collision lifetime and geometry.

The above offers important guidelines for interpreting the emission spectra presented in Chapter III. The emission spectra of transient species such as N$_2$(C) (radiative lifetime ca 50 nsec) derived from the metastable nitrogen reveal the electronic relaxation mechanism. The fraction of N$_2$(C)-population which demonstrates low r-temperatures derive from metastable nitrogen (one or more species) via a radiative process. This fraction has a relaxation history in which electronic (e) and v-degrees of freedom are uncoupled to the t- and r- degrees of freedom. The fraction of N$_2$(C)-population whose spectra demonstrate r-temperatures $\gg$ T$_t$ derive from electronic relaxation by collision. This N$_2$(C)-population has a history marked by at least one irreversible electronic relaxation.

The above neglects several kinetic factors of supersonic nitrogen discharges, for example, the different cooling rates
for the different r-levels. The high pre-expansion temperatures mean that high-lying r-levels are heavily populated. With $T_0 \approx 2100$ K, the maximum in the rotational population distribution $P(J)$ of a diatomic occurs at

$$J^* = \left( \frac{k_B}{2} \frac{T_0}{h c B} \right)^{1/2} - 1/2$$

$$\approx 19$$

where $h$, $c$, and $B$ (ca. 2 cm$^{-1}$ for nitrogen) are Planck's constant, the speed of light, and the rotational constant [40]. In the experiments present in Chapter III, the r-level most heavily populated maximum corresponds to an energy 760 cm$^{-1}$ above the $J = 0$ level. For most of nitrogen's electronic states, the separation between individual rotational levels near $J^* = 19$ is 76 cm$^{-1}$. For cooling to be effective in the supersonic discharge, r-quanta which are a factor of three greater than those of room temperature ($T_0 \approx 300$ K) expansions would have to be converted to directed mass flow [34]. Effects due to different cooling kinetics are anticipated in supersonic discharges (those of Chapter III and otherwise), given that lower J-levels are more easily cooled than higher J-levels. As a result, the spectra of transient emitters such as $N_2(C)$ observed sufficiently far from the expansion point highlight unusual cooling phenomena. This is because far downstream in the expansion, radiative relaxation (with $\Delta J$
constraints) of the nitrogen metastables dominates electronic relaxation by collision.

In reviewing the pure nitrogen data of Figure Chapter III (Figure 12-14), the lowest $r$-temperature, $65 \text{ K} \sim J^* \approx 3$, suggested by the best-match $P(J)$ is reasonable for $T_i$ obtained by supersonic cooling. This lowest temperature is taken as the signature of the radiative mechanism by which $N_2(C^3\Pi_u)$ is formed in the supersonic discharge. One or more emitting precursors operate independently in this mechanism

$$N_2^* \rightarrow N_2(C^3\Pi_u) + \text{photon}$$

where $N_2^*$ represents a form of metastable nitrogen.

An intermediate temperature, $160 \text{ K} \sim J^* \approx 5$, suggested by the best-match $P(J)$ was observed only in spectra collected within a few cm of the expansion aperture. This temperature is allied with the collisional mechanism leading to $N_2(C^3\Pi_u)$

$$N_2^* + N_2(X^1\Sigma_g^+) \rightarrow N_2(C^3\Pi_u) + N_2(X^1\Sigma_g^+)$$

The collision rates near 4 cm are of order $10^3 \text{ sec}^{-1}$. It is near this point that the radiative relaxation mechanism begins to dominate collisional relaxation. Thus $10^3 \text{ sec}^{-1}$ can be taken as an upper limit estimate of the radiative rate of
the metastable precursor(s) of \( N_2(C^3\Pi_u) \).

Rotational temperatures \( \geq 5500 \, \text{K} \) \( (J^* \approx 32) \) were indicated only in spectra collected from points close to the expansion source. Such temperatures most likely derive from collisional relaxation of metastable nitrogen—a form different from that responsible for the \( J^* \approx 5 \) maximum. Rotational temperatures \( 1600 - 1800 \, \text{K} \) \( (J^* \approx 16 - 18) \) were indicated in spectra recorded at points as far as 12 cm from the source. These temperatures most likely derive from radiative relaxation of metastable nitrogen. These high temperatures indicate significant differences in the cooling rates of low and high lying \( J \)-levels. Another explanation involves electronic relaxation by collision followed by radiative relaxation. The experiments demonstrate that unusual rotational population distributions—inversions among the \( J \)-levels—can be obtained for metastable nitrogen and derivatives in a supersonic discharge.

