LASER PROBING of
TRANSPORT PROPERTIES and
ROTATIONAL ALIGNMENT of
N$_2^+$ DRIFTED in He

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Laser Probing of Transport Properties and Rotational Alignment of $\text{N}_2^+$ Drifted in He

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Results of transport property and rotational alignment experiments of the atmospherically important molecule $\text{N}_2^+$ are presented, as measured in a flow-drift apparatus using the technique of single-frequency laser-induced fluorescence (LIF). A trace amount of $\text{N}_2^+$ is drifted in helium as a buffer gas; the external axial electric field of the drift tube varies the center-of-mass collision energy of the ion-neutral pair. The net effect over hundreds of buffer gas collisions is to establish a steady-state anisotropic ion velocity distribution, the precise character of which is determined by the ion-neutral interaction potential, mass ratio, and field strength. A single-frequency ring dye laser is used to probe Doppler profiles of various rotational lines of the $(v',v'') = (0,0)$ band in the $B ^2\Sigma_u^+ - X ^2\Sigma_g^+$ system at 390 nm. The single-frequency cw laser technique allows one to measure the velocity component distribution function (VCDF) along the laser propagation direction $k$; the VCDF is a projection of the complete ion velocity distribution function. Additionally, the rotational alignment of the ions as a function of one component of sub-Doppler laboratory velocity is probed by polarized LIF.

Drift velocities and ion mobilities are determined from the shift of the first moments of the coaxial LIF Doppler profiles, while perpendicular and parallel translational temperatures are determined from the widths or second central moments of the profiles in the direction probed. Drift velocities measured up to a field strength
of 16 Td appear to be in good agreement with data derived from earlier arrival-time measurements. A small but definite increase in mobility with increasing rotational state from J=13.5 to J=22.5 is observed. A significant difference of over 100 K between the parallel and perpendicular temperatures is measured at the highest field strength employed (16 Td). A small degree of positive skewness or third central moment is observed as well in the parallel VCDF's, which is of particular interest since a high-velocity tail has not been previously reported for any molecular ion system. Additionally, by probing with linearly polarized light and measuring the degree of polarization of the resultant LIF, the collision-induced quadrupole rotational alignment parameter $A_0^{(2)}$ is determined as a function of field strength and velocity subgroup. A strong correlation is found between the degree of rotational alignment and the velocity subgroup when probed parallel to the field direction, with the alignment parameters generally increasing monotonically across the distribution. A dramatic difference in velocity-selected alignment as a function of rotational state is observed as well, for experiments conducted on various rotational lines at a fixed field strength of 12 Td. For sufficiently low rotational state (J about 9), it appears that $A_0^{(2)}$ changes sign across the Doppler profile.
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As I reach the end of the valley of sweat, blood, and tears (in approximately that order) that has been the graduate school experience for me, I become very much aware that, although it has been largely a solitary enterprise, I didn’t get through it alone. There is a long list of “invisible contributors” that I need to thank somehow. Coupled with the frustration, at the end, of realizing that I seemed to have had to learn absolutely everything the hard way, is the realization that it would have been infinitely worse without the many people I’ve interacted with along the way.

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CHAPTER I

INTRODUCTION

A. General motivation

The motion of a swarm of ions in a gas under the influence of an external electric field has been the subject of intense study both experimentally and theoretically for over 100 years. The birth of gaseous electronics can be traced to the discovery of X-rays in a cathode-ray tube by Roentgen in 1895. In drift tube studies, the charge of the ions provides a convenient "handle" that can be used by the external electric field to "drag" them through a buffer gas, often a noble gas. More precisely, the external drift field serves to vary the average center-of-mass collision energy of the ion-neutral pair. As ions undergo collisions with the buffer gas, a steady-state balance is achieved between the acceleration or energy imparted by the drift field and the energy or momentum lost to buffer gas collisions. The net result over hundreds of collisions is a steady-state anisotropic ion velocity distribution function $F(v)$, the precise character of which is determined by the ion-neutral interaction potential, mass ratio, and field strength. Additionally, the plane of rotation of a molecular ion can be altered by repeated directed collisions with the buffer gas, which is the phenomenon of collision-induced rotational alignment.

Mathematically, the ion velocity distribution $F(v)$ is described by integrodifferential equations. Much theoretical effort, dating from the initial work of Maxwell and Boltzmann, has been expended to find solutions to equations of this sort, and this theoretical work had been instrumental in developing many areas of
statistical physics. Experimentally, starting with work in the 1930's, drift tube experiments have focused on measuring the motion of ions in gases—i.e., their transport properties—in the hopes of obtaining a glimpse of the underlying ion velocity distribution.

There are several fundamental reasons why one would want to know $F(v)$. For one, knowledge of the ion velocity distribution function would in principle allow calculation of any ion transport property. More importantly for chemical physics, $F(v)$ is the key microscopic-to-macroscopic conversion entity, relating through its average, for example, a microscopic reaction cross-section to a macroscopic and observable rate constant. Because the ion velocity distribution function can “tailor” the observable outcome, manipulation of both ion and neutral velocity distribution functions is a subject of considerable technological interest, for example in kinetic-energy enhanced ion and neutral etching for semiconductor processing.

Traditionally, drift tube experiments, in which the external electric field strength is on the order of 1 V cm$^{-1}$, have bridged the energy gap of approximately 10 meV to 1 eV between “cold” supersonic jet expansion experiments and “hot” single-collision beam experiments. One of the primary motivations for the extensive research conducted on flow-drift apparatuses in the past 30 years has been to measure ion-molecule reaction rates. Drift tubes, which have an easily varied electric field that essentially plays the role of temperature, have permitted the study of ion-molecule reactions at above-thermal energies.$^1$ It was recognized by Wannier in 1953 that, by assuming a constant mean free time between ion-neutral collisions, the Boltzmann
equation can be solved exactly (in the high-field case) for the attractive \( r^{-4} \) potential characteristic of all ion-induced dipole interactions. The resulting average lab-frame energy of the ion swarm is given by the surprisingly simple expression,

\[
\langle KE_{\text{lab}} \rangle = \frac{1}{2} m \langle v_i^2 \rangle = \frac{3}{2} k_B T_{\text{buffer}} + \frac{1}{2} m v_d^2 + \frac{1}{2} M v_d^2 \tag{1.1}
\]

where \( m \) is the ion mass, \( M \) is the buffer mass, and \( v_d \) the ion drift velocity. As can be seen from Eq. (1.1), superimposed on the purely thermal, isotropic energy are two additional terms. The first is associated with the directed motion of the ions in the buffer; the second accounts for the randomizing effect of collisions with the buffer. This expression turns out to work astonishingly well in yielding average kinetic energies provided that the measured values of ion drift velocities are used. This fact was the impetus for much of the ion transport work conducted in the 1970's.

Recently, there has been a resurgence of interest in these old methods. The technique of ion mobility spectrometry has been used to study cluster mobilities, which depend on the angle-averaged collisional cross sections of the clusters. For example, the mobilities of \( \text{NO}^+(\text{CH}_3\text{CN})_n \) clusters drifted in He will monotonically decrease with increasing cluster size \( n=0-3 \) at a fixed field strength. Actual cluster structure information can be gleaned from differences in the mobility of isomers of various mass-selected species. The structure of silicon, germanium and aluminum clusters have been studied by injecting mass-selected clusters into a drift tube at various injection energies. Proposed formation mechanisms of fullerenes from cyclic carbon rings have been studied by this technique as well.
It is hoped that the work presented here is in a similar spirit of “teaching a very old dog yet one more new trick”! The experimental technique of single-frequency laser-induced fluorescence (LIF) is employed in this work to study both transport properties and collision-induced rotational alignment of one particular ion, $N_2^+$, drifted in helium in a drift-tube apparatus. The single-frequency ring dye laser beam can be thought of as a “delta function” in frequency space that selects out one laboratory ion velocity component along its propagation direction $\hat{k}$. This technique permits one to map out the steady-state ion velocity distributions more-or-less directly as a function of field strength and rotational state. Additionally, by measuring the polarization of the resultant LIF, the degree of rotational alignment of $N_2^+$ can be studied as a function of one component of laboratory-selected velocity.

In some ways, $N_2^+$ is a molecule ideally suited for study with the technique of single-frequency LIF. The ion can be made cleanly and easily in a flowing afterglow or plasma discharge. It has two fairly low-lying excited electronic states ($A^2\Pi_u$ and $B^2\Sigma_u^+$) that are optically accessible with visible photons. In particular, the $B^2\Sigma_u^+$ state has a fluorescence lifetime (62 ns) short enough to insure that the molecule spends the majority of time in the ground $X^2\Sigma_g^+$ state, but not so short that the natural linewidth of the transition must be taken into consideration in line shape analysis. Additionally, the Franck-Condon factors for the ground vibrational state of the $B^2\Sigma_u^+ - X^2\Sigma_g^+$ system are quite strong. The primary disadvantage of the molecule is its nonzero nuclear spin; the presence of unresolved hyperfine structure
underlying each rotational line somewhat complicates the data analysis for both the transport property and alignment experiments.

Because of these factors, $\text{N}_2^+$ is a natural “chromophore” for use in plasma environments. For example, $\text{N}_2^+$ has been studied via LIF in an electron cyclotron resonance (ECR) plasma to characterize transverse ion translational temperatures and obtain the “pitch angle” that determines the plasma etch anisotropy. Both translational and rotational ion temperatures were obtained by LIF in a pulsed RF-generated nitrogen plasma to study the transient plasma heating and cooling. Doppler shifts of the $B - X$ and $A - X$ emission of $\text{N}_2^+$ in a He glow discharge, measured by Fourier transform emission spectroscopy, are used as a probe of the plasma dynamics; the discharge electric field can be measured by this technique.

Additionally, because of its atmospheric and interstellar importance, $\text{N}_2^+$ is a molecular ion of intrinsic interest. It is one of the major constituents of the F-region of the ionosphere (altitude > 120 km), and the $\text{N}_2^+ + \text{O}$ reaction is key in controlling the amount of $\text{O}^+$ and $\text{NO}^+$ in this region. Atmospheric models and measurements differ on the amount of $\text{N}_2^+$ in this region by a factor of greater than two, yet the $\text{N}_2^+ + \text{O}$ rate constants and branching ratios have been confirmed by several independent measurements. Work from this laboratory on a SIFT/LIF apparatus reveals a previously undetected channel of simultaneous charge and vibrational transfer between reactions of $\text{N}_2^+$ and neutral $\text{N}_2$, which may provide clues to the solution of this puzzle.
However, this work concerns solely the nonreactive scattering properties of the \( \text{N}_2^+ \)-He system. Two basic categories of experiments will be discussed. The transport property experiments, covered in Chapter III, involve characterizing the ion velocity distribution function \( F(v) \) as a function of field strength and attempting to understand some of the mechanisms leading to this behavior. The rotational alignment experiments, discussed in Chapter IV, seek to measure the degree of rotational alignment as a function of velocity sub-group and probe direction, and to understand the underlying dynamics.

**B. Interaction potential**

A distinguishing feature of ion-molecule interactions is that they are always dominated by the attractive, long-range \( r^{-4} \) ion-induced dipole term in the potential. Traditionally, the motivation for much of the older ion transport work was to obtain a more detailed picture of the interaction potential by extracting this information from the measured transport property data (i.e., the inversion problem). A more modern approach is to calculate what is believed to be an accurate \textit{ab initio} interaction potential and then test the accuracy of this potential by calculating “forward” to transport properties that can be compared with actual measurements. For example, a recent calculation found good agreement between measured and theoretical mobilities derived from classical trajectory calculations run on an \textit{ab initio} NO\(^+\)-He interaction potential.\(^{12}\) Unfortunately, there are still a small number of calculated ion-molecule interaction potentials for systems of interest.
The \( \text{N}_2^+ \)-He system is unusual in this regard because high-level interaction potentials have been calculated several times. In an early calculation from the group of H.-J. Werner, Miller et al.\textsuperscript{13} performed an \textit{ab initio} calculation using multi-configuration self-consistent field, configuration interaction (MCSCF-CI) wave functions to determine the 2-D interaction potential as a function of the \( \text{N}_2^+ \)-He internuclear distance \( R \) and angle \( \theta \) between the diatomic bond and \( R \). The calculations were carried out for the equilibrium \( \text{N}_2^+ \) bond length of 2.11 bohr radii (\( a_0 \)) and for three discrete angles, \( \theta = 0, 45 \) and 90 degrees with \( R \) varying from 3.5 to 25.0 \( a_0 \). The resulting energies were then fit to an interpolating function to obtain an analytic interaction potential \( V_{\text{int}}(R, \theta) \) as a continuous function of the two coordinates, as shown in Fig. 1. Note that the depth of the well minimum (approximately 140 cm\(^{-1}\)) is almost independent of orientation, but the position of both the minimum and the repulsive wall of the bare potential vary considerably with angle. Qualitatively, it is this angular variation that produces rotational alignment in the collision dynamics of \( \text{N}_2^+ \)-He. Additionally, the well is sufficiently deep to give rise to a number of bound rovibrational states of the \( \text{N}_2^+ \)-He complex.

In a more recent and detailed calculation, Berning and Werner\textsuperscript{14} use multireference configuration interaction (MRCI) expansions to calculate 3-D adiabatic \( \text{N}_2^+ \)-He potential energy surfaces for the first three electronic ground states of \( \text{N}_2^+ \) as a function of \( R, \theta \), and bond length \( r \). A grid of four discrete values of \( \theta = 0, 30, 60, \) and 90 degrees, and three values of \( r = 1.90, 2.11, \) and 2.65 \( a_0 \) were
Fig. 1.1: $N_2^+$-He *ab initio* interaction potential of Miller *et al.* in Jacobi coordinates.
calculated, for distances $R$ between 3 and $11\ a_0$. These adiabatic surfaces were then transformed into a diabatic representation to study electronically inelastic scattering dynamics of $N_2^+$-He. Although not explicitly compared to the first calculation, diagrams of the ground-state adiabatic potential indicate it is quite similar to the earlier potential.

**C. Ion transport properties**

Although the study of ion transport properties is a mature field, ongoing experimental work continues to yield surprises. For example, the mobilities of $O^+$ and $O^-$ in He are considerably different over the same range of effective temperatures, due to the different interaction potential well depths of the HeO$^+$ and HeO$^-$ systems.\(^{15}\) New techniques are continually being developed that enhance the field. For instance, a recent modification of the zero-kinetic energy photoelectron spectroscopy technique promises the possibility of near-complete rotational and vibrational state molecular ion preparation for the investigation of state-selected ion-molecule reactions.\(^{16}\)

The single-frequency LIF transport property experiments in this work are primarily concerned with measuring $N_2^+$ mobilities and translational temperatures as a function of rotational state and field strength. The advantages of the LIF technique are that it provides a state-selective, non-obtrusive, *in situ*, direct measurement of velocity component distribution functions. Additionally, the LIF technique can reveal information—such as translational temperatures and a relative measure of local ion number densities—that can not be obtained from other techniques traditionally used to measure ion transport properties.\(^{17,18}\)
Mobility is the phenomenological proportionality "constant" between applied electric field and observed steady-state drift velocity. This constant in general depends on field strength and contains structure information about the interaction potential. In this technique, measured mobilities are directly proportional to the Doppler shift in line center or first moment of a LIF transition for a given field strength. Translational temperatures are an indicator of how the resultant randomizing energy of the ion-buffer gas collisions is being disposed of, on average, between the directions parallel and transverse to the field. For LIF, measured translational temperatures are proportional to the square of the linewidth or the second central moment of the line shape. Higher line shape moments, such as the third central moment, which reveals skewness information, can be studied as well. Details of these measurements and results are presented in Chapter III.