2. Discussion of the Sidebands of the 2+ Emission

There are many studies of nitrogen clusters in the condensed phase [41-44] or trapped in van der Waals ground state potentials [45,46]. Ionic species, such as \( \text{N}_2^+(X^2\Sigma_g^+) \), participate in stable clusters of molecular nitrogen [47-50]. However, experiments prior to this thesis have not revealed
the presence of neutral, transient bimolecular clusters, 
\(N_2(C^3\Pi_u) - N_2(X^1\Sigma_g^+)\) and \(N_2(B^3\Pi_g) - N_2(X,^1\Sigma_g^+)\) in an electric 
discharge, or any other source.

The cluster experiments of Chapter III demonstrate 
several features of \(N_2(C^3\Pi_u) - N_2(X^1\Sigma_g^+)\) and \(N_2(B^3\Pi_g) - N_2(X,^1\Sigma_g^+)\). 
First, \(N_2(X^1\Sigma_g^+)\) bound to \(N_2(C^3\Pi_u)\) and \(N_2(B^3\Pi_g)\) exerts a 
relatively small electronic and vibrational perturbation. One 
interprets this from the small spectral shifts (100 cm\(^{-1}\)) 
relative to the monomeric \(N_2\ C^3\Pi_u \longrightarrow B^3\Pi_g\) emission. This is 
supported by the fact that intensity distributions observed 
for the cluster transitions agree with ones predicted by the 
\(N_2\ C^3\Pi_u \longrightarrow B^3\Pi_g\) Franck-Condon factors.

No emission was observed from clusters \(N_2(C^3\Pi_u, v > 1) - N_2(X^1\Sigma_g^+)\). It is likely that \(N_2(C^3\Pi_u, v' \geq 2) - N_2(X^1\Sigma_g^+)\) 
predissociates in a time less than the radiative lifetime. 
This would be ca. 50 nsec on the basis of radiative \(N_2(C^3\Pi_u)\) 
[32] and means that radiative relaxation of \(N_2(C^3\Pi_u, v' = 0,1) - N_2(X^1\Sigma_g^+)\) 
competes favorably with predissociation. This would 
be the case if the cluster binding energy is on the same order 
as the vibrational quantum of \(N_2(C^3\Pi_u) (1991 \text{ cm}^{-1})\).

The blue-shifts reveal details of the binding affinity 
of \(N_2(C^3\Pi_u)\) and \(N_2(B^3\Pi_g)\) to \(N_2(X^1\Sigma_g^+)\). Spectroscopic blue-shifts 
are uncommon in experiments with molecular complexes, since
a complex is generally bound more strongly in the upper electronic state than in the lower state. The shifts reported in this thesis deal with species which are of an open shell nature in both upper and lower states. Also, the shifts are of the same order as those reported by Tinti and Robinson in their study of nitrogen isolated in frozen neon [51]. That the blue-shifts observed in this thesis work exceed those reported for nitrogen-neon clusters is likely due to the greater polarizability of nitrogen relative to neon. The observed spectral shifts demonstrate the electronic levels of $N_2(C^3\Pi_u) - N_2(X^1\Sigma_g^+)$ and $N_2(B^3\Pi_g) - N_2(X^1\Sigma_g^+)$ to be displaced slightly from the energy levels of the separated molecule limits $N_2(C^3\Pi_u) + N_2(X^1\Sigma_g^+)$ and $N_2(B^3\Pi_g) + N_2(X^1\Sigma_g^+)$. The shifts also indicate that the complexation of excited $N_2$ with ground state $N_2$ leads to a stronger bond for $N_2(B^3\Pi_g)$ than for $N_2(C^3\Pi_u)$.

Studies have shown that nozzle conditions such as pressure, temperature, and aperture size determine the nucleation, growth, and relaxation of molecular clusters [52]. The experiments described in this thesis demonstrate that nitrogen cluster formation is encouraged in a supersonic discharge by moving the excitation events further from the expansion aperture. This is reasonable given that larger electrode-aperture gaps increase the expansion time and allow further cooling and three-body collisions to take place. The experiments also show that the cluster formation is enhanced
when monatomics are included in the supersonic discharge. This is reasonable given that the three-body collisions

\[ N_2^* + N_2(X^1\Sigma^+_g) + M \longrightarrow N_2^* - N_2(X^1\Sigma^+_g) + M \]

are essential to all cluster nucleation. Here the asterisk denotes a form of metastable nitrogen while \( M \) denotes a colliding species which absorbs the heat of complexation early in the expansion. Over the course of this thesis work, experiments demonstrated \( N_2(X^1\Sigma^+_g) \), helium, and argon as effective third bodies in the cluster nucleation step. It appears that monatomics (He and Ar) absorb the heat of complexation more readily than \( N_2(X^1\Sigma^+_g) \) without quenching the excited precursor \( N_2^* \). Experiments revealed no evidence of excited clusters involving nitrogen-argon or nitrogen-helium in the supersonic discharge. One would anticipate nucleating excited nitrogen-argon clusters as easily as nitrogen-nitrogen. Thus, a search for conditions favorable to nitrogen-argon transient clusters is advisable for future work built upon this thesis. The emission wavelengths of \( N_2(C^3\Pi_u, v'=0,1) - \text{Ar} \) should be nearly equal to those of \( N_2(C^3\Pi_u, v'=0,1) - N_2(X^1\Sigma^+_g) \).