D. Collision-induced rotational alignment

Alignment phenomena are ubiquitous in chemical physics. Their appearance in such a diversity of experiments makes alignment a simultaneously fascinating and frustrating subject to study. Rotational alignment, the preferential arrangement of the angular momentum vector associated with a molecule's rotation, can be created in a variety of ways. For example, the intense electric fields associated with a pulsed laser can be used to induce a dipole in the molecule that effectively "traps" the molecule into pendular motion around the polarization vector of the laser. Pendular motion of the linear molecules CO$_2$ and CS$_2$ has been demonstrated by examining the angular distribution of O$^+$ or S$^+$ fragments relative to the electric field of the laser.\textsuperscript{19} The "brute force technique" of orienting polar molecules with a strong DC electric field
(linear Stark effect) has recently been applied to orient the asymmetric top molecule C₆H₅I and study steric effects in the reaction K + C₆H₅I → KI + C₆H₅.²⁰ Gas-phase chemical reactions can create alignment. To cite just one example from the vast field of stereochemistry, a strong steric effect is observed for the “benchmark” reaction O(¹D₂) + H₂(v = 0) → OH(X ²Πᵣ, v' = 0, N', f) + H when the final states are resolved.²¹ Reactive scattering with surfaces can also generate alignment. For example, D₂ exhibits strong preference for desorption from a Cu (111) surface in a helicopter alignment, indicating a smaller activation barrier for adsorption onto the surface for this approach.²²

This particular work is concerned with collision-induced rotational alignment in a drift tube environment. It has been known for many years that there is an intimate relationship between transport properties and molecular alignment. The so-called Senftleben-Beenaker effect²³ historically refers to the change in thermal conductivity of neutral paramagnetic gases in the presence of an external magnetic field. However, to the best of this investigator’s knowledge, collision-induced rotational alignment has not been previously reported in any ion-molecule system outside of this group. Chapter IV covers the details and results of alignment experiments on the N⁺₂-He system, with the unique twist of partial velocity selection. Indeed, evidence presented there suggests a hypothesis that velocity-subgroup alignment is the “generic” behavior of any gas phase system in which there is some sort of anisotropic (i.e., non-Maxwell-Boltzmann) velocity distribution.
References for Chapter I


CHAPTER II

GENERAL EXPERIMENTAL TECHNIQUES

A. Introduction

An overall schematic of the experimental apparatus is shown in Fig. 2.1. The apparatus comprises a flowing afterglow ion source coupled to a drift tube and has undergone continual modifications since its inception.1 A goodly majority of the current incarnation of the apparatus is identical with a previous configuration, and is discussed in further detail in the thesis of Michael Bastian.2 Substantive differences and important points for this work are discussed in the following sections. Section II.B covers ion production conditions and details of the flow-drift portion of the apparatus. The details of the ring dye laser system and relevant diagnostics are discussed in Sec. II.C. The detection of both unpolarized and polarized fluorescence is discussed in Sec. II.D. Sections II.E and II.F cover the necessary electronics and data acquisition programming, and some minor details of data analysis. Details of the spectroscopy of the \((v',v'\prime) = (0,0)\) band of the \(N_2^+ B^2 \Sigma_u^+ - X^2 \Sigma_g^+\) system are discussed in Sec. II.G.

B. Ion source & flow-drift region

Because proper ion production and charge-separation conditions are essential to the correct measurement of transport properties, a brief discussion is given of these issues in this section. The ion are generated by a traditional flowing afterglow; ion production details are discussed in Sec. II.B.1. A brief discussion of the relevant
Fig. 2.1: Overall schematic of experimental apparatus.
hydrodynamics of the flow tube is presented in Sec. II.B.2. Sec. II.B.3 discusses the drift region of the apparatus.

1. Ion source & production conditions

The flowing afterglow characteristics are dominated by the buffer gas, which is helium for all work presented here. Approximately $5.1 \times 10^{21}$ atoms s$^{-1}$, corresponding to a typical flow rate of 11.4 standard liters min$^{-1}$ (slm), of industrial-grade He (nominal 99.995% purity) is passed through two liquid-nitrogen cooled cold traps containing 5 Å molecular sieves. The traps are pumped on and baked out continuously when not in use by custom heating mantles (Glas-Col) regulated by an autotransformer. The He flow rate is regulated by a mass flow controller (Tylan FC-280). The controller calibration, which is important for determining the bulk flow velocity of the buffer gas, can be checked with a wet test meter (Precision Scientific), as discussed more below.

The helium buffer then flows over an electron impact ion source, as detailed in Fig. 2.2. The ion source consists of a thoriated iridium filament, with a repeller plate directly behind and fine mesh grid directly in front of the filament. The entire source is covered by a slotted metal cup. Construction details of the filament and ion source are given in Bastian.\textsuperscript{2} The ion source is biased by regulated voltage and current supplies (Kepco) that float with respect to the tube voltages. For all work presented here, the ion source was configured as an electron gun, in which the filament is biased at a voltage $V_G$ that is negative relative to the “local ground”, (i.e., the ion source flange). Electrons are boiled off the filament by a filament current $I_F$ (with associated
Fig. 2.2: To-scale diagram of ion source region. Electrical connections are shown schematically in Fig. 2.5 (after Ref. 2).
ohmic drop $V_F$), maintained at a value by the regulated current supply such that the emission current $I_E$ collected by the mesh grid is held to a constant value, chosen by a potentiometer. For the electron gun configuration, the repeller plate is held at approximately $-V_G$ by tying it to the negative end of the filament. The fine mesh grid and slotted cup are at the potential of the source flange, which is in turn floated on top of the charge separation and drift voltage power supplies, as discussed below. Gas inlets for the buffer and neutral reagent gases are electrically insulated by glass tube and Cajon connector assemblies.

Because the cross sections for direct electron impact ionization for most small molecules are considerably less than the reactive cross sections at electron energies of 1-100 eV, the desired ions in a flowing afterglow are invariably formed through some sort of ion-molecule reaction. The dominant production reactions for $N_2^+(v'' = 0)$ are Penning ionization by metastable singlet and triplet helium and charge transfer with singly-ionized helium:\(^{3,4}\)

$$
\begin{align*}
N_2 + He^* \left(2^1S, 2^3S\right) &\rightarrow N_2^+ \left(B^2\Sigma_u^+, v'\right) + He + e^- \\
N_2 + He^+ \left(2S\right) &\rightarrow N_2^+ \left(C^2\Sigma_u^+\right) + He^1S 
\end{align*}
$$

(2.1)

The singlet He metastable state is known to be efficiently quenched by superelastic electronic collisions in the afterglow,\(^5\) so the triplet state is assumed to be the dominant Penning ionization production channel. The primary loss mechanism for $N_2^+$ is the exothermic charge-transfer reaction with $H_2O$:

$$
N_2^+ + H_2O \rightarrow N_2 + H_2O^+ + 2.96 \text{eV}
$$

(2.2)
that accumulates in the tube or starts desorbing from the traps as they get saturated.

Although considerable time was spent searching for optimal production conditions, a small number of conditions were actually used in practice for the data presented here. Ion production conditions are monitored by a quadrupole mass spectrometer (Extranuclear/Extrel) located downstream of the flow-drift region, as shown in Fig. 2.1. Mass spectra were taken every time the experiment was run to monitor the production conditions and the cleanliness of the drift tube. Details of this particular ion detection system are given by Zwier, Smith, Hamilton, and Bastian; since just qualitative information was extracted from the mass spectra for this work, the mass spectrometer will not be discussed further.

The production condition mass spectra used for the two major sets of experiments in this work conducted in the Fall of '95 and the Fall '97/Spring '98 are shown in Figs. 2.3 and 2.4, respectively. The figure captions detail the specific conditions used. For the majority of the work, neutral $N_2$ alone was added via the upstream effusive inlet shown in Fig. 2.2; some early work was done by adding neutral Ar as well. The flow of neutral reagents are monitored by mass flow meters (Tylan FM-360V) and regulated by needle valves. The removable stainless steel aperture in the source region 9 cm downstream of the filament increases the residence time of the gases in the source region to help drive the ion chemistry to completion before the drift region. Additionally, it was found that both the measured axial ion flow velocity and the apparent measured ion mobilities were greatly affected by the aperture size, as discussed in detail in Sec. III.E. Note that for cw LIF work, it is particularly important to choose production conditions that quench the flowing
Fig. 2.3: Representative mass spectra for Fall '95 experiments.
Fig. 2.4: Representative mass spectra for Fall '97 and Spring '98 experiments.
afterglow fluorescence, which is primarily due to collisional deactivation of He(2\(^3\)S) with various buffer gas impurities such as H\(_2\)O and O\(_2\).\(^5\) The addition of neutral N\(_2\) in the source region efficiently quenches this fluorescence.

As the above discussion indicates, a clean, dry flow-drift apparatus is a prerequisite for successfully making ions of reactive species such as N\(_2^+\). It was found helpful to wrap the source elbow, upstream and downstream tee's and all baffle arms with heating tape and "bake out" these regions between runs of experiments. Unfortunately, not all regions of the apparatus were accessible for baking; in particular, the Teflon rods and mylar spacers in the drift LIF assembly tend to trap water and cannot be baked out effectively. The best mass spectra were obtained when the apparatus was not vented for months and thus never exposed to atmosphere. Venting frequently would noticeably affect ion yield both in the mass spectra and in the LIF signal. Additionally, when running, it was found important to keep the trap dewars full of liquid nitrogen to prevent water from desorbing from the top of the traps and accumulating in the tube.

2. Flow tube considerations

The flow tube (i.e., the portion of a flow-drift apparatus with no applied fields) is a flowing system dominated by the buffer gas behavior. A brief discussion is given of the relevant hydrodynamics of the flow tube portion of the apparatus, focusing on relations important for arguments given later in Chapter III.

The bulk or "plug flow" velocity \(v_0\) of the buffer gas is linearly related to the buffer gas throughput \(Q_{buffer}\) and is given by\(^8\)
\[ v_0 = \frac{Q_{buffer}}{\pi a^2} \times \frac{760 \text{Torr/atm}}{P(\text{Torr})} \times \frac{T(K)}{273.16 \text{K}} \]  

where \( v_0 \) is in cm s\(^{-1}\), \( Q_{buffer} \) is in atm cm\(^3\) sec\(^{-1}\) and \( a \) is the radius of the flow tube in cm. With \( a = 3.65 \text{ cm} \) for this apparatus, and expressing \( Q_{buffer} \) in the more convenient units of standard liters min\(^{-1}\) (slm), this gives

\[ v_0 = 1.108 \times 10^{-2} \frac{Q_{buffer}}{P(\text{Torr})} \frac{T(K)}{273.16 \text{K}} \]

with \( v_0 \) now expressed in m s\(^{-1}\). Thus, if the He flow controller is calibrated with a wet test meter, the bulk velocity can be determined. For typical calibrated flow conditions of 11.4 slm of He at \( P = 0.50 \text{ Torr} \) and \( T = 298 \text{ K} \), \( v_0 \) is about 75 m s\(^{-1}\).

The buffer gas under laminar flow conditions will assume a parabolic velocity profile, with the velocity as a function of the radial position \( r \) from the tube axis given by

\[ v(r) = 2v_0 \frac{\left[ 1 - \left( \frac{r}{a} \right)^2 + \left( \frac{2s}{a} \right) \right]}{\left[ 1 + \left( \frac{4s}{a} \right) \right]} \]  

where \( s = s'/P \) is the slip coefficient. For negligible buffer gas slip at the flow tube walls (i.e., \( s/a = 0 \)), this reduces to

\[ v(r) = 2v_0 \left[ 1 - \left( \frac{r}{a} \right)^2 \right] \]

Note in particular Eq. (2.5) predicts an on-axis \((r = 0)\) buffer flow velocity of \( 2.0v_0 \) for no slip; for \( s/a = 0.02 \) (a couple percent slip), the axial flow velocity is about \( 1.9v_0 \). Thus, a well-behaved flow tube operating in the laminar flow regime should have a ratio of axial ion flow velocities to buffer gas bulk velocities of 1.9 to 2.0.
The conventional indicator of laminar/turbulent flow is the Reynolds number, given by

\[ R_e = \frac{\rho v_0 a}{\eta} \]  

(2.7)

where \( \rho \) is the buffer gas mass density in g cm\(^{-3} \), \( v_0 \) is the buffer bulk flow velocity in cm s\(^{-1} \), \( a \) is the tube radius in cm, and \( \eta \) is the buffer gas viscosity in poise \( (\eta_{\text{He}} = 189.6 \times 10^{-6} \, \text{P}) \). For the typical conditions given above, \( R_e \approx 16 \), indicating that conditions are well within the laminar flow regime. The entry length, the minimum length needed to establish laminar flow, is given by

\[ L_e = 0.227 a R_e \]  

(2.8)

which gives an entry length of approximately 13 cm for typical conditions. The length of the flow region elbow alone shown in Fig. 2.1 is 28 cm. These calculations, along with calibration measurements discussed in Chapter III that consistently produce an axial ion flow velocity of 1.9 to 2.0 times the bulk flow in flow tube (zero-field) conditions, strongly suggest that the buffer gas flow in this apparatus is laminar and well-behaved. In particular, the anomalous axial ion velocity systematics observed in drift tube conditions that are discussed in Chapter III are not believed to be due to turbulent flow or insufficient entry length.

3. Drift & charge separation regions

The resulting space-charge neutral plasma from the flowing afterglow source flows through a 44-cm-long field-free region to the drift region. An electrical schematic of the drift region and its relation to the source and flow regions is shown
in Fig. 2.5. The drift region consists of a total of either 45 or 51 guard rings (depending on configuration; Fig. 2.5 shows the 51-ring apparatus), 1-cm-wide by 7.3-cm-i.d., electrically insulated by mylar spacers and connected in series by a network of precision 500 Ω vacuum resistors (Caddock). The resistor values are chosen to keep the network biasing current much larger than the ion recombination current at the walls. The entire drift assembly is held together by compression between two gold-plated aluminum flanges, as indicated in the figure. Two voltage supplies are used for the drift region. The charge separation supply, which floats on top of the drift voltage supply, is used to establish the charge separation field in the first portion of the drift region, as discussed further below. A drift voltage supply across the remaining guard rings is used to establish a uniform variable axial electric field in the drift region proper. The drift supply has its ground lead tied to the downstream flow region.

In a drift tube apparatus, the field parameter is the ratio $E/N$ of external applied electric field to buffer gas number density, conventionally measured in Townsend (1 Td = $10^{-17}$ V cm$^2$). A convenient conversion factor between $E/N$ and $E/P$ can be produced from the ideal gas law:

$$
\frac{E}{N} = k_B T \frac{E}{P} \quad \text{or} \quad \left( \frac{E}{N} \right) = 1.0356 \times 10^{-2} \ T \left( \frac{E}{P} \right) \quad (2.9)
$$

with $E/N$ in Td, $T$ in degrees Kelvin, and $P$ in Torr. We desire a formula for $E/N$ at the LIF imaging region of the drift tube, $(E/N)_{LIF}$. The external applied electric field is assumed to be the applied drift voltage across the drift region of the tube
Fig. 2.5: Schematic of drift tube electrical connections.
divided by the effective tube length, as measured from ring center to ring center. Simulations in Simion show this to be an excellent approximation for the axial field strength, and the field remains uniform to within 1% up to about 80% of the tube radius. $P_{LIF}$ is determined by linear interpolation of readings taken at two pressure ports 17 cm up and downstream of the LIF region, as shown in Fig. 2.5. These ports are connected to a 1 Torr capacitance manometer (MKS Baratron), which is referenced to the quadrupole chamber pressure (effectively zero Torr). By convention, the tube pressure is measured downstream at port B and multiplied by a scale factor $s$ to obtain the pressure at the LIF region. Taking then:

$$E_{LIF} = \frac{V_{\text{drift}}}{L_{\text{eff}}}, \quad P_{LIF} = sP_B, \quad T = T_{\text{room}},$$

(2.10)
gives a field strength formula for $E/N$ at the LIF region:

$$\left(\frac{E}{N}\right)_{LIF} = 1.0356 \times 10^{-2} \frac{V_{\text{drift}} T_{\text{room}}}{s P_B L_{\text{eff}}}$$

(2.11)

with $E/N$ in Td, $V_{\text{drift}}$ in volts, $T_{\text{room}}$ in Kelvin, $P_B$ in Torr and $L_{\text{eff}}$ in cm. The room temperature is measured by a mercury thermometer adjacent to the apparatus. The pressure scaling factor must be empirically determined for each apparatus assembly. For the assembly used for the majority of this work, $s$ was found to be 1.022 from repeated measurements of $P_A$ and $P_B$. A typical running $P_B$ was about 0.4905 Torr.

To measure proper transport properties in a drift-tube apparatus, it is necessary to separate the negative species (primarily electrons) from the plasma to achieve a space-charge limited density of ions drifting in neutral buffer gas. A simple estimate
produced from a one-dimensional Poisson’s equation argument\textsuperscript{10} yields an upper bound of approximately $10^6$ ions cm$^{-3}$ for negligible space charge effects for the dimensions of this apparatus. The conventional way of insuring both these conditions is to create a charge separation region, consisting of a number of rings prior to the drift region proper that are maintained at a separate field strength than the drift region. Ideally, the charge separation region creates a barrier for all free electrons in the plasma, and one is left with a space-charge-limited density of positive ions alone in the drift region. Unfortunately, it was found that the apparent axial ion flow velocities can be significantly altered by the length and position of the charge separation region, probably indicating that the ion density is above the space-charge limit. For the majority of the work presented here, the charge separation region consisted of 11 rings (10 resistors) with 10.0 V across these resistors for a nominal 1 V cm$^{-1}$ external electric field. A discussion of artifacts introduced by possible space-charge effects due to either too high ion density or free electrons is deferred to Sec. III.E.

C. Ring dye laser system & diagnostic tools

The resultant $N_2^+$ ions in the drift tube are probed by a single-frequency ring dye laser system, as discussed in this section. Ring dye “laserology” turns out to be particularly important for this experiment due to its inherent repetitiveness. Additionally, operating at and below 390 nm required using a near-UV dye that is costly, short-lived, and sometime difficult to achieve consistent results. It should be mentioned that if future experiments requiring a cw laser in this wavelength range are attempted, the acquisition of a Ti:Sapphire ring system and the construction of an
external actively-stabilized doubling cavity with a BBO, LBO, or LiIO$_3$ crystal as a second-harmonic generation medium should be seriously considered.$^{11}$ The laser pump requirements would be in the visible (514 nm) and much less stringent. The additional power stability and reliability would permit longer scan times and more coadds. Lastly but not leastly, an all solid-state system would relieve some of the pain and suffering commonly associated with ring dye lasers, with which this investigator is intimately familiar. This is an important consideration, as chemical physics experiments are becoming more complex, and single-frequency lasers are now often just one of several lasers employed in an experiment, used perhaps for intermediate-state preparation.$^{12}$

1. General description

An optical and electronics schematic of the relevant portions of the ring dye laser system (Coherent 699-21) is shown in Fig. 2.6. The basic concepts of a moderate-resolution, actively-stabilized ring dye laser are well-described in the literature.$^{13-15}$ Briefly, the laser consists of a vertically-folded ring cavity defined by four mirrors. A thin ribbon of dye jetted into the cavity serves as the lasing medium and is pumped by an argon ion laser. A hierarchy of three increasingly selective frequency elements (i.e., the birefringent filter, thin etalon, and thick etalon) force the laser to run in a single longitudinal cavity mode, with an actively-stabilized linewidth of less than 1 MHz. The scanning elements ($\alpha, \beta, \chi, \gamma$ in Fig. 2.6) are controlled by a cavity-side-lock system which employs a temperature and pressure stabilized confocal Fabry-Perot reference cavity with a free spectral range of 1.0 GHz. The
Fig. 2.6: Coherent 699-21 ring dye laser optical & electronics schematic.
electronics consist of essentially two servo loops. The air-spaced thick etalon is translationally tuned by a separate dither-and-track loop that keeps the thick etalon centered on the chosen longitudinal mode. The second servo loop is the cavity-side-lock that uses the reference cavity as a frequency discriminator. The reference cavity Brewster plate (δ) is scanned under either internal or external control and the scan is fed-forward to the thick and thin etalons and intracavity Brewster plate (χ, β, and γ) to roughly position these tuning elements as the laser is scanned. Feed-back information derived from the reference cavity is used by the second servo loop to actively stabilize the laser by continuously positioning the fast (tweeter, α) and slow (Brewster plate, γ) intracavity elements to keep the frequency error signal at the lock point. These elements compensate primarily for dye jet jitter and air temperature and pressure perturbations to the cavity, respectively.

Dye preparation and use was (unfortunately) a significant practical consideration for this experiment due to the expense and short life of the dye. The dye used was Exalite 392E, a proprietary near-UV dye (Exciton Chemical Co.) with a molecular weight of 723 amu, and useful single-frequency spectral range of approximately 388 to 392 nm. Although significantly more robust than the polyphenyl dyes it was developed to replace,16 this dye still requires special preparation and handling. Recommended concentrations for CW ring dye laser use vary from 1.6 to 4.15 millimolar (mM) solutions of dye in ethylene glycol. Two grades of glycol were used over the course of this experiment (Mallinckrodt AR and Fisher Certified), both with a typical water content of 0.05% or less; glycol lots should always be chosen with the lowest water content available. Pragmatically, the dye recipe used for the
majority of this work consisted of adding 3.00 g of pulverized dye to 300 ml of ethylene glycol to form a premix solution. The dye is supplied in microcrystalline form and must be crushed in a mortar and pestle to the consistency of talcum powder to insure that it goes systematically into solution. The premixes were prepared two at a time, sonicated and then mixed for at least 24 hours on a stirplate. After flushing the old dye from the jet system, 900 ml of glycol was added and the dye circulator checked for leaks before adding the 300 ml of dye premix, resulting in a 3.46 mM operating solution. It should be pointed out that the only way to be certain of the correct dye concentration is to check the dye jet absorption of the pump beam as a function of dye solution molarity (80-85% absorption is optimal); this was done several times in the course of the work.

Exalite 392E is optimally pumped by the mid-UV lines (333.6 to 363.8 nm, "all lines") generated by Ar$^{2+}$ in an argon ion laser. Two large-frame argon ion pump lasers were used in the course of this work. The original pump laser (Coherent Innova 20) had a passively stabilized quartz crystal resonator structure which required continual repeaking, noticeably affecting the beam-pointing stability. When the cathode sagged on the tube in this laser, a tube refurbishment procedure was attempted, with decidedly mixed results. With "20-20 hindsight", it was recognized that the pump requirements for this experiment were probably too demanding to be met by a refurbished laser tube. The second pump laser (Coherent Innova 400) has an actively-stabilized Invar resonator; the ring dye laser output is noticeably more consistent and stable over time with this pump source. For near-UV dyes, the pump mode is very important for achieving optimal results; pump mode can be observed in
the far field by splitting off a fraction of the pump beam with a simple beamsplitter and expanding it with a lens onto a white card. The “donut mode” (linear combination of $\text{TEM}_{01}$ & $\text{TEM}_{10}$ modes)\textsuperscript{18} is a particular and well-known problem with these lasers. These modes develop over time because of color centers formed on the crystalline quartz Brewster windows of the laser tube. Donut modes can be eliminated by aperturing down intracavity, at the expense of output power. It was found that for this dye, optimal results were always achieved with larger pump mode volumes, even if these volumes included some “donuts”.

The highest single-frequency power achieved with this dye was 105 mW at the output coupler; a more typical running power is 80 mW with fresh dye. Dye lifetimes depend on several factors, including pump laser power and mode, ring cavity alignment, and cooling water temperature. A typical value is fifteen running hours to approximately one third of initial power. The dye solution will turn from clear when new, to pale straw, to a dark urine color when completely oxidized. For optimal dye lifetime, it was found necessary to eliminate all brass parts from the dye utility module and replace them with stainless steel. Additionally, it was found helpful to time dye use with a stop-watch in order to know the usable dye lifetime left, so that future experiments could be planned. The need to work quickly on the ring dye laser with this dye, to know when and when not to make compromises, and always, to be flexible in experiments performed cannot be overemphasized.

2. Diagnostic tools

The ring dye laser is used in conjunction with other diagnostic tools, as shown in the optics table schematic of Fig. 2.7. A fraction of the output beam from the laser
Fig. 2.7: Optics table schematic, showing ring dye laser and associated diagnostic tools.
is split off by a primary coated 85/15% beamsplitter (CVI Laser Corporation). This beamsplitter is sufficiently thick such that the secondary reflection off of the nominally AR-coated back surface is spatially well-separated from the primary split-off beam. This secondary reflection was put to good use by directing it via a pick-off mirror to an external photodiode (EG&G FND-100Q), used as input to the laser power channel for the transport property experiments, and as the normalizing photodiode for the analog divider (discussed below) in the alignment experiments.

A second coated beamsplitter splits the primary diagnostic beam 80/20%. For typical data-taking conditions on the transport property experiment, these beams were directed to the two confocal Fabry-Perot spectrum analyzers used in the course of this work. One is a commercial Invar cavity (Coherent Model 240), 5 cm in length, with a free spectral range \( (\text{FSR} = \frac{c}{4L}) \) of 1.50 GHz. This cavity has a piezoelectric translator on the back mirror which enables the transmission fringes to be tuned or dithered in frequency by applying either a DC voltage or a ramp. A simple "high-voltage" piezo ramper was constructed to exploit this capability (schematic in appendix A). This proved quite useful; the consistently downward slope of laser power with time meant that with each dye change, inevitably there would be a point at which not enough power was available to obtain an external wavemeter reading. The 5 cm long Invar cavity could then be used as an \textit{ad hoc} wavemeter. The laser beam is multiplexed quickly between the wavemeter and the Fabry-Perot cavity by a simple mirror mounted on a 1-D translation rail.

Although convenient to use at times, the commercial 5 cm Invar cavity is not particularly stable in frequency. Also, its relatively long free spectral range means that
few frequency markers appear in the framing of a short laser scan; a cavity with a shorter FSR was desired in order to compute scan widths more accurately for the transport property experiments. Additionally, a stable frequency marker cavity was needed for the sub-Doppler alignment experiment. For these reasons, a simple “ultrastable” confocal Fabry-Perot cavity, 20 cm in length, with a free spectral range of 0.375 GHz was constructed, as diagrammed in Fig. 2.8. The cavity mirrors are two stock plano-concave spherical mirrors (CVI Laser Corporation) of 20.0 cm radius and a surface figure of $\lambda/10$, with a reflectivity of 99.5% over the wavelength range 388 to 392 nm. A ultra-low thermal expansion (Corning “ULE”) titanium silicate glass cylindrical piece of indicated dimensions was bored and countersunk by the JILA instrument shops. The ULE cylinder was mounted in a JILA lens mount, and the mirrors were arranged perpendicular to the bore. The mirror spacing was adjusted to maximize finesse, and the mirrors affixed to the ULE with Torr-Seal, following the construction technique of Hall labs. Note that the mirror holes and cavity should be completely sealed immediately to prevent debris from migrating into the cavity and destroying the reflectivity finesse (this initially occurred with this cavity). A simple photodiode circuit was constructed to detect the transmission fringes.

A scope trace of the 20 cm ULE cavity’s transmission fringes, with the 5 cm Invar cavity fringes shown for comparison, is given in Fig. 2.9. The total instrument finesse may be estimated from such a diagram; the finesses are approximately 100 and 25 for the 5 cm Invar and 20 cm ULE cavities, respectively. Because the performance of the ULE spectrum analyzer in a reasonably draft-free room was adequate for these purposes, no attempt was made to temperature-stabilize it.
Fig. 2.8: Construction schematic of 20 cm ULE confocal Fabry-Perot cavity.
Fig. 2.9: Representative scope trace of 20 cm ULE cavity, with 5 cm cavity trace shown for comparison.
However, it was found important to construct plexiglass boxes around both cavities to minimize convective temperature cycling. The coefficient of thermal expansion of ULE is specified as $\alpha_{ULE} = 0 \pm 30 \times 10^{-9}/^\circ C$, with a maximum variation of 15 ppb per degree C in a boule of material. A simple analysis with these numbers give a thermal shift in frequency of a transmission fringe of approximately 20 MHz $^\circ C^{-1}$. The constructed ULE cavity is considerably less stable than this figure would imply primarily due to its low thermal mass. With a density $\rho_{ULE} = 2.21$ g cm$^{-3}$ and specific heat $c_{ULE} = 0.183$ cal/g$^0$C, the thermal mass of this cavity is approximately 36 cal $^0$C$^{-1}$. Additional long-term frequency stability could undoubtedly be achieved by the construction of a simple "hot box" as a temperature stabilizer.

For the rotational alignment experiment, the 20 cm ULE cavity was used to generate frequency markers for sub-Doppler data acquisition. The reference cavity Brewster plate (δ in Fig. 2.6) can be simply modeled as a critically-damped oscillator driven by the internal or external scanning ramp (i.e., as a "screen door" pushed and pulled by the ramp). If a marker cavity such as this one is used as feedback to position the laser in frequency, and the external ramp simply stopped once the maximum of a transmission fringe appears, the reference cavity Brewster plate will overshoot the target position, and the laser frequency will end up in some unknown location between free spectral ranges. A simple scheme was adopted to get around this problem. An analog divider circuit which mimics the electronics of a cavity-side-lock system was constructed (schematic in appendix A) to divide out the laser power dependence of the cavity transmission and to insure that each transmission peak is the
same amplitude. The numerator input is the 20 cm ULE cavity photodiode and the
denominator input the aforementioned laser power photodiode. The output is a 0-to-
10 V signal sampled by the microcomputer’s analog-to-digital converter. Two
empirically-determined voltage thresholds are used in conjunction with a simple step-
and-sample algorithm in the acquisition program (Eta-Spex) to position the laser
frequency onto an arbitrary cavity transmission fringe. One voltage threshold is used
simply to count passing fringes as the laser is slewed. Once the fringe immediately
prior to the target fringe has appeared, the slew rate is slowed and the threshold
lowered. The external ramp is then stopped as soon as this lower voltage threshold is
reached; the additional “creep” of the Brewster plate alone will consistently position
the laser frequency above 80% of fringe peak height in under a second. False fringes
caused by noise or the laser coming momentarily out of lock can be easily
discriminated against by keeping track of the fringe width. Although this scheme
works remarkably well in practice for the relatively coarse (± 30 MHz) frequency
positioning needs of this experiment, because the 20 cm ULE cavity is still quite
unstable, no attempt was made to transfer the frequency lock to this cavity.

Although the Fabry-Perot spectrum analyzers are useful for scan width
analysis and frequency positioning within a scan width, a spectrometer of some sort is
needed to make rotational line identifications. The external scanning Michelson
interferometer wavemeter employed here (Burleigh Model WA-20) has an absolute
accuracy of ± 0.001 nm, and its resolution of ± 0.01 cm⁻¹ is sufficient to distinguish
between thick etalon modes of the ring laser. The wavemeter was usually not
employed for the transport property experiments once the desired LIF transition was
found. For the sub-Doppler alignment experiments, the wavemeter was useful as a diagnostic while running (if sufficient power was available) to verify the laser had not mode-hopped during a data acquisition sequence.

A rough diagnostic of how well the ring dye laser was running on a particular day could be obtained by counting how frequently the cavity-side-lock servo loop broke lock due to microbubbles in the dye stream, dye jet pressure fluctuations, or environmental perturbations. Each time the servo loop breaks lock, the intracavity Brewster plate ($\gamma$ in Fig. 2.6) will attempt to compensate. If too much error accumulates such that the Brewster plate will tip out of range if it attempts to compensate for additional cavity length variations, a galvo recentering circuit automatically breaks lock and recenters the Brewster plate. These recenterings are undesirable, as they will often induce a longitudinal mode hop while all servo loops are open. To monitor the number of unlock/lock transitions, a simple window detector circuit (schematic in appendix A) was constructed to detect and count these transitions. The input of the detector is the reference cavity error signal, and its output is a logic-level pulse, one for each transition. Front-panel LED’s provide additional visual cues, which are very convenient for monitoring across the room, as the rapid scope transitions cannot be seen from a distance. Discriminator levels were arbitrarily set at $\pm 1V$ above the lock point (ground) to count the largest, slowest unlock/lock transitions, which lead to the most rapid accumulation of Brewster plate error. Although originally constructed for the alignment work, the window detector proved so useful in practice that it was used constantly.
Lastly, note that for a Coherent 699-21, both the intracavity Brewster plate and thick etalon error signals are accessible for diagnostic purposes. The thick etalon error signal can be monitored directly from the back-panel of the ring dye laser control box. This signal was monitored continuously for both sets of experiments. A discontinuity in the thick etalon error signal usually reflects a mode hop, as the etalon is now being dithered about a different longitudinal mode, and monitoring the signal can be an immediate way to determine this. The intracavity Brewster plate error signal is displayed on the front-panel of the ring dye laser control box, and can be monitored internally at TP5 of the 1A9 circuit board; if the voltage at this test point exceeds ±0.9V (corresponding to 80 to 20 μA on the front-panel meter), the galvo will recenter.

3. Beam transport & polarization control

The output laser beam is transported to the apparatus table and into the baffle arms by a set of mirrors, as shown in Figs. 2.1 and 2.7. Two mirrors were needed for the perpendicular laser probe direction, and three for parallel (coaxial) probe. The mirror sets were independent, and the probe directions could be easily switched by sliding into place or aside the first perpendicular probe mirror, which was mounted on a 1-D translation stage, as shown in Fig. 2.7. The ability to quickly toggle between the two probe directions was particularly important for measuring axial ion flow velocities, as discussed in Sec. III.E. Unfortunately, mirrors with ordinary (i.e., uncoated, oxidized) aluminum surfaces will have losses of 50% or greater per mirror at \( \lambda \leq 390 \text{ nm} \). Special "UV-enhanced" aluminum mirrors with MgF\(_2\) dielectric coatings (Melles Griot, coating code 028) were employed to keep mirror losses at a tolerable 2 to 5% level. The baffle arm entrance windows were fused silica and
mounted between two O-rings to minimize strain and avoid possible stress-induced birefringent effects. The exit baffle arms are terminated in Brewster-angle window beamstops that were rotated into the plane of the dominant polarization sense of the probe beam (usually vertical).