The lifetimes of \( N_2(C^3\Pi_u, v'=0,1) - N_2(X^1\Sigma^+_g) \) and \( N_2(B^3\Pi_g, v'') - N_2(X^1\Sigma^+_g) \) are short due to efficient radiative relaxation. Thus, emission spectroscopy is likely the most suitable, probe
of the transient clusters. The parent metastable $N_2^+ - N_2(X^1\Sigma_g^+)$, however, may likely be investigated using laser induced fluorescence or mass-selective techniques. Emission spectra carry certain shortcomings, at lower resolution where cluster bands overlap the monomer bands. Table I thus contains only a partial listing of the allowed transitions between $N_2(C^3\Pi_u) - N_2(X^1\Sigma_g^+)$ and $N_2(B^3\Pi_g) - N_2(X^1\Sigma_g^+)$. 

B. Nitrogen-Helium Supersonic Discharge Experiments

Excitation using an electric discharge would not be expected to be a selective process. In the helium-nitrogen experiments of the previous chapter (Section IIIB), electrons accelerated between the cathode and anode prepared any number of excited species in the nozzle throat. Species such as He$(2^3S)$, $N_2^+(B^2\Sigma_u^+)$, $N_2^+(X^2\Sigma_g^+)$, $N_2(A^3\Sigma_g^+)$, $N_2^+(A^2\Pi_u)$ are a partial list [44]. These excited species collided with $N_2(X^1\Sigma_g^+, v'')$ prior to expansion in numbers which depended on such things as the nitrogen/helium ratio and the discharge-expansion coupling.

The experiments demonstrated that when conditions (extremely low nitrogen/helium ratios) favored only atom-diatom collisions, the lower-lying $v''$-populations of $N_2(X^1\Sigma_g^+, v'')$ were Boltzmann-like. When collisions between diatomics were encouraged (higher seeding), a selective "up-
pumping" happened which favored population of the even-numbered $v''$-levels of ground state nitrogen.

There are at least two ways of viewing and attributing the experimental results of nitrogen/helium supersonic discharges. The first is that the discharged and expanded mixtures were thermodynamic systems very far from equilibrium. Extremely sharp temperature gradients involving different degrees of freedom were in effect. Localized portions of discharged gas could then be characterized by high $e^-, v^-, r^-, t$-temperatures, relative to those of surrounding gas.

Partial equilibration involved collisions between $N_2(X^1\Sigma_g^+, v'')$ and high-temperature components of the discharge. If local temperature gradients were sufficiently large, the $N_2(X^1\Sigma_g^+, v'')$ would serve as an energy sink. Transfer of multiple $v$-quanta would be encouraged in the collisions taking place during the supersonic expansion. This is one way attributing results (Figure 17-19, Table II) which showed $>1$ $v$-quanta exchanges to dominate the equilibration process.

A second explanation is on symmetry grounds. The experiments revealed nitrogen molecules (charged and/or electronically excited) to perturb $N_2(X^1\Sigma_g^+, v'')$ in a totally symmetric way. This perturbation had the effect of pooling discharge energy in ground-state nitrogen levels described by
symmetric oscillator wavefunctions. These levels were the low-lying ones with even vibrational quantum numbers.

The role of symmetry in collisions between diatomics has been examined in several previous studies [53–55]. Beam experiments have demonstrated a high propensity for even numbers of vibrational quanta to be transferred during collisions between $N_2(X^1\Sigma_g^+)$ and $N_2^+(X^2\Sigma_g^+)$. Such phenomena originate from a totally symmetric operator which controls the exchange of charge, electronic excitation energy, and coupled vibrational quanta between colliding molecules. It appears that symmetry plays a critical role in the redistribution of energy among nitrogen molecules in the seeded discharges of these experiments. It is difficult to identify the species most responsible for the totally symmetric perturbation of $N_2(X^1\Sigma_g^+,v^\text{m})$ during collisions. However, such perturbations apparently cause up-pumping/pooling effects which are very discriminating. These effects may be quite general traits to be observed and exploited in supersonic discharges.

C. Fluorobenzene-Argon Supersonic Discharge Experiments

What is most interesting about these experiments is the excitation mechanism underlying the fluorescence of hexafluorobenzene cations and derivatives. Collisions between the neutral aromatic precursors and metastable argon are
presumed to give rise to the fluorescent species. However, the energy levels of metastable argon \( ^3P_{2,0} \) lie at 11.8 and 11.6 eV [56]. Such energies are insufficient to ionize and electronically excite molecules such as \( \text{C}_6\text{F}_6 \) and \( \text{C}_6\text{F}_5\text{H} \) to produce \( \text{C}_6\text{F}_6^+(B^2A_{2u}) \) and \( \text{C}_6\text{F}_5\text{H}^+(B^2B_2) \). This is the reason that conventional argon discharges seeded with \( \text{C}_6\text{F}_6 \) and \( \text{C}_6\text{F}_5\text{H} \) are "dark".

An alternative excitation mechanism is proposed in this thesis which involves metastable forms of the aromatic precursors. In the thesis work using supersonic argon discharges, collisions between metastable argon and metastable, triplet \( \text{C}_6\text{F}_6 \) and \( \text{C}_6\text{F}_5\text{H} \) are facilitated. Since the triplet states of these species lie at energies > 3.5 eV, collisions between molecules such as \( \text{C}_6\text{F}_6 \) and \( \text{Ar}(^{3}P_{2,0}) \) can yield products \( \text{C}_6\text{F}_6^+(B^2A_{2u}) \). This mechanism is proposed to account for the spectra presented in this thesis. Further reasoning is as follows.

The radiative lifetimes of \( \text{C}_6\text{F}_6^+(B^2A_{2u}) \) and \( \text{C}_6\text{F}_5\text{H}^+(B^2B_2) \) are ca. 50 nsec [27]. This taken with the ion/jet emitting length (\( > 5 \text{ cm} \)), the jet velocity (ca. \( 10^5 \text{ cm/sec} \)), the aromatic/argon seed ratios (ca. 0.0001), and the fluorescence intensity distribution, indicated that collisions exterior to the nozzle were the excitation mechanism underlying ionization and electronic excitation. All factors pointed to ionization
of neutral C₆F₆ and C₆F₅H by metastable argon, promptly
followed by emission from C₆F₆⁺(B₂A₂u) and C₆F₅H⁺(B₂B₂) in the
expansion core. This was consistent with the low voltages (<
100 V) employed in the nozzle throat, the collision rates
along the expansion axis (10³ sec⁻¹ at 5 cm downstream), and
the electric field structure of the nozzle. The latter
discouraged effectively all ions--C₆F₆⁺, C₆F₅H⁺, Ar⁺-- from
passing through the expansion aperture. In the expanded
discharges, distributions of C₆F₆ and C₆F₅H were excited into
metastable triplet states and were essentially frozen after
a certain number of collisions at the nozzle throat. Such
distributions yielded radiative ions as a result of ³C₆F₆⁻ and
³C₆F₅H⁻-Ar⁺ (³P₂₂) collisions downstream.

The above mechanism focuses attention on the electronic
spin wavefunctions of the collision complexes such as ³C₆F₆⁻-
Ar⁺(³P₂₂) and ³C₆F₅H⁻-Ar⁺ (³P₂₂). These spin wavefunctions are
superpositions of singlet, triplet, and quintet terms. The
electronic spin wavefunctions for collision products
C₆F₆⁺(B₂A₂u)-Ar(¹S₀)-e⁻ and C₆F₅H⁺(B₂B₂)-Ar(¹S₀)-e⁻ are
superpositions of singlet and triplet terms. In the
conversion of ³C₆F₆⁻-Ar⁺(³P₂₂) and ³C₆F₅H⁻-Ar⁺ (³P₂₂) to
C₆F₆⁺(B₂A₂u)-Ar(¹S₀)-e⁻ and C₆F₅H⁺(B₂B₂)-Ar(¹S₀)-e⁻, the radiative
ion yields scale with the overlap of collision complex and
product wavefunctions. As these yields depend on the
projection of spin angular momentum relative to the collision
axis, experiments which should follow this thesis are suggested.