To aid in the beam transport, drilled table extensions were constructed for the apparatus table and a breadboard assembly made for the coaxial probe baffle arm. Additionally, counterpropagating HeNe laser beams were employed in each probe direction to get the beam transport near-perfect and thus minimize background contributions from scattered laser light. The HeNe lasers were mounted behind the Brewster-angle windows and were prealigned with the aid of a target that fit into the baffle arms. Once aligned, the HeNe beams allowed the investigator to iterate through the set of mirrors for a given probe direction very quickly to get the ring dye laser beam alignment close to optimal. Fine adjustment was always done by observing the PMT signal and comparing the scattered laser light levels with the PMT dark-count rate. The use of a multi-channel scalar (Nicolet) as a "stripchart" to check scattered laser light proved quite useful. It was particularly important for the alignment experiment to get the background contributions from scattered laser light as low as possible. As a residual beam-transport note, it was also found necessary to refrain from adjusting the lower fold mirror (tweeter) of the ring dye laser cavity once the laser was initially peaked with fresh dye. This intracavity mirror most affects the pointing of the output beam, and even a small adjustment of the tweeter would be magnified by the long beam throws of this experiment and noticeably perturb the beam transport.
The output beam of the ring dye laser is nominally vertically polarized; this s-wave polarization sense is preserved by the beam transport mirrors to the apparatus table. The transport property experiments did not necessarily require modification of the polarization state. For the rotational alignment experiments however, polarization control of the probe beam is crucial. A zero-order polymer half-wave plate (Meadowlark Optics) with \( \lambda_c = 390 \text{ nm} \) was used to rotate the plane of polarization of the probe beam. Primarily, the half-wave plate was used as a compensator to match the "vertical" of the probe beam with the "vertical" of the fluorescence imaging axis and to correct for small polarization rotations that occur in the beam transport. A Glan-Taylor polarizing prism (Melles Griot) was used following the wave plate to insure linear polarization purity of the probe beam. Any residual elliptical polarization present in the incident beam, whether due to imperfect ring dye laser alignment, beam transport, or partial-wave retardation of the wave plate, will be extinguished by the Glan prism. Note in particular that Fig. 2.1 is somewhat misleading; there are no additional optics of any sort (besides the baffle arm entrance windows) after the polarization optics. The retardance of polymer wave plates is fairly insensitive to incident angle, so the wave plate was mounted in a simple one-axis rotary stage; the Glan prism was mounted in a three-axis rotary stage with separate tilt adjustments. For proper operation, both polarization optics must be aligned normal to the laser beam. This can be accomplished by locating the retro-reflection off the front surface of the optic and then adjusting the tilt of the optic to make the retro coincide with the incident beam. Lastly, a very simple pragmatic way of setting a desired probe polarization angle is to first rotate the Glan prism so its polarization transmission axis
is at right angles to the desired setting. Then, place a white card after the Glan prism and rotate the half-wave plate to whatever setting achieves extinction of the output beam, by visual inspection of the card. The major axis of the polarization ellipse is now at right angles to the transmission axis of the Glan; rotating the Glan back 90 degrees to the desired setting will pass the major axis while extinguishing the minor.

D. LIF Detection: unpolarized and polarized fluorescence detection

The geometrical relationship between the two probe beam directions and the fluorescence imaging region in the drift section of the apparatus is shown in the perspective view of Fig. 2.10. Laser-induced fluorescence is always detected orthogonal to both probe directions by a blue-sensitive photomultiplier tube (PMT) through a series of optics referred to as the PMT “stack”. Although a number of stack configurations were employed throughout the course of this work, in practice, the data presented here were taken with a small number of configurations; the stack was “frozen” into one of these particular configurations for the course of an experiment. While important for both experiments, the stack configuration is particularly crucial for polarized LIF detection used in the rotational alignment experiments. General unpolarized fluorescence detection issues are briefly discussed in Sec. II.D.1; details of polarized fluorescence detection are summarized in Sec. II.D.2.

1. Unpolarized detection

The \( \text{N}_2^+ \) fluorescence passes through apertures cut into three drift rings at the center of the apparatus (the LIF region). Experimental tests by previous investigators, as well as the \textit{Simion} modeling of Bastian\(^2 \) demonstrate that these cuts make a
Fig 2.10: Perspective view of apparatus, showing relation between probe beams & LIF detection.
negligible perturbation in electric field uniformity at the LIF region. Two sets of three cut rings were used in practice. The first set, previously employed by other investigators on this project, have a single square-cut opening in the shape of a cross. These rings were used for the first rotational alignment experiments conducted in the Fall of '95. Subsequently, to address a possible LIF polarization systematic in this experiment, these rings were replaced by another set. The new rings have relieved-cut cross-shaped apertures cut into both the top and bottom of the rings. These reliefs were cut to eliminate possible glancing-angle, partially-polarizing fluorescence reflections off of the flat-cut metal surfaces that could be imaged by the PMT. However, diagnostic tests taken with this new set of rings indicate that glancing-angle polarizing reflections off of the surfaces of the original pieces probably made a negligible contribution to the polarization systematic. These relieved-cut rings were employed in both the Fall '97 transport property work and the Spring '98 rotational alignment work.

The LIF then passes through a vacuum window into the light-sealed PMT stack. The LIF windows (Esco Products) used here are made of fused silica. The windows are mounted between two O-rings with an anodized aluminum window holder to minimize possible strain. The window holder has an effective aperture size; two sizes were used in practice. The original window holders had 2.86 cm (1.125 inch) apertures. To narrow down the effective imaging solid angle for the alignment experiments, a second window holder was constructed, with a 1.59 cm (0.625 inch) aperture. Ironically, it now appears that possible polarizing reflections off of the square-cut walls of this aperture piece may have been contributing to the polarization
systematic. Two biconvex fluorescence imaging lenses (Newport) made of BK-7 (one AR coated, one uncoated) and of focal length \( f = 6.3 \) cm were employed. Although experiments were attempted with the lens at various positions, the best signal-to-background was invariably obtained with the lens as close to the window as possible. The lens focal length was chosen to give approximately 1:1 imaging of the fluorescence in the source region, although this imaging restriction on distances in the PMT stack was not found to be very important in practice.

Even with the most careful production conditions and laser beam alignment, the amount of residual flowing afterglow fluorescence and scattered laser light completely precludes attempting experiments without an interference filter in the fluorescence channel. Two bandpass interference filters were used throughout this work and their transmission functions were characterized on the JILA Cary spectrophotometer. The choice of interference filter for the transport property experiments was somewhat arbitrary and simply based on best signal-to-background. However, for the alignment experiments, it is necessary to know the P/R branch-weighting of the observed fluorescence in order to properly calculate alignment parameters from polarized LIF measurements, as discussed in Sec. IV.B. The interference filter fits into a square-cut “shelf” in a filter assembly that is light-sealed by a half-cylindrical piece of black Delrin plastic.

Only one type of photomultiplier tube was used for this work, the Thorn EMI 9813QB; which is optimized for photon-counting in the blue. The 9813QB has a quartz window leading to an end-on bialkali photocathode with an effective cathode diameter of 46 mm and a quantum efficiency of approximately 23% at 425 nm.
Photoelectron multiplication is achieved through 14 beryllium copper dynodes in a linear focused structure with an approximate gain of $7 \times 10^7$. Standard photon-counting biasing networks for the dynodes are used; the photocathode high-voltage is usually run at -2200 V. The photocathode could be completely shuttered from all fluorescence for a thermionic dark count check, which was particularly important for the alignment experiments. Various 9813QB's will have different dark counts; a tube with a particularly low dark count (serial #4970) was used for most of the experiments conducted.

2. Polarized detection

For the rotational alignment experiments discussed in Chapter IV, it was necessary to resolve the polarization of the fluorescence. Although other techniques were considered, including the use of a photoelastic modulator in the laser probe beam to modulate the laser polarization, a dual PMT setup with two orthogonal polarizers, and the use of a liquid crystal variable retarder in the fluorescence channel, a very simple fluorescence polarization detection scheme was ultimately chosen. The reasons for using this particular scheme are discussed more fully in Sec. IV.B, and the mechanics of this data acquisition scheme are discussed in Sec. IV.C. Although several different dichroic polarizers were experimented with, in practice a pair of 5.1-cm (2-inch) diameter dichroic polarizers (Optics for Research) with an extinction ratio of better than $10^{-3}$ were used for all the work presented here.

Several different methods were used to set the angle of the fluorescence polarizer transmission axis. The simplest technique, employed in the earliest alignment experiments, involved mounting the polarizer in a square-cut frame that fits
snugly into one of the shelves of the interference filter assembly. The polarizer transmission axis was indicated to the drift tube axis and firmly taped into place in the frame. To change the polarizer setting, the polarizer frame was rotated 90 degrees and replaced in the stack shelf. This simple method is useful for measuring linear polarization coefficients, which require just two orthogonal polarizer settings; however, this technique suffers from several disadvantages. The primary disadvantage of this method is that it requires breaking the light-seal of the stack for each polarizer rotation. For each rotation, the PMT shutter has to be closed, the black Delrin light seal of the interference filter assembly rotated open, and the polarizer itself rotated, a time-consuming and tedious process. Early diagnostic data indicated that good time correlation between the sequential polarization measurements was essential, so this method was inherently problematic. Additionally, the polarizer setting could not be checked once the light seal was closed, introducing the possibility of operator error in the polarizer rotations.

To address these shortcomings, a slightly more sophisticated approach was taken. A new lens barrel and adapter were built such that the entire PMT stack could be mounted on a commercial 2-inch manually-driven rotation stage (Newport). This particular stack configuration is shown in Fig. 2.10. The interference filter holder assembly is identical to the old stack, and the polarizer is still mounted in one of the shelves. However, the entire stack is rotated to set the polarizer transmission axis to a particular angle. The primary advantage of this technique is that the light seal of the PMT stack is not broken for polarizer rotations, greatly speeding the data acquisition. Additionally, the polarizer settings can be checked by the marking on the rotation
stage to verify that a clerical error had not been made on a particular trial. Unfortunately, there are still disadvantages to this method. Although the stage permitted setting the transmission axis of the polarizer to any angle, usually trials were taken at only two angles (0 and 90 degrees) or just a few angles. This scheme required the investigator to manually rotate the stage to the specified angle in the sequence as often as once every eight seconds. These rotations need to be performed repeatedly as rapidly as possible and without clerical error, often for several hours under conditions of considerable duress and fatigue. More importantly, diagnostic data taken with this stack indicated that it was introducing polarization systematics (discussed in Sec. IV.D.1) due to the "wobble" or effective modulation of the detection solid angle as the stack was rotated.

To address these shortcomings, a detection stack was constructed with the polarizer mounted in an integrated rotation stage and driven by a stepper motor. A scale drawing of this stack and stage is shown in Fig. 2.11. The rotation stage is driven by a Geneva mechanism\textsuperscript{21} discretely indexed to 15-degree steps by a detent, which consists of a stainless steel ball constrained by a bushing consisting of four stainless steel rods mounted in a brass sleeve. The stage itself rides on two sets of 2.5 inch i.d. by 3 inch o.d. bearing races (Kaydon). Twenty-four hardened steel pins equally spaced on the diameter of the stage engage both the star wheel of the Geneva mechanism and the ball detent. This design insures that the stage is discretely indexed to 15 degree steps by the detent and that the stage positioning is completely reproducible; the positioning error is estimated to be less than 0.1 degree. The symmetry of the drift tube means seven distinct polarization angle measurements are
Fig. 2.11: To-scale plan view of stepper-motor driven PMT stack.
possible. The entire assembly is light-sealed so that light seal is never broken to rotate the polarizer. The dichroic polarizer is Torr-Sealed in a 2-inch diameter adapter piece and held in place by three set screws; the stage design permits fine adjustment of the polarizer to match up its transmission axis with the geometry of the apparatus.

A stepper motor is the “torque engine” that drives the stage to a specific detent position. The design goal was to take advantage of the inherent simplicity of stepper motors to produce a system with nearly 100% mechanical reliability. A small stepper motor (Airpax; nominal 5 V, 6.25 ohms/coil) with a 7.5 degree full-step was used for this particular design. The stage is geared such that four stepper motor steps are needed to produce one stage step. A circuit was designed and constructed to drive the stepper motor in the necessary burst mode (circuit schematic in appendix A). The circuit is designed with three inputs from the outside world: a command for a single stage step, which can come from either a front-panel push-button or remotely from a computer, a direction (CW/CCW) flag, and a “Hold/Let go” that effectively shunts the stepper motor coil current, making it impossible for the stage to take a step. This latter feature is crucial, as it was found that just moving around the lab could produce large noise spikes on the stepper motor driver ground plane, triggering a spurious stage step and throwing off the sequencing of the stage. The three inputs are normally driven by digital output signals from the acquisition computer.

The stage is designed to be inherently almost 100% reliable; however, the system is run “open-loop” without verification of angle positioning. An attempt was made to integrate a microswitch into the stage to verify the number of stage steps taken. However, it was found that the microswitch itself would be unreliable unless
carefully positioned. Additionally, the drag on the stage caused by the switch made the assembly considerably more unreliable. The simplest and most practical solution was found to be periodically opening the PMT stack at the filter holder and checking the stage position visually. The polarizer sequences were programmed such that the stage was slewed to a “home” position (arbitrarily 0 degrees) between sequences. The stack could then be opened and checked at the sequence boundaries if so desired. The PMT stack was designed to come apart easily in under five minutes at the stage with the PMT shuttered, which permitted “hot” checking of the stack with the PMT voltages still on. Additionally, the stage makes a characteristic chattering noise when slewing, which is noticeably different than the sound produced if it is out of detent. Using the unique acoustic signature of a successful stage step would be the most promising avenue of designing a non-obtrusive closed-loop system for future work.

E. Electronics and data acquisition programming

A brief description is given of the relevant electronics and computer programming issues that arose in the course of the two experiments. The data acquisition is computer-controlled, so these two topics are naturally tied together. All data acquisition programming for both experiments was performed in C (Borland Turbo C 2.01) for a DOS-based computer and integrated into a single program called Eta-Spex. The length of the total program (approximately 13,000 lines with user-interface code and look-up tables) precludes including a print-out; a diskette is enclosed with the source code in Appendix B. Key features of the program are discussed briefly below. The acquisition programming turned out to be particularly important for the alignment experiment; it was recognized early on that to obtain good
statistics, many repetitions would have to be performed of basic acquisition tasks. The philosophy was to use the natural strengths of a computer to handle the clerical and "grunt" repetitive work of the experiment.

All data acquisition in the program is hardware interrupt-driven,\textsuperscript{22} which means that the user can perform tasks like rescaling the spectra graphics screen or move the graphics cursors while data is being acquired, with the assurance that no data points are being missed. The timing of both the hardware interrupts and counter gates is derived from a 1 MHz crystal, making any timing jitter issues negligible. The program is menu-driven, with the particularly useful feature that numerical parameters such as gate widths are extracted directly from the menu text and not stored in internal look-up tables. Pragmatically, this means a menu parameter can easily be changed and the program recompiled "on the fly" while the experiment is running. The acquisition filename prompting is virtually fool-proof, which insures that files are not lost through operator error. Additionally, the program has filename generation capabilities through a templating mechanism that automatically generates a sequentially numbered filename, which can then be accepted by a single keystroke. This is particularly useful for the transport property experiments, which tend to be file-intensive. The file format is multi-column, tab-delimited ASCII, which can easily be imported into virtually any data analysis or plotting program.

A block schematic of a portion of the acquisition system is shown in Fig. 2.12. There are three data acquisition and control boards (MetraByte) in the laboratory computer. A five-counter card based on the AMD 9513 system timing controller\textsuperscript{23} is used for event counting; some of the counters are used to gate other counters and
Fig. 2.12: Block schematic of counter portion of acquisition system.
trigger interrupts. A digital-to-analog (D/A) converter card is used primarily to ramp and position the ring dye laser through external control. The second D/A channel is used to control the programmable floating voltage supply for the experiments discussed in Sec. III.E. An analog-to-digital (A/D) converter card is used to sample the 20 cm ULE Fabry-Perot transmission peaks for the hardware marker positioning method discussed above. Three digital outputs on this card are also used to control the stepper motor-driven rotation stage electronics.

Four event counters of the AMD9513 are used in the transport property experiments. Counter 5 is tied to a crystal-locked 1 kHz signal, which is used as time base to periodically generate HW interrupts for event counter sampling. The PMT signal was amplified and pulse-height discriminated by a preamp/discriminator (Pacific Instruments) located adjacent to the PMT stack. The PMT pulses are sent to the electronics rack, regenerated by a pulse generator, and sent to a 9513 event counter. A “local” measure of ring dye laser power is derived from either the normalizing photodiode of the cavity-side-lock system or a separate photodiode, as discussed in Sec. II.C. The ring dye laser power signal was always converted into the digital domain by a JILA electronics shop built voltage-to-frequency converter, based on the Raytheon RM4151. It was confirmed that V/F converter used is completely linear over its entire 0-10V range (nominal 1 kHz/V calibration), and always properly zero-offset; this detail is particularly important for the alignment experiments because all the LIF signals are laser-power normalized. The Fabry-Perot signals are digitized by two more V/F’s and sent to two more event counters. For the sub-Doppler alignment experiments, a slightly different configuration is employed. Three event
counters are used; the PMT and laser power signals are treated the same as for the transport property experiment. The third counter receives pulses from the window detector discussed above. Counters 4 and 5 of the 9513 are tied together and used to generate both a hardware gate and periodic sampling interrupt for the event counters. This permits an assessment of the statistical spread in the counting trials to be made.

**F. General data analysis considerations**

A brief discussion is given of general data analysis issues involved in both experiments. For the transport property experiments, extensive use was made of a commercial non-linear curve fitting program (PeakFit; Jandel Scientific). This program uses the Marquardt-Levenberg algorithm\(^2\) to fit a number of library functional forms to user-supplied data. The two functional forms used primarily in this work are discussed in Chapter III. The fitting program calculates a standard error in the fit for each fit parameter that is subsequently used as a measure of fit uncertainty in the error analysis. The standard errors in the fit parameters are obtained from the covariance matrix \(C\). Specifically, for a fitting functional form \(y(x;\bar{a})\) depending on \(K\) fit parameters \(a_1..a_K = \bar{a}\), the covariance matrix is defined as

\[ C = \alpha^{-1}, \]

with the matrix elements of the matrix \(\alpha\) given by\(^2\)

\[ \alpha_{kl} = \sum_{i=1}^{N} \left( \frac{\partial y(x_i;\bar{a})}{\partial a_k} \right) \left( \frac{\partial y(x_i;\bar{a})}{\partial a_l} \right) \]  

(2.12)

where the sum runs over the number of data point \(N\). The square roots of the diagonal elements of the covariance matrix multiplied by the chi-squared per degree of freedom are the standard errors \(\delta a_i\) corresponding to the fit parameters:
\[ \delta a_i = \sqrt{\frac{\chi^2}{N_{\text{dof}}}} \sqrt{C_{ii}} \] with \[ \chi^2 = \sum_{i=1}^{N} (y_i - y(x_i; \bar{a}))^2, \quad N_{\text{dof}} = N - K \]

The off-diagonal elements of the covariance matrix provide information about how the various parameters are correlated. Although the commercial program does permit user-supplied fitting functions to be used, these functional forms are not pre-compiled, and thus fitting to these forms is agonizingly slow. In the very latter stages of this work, an attempt was made to integrate non-linear fitting routines into Eta-Spex to fit the functional forms discussed in Chapter III to the individual hyperfine components of a line shape. Although this work was not completed, this is the most promising approach for future work. Some basic file analysis capabilities were integrated into Eta-Spex. In particular, it was found useful to be able to quickly “page” through and review acquisition files in a particular run. The graphics screen cursors permitted the Fabry-Perot spectrum analysis to be performed visually and thus reasonably quickly. Additionally, since the transport property experiments are file-intensive, some of the diagnostic data (for example, to resolve the axial ion flow systematics) was analyzed “on the fly” by using a Savitzky-Golay smoothing routine to smooth the LIF spectrum and then determine the first and second central moments numerically. These numbers (but no file) were then recorded.

**G. Spectroscopy of the \textit{N}_2^+ B ^2\Sigma_u^+ - X ^2\Sigma_g^+ system**

A typical LIF spectra of the \textit{R}_1(15) spin-rotation line of \textit{N}_2^+ is shown in Fig. 2.13. Because of both its importance in atmospheric and astrophysical work, and
Fig. 2.13: Typical LIF spectra of a single spin-rotation line, illustrating the Doppler-broadened, unresolved hyperfine structure. Three Gaussians of equal linewidth are placed on each of the components in the stick spectra.
because of the ubiquitous nature of the $N_2^+$ molecule in plasma environments, its electronic spectroscopy has been quite extensively studied. Additionally, the hyperfine (hf) structure of a number of vibrational bands in the $B^2\Sigma_u^+ - X^2\Sigma_g^+$ system has been studied experimentally. Until quite recently, the hf structure of the $(v', v'') = (0,0)$ band that this work is concerned with remained unmeasured with sub-Doppler resolution. However, it now appears that high-resolution measurements have been made, and an analysis of this band is underway at the time of this writing.\footnote{26} Section II.G.1 discusses the general spectroscopic structure of the $B^2\Sigma_u^+ - X^2\Sigma_g^+$ system, while Sec. II.G.2 covers the details of the hyperfine structure.

**1. General spectroscopic structure**

The general spectroscopic structure of the ${}^{14}N_2^+ B^2\Sigma_u^+-X^2\Sigma_g^+$ first negative system is very well known.\footnote{27} The higher-lying rotational levels ($N'' > 4$) of the ground electronic state are best described by a Hund's case $b^\beta_j$ coupling scheme,\footnote{28} in which the total orbital angular momentum $\mathbf{N}$ of the electrons and nuclei is added to the unpaired electronic spin angular momentum $\mathbf{S}$ to form $\mathbf{J}$, which is then added to the coupled nuclear spins $\mathbf{I}$ to form $\mathbf{F}$, the total angular momentum of the molecule. The presence of a single unpaired electron leads to an electronic spin-rotation splitting of each rotational line $N$ into two spin doublets with resulting $J$ values $J_1 = N + \frac{1}{2}$ and $J_2 = N - \frac{1}{2}$. Each of these spin-rotation levels is further split by nuclear spin interactions into either (effectively) five or three hyperfine levels, depending on the symmetry of the rotational level. Each $^{14}N$ nucleus is a boson with spin 1; these spins
couple together to give a total nuclear spin of \( I = 0, 1, \) or \( 2 \). The requirement that the total wavefunction of the molecule be symmetric under interchange of the nuclei leads to even \( N'' \) rotational levels associated with \( I = 0 \) or \( 2 \) for a total of six hyperfine components, two of which are nearly degenerate. The odd \( N'' \) rotational levels are associated with \( I = 1 \) and have three non-degenerate hyperfine components. The familiar 2:1 even/odd \( N'' \) intensity alternation of the rotational spectrum of \( \text{N}_2^+ \) is a consequence of these spin statistics. The consequence for the dynamics is that there are two non-interacting rotational manifolds, the ortho \( (N'' \) even) or para \( (N'' \) even) states, which leads to an effective doubling of the rotational constant for the spacing of adjacent rotational levels within a given manifold.

Figure 2.14 shows this general spectroscopic structure for the \( R_1^{(15)} \) LIF transition, with the dominant radiative transitions obeying the propensity rule \( \Delta F = \Delta J = \Delta N = \pm 1 \). Since the spin-rotation splitting of the spin doublet varies as \( \gamma N \), with an effective spin-rotation constant \( \gamma_{v=0} = 272.8 \text{ MHz} \),\(^{29}\) the \( J_1 \) and \( J_2 \) branches can be easily resolved by the resolution of this experiment. Figure 2.15 shows LIF survey spectra of five rotational lines in the para manifold. Note that the wingss of the lines begin to overlap around \( N''=7 \). Table 2.1 gives the relevant rest transition frequencies for the lines studied in this experiment, as calculated from a standard Dunham expansion\(^{30}\) with known molecular constants.

### 2. Hyperfine spectroscopy

There is unresolved Doppler-broadened hyperfine structure underlying each of the spin-rotation branches, as shown in Fig. 2.13. For optical transitions, the hyperfine
\[ \text{LIF spectroscopy: pump (0, 0) observe (0, 1)} \]

All lines shown obey:
\[ \Delta F = \Delta J = \Delta N = -1 : P \]
\[ \Delta F = \Delta J = \Delta N = +1 : R \]

**Fig 2.14:** Pump-fluoresce diagram for \( R_{1}(N''=15) \), showing typical spectroscopic structure for para manifold.
Fig. 2.15: LIF survey spectra of five rotational lines in the para manifold.
<table>
<thead>
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<th>Transition</th>
<th>( J'' )</th>
<th>( \bar{v}_0 ) (cm(^{-1}))</th>
<th>( \lambda_0 ) (nm)</th>
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**Table 2.1:** Relevant rest transition frequencies for the R-branch of the (0,0) band of the \( \text{N}_2^+ \, B \ ^2\Sigma_u^+ - X \ ^2\Sigma_g^+ \) system, as calculated from Eq. (2.x).
interaction is primarily due to the magnetic interaction of electronic and nuclear spins. The energy spacing of the hyperfine components has been well-studied for the $(\nu',\nu'') = (0,1)^{31}$ and $(1,2)^{32}$ bands of $^{14}\text{N}_2^+$ by the technique of fast ion-beam laser spectroscopy, which permits kinematic compression of the hyperfine Doppler widths to less than 100 MHz. Somewhat surprisingly, it appears that precise spectroscopic magnetic hyperfine parameters for $\nu'' = 0$ have not previously been measured or calculated. In particular, the Fermi contact interaction coupling constant $b_F$ and the dipole interaction coupling constant $t$ are necessary to calculated the needed matrix elements. A simple linear extrapolation of the known $b_F''$ and $t''$ coupling constants for $\nu'' = 2$ and 1 gives an estimate of $b_F'' \approx 90$ MHz and $t'' \approx 20$ MHz. It might be anticipated that these magnetic hyperfine parameters would depend quite sensitively on the structure and extent of the $\nu'' = 0$ electronic wavefunction in the vicinity of the $^{14}\text{N}$ nuclei and that using the known $(0,1)$ spectroscopy could lead to significant error. However, most of the hf splitting observed in optical transitions in the $(0,0)$ and $(1,0)$ bands is actually due to splitting in the upper $(B)$ state, common to both $\nu'' = 0$ and $\nu'' = 1$. Thus, throughout most of this work, we approximate the $\nu'' = 0$ hf spectroscopy with known $\nu'' = 1$ spectroscopy. Specifically, we use the tabulated hf spacings for $\nu'' = 1$. For the relative hyperfine intensities within a spin-rotation line, explicit intensity formulas can be worked out, starting from the assumption that the individual hf intensities vary as the product of two dipole reduced matrix elements, as per Eq. (2.14). However the algebraic formulas are too lengthy to include here.

$$I(F_i) \propto \left| \left< F_f \right| r^{(1)} \left| F_e \right> \left< F_e \right| r^{(1)} \left| F_i \right> \right|^2$$  \hspace{1cm} (2.14)
References for Chapter II


CHAPTER III

ROTATIONALLY-RESOLVED TRANSPORT PROPERTIES OF $N_2^+$ DRIFTED IN He

A. Introduction

This chapter concerns the measurement of transport properties by single-frequency LIF. Since transport property background material has already been presented in Chapter I, no further discussion is given. A more in-depth experimental background is presented here than usual because this experimental apparatus is undergoing revision once again, and the present investigator is attempting to insure some of this information and "lore" is preserved. A descriptive theory of single-frequency LIF transport property measurements is given in Sec. III.B. Details of measurement and analysis techniques are given in Sec. III.C. Results of the experiments conducted are presented in Sec. III.D. Section III.E outlines some systematic problems and other "weird stuff" present in the measurements. A discussion of the results, along with a comparison to the previous LIF studies on $\text{CO}^+\text{-He}$ is given in Sec. III.F. Section III.G wraps up with a conclusion.

B. Descriptive theory

A brief discussion is given of the relations relevant for extracting both velocity distribution functions and transport property data from LIF Doppler profiles. The outline of the theory for a single LIF transition is presented here; the additional complications introduced by the unresolved Doppler-broadened hyperfine structure present in this system are discussed in Sec. III.C below.
The fundamental entity in the study of ion transport properties is the ion velocity distribution function $F(v)$. By definition, $F(v) \, dv_x \, dv_y \, dv_z$ is the probability of measuring an ion velocity vector $v$ between $v_i$ and $v_i + dv_i$ for each of the dimensions in the problem. Formally, for atomic ions undergoing elastic collisions, $F(v)$ represents the solution to the Boltzmann equation. For molecular ions undergoing both elastic and inelastic collisions, the appropriate starting point is either the Wang Chang-Uhlenbeck-de Boer\textsuperscript{1} or Waldmann-Snider\textsuperscript{2} equations. There is an extensive body of theoretical literature concerning the solution to these equations that would not be possible to summarize here. Several review articles by Kumar as well as the texts by Mason and McDaniel\textsuperscript{3,4} cover this material; a brief historical sketch is given by Bastian\textsuperscript{5}.

The velocity component distribution functions (VCDF) $f(v_k, \hat{k}_{laser})$ measured in this experiment are related to the complete ion velocity distribution function $F(v)$ through the relation:

$$f(v_k, \hat{k}_{laser}) = \int d^3v \, F(v) \, \delta(v_k - v \cdot \hat{k}_{laser})$$ (3.1)

where the delta function picks out the projection $v_k$ of ion velocities along the laser probe direction $\hat{k}_{laser}$ that are in resonance with the LIF transition. In words, $f(v_k, \hat{k}_{laser}) \, dv_k$ is the probability of measuring an ion velocity component along $\hat{k}_{laser}$ between $v_k$ and $v_k + dv_k$. As pointed out by Bastian,\textsuperscript{5} there is an alternative
definition of velocity component distribution functions in the theoretical literature; we
will be concerned only with the definition given here.

If the ion velocity distribution \( F(v) \) is separable, i.e., if it can be written as

\[
F(v) = F_x(v_x) F_y(v_y) F_z(v_z),
\]

(3.2)

the product of three component functions, and the distribution is probed along one of
these coordinate directions—say the Z-direction—then Eq. (3.1) becomes

\[
f(v_k, \hat{k}_{\text{laser}}) = \left\{ \int_{-\infty}^{\infty} dv_x' F_x(v_x') \int_{-\infty}^{\infty} dv_y' F_y(v_y') \right\} F_z(v_z) = CF_z(v_z) \quad (3.3)
\]

and the measured VCDF is identical (within an ignorable rescaling factor) to one of
the component functions. In words, Eq. (3.2) just says velocity components along
orthogonal directions are completely uncoupled or uncorrelated. If \( F(v) \) is separable,
then by measuring \( f(v_k, \hat{k}_{\text{laser}}) \) at three orthogonal directions, the components of the
velocity distribution are mapped out, and \( F(v) \) can be unambiguously reconstructed.

If \( F(v) \) is not separable, in general one must use the technique of Fourier transform
Doppler spectroscopy\(^6,7\) to reconstruct the complete velocity distribution function.

We will assume for the analysis of this experiment that separability holds, although
this does not necessarily have to be the case. Velocity component correlation has been
demonstrated theoretically in Monte Carlo simulations on the Na\(^+-\)Ne system,\(^8\) and
eperimentally in previous work on the Ba\(^+-\)Ar system performed on this apparatus.\(^9\)

The experimental quantities measured in this work are obtained from moment
and line shape analysis of the LIF Doppler profiles. LIF frequencies are related to
velocity components through the first-order Doppler shift expression,
where $v_0$ is the rest absorption frequency of the LIF transition, and $v_k = \mathbf{v} \cdot \mathbf{k}_{\text{laser}}$ is the velocity component projection in the direction probed. Essentially, Eq. (3.4) just maps velocity components linearly into LIF frequencies, so we are free to rewrite any velocity component expression in terms of frequencies or vice versa. We will assume throughout that the velocity component distribution functions are normalized so that

$$\int_{-\infty}^{\infty} dv_k \ f(v_k; \mathbf{k}_{\text{laser}}) = 1$$  \hspace{1cm} (3.5)$$

Also, in the following definitions, the $\langle \rangle$'s always denote an average of the quantity in the brackets over the appropriate velocity component distribution function.

The drift velocity $v_d$ and ion mobility $K$ are related through the phenomenological equation

$$v_d = KE$$  \hspace{1cm} (3.6)$$

The measurable quantity is the drift velocity, which is related to the first moment of the velocity component distribution along the external field direction. If the field is along $Z$, then the first moment of this distribution is given by

$$\langle v_z \rangle = \int_{-\infty}^{\infty} dv_z \ v_z \ f(v_z; \mathbf{k}_{\text{laser}} \parallel Z)$$  \hspace{1cm} (3.7)$$

which would be identical to the drift velocity $v_d$ in a stationary system. For a flow-drift experiment, the zero-field flow velocity of the buffer gas must be subtracted off from the total velocity, and drift velocities are found then by:
\[ v_d = \langle v_z \rangle_{E/N} - \langle v_z \rangle_{E/N=0} \]  

(3.8)

Literature values are almost invariably given in terms of standard or reduced mobilities, \( K_0 \), effectively normalized to standard temperature and pressure:

\[ K_0 = \left( \frac{P}{760 \text{ Torr}} \right) \left( \frac{273.16 \text{ Kelvin}}{T} \right) K \]  

(3.9)

where \((P, T)\) are the conditions under which \( K \) was actually measured. The reduced mobility is related to \( v_d \) by:

\[ v_d = K_0 N_0 \left( \frac{E}{N} \right) \]  

(3.10)

where \( N_0 = 2.69 \times 10^{19} \text{ cm}^{-3} \) is the gas number density at standard temperature and pressure. Explicitly, the relationship between reduced mobility and measured drift velocity at a specific \( E/N \) in conventional units is:

\[ K_0 = (0.37221) \frac{v_d}{E/N} \]  

(3.11)

where \( K_0 \) is in \( \text{cm}^2 \text{ V}^{-1} \text{ s}^{-1} \), \( v_d \) is in \( \text{m s}^{-1} \), and \( E/N \) is in Td.