Magnetic sublevels of triplet aromatics such as $^3C_6F_6^*$ are distinguished by different projections (with respect to symmetry axes) of the spin angular momentum and degrees of coupling with the rotational angular momentum. However, very little experimental information is available regarding the splittings of these magnetic sublevels due to resolution problems. In supersonic discharge experiments such as those described in Chapter III, it should be possible to change the projection of the spin angular momentum of triplet aromatics such as $C_6F_6$ and $C_6F_5H$ prior to collision with $Ar^*(^3P_{2,0})$ using a resonant rf field $H_1$. The yield of fluorescent $C_6F_6^+(B^2A_{2u})$ and $C_6F_5H^+(B^2B_2)$ will be different for resonant-versus-non-resonant conditions, provided the ionization yields depend on the collision complex geometries. This would offer a high resolution, optical way to investigate magnetic sublevels of aromatics such as $C_6F_6$ and $C_6F_5H$ in triplet states under cold, isolated conditions.
1. The experiments of this thesis demonstrated that supersonic discharges prepare metastables such as nitrogen under translationally and rotationally cold conditions. These metastables relax electronically in the post-nozzle gas flow by two mechanisms, radiative and collisional. The rotational distributions demonstrated by the emission spectra reveal the nature of these mechanisms and their efficiency. In the case of nitrogen, metastables produced in a supersonic discharge relax by radiative and collisional channels and strongly favor $N_2(C^3\Pi_u)$ as the product. The rotational population distributions are unusual downstream due to different cooling rates of individual J-levels, and/or by multiple (collision followed by radiative relaxation) processes.

2. The spectra of this thesis demonstrate the presence of transient nitrogen clusters in a supersonic discharge. This is important given that supersonic jets have generated many clusters over the years, but few reports have been made of neutral, excited clusters with triplet spin multiplicity.
3. In the nitrogen/helium experiments, an unusual vibrational distribution was revealed by the Penning ionization reaction between nitrogen and metastable helium. A propensity rule governs the vibrational distribution of ground state nitrogen $N_2(X^1\Sigma_g^+,v^\prime\prime)$. The even-numbered ground state vibrational state $v^\prime\prime$ is favored during the collisions between $N_2(X^1\Sigma_g^+,v^\prime\prime)$ and excited nitrogen species prior to expansion.

4. Experiments and principles presented in this thesis can be adapted to other molecular systems, including large molecules such as aromatics. A supersonic jet method of accessing and probing the excited triplet states of closed shell molecules is offered in both the hexafluorobenzene and nitrogen experiments. This method entails observing how electronic relaxation, by either collision or radiative pathways, leads to states which are strongly radiative.
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APPENDIX

A. VITAE

The author of this dissertation, Jing-chen Luo was born on Oct. 31, 1962 in Beijing, the People's Republic of China.

He obtained his B.S. degree in Physics, July 1983, Changchun University, Changchun, Jilin, China. Then, he became a research assistant in Changchun Institute of Optics and Fine Mechanics, Academia Sinica. During 1983-1985, his research focused on developing a new ring-cavity dye-laser system.

In 1986, he went to University of Edinburgh, U.K. After 4 month English language training, he registered as a graduate student in the chemistry department leading to a Ph.D degree. His major research included: (1) Laser Induced Multi-photon Ionization in Supersonic Jet (gas phase); (2) Multi-photon Ionization in Liquid Phase, and (3) Metal Elements Analysis Using Laser Induced Breakdown Spectroscopy. He was awarded British Petroleum EMRA award for graduate research, 1986-1987. E.E.C. graduate student research grant, 1987-1988.
In 1989, he transferred to Loyola University Chicago, U.S.A, was granted graduate student assistantship in chemistry department. In 1992, he received the University Fellowship. His research area are on Spectroscopy, such as, Spectroscopic Study of Triplet State Molecules in Corona Supersonic discharge and Laser Excitation Spectroscopy. He is currently completing the Ph.D degree in Loyola University Chicago. He ia also a member of The American Chemical Society and The Coblentz Society of Spectroscopy.
The Dissertation submitted by Jing-chen Luo has been read and approved by the following committee:

Dr. Daniel J. Graham, Director  
Assistant Professor, Dept. of Chemistry  
Loyola University Chicago

Dr. Leslie W-M. Fung  
Professor, Dept. of Chemistry  
Loyola University Chicago

Dr. Gordon P. Ramsey  
Associate Professor, Dept. of Physics  
Loyola University Chicago

Dr. Elliot Burrell  
Associate Professor, Dept. of Chemistry  
Loyola University Chicago

Dr. Victoria Buch  
Assistant Professor, Dept. of Chemistry  
University of Illinois at Chicago

The final copies have been examined by the director of the Dissertation Committee, Dr. Daniel J. Graham and the signature which appears below verifies the fact that any necessary changes have been incorporated and that the dissertation is now given final approval by the Committee with reference to content and form.

The dissertation is, therefore, accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

Date 9-7-93  Director's Signature Daniel J. Graham