The second and third central moments of the VCDF's determine the width and asymmetry, respectively, about the line center. The second central moment is

\[ \left\langle \left( v_k - \langle v_k \rangle \right)^2 \right\rangle = \int_{-\infty}^{+\infty} dv_k \left( v_k - \langle v_k \rangle \right)^2 f(v_k; \hat{k}_{\text{laser}}) \]  

(3.12)

The second central moment is related to a translational temperature in the direction probed by

\[ T_k = \frac{m}{k_B} \left\langle \left( v_k - \langle v_k \rangle \right)^2 \right\rangle \]  

(3.13)
Only $T_\perp$ and $T_\parallel$, the temperatures perpendicular and parallel to the field, are measured in this work. Translational temperatures are indicators of how random energy acquired from the external field is partitioned by the interaction potential into directions either parallel or transverse to the field. If a single LIF transition is purely Doppler broadened, then the translational temperature in the direction probed is related to the linewidth by\(^\text{10}\)

$$T_k = \frac{c^2}{8\ln 2} \frac{M}{R} \left( \frac{\delta\nu_{\text{FWHM}}}{\nu_0} \right)^2$$  \hspace{1cm} (3.14)

where $M$ is the molecular weight of the species and $\delta\nu_{\text{FWHM}}$ is the full width at half-maximum of the Doppler profile in frequency units. Alternatively, if the linewidth is expressed in terms of the root-mean-square second central moment $\delta\nu_\sigma$ discussed below, where $\delta\nu_{\text{FWHM}} = \sqrt{8\ln 2} \delta\nu_\sigma$, then Eq. (3.14) can be rewritten as:

$$T_k = \frac{c^2}{R} M \left( \frac{\delta\nu_\sigma}{\nu_0} \right)^2 = \left( 1.08096 \times 10^{13} \right) M \left( \frac{\delta\nu_\sigma}{\nu_0} \right)^2$$  \hspace{1cm} (3.15)

with $T_k$ in Kelvin and $M$ in g mole\(^{-1}\). The third central moment is

$$\left\langle \left( v_k - \langle v_k \rangle \right)^3 \right\rangle = \int_{-\infty}^{+\infty} dv_k \left( v_k - \langle v_k \rangle \right)^3 f\left(v_k; k_{\text{laser}}\right)$$  \hspace{1cm} (3.16)

It is conventional in the literature to report a dimensionless skewness parameter $\delta$, usually defined as\(^\text{11}\)

$$\delta = \frac{\left\langle \left( v_k - \langle v_k \rangle \right)^3 \right\rangle^{1/3}}{\left\langle \left( v_k - \langle v_k \rangle \right)^2 \right\rangle^{1/2}}$$  \hspace{1cm} (3.17)
Skewness is a measure of the asymmetry of a velocity distribution about its mean. A positive skewness $\delta$ indicates the presence of a “high-velocity tail”. A more specific formula relating skewness to a measurable quantity cannot be given without choosing an appropriate line shape model, as discussed in detail in Sec. III.C. Note in particular that the canonical Gaussian line shape has no cumulatives higher than the second. Although higher moments, such as the fourth central moment or “excess” can be considered, this was not done in this work; indeed, the experimental third central moment information presented here is only semi-quantitative at best.

**C. Measurement & analysis techniques**

Measurement and analysis details are given in this section on both the “first moment” experiments performed, in which the coaxial laser probe data are used to extract drift velocities and corresponding mobilities, and the “central moment” experiments, in which both perpendicular and coaxial laser probe data are taken to obtain translational temperatures and skewness parameters.

**1. Measurement details**

In general, line profiles at a specific field strength ($E/N$) and probe direction (perpendicular or parallel) are obtained by scanning the ring dye laser over the LIF transition of interest for one or more coadds, as discussed in Sec. II.E. The raw data then consists of acquired counts or signal vs. channel number; a frequency scale is needed to convert channel numbers into physical units. Here, frequency calibration is provided by Fabry-Perot spectrum analysis, which gives an average frequency interval per channel number or, equivalently, a scan width $W_{\text{scan}}$ for each file acquired. Typical Fabry-Perot data acquired concurrently with the LIF data is shown in Fig. 3.1.
Fig. 3.1: Representative first moment data exhibiting the characteristic shift in frequency of the field-on line center. The shift of 1.75 GHz for a field of 12.0 Td shown in the figure corresponds to a drift velocity of about 682 m s$^{-1}$, and a reduced mobility of about 21.2 cm$^2$ V$^{-1}$ s$^{-1}$. 
Scan widths were found by determining the first and last clean transmission fringe or peak in the spectra; systematic care was taken to avoid fringes at the very beginning of scans, which tend to be nonlinear. Since both cavities used were of reasonably high (> 25) finesse, the centers of the transmission fringes were located by finding the channel number corresponding to the highest point. Although technically, the fringe centers could be found more precisely by numerically integrating over the accumulated counts for each peak, this analysis would be too involved for the number of data files taken and was felt to be unnecessary given the other uncertainties in the experiment. Indeed, a straightforward uncertainty analysis, as discussed below in Sec. III.D, will reveal that scan width uncertainty is a minor contributor to the overall uncertainty of the transport property data.

Once the channel number locations of the first and last transmission fringes has been found, the number of free spectral ranges (FSR’s) bracketed by these transmission fringes is counted. Scan widths are calculated by multiplying the number of FSR’s by the FSR frequency interval, dividing by the number of channel numbers between the first and last fringe, and multiplying by the total number of channels in the scan. Explicitly, the formula used is:

\[
W_{\text{scan}}(\text{GHz}) = \frac{\# \text{ of FSR's bracketed}}{(\text{HI} - \text{LO}) \text{ ch} \# \text{ of last & first fringe}} \times \frac{N \text{ GHz}}{1 \text{ FSR}} \times \frac{\# \text{ of channels}}{1 \text{ scan}} \tag{3.18}
\]

Using Eq. (3.18), the Fabry-Perot spectrum from the 0.375 GHz FSR cavity shown in Fig. 3.1 yields a scan width of 8.855 GHz for a 512-channel scan. Note that an average frequency interval per channel number can be found just by dividing the scan widths by the number of channels, which is effectively what is done to compute
frequency shifts and linewidths. To avoid roundoff error in subsequent calculations, scan widths were always recorded to four significant digits, even though these measurements have uncertainty in the fourth, and in the case of the 5 cm Invar cavity, even the third digit. For the majority of the transport property data presented here, a dual Fabry-Perot setup was used, in which spectra from both the 5 cm Invar and 20 cm ULE cavities discussed in Sec. II.C were acquired in tandem. This was done primarily as a consistency check on the previous CO$^+$-He LIF transport property work from this apparatus,$^5,12$ which used only the 5 cm Invar cavity. Transport properties were calculated from both scan widths and were found always to agree within the error bars of the experiment.

Drift velocities for a specific field strength are found by the difference between line centers of a pair of field-off and field-on coaxial line profiles; representative data is shown in Fig. 3.1. A switchbox, as shown in the schematic of Fig. 2.5, was used to switch rapidly the drift voltage supply, preset to the appropriate voltage for the target $E/N$, between sequential field-off and field-on measurements. The OFF setting effectively shorts the supply by tying the first and last rings of the drift region together. The field-on measurement scans began within at most 30 seconds after the field-off scan coadds; the automated filename templating capabilities of Eta-Spex helped greatly in speeding the data acquisition. The emphasis in general was on acquiring a field-off/field-on pair that was as well-correlated in time as possible.

This technique differs slightly from the one previously employed on the first moment experiments performed by Bastian et al. on CO$^+$-He$^{12}$ and Ba$^+$-Ar.$^9$ The
previous method involved taking three data files for each drift velocity determination, two field-off measurements which bracket the field-on measurement. The field-off line center was determined from an average of these two measurements. Additionally, the drift voltages were set by manually changing the front-panel settings of the drift voltage supply, a time-consuming affair. The reasoning behind using bracketing field-off measurements was to compensate for perceived systematic center-frequency drift of the ring dye laser. However, the construction of a considerably more stable Fabry-Perot cavity (Sec. II.C) allows for a better assessment of long-term laser drift. Diagnostic data suggests that short-term (< 10 minutes) ring dye laser drift is negligible, and that drift of the Roots blower pumping speed is a more significant issue. Ring dye laser drift alone can be assessed by taking repeated perpendicular probe scans over a transition. Systematics of this nature are discussed more in Sec. III.E.

To obtain drift velocities, some method must be found of making a correct determination of the first moments of the field-off and field-on line profiles. A discussion of the line shape analysis issues involved in this experiment follows in Sec. III.C.3. If the first moments (in channel numbers) of the field-off/field-on pair determined from this analysis are denoted as \( \mu \), the frequency shift can be found as:

\[
\Delta \nu = \left( \mu_{E/N} - \mu_{E/N=0} \right) \times \frac{\overline{W}_{\text{scan}}}{\text{# of channels}} \times \frac{1 \text{ scan}}{\text{# of channels}} \tag{3.19}
\]

where \( \overline{W}_{\text{scan}} \), the average scan width of the field-off/field-on pair, is used to convert this channel difference into a frequency. Equation (3.8) can be rewritten in terms of frequencies as:
\[ \Delta u = \langle u \rangle_{E/N} - \langle u \rangle_{E/N = 0} \]  

(3.20)

From Eq. (3.4), the drift velocity is related to the Doppler shift in the first moment of the transition frequencies as

\[ v_d = \lambda_0 \Delta u \]  

(3.21)

where \( v_d \) will be in m s\(^{-1} \) if \( \lambda_0 \) is in nm and \( \Delta u \) is in GHz. Each measured \( v_d \) at a specific field strength yields a corresponding \( K_0 \) as given by Eq. (3.11) above. The actual field strength for each measurement is calculated from Eq. (2.11); note in particular that to extract the small differences in rotor-state mobility shown in Sec. III.D, an accurate field determination is needed for each pair of measurements.

Perpendicular and parallel translational temperatures for a specific field strength are obtained from the second central moments of the LIF spectra. Six or seven line profiles taken at a fixed field strength comprise one observation; these profiles are simply taken sequentially. Parallel and perpendicular measurements were interwoven in data-taking sessions to establish correlation between differences in these temperatures. The representative data in Fig. 3.2 compares the full-width half-maximum of plasma (field-off) and 16 Td data taken with parallel laser probe. If a correct determination of the root-mean-square (rms) second central moments \( \delta u_e \) is obtained through line shape analysis, then the translational temperatures are given by Eq. (3.15) above. For \( N_2^+ \), with \( M = 28.0056 \) g mole\(^{-1} \), Eq. (3.15) gives

\[ T_k = \left( 3.36832 \times 10^{11} \right) \left( \frac{\delta u_e}{u_0} \right)^2 \]  

(3.22)
Fig. 3.2: Representative second central moment data, showing the increase in Doppler broadening with increasing field strength. The Gaussian fit is shown, with temperatures corrected for underlying hyperfine structure.
with $T_k$ in $K$, and where $\delta v_\sigma$ is expressed in GHz, and $\bar{v}_0$ in cm$^{-1}$. The rest transition frequencies for the various rotational lines probed are listed in Table 2.1.

2. **Velocity component distribution functional forms**

The above analysis has deferred discussion of several line shape complications that turn out to be important in practice. Because the natural linewidth of the $B^2 \Sigma_u^+ - X^2 \Sigma_g^+$ transitions for $N_2$ $\left( v''=0 \right) \left( \delta v_{FWHM} < 3 \text{ MHz} \right)$ is much smaller than the Doppler linewidths ($\delta v_{FWHM} = 1.8 \text{ GHz for } T_k = 300 \text{ K}$), the effects of this homogeneous broadening upon the line shape can be safely neglected. Thus, no convolution integral over a Lorentzian is present in Eq. (3.1). However, as discussed in Sec. II.G, there is still Doppler-broadened and hence unresolved hyperfine (hf) structure underlying each spin-rotation line, with presently uncertain hf spectroscopy. Additionally, to extract proper central moment information, an appropriate line shape model must be chosen, yet there is currently little theoretical treatment of velocity distribution functional forms for molecular ions with accessible internal degrees of freedom.$^{13}$ Accordingly, several different approaches of increasing sophistication were taken towards the line shape analysis.

A natural starting point for a low-field molecular ion velocity distribution would be the standard "three-temperature" model,$^4$

$$ F(\mathbf{v}) = f_0(\mathbf{v}; v_d, T_\parallel, T_\perp) $$

$$ = \left( \frac{m}{2\pi k_B T_\perp} \right)^{3/2} \left( \frac{m}{2\pi k_B T_\parallel} \right)^{1/2} \exp \left[ -\frac{m}{2k_B T_\perp} \left( v_x^2 + v_y^2 \right) - \frac{m}{2k_B T_\parallel} (v_d - v_z)^2 \right] $$  \hspace{1cm} (3.23)

with $\int_{-\infty}^{+\infty} d^3 v f_0(\mathbf{v}; v_d, T_\parallel, T_\perp) = 1$ for any choice of parameters $(v_d, T_\parallel, T_\perp)$. 

This is simply a Gaussian displaced in the field direction by the ion drift velocity $v_d$ and characterized by two widths, the parallel and perpendicular translational temperatures $T_{||}$ and $T_{\perp}$. In three-temperature theory, Eq. (3.23) is taken as the zeroth-order or starting-point solution to the Boltzmann equation.

This velocity distribution has several advantages. For one, since the range of field values employed in this experiment is quite low, the true velocity distribution function would not be expected on physical grounds to deviate much from this form. Equation (3.23) is separable into components parallel and transverse to the field, so measurements in just two directions are sufficient to recover the complete velocity distribution function. Additionally, this form has the advantage of being very tractable both analytically and numerically; this is an easy functional form to use as a model and to fit to. Its primary disadvantage is that Eq. (3.23) is a completely symmetric line shape incapable of representing any skewness in the experimental data.

An appropriate parametrization of the symmetric Gaussians in Eq. (3.23) is

$$y(x; a_0, a_1, a_2, b) = a_0 \exp \left[ -\frac{1}{2} \left( \frac{x - a_1}{a_2} \right)^2 \right] + b \tag{3.24}$$

with a total of four adjustable parameters (the $a_n$'s discussed in this chapter should not be confused with the alignment parameters discussed in Chapter IV). The constant background $b$ and rescaling amplitude $a_0$ are needed to fit experimental data. The parameter $a_1$ is the first moment $\mu$, and $a_2$ is root mean square second central moment $\sigma$. 
If the perpendicular velocity component is still represented by a symmetric Gaussian, but an asymmetric line shape is introduced in the field direction, we can represent skewness in the experimental data. There are several choices of functional forms in the literature. Perhaps the simplest form that comes out of a physical model is the velocity distribution of Whealton and Woo:\textsuperscript{14}

\[
f_{ww}(v; \langle v_z \rangle, T_\perp, \beta_\parallel, \alpha \tau) = \left( \frac{m}{2\pi k_B T_\perp} \right) \exp \left[ -\frac{m}{2 k_B T_\perp} (v_x^2 + v_y^2) \right] \times \\
\left( \frac{1}{2\alpha \tau} \right) \exp \left[ -\left( \frac{v_z - \langle v_z \rangle}{\alpha \tau} \right) + \frac{1}{4\beta_\parallel (\alpha \tau)^2} - 1 \right] \times \\
\text{erfc} \left[ \sqrt{4\beta_\parallel (\alpha \tau)^2} \left( \frac{1}{4\beta_\parallel (\alpha \tau)^2} - \left( \frac{v_z - \langle v_z \rangle}{2\alpha \tau} \right) - \frac{1}{2} \right) \right]
\]

(3.25)

with \( \beta_\parallel = \frac{1}{2 \left( \langle (v_z - \langle v_z \rangle)^2 \rangle - (\alpha \tau)^2 \right)} \), \( \int_{-\infty}^{+\infty} d^3v \ f_{ww}(v; \langle v_z \rangle, T_\perp, \beta_\parallel, \alpha \tau) = 1 \)

for any choice of \( \langle (v_z, T_\perp, \beta_\parallel, \alpha \tau) \)

where \( a = qE/m \) is the ion acceleration due to the field and \( \tau \) the mean free time between collisions. Note that Eq. (3.25) is separable and that the transverse velocity component distribution is identical to Eq. (3.23). The distribution for the field direction is a kinetic-model solution to the Boltzmann equation, with the approximation that the mean free time \( \tau \) between ion-neutral collisions is independent of ion velocity. This method requires a reasonable guess for a zeroth-order solution \( f_{(0)} \); the kinetic-model solution is then obtained from the zeroth-order solution through an integral relation. Whealton and Woo use the above three-temperature form; Eq. (3.23), for \( f_{(0)} \) to produce Eq. (3.25).
An appropriate parametrization of the Whealton-Woo distribution in the field direction is obtained by setting the second central moment to $a_2$, and the product $a\tau$, the average "terminal velocity" acquired by an ion before a collision, to $a_3$,

$$y(x; a_0, a_1, a_2, a_3, b) = a_0 \exp\left[ -\frac{x - a_1}{a_3} + \frac{1}{4\beta(a_2, a_3) a_3^2} - 1 \right] \times$$

$$\text{erfc}\left[ 2a_3\sqrt{\beta(a_2, a_3)}\left( \frac{1}{4\beta(a_2, a_3) a_3^2} - \frac{x - a_1}{2a_3} - \frac{1}{2} \right) \right] + b \quad (3.26)$$

with $\beta(a_2, a_3) = \frac{1}{2(a_2^2 - a_3^2)}$

Figure 3.3 show plots of Eq. (3.26) for fixed $(a_0, a_1, a_2)$ and several different values of $a_3$. Note in particular for $a_3 \to 0$, we recover a Gaussian distribution.

A functional form related to the Whealton-Woo functional form is given by Makabe, Misawa and Mori,\textsuperscript{11} and was used in previous Ba\textsuperscript{+}-Ar work conducted on this apparatus\textsuperscript{9,15} to fit experimental data. The form is

$$f_{\text{MMM}}(v; \langle v_z \rangle, T_\perp, \beta_\parallel, a\tau) = \left( \frac{m}{2\pi k_B T_\perp} \right)^{\frac{3}{2}} \exp\left[ -\frac{m}{2k_B T_\perp}\left( v_x^2 + v_y^2 \right) \right] \times$$

$$\left( \frac{1}{2a\tau} \right)^{\frac{3}{2}} \exp\left[ -\left( \frac{v_z - \langle v_z \rangle}{a\tau} \right)^2 + \frac{1}{4\beta_\parallel(a\tau)^2} - 2 \right] \times$$

$$\int_{-\infty}^{v_k} d\xi \text{erfc}\left[ \sqrt{4\beta_\parallel(a\tau)^2}\left( \frac{1}{4\beta_\parallel(a\tau)^2} - \frac{\xi - \langle v_z \rangle}{2a\tau} \right) - 1 \right] \quad (3.27)$$

with $\beta_\parallel$ defined as in Eq. (3.25). Note the formal similarity between this expression and Eq. (3.25). Equation (3.27) is obtained by using the Whealton-Woo expression as the zeroth-order $f_{(0)}$ in the same integral relation for the kinetic-model solution. The additional factors of two in Eq.(3.27) arise from this integration. Although used
Fig. 3.3: Wheaton-Woo velocity distribution function in the form of Eq. (3.26), plotted at four different values of $a_3$; the other parameters are fixed at $a_0 = 1$, $a_1 = 256$, and $a_2 = 64$. A symmetric Gaussian of the form of Eq. (3.24) with these same parameter values is shown for comparison.
successfully for the Ba⁺-Ar work, this functional form was not employed here for several reasons. For one, Eq. (3.27) requires performing an integral for every function evaluation, slowing down the fitting computations considerably. Additionally, for the low fields and relatively small degrees of skewness observed in this experiment, the Whealton-Woo form is a more appropriate fitting function.

Another convenient functional form that incorporates a moderate degree of skewness is the Haarhoff-Van der Linde (HVL) function. The HVL function in parameterized form is

\[
f_{HVL}(x;a_0,a_1,a_2,a_3) = a_0 a_2 \sqrt{2\pi a_1 a_3} \exp\left[-\frac{1}{2}\left(\frac{x - a_1}{a_2}\right)^2\right] \left[\exp\left[\frac{a_1 a_2}{2 a_2} - 1\right] - 1\right]^{-1} + \frac{1}{2} \left[1 + \text{erf}\left(\frac{x - a_1}{\sqrt{2} a_2}\right)\right]
\]

(3.28)

Although the physical model associated with this function is not appropriate for this experiment, the \(a_3\) parameter of this form was found to be a convenient empirical method of characterizing the third central moments in the experimental line shapes.

Lastly, for completeness, we note that the helium buffer is invariably assumed to have a thermal, isotropic Maxwell-Boltzmann velocity distribution characterized by a single temperature \(T\)

\[
F_B(V;T) = \left(\frac{M}{2\pi k_B T}\right)^{3/2} \exp\left[-\frac{M}{2k_B T} V^2\right] \quad \text{with} \quad \int_{-\infty}^{+\infty} d^3V F_B(V;T) = 1 \quad (3.29)
\]

The Maxwell-Boltzmann distribution follows from the assumption of a trace number density of ions; the buffer always acts as a thermal bath that is completely unperturbed by the presence of ions.
3. Line shape analysis

If we assume the simplest functional form, i.e. the three-temperature model given in Eq. (3.23), the composite line shape for a given spin-rotation transition, for a fixed field strength and probe direction, can be modeled by associating a symmetric Gaussian with each underlying hyperfine component in the spin-rotation line, of form

\[ y_i(v; A_i, \mu_i, \sigma) = A_i \exp \left[ -\frac{1}{2} \left( \frac{v - \mu_i}{\sigma} \right)^2 \right] \]  

(3.30)

where the individual hf transitions are indexed by \( i \); \( A_i \) and \( \mu_i \) denote the intensity and relative placement of the hf transitions within the group, as illustrated by the stick spectrum in Fig. 3.4 (a). Note that all of the underlying Gaussians are characterized by the same width \( \sigma \) and hence the same translational temperature. It is assumed throughout that the spacings \( \mu_i \) are nearly equal and much less than \( \sigma \).

The most straightforward approach to fitting the experimental LIF line shapes is to just fit to a composite line shape that is the sum of the \( y_i \)'s of Eq. (3.30), i.e.,

\[ y_{total} = \sum_i y_i(v; A_i, \mu_i, \sigma) \]  

(3.31)

Unfortunately, to do this properly requires precise knowledge of the underlying hf spectroscopy for \( N_2^+ (v''=0) \), which is currently not exactly known (see Sec. II.G). However, we can make an assessment of how sensitive the moments of the overall spin-rotation line shapes are to these relative intensities and placements by calculating the first and second central moments of the composite line shape of Eq. (3.31) analytically. Performing a straightforward set of Gaussian moment integrals gives for the moments of the overall line shape for a three-hf-component (para) line:
Fig. 3.4: Simulated spectra of underlying hf structure. a) stick spectra for R₁(15) transition. b) synthetic spectra fit to a single Gaussian + constant background. Fit residuals are shown in the lower panel.
\[ \langle \mu \rangle = \frac{A_c \mu_c - A_a \mu_a}{A_{\text{total}}}, \quad \text{with} \quad A_{\text{total}} = A_a + A_b + A_c \]

\[ \left( \langle \mu \rangle - \langle \mu \rangle \right)^2 = \sigma^2 + \frac{A_a \mu_a^2 + A_c \mu_c^2}{A_{\text{total}}} + 2 \langle \mu \rangle \left\{ A_c \mu_c - A_a \mu_a \right\} \]

\[ \langle \mu \rangle = \frac{A_a \mu_a + A_c \mu_c}{A_{\text{total}}} - \left( \frac{A_a \mu_a + A_c \mu_c}{A_{\text{total}}} \right)^2 \]

(3.32)

where the hf components are indexed by letter from low to high frequency. The expressions for the five-component (ortho) lines are obvious extensions to Eq. (3.32). Note in particular the first moment of the overall spin-rotation line shape is independent of the width of the underlying components. Also, the overall second central moment is larger than the second central moment \( \sigma^2 \) of the underlying components by a simple algebraic combination of the hf spacings and intensities. If translational temperatures are derived from the second central moments of the overall line shape, these will be systematically too large, but these temperatures can be corrected if the hf spacing and intensities are known, via Eq. (3.32). Note both of these expressions have the correct limiting form for \( \mu_i = 0 \) or \( A_a = A_c, \mu_a = \mu_c \).

In the above model of Eq. (3.31), there are still a total of four "orthogonal" fit parameters: a constant background, an overall scaling of the three component Gaussians, an overall placement of the stick spectra within the line shape, and the shared width of the three Gaussians. Noting that a single Gaussian of the form of Eq. (3.24) has the same number of parameters, a very reasonable approach for determining drift velocities and translational temperatures is to fit the individual spin-rotation lines to single Gaussians and moment-match the single Gaussian fit parameters to the moments of the overall line shape to recover line centers and
widths. Note in particular that if the fit parameter $a_1$ is taken as the estimator of the first moment $\mu$, this first moment will be systematically offset, but the magnitude of the offset is independent of the underlying temperature of the components (i.e., independent of field strength). Thus, when differences in field-off/field-on pairs are calculated by Eq. (3.19), this constant offset will be subtracted off, yielding correct $\Delta \nu$'s and corresponding drift velocities through Eq. (3.21). Likewise, $a_2 \cdot W_{\text{scan}}$ can be taken as an estimator of $\delta \nu_0$; uncorrected temperatures can be calculated directly by Eq. (3.22), or these widths can first be corrected by Eq. (3.32) to yield corrected translational temperatures.

An assessment of how well this moment-matching approximation works in practice can be made by synthesizing some data with known moments and studying out how well a single Gaussian analysis can recover these moments. For example, the best estimate of the hf stick spectra for $R_1(15)$ is shown in Fig. 3.4 (a). A composite line shape was created by assigning three Gaussians of the form of Eq. (3.30) to each of these transitions. The composite line shape was rescaled and a background added such that the resulting signal-to-background would be representative of experimental values. Then, the line shape was run through a Poisson "noise-generator" that generates Poisson deviates according to $f_y(n)$, with $y$ being the total $y$-value at the particular point. This is necessary for the non-linear least squares fitting routines, and is a very pragmatic way of modeling the noise-in-signal of the experimental data. These simulated spectra were fit to a single Gaussian line shape of form Eq. (3.24); a typical composite simulated spectra and fit Gaussian is shown in Fig. 3.4 (b).
Twelve “observations” each were synthesized for a range of translational temperatures of the underlying Gaussians from 300 to 600 Kelvin, in 50 K steps, for “scan widths” of 7.850 GHz. The fit parameter $a_1$ was systematically offset high by 23 MHz, but this offset remains completely invariant as a function of temperature, within the standard error of the fit (2 MHz). The offset predicted from Eq. (3.32) is 22 MHz, independent of temperature. The uncorrected temperatures calculated from the fit parameter $a_2$ are systematically too high by 35 K, independent of underlying width $\sigma$; the prediction from Eq. (3.32) is 33 K. Corrected temperatures obtained from Eq. (3.32) are still high by 2 K from the true underlying temperatures; however, the standard error in the fit parameter alone yields error bars of $\pm$ 3 K for these temperatures. In summary, this single Gaussian moment approximation yields true first-moment differences to an excellent approximation, and true second-central moments within a systematic error that is smaller than the random error bars of the experiment. Loosely, this approximation works well because of the closeness of spacing and approximately equal amplitudes of the hf components within the group. The primary shortcoming of the above analysis is that it is incapable of yielding quantitative third moment information. Note however, that the fit residuals of the 600 K simulated spectra shown in Fig. 3.4 (b) scatter evenly about zero, which is taken as additional confirmation that the experimentally-observed skewnesses discussed below are not artifacts of the unresolved hf structure underlying each spin-rotational line.

D. Results

This section discusses transport property results obtained in several sets of LIF experiments. The results are presented by corresponding moment, even though some
of the data sets are overlapping. Section III.D.1 presents the “first moment” experiments that determine drift velocities and mobilities, Sec. III.D.2 presents “second central moment” experiments that determine parallel and perpendicular translational temperatures, and Sec. III.D.3 presents “third central moment” experiments that attempt to characterize the skewness believed present in the parallel velocity component distributions. Discussion of these results in the context of the literature and previous work on CO⁺-He is presented in Sec. III.F.

1. First moments: drift velocities & mobilities

Results are presented in this section for two sets of first-moment experiments conducted on \( N_2^+ (v'' = 0) \), using the methods previously discussed in Sec. III.C. The goal of the first set of experiments was to determine drift velocities and corresponding mobilities as a function of \( E/N \) for a single rotational line, \( R_1 (N'' = 15) \). The second set of experiments involved the measurement of mobilities at a single fixed field strength, 12.0 Td, as a function of rotor state to ascertain whether J-state dependent transport properties would occur in the \( N_2^+ \)-He system.

Results from the first-moment measurements on the transition \( R_1 (15) \) are presented in Figs. 3.5 and 3.6, and tabulated in Table 3.1. Each of the twelve data points shown in Fig. 3.6 is composed of a weighted average of at least two sets of observations taken on separate days. Each observation consists of six or seven field-off/field-on pairs taken in sequence. From previous experience, it was felt that a minimum of six pairs were necessary to obtain a statistically meaningful mobility
Fig. 3.5: a) Drift velocities obtained from $R_i(15)$ as a function of field strength from 1.5 to 16 Td. The measurement uncertainties are well-represented by the size of the symbols in the plot. b) Corresponding effective temperatures.
Fig. 3.6: Experimental LIF mobilities obtained from $R_1(15)$ as a function of field strength from 1.5 to 16 Td. The white diamonds are the arrival-time results from Ref. 27, discussed in more detail in Sec. III F.
### a) $R_1(15)$ LIF drift velocities & reduced mobilities.

<table>
<thead>
<tr>
<th>Field $E/N$ (Td)</th>
<th>Average Field $E/N$ (Td)</th>
<th>Total No. of observations</th>
<th>$v_d$ (m s$^{-1}$)</th>
<th>$K_0$ (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>1.50</td>
<td>14</td>
<td>90 ± 3</td>
<td>22.4 ± 0.7</td>
</tr>
<tr>
<td>2.0</td>
<td>2.00</td>
<td>13</td>
<td>117 ± 2</td>
<td>21.8 ± 0.3</td>
</tr>
<tr>
<td>3.0</td>
<td>3.00</td>
<td>14</td>
<td>175 ± 3</td>
<td>21.8 ± 0.3</td>
</tr>
<tr>
<td>4.0</td>
<td>4.00</td>
<td>13</td>
<td>235 ± 2</td>
<td>21.9 ± 0.2</td>
</tr>
<tr>
<td>5.0</td>
<td>4.99</td>
<td>13</td>
<td>295 ± 4</td>
<td>22.0 ± 0.3</td>
</tr>
<tr>
<td>6.0</td>
<td>5.99</td>
<td>11</td>
<td>347 ± 3</td>
<td>21.6 ± 0.2</td>
</tr>
<tr>
<td>7.0</td>
<td>6.99</td>
<td>13</td>
<td>407 ± 2</td>
<td>21.6 ± 0.1</td>
</tr>
<tr>
<td>8.5</td>
<td>8.49</td>
<td>13</td>
<td>487 ± 3</td>
<td>21.3 ± 0.2</td>
</tr>
<tr>
<td>10.0</td>
<td>9.97</td>
<td>13</td>
<td>570 ± 3</td>
<td>21.3 ± 0.1</td>
</tr>
<tr>
<td>12.0</td>
<td>11.96</td>
<td>14</td>
<td>683 ± 3</td>
<td>21.2 ± 0.1</td>
</tr>
<tr>
<td>14.0</td>
<td>14.00</td>
<td>14</td>
<td>811 ± 6</td>
<td>21.6 ± 0.2</td>
</tr>
<tr>
<td>16.0</td>
<td>15.99</td>
<td>7</td>
<td>913 ± 5</td>
<td>21.3 ± 0.2</td>
</tr>
</tbody>
</table>

### b) LIF drift velocities & reduced mobilities for 8 rotational lines, measured at 12.0 Td.

<table>
<thead>
<tr>
<th>Transition (probed)</th>
<th>$J''$</th>
<th>Total No. of observations</th>
<th>$v_d$ (m s$^{-1}$)</th>
<th>$K_0$ (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_1(13)$</td>
<td>13.5</td>
<td>12</td>
<td>685.9 ± 1.7</td>
<td>21.27 ± 0.08</td>
</tr>
<tr>
<td>$R_1(14)$</td>
<td>14.5</td>
<td>13</td>
<td>687.2 ± 1.3</td>
<td>21.36 ± 0.07</td>
</tr>
<tr>
<td>$R_1(15)$</td>
<td>15.5</td>
<td>14</td>
<td>682.5 ± 1.9</td>
<td>21.21 ± 0.08</td>
</tr>
<tr>
<td>$R_1(16)$</td>
<td>16.5</td>
<td>13</td>
<td>693.7 ± 1.9</td>
<td>21.53 ± 0.08</td>
</tr>
<tr>
<td>$R_1(18)$</td>
<td>18.5</td>
<td>13</td>
<td>694.6 ± 2.0</td>
<td>21.57 ± 0.08</td>
</tr>
<tr>
<td>$R_1(19)$</td>
<td>19.5</td>
<td>12</td>
<td>695.5 ± 1.9</td>
<td>21.59 ± 0.09</td>
</tr>
<tr>
<td>$R_1(20)$</td>
<td>20.5</td>
<td>14</td>
<td>702.8 ± 2.0</td>
<td>21.87 ± 0.08</td>
</tr>
<tr>
<td>$R_1(22)$</td>
<td>22.5</td>
<td>14</td>
<td>704.6 ± 1.6</td>
<td>21.91 ± 0.07</td>
</tr>
</tbody>
</table>

**Table 3.1:** Tabulated results of first moment experiments. a) $R_1(15)$ drift velocities and corresponding mobilities; b) $J$-state dependent drift velocities and corresponding mobilities.
measurement. The majority of the files, in particular all data points below 8 Td, consist of 1024 points.

The drift velocities plotted in Fig. 3.5 exhibit the usual quasi-straight-line behavior. Note that the mobilities shown in Fig. 3.6 show almost no variation with field strength. There is evidence of a slight mobility maximum at the lowest field strength studied (1.5 Td); the mobilities gradually decrease with increasing field strength. This behavior, discussed in more detail in Sec. III.F, is typical for systems in which the average thermal energy at room temperature alone causes sampling of the repulsive wall of the interaction potential.

The grid of field strengths $E/N$ was specifically chosen to investigate whether the anomalous behavior seen in the LIF-determined mobilities of the CO$^+$-He system would occur in the N$_2^+$-He system. A discussion of the cause of the systematics believed present in both this experiment and in the previous CO$^+$-He work is deferred until Secs. III.E and III.F, respectively. Additionally, several sets of data at the same field strength were taken in order to assess whether any one-time charging or arcing behavior in the drift tube was responsible for the unusual CO$^+$-He mobilities. Data taken days or even weeks apart showed remarkably little variation, strongly suggesting that this is not the case for either system. Only data analyzed using the scan widths derived from the 20 cm Fabry-Perot cavity are presented here. However, as previously mentioned, as a consistency check on the prior CO$^+$-He work, scan widths from the 5 cm Invar cavity used in that work were recorded concurrently. Comparison of data analyzed with scan widths derived from both cavities shows no
significant difference. Although the 20 cm cavity employed in this work is
demonstrably superior to the 5 cm cavity, it is not believed that erroneous results in
previous work were obtained through use of this cavity or misanalysis of scan widths.

In a second set of experiments, the possibility of J-dependent transport
properties was investigated at a single field strength. A total of eight different
rotational lines in both the ortho and para manifolds (including results from the
$R_1(15)$ measurements) were investigated, all at a fixed field strength of 12.0 Td. On
physical grounds, one would expect any state-dependent effects to be most
pronounced at high field strengths; additionally, high field strengths have larger
frequency shifts and thus smaller fractional errors and so are easier to measure
precisely. The choice of 12 Td was made as the highest field strength possible that
would permit sufficient signal-to-background for measurements on the greatest
number of lines. A summary of results is presented in Fig. 3.7 and tabulated in Table
3.1. Each data point is a weighted average of two observations consisting of six or
seven pairs taken on separate days.

These data show a small but quite definite trend of increasing mobility with
increasing rotational state. Additional corroborating evidence of this claim is provided
in Fig. 3.8. Both “high-J” and “low-J” observations were taken on the same day to
determine how well the effects would correlate. Figure 3.8 shows some of the data in
Fig. 3.7 broken out by data-taking session; note that the general trend of each line is
the same. Similar quantum-state transport effects have been previously reported, both
in the literature and in the previous experiments on $\text{CO}^+\text{-He}$ on this apparatus and are
discussed in more detail in Sec. III.F.
Fig. 3.7: Drift velocities (a) and corresponding mobilities (b) for eight rotational lines at 12.0 Td.
Fig. 3.8: J''-state dependent mobility data at 12.0 Td, broken down by day of observation. The general trend for higher rotational lines to have higher mobilities can be seen in "high-J''/"low-J'' data taken in the same experimental run.
All data presented here were analyzed from first-moment differences from fits of a single Gaussian plus constant background to the full spin-rotation line shape, as discussed in detail in Sec. III.C.3. The stated error bars are standard deviations of the weighted means of all measurements. The measurement uncertainties in drift velocities and mobilities were calculated for each set of observations using standard uncertainty propagation formulas.\(^{18,19}\) For each set of observations, the error bar was then taken to be either the statistical spread in the data set (i.e., the sample standard deviation) or the calculated uncertainty, whichever was larger. This error bar was then divided by the square root of the number of field-off/field-on pairs, and multiplied by the appropriate Student's t-distribution factor\(^{20,21}\) to account for the finite number of observations in each set. Each final data point is the average of all sets of observations, each weighted by the inverse of their variances. For the drift velocities, the statistical spread in the data was invariably larger than the calculated uncertainty; for the mobilities, the calculated uncertainty was almost always larger. The largest contributor to the error bars of the mobilities is the uncertainty in external field strength (\(E/N\)), which in turn is dominated by uncertainties in knowing the local temperature and pressure at the LIF region.

2. Second central moments: translational temperatures

Results are presented here for second central moment experiments to extract parallel and perpendicular translational temperatures. Rough temperature measurements extracted from the “calibration files” of the first (Fall '95) sub-Doppler alignment experiments suggested that there was a significant difference of over 100 K between \(T_{||}\) and \(T_{\perp}\) for \(J'' = 15.5\) at the highest field strength measured (16 Td). This
The anomalous axial ion flow velocity systematics discussed in Sec. III.E below call these results somewhat into question, and the $J'' = 15.5$ temperatures were remeasured in the Fall of '97.

Figure 3.10 presents the results of these measurements. Shown are both parallel and perpendicular temperatures corrected for the underlying hf structure, as discussed in Sec. III.C.3; Table 3.2 summarizes these measurements. The parallel temperatures were extracted from the same data set used to obtain the first moment $R_1(15)$ results presented above, while the perpendicular temperatures were extracted from a separate set of data. Because the first moment data was acquired in a different fashion than the perpendicular central moment data, coaxial and perpendicular measurements were made back-to-back under identical drift tube conditions to verify that the measured differences were not artifacts due to the changes in tube voltage settings that could possibly alter the ion production conditions over time. Effects such as these have been observed previously, as shown in Sec. III.E. Note that the same general trend first observed in Fall '95 is present in this data set as well. The parallel translational temperatures are significantly greater than the perpendicular translational temperatures, indicating a strong propensity for the interaction potential to scatter trajectories such that a large portion of the directed energy is preserved.

3. Third central moments: direct measure of skewness

The sub-Doppler calibration files acquired in the fall of '95 revealed more than just a significant difference between the parallel and perpendicular temperatures. This data was analyzed by fitting to a single symmetric Gaussian plus constant background, as discussed in Sec. III.C.3. Inspection of the fit residuals (= observed
Fig. 3.9: a) Second & b) third central moment data on $R_1(15)$, extracted from alignment calibration files taken Fall '95.
Fig. 3.10: Corrected perpendicular & parallel translational temperatures for the $R_1(15)$ transition.
### Second central moment results.

Both uncorrected temperatures derived from the full linewidth and temperatures corrected for the underlying hyperfine structure are presented.

<table>
<thead>
<tr>
<th>Field (Td)</th>
<th># of obs</th>
<th>Uncorrected $T_\parallel$ (K)</th>
<th>Corrected $T_\parallel$ (K)</th>
<th># of obs</th>
<th>Uncorrected $T_\perp$ (K)</th>
<th>Corrected $T_\perp$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>7</td>
<td>$329 \pm 3$</td>
<td>$296 \pm 3$</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>2.0</td>
<td>13</td>
<td>$337 \pm 3$</td>
<td>$304 \pm 3$</td>
<td>12</td>
<td>$332 \pm 2$</td>
<td>$299 \pm 2$</td>
</tr>
<tr>
<td>3.0</td>
<td>14</td>
<td>$341 \pm 3$</td>
<td>$308 \pm 3$</td>
<td>6</td>
<td>$337 \pm 2$</td>
<td>$304 \pm 2$</td>
</tr>
<tr>
<td>4.0</td>
<td>13</td>
<td>$353 \pm 5$</td>
<td>$319 \pm 5$</td>
<td>12</td>
<td>$337 \pm 3$</td>
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<td>6</td>
<td>$340 \pm 3$</td>
<td>$306 \pm 3$</td>
</tr>
<tr>
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<td>11</td>
<td>$380 \pm 5$</td>
<td>$347 \pm 4$</td>
<td>6</td>
<td>$350 \pm 2$</td>
<td>$316 \pm 2$</td>
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<td>$397 \pm 5$</td>
<td>6</td>
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<td>$428 \pm 8$</td>
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<td>$562 \pm 11$</td>
<td>6</td>
<td>$440 \pm 6$</td>
<td>$407 \pm 6$</td>
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</table>

*Table 3.2:* Second central moment results.
(data value minus fit value) for both field-off and field-on coaxial probe data reveals a
pattern suggesting that a small but measurable degree of skewness is present in the
parallel velocity component distributions. Representative data are shown in Fig. 3.11.
The left-hand panel is a 0 Td Doppler profile of $R_1(15)$; the right-hand panel is the
same profile at 16 Td. The symmetric Gaussian fits are shown, with fit residuals
displayed in the lower panels. The 0 Td residuals scatter evenly about zero, indicating
that a symmetric functional form can adequately describe the composite line shape.
However, the 16 Td residuals are systematically negative (positive) in the low (high)
velocity tail, indicating that a symmetric function can no longer adequately describe
this line shape.

This pattern of residuals indicates a small positive skewness or "high-velocity
tail" may be present in the parallel VCDF. Although it is well-known that atomic ion
systems can exhibit pronounced skewness in the field direction, to the best of this
investigator's knowledge, skewness in a molecular ion system (other than $N_2^+$ in
$N_2$) has not previously been reported. In this first work, the skewness was
characterized by fitting the entire line shape to the HVL functional form, Eq. (3.28)
above. The $a_3$ parameter was taken as an empirical measure of skewness. The results
are shown in Fig. 3.9 which confirm the qualitative observations.

For the Fall '97 transport property work, an attempt was made to incorporate
non-linear-fitting routines into Eta-Spex so that these line shapes could be fit to the
Wheaton-Woo functional form of Eq. (3.26). Unfortunately, this work was not
entirely completed, so no plots are presented here. However, the pattern of residuals
**Fig. 3.11:** Evidence of positive skewness in the coaxial probe data. The residuals of a fit to a symmetric Gaussian lineshape indicate that the 16 Td data has a small but discernable high-velocity tail.
shown in Fig. 3.11 was consistently observed in the course of fitting coaxial probe
tline shapes to symmetric Gaussians. Although there was some concern that the
systematics discussed in the next section were responsible for these observations, this
trend is also present in the coaxial and perpendicular measurements, made back-to-
back without any variation in the tube voltages. This observation strongly suggests
that there is indeed a small degree of positive skewness in the parallel VCDF's.

E. Possible systematics

The list of possible experimental artifacts in the measurement of ion
transport properties in a drift tube is daunting. First, there is the possibility of
turbulent gas flow or other hydrodynamic problems associated with the bulk flow of
buffer gas. Either the target ions or undesirable ion-neutral clusters can be produced
within the drift region itself, if incorrect ion chemistry is being employed that makes
the production reactions occur "late". Additionally, long-lived ion-neutral collision
complexes from the ion source may be surviving to the drift region. Surfaces in the
drift tube can be either systematically (i.e., reproducibly) or "randomly" charging, a
maddening problem to track down. Arcing behavior—the breakdown of the partially
ionized gas under the application of a sufficiently high drift field—can occur, often
without the investigator being aware. Inadequate charge separation of the flowing
afterglow plasma can result in a significant density of electrons still present in the
drift region, partially shielding the positive ions from the external electric field and
seriously affecting the measured transport properties. Lastly, there is the possibility of
space-charge perturbation of the applied external electric field if the density of ions in
the drift region is greater than approximately $10^6$ ions cm$^{-3}$.
All of the items on this list are a particular problem for the measurement of transport properties via single-frequency LIF precisely because it is a sensitive, in situ, non-obtrusive measurement technique. Loosely, with the LIF technique, one “sees” everything going on within the drift tube or plasma environment, even if one would at times prefer not to! Thus, it can be difficult to disentangle the various processes occurring in the drift tube to extract the desired transport properties one wishes to measure. Additionally, because the major disadvantage of the technique is that the signal-to-background is limited, compromises must be made on ion production conditions that may unavoidably affect the measurements.

Without exaggeration, easily twice as much work was performed to characterize and attempt to solve systematic problems present in the transport experiments than to take the data in Sec. III.D; this aspect of the experiment was plagued by setbacks and frequently discouraging. The results presented in this section summarize the findings of this work. Sec. III.E.1 discusses the axial ion flow velocity experiments that revealed an anomalous dependence of the axial ion “flow velocity” on charge separation voltage. Section III.E.2 summarizes some truly bizarre results obtained by adiabatically scanning either the charge separation or drift voltage.

The material of this section is of far more than incidental interest. Previous measurements of both the CO\(^+\)-He system and the Ba\(^+\)-Ar system performed on this apparatus revealed significant differences between the reduced mobilities obtained by single-frequency LIF and the traditional pulsed-field arrival time measurements.\(^{23}\) Additionally, both because the CO\(^+\)-He LIF mobility curves have unusual structure and because the arrival-time technique is well-entrenched in the literature as the
"correct" way of measuring mobilities, the LIF technique has become suspect. Certainly, these discrepancies call into question our understanding of the measurements; the results presented in this section suggest that the previous CO\(^+\)-He LIF work was hampered by some of the same problems encountered in N\(_2^+\)-He.

1. Axial ion flow-velocity experiments

This section discusses measurements investigating anomalous shifts in the apparent ion axial flow velocity as a function of charge separation voltage. These effects were noted as early as the first alignment work conducted during the fall of '95. The method used to locate a specific rotational line is to first probe in space-charge neutral plasma, and, once the transition is found and framed within the laser scan, then to turn up the charge separation supply to the desired voltage. As a matter of course, the "A" cursor of the acquisition program (Eta-Spex) was positioned to continuously track the first moment, both for laser diagnostic purposes and in preparation for the placement of "software" sub-Doppler markers for rotational alignment measurements. For coaxial laser probing, a noticeable shift in the first moment between charge-separation off and charge-separation on was repeatedly observed—the transition would be "off mark", as indicated by the software cursor, after the charge-separation voltage was on. At the time of those measurements, it was believed that this effect was due to surface charging of either the aluminum compression flanges that hold together the drift assembly, or the LIF box end-cap drift rings, known to be constructed of aluminum and to have caused charging problems for the CO\(^+\)-He arrival-time work previously conducted on the apparatus. Since the
emphasis of the experimental work was initially on alignment rather than transport measurements, no action was taken to remedy this perceived problem at that time. Subsequently, after the Fall '95 alignment work was completed, the apparatus was disassembled and cleaned, the aluminum compression flanges sent out for gold coatings, and the LIF box end-caps rebuilt in stainless steel.

The same effects were reobserved and measured in the course of diagnostic work on first moment experiments taken in the fall of '96. Figure 3.12 shows representative diagnostic data on $R_1(9)$, at a drift field corresponding to 1.50 Td; field-off/field-on pairs were acquired as a function of charge separation voltage. For this apparatus configuration, five guard rings (four resistors) were used as a charge separation region. What is unusual about this data is the shift in position of the field-off line center with increasing charge separation voltage. Naively, one might anticipate a shift in the field-on line center towards higher frequencies as the charge separation voltage is increased; the simple explanation would be that as the shielding effects of the sheath of electrons are diminished in the plasma by the increasing voltage, the positive ions "see" more of the external applied drift field, and their first moments shift accordingly. This qualitative behavior was observed in the CO$^+$-He system and explained in this fashion. However, the field-off line centers should not shift as a function of charge separation voltage, as the field-off measurements (ideally) represent the true axial ion flow velocity of the ion, which should be identical with the axial buffer gas velocity. The lower panel of Fig. 3.12 displays the nonsensical "mobilities" that would be obtained from such measurements if taken at
Fig. 3.12: Field-off & field on line center shifts as a function of charge separation voltage, showing representative axial ion flow velocity shift. The data is on $R_1(9)$, with the drift field corresponding to 1.50 Td. The bottom panel shows "mobilities" derived from these differences, irrespective of charge separation voltage value.
face value, underscoring the importance of proper ion production conditions and charge separation to transport property measurements.

Subsequent data taken at other field strengths confirmed this qualitative behavior. Additionally, the ion's axial flow velocity was measured for this apparatus configuration. True axial ion flow velocities can be measured by this technique by back-to-back pairs of perpendicular and parallel laser probe scans, made under flow-tube conditions (both charge-separation and drift fields off). No Doppler shift whatsoever is present in the perpendicular probe line center, which effectively fixes a laboratory “zero” of velocity (i.e., $\bar{u}_0$ is measured). An immediate coaxial probe measurement yields the Doppler shift of the ions on the drift-tube axis due to the bulk flow of the buffer gas alone. It is well-known that the ratio of the average ion flow velocity to buffer gas bulk flow velocity, $v_0$, is 1.6;\textsuperscript{24} however, because this technique samples only ions on the axis of the flow tube, what is measured here is the axial ion flow velocity, which should the same as the axial buffer velocity of 1.9 to 2.0 times $v_0$, as discussed in Sec. II.B.2. A helpful analogy is the motion of leaves (ions) sprinkled on top of a flowing stream (buffer gas). These LIF measurements yielded an axial ion flow velocity of $137 \pm 2$ m s\textsuperscript{-1}; the known calibrated flow of buffer gives a $v_0 = 71$ m s\textsuperscript{-1}, for a ratio of 1.9, as expected.

To summarize a lengthy set of experiments conducted, it is now believed that this systematic is due to space charge effects. Fig. 3.13 summarizes the results of several diagnostic experiments conducted in which the axial ion velocity was measured by back-to-back perpendicular and coaxial laser scans for two different
10 cm charge-separation region, two source aperture sizes:

\[ V_G = 23.0 \text{ V}, \ I_E = 1.25 \text{ mA throughout} \]

1.125" dia: \( N_2 \) flow approx. 23 sccm
0.389" dia: \( N_2 \) flow approx. 10 sccm

Fig. 3.13: "Working" plot summarizing some results of axial ion flow experiments. Shown are several sets of data acquired with two source aperture sizes.
source aperture sizes, as shown in Fig. 2.2. Note the large rise in axial ion velocity with charge-separation voltage for the larger aperture size. Additional experiments conducted with an even small aperture confirm this trend. It is believed that this space charge effect is due an enhanced axial ion density gradient that becomes established with non-zero charge separation voltage. The transport property data in Sec. III.D was acquired with the 0.389-inch dia aperture, the smallest aperture possible that still permitted measurements to be made with adequate signal-to-noise.

2. LIF intensity vs. tube voltage experiments

Another class of experiments was attempted on this apparatus. The basic idea was to scan either the charge-separation voltage or the drift voltage slowly in time while monitoring the LIF signal. The laser frequency is positioned at line center on a rotational transition, and the laser probe direction is always perpendicular, so the transition cannot be Doppler-shifted out of resonance with changes in either tube voltage. What is measured is the relative ion number density in the LIF region, as a function of the tube voltages. The conception of the charge-separation scanning experiment was as a diagnostic tool for performing production condition checks. The original idea behind the drift voltage scanning experiment was to obtain scans for several different rotational lines, in the hopes of extracting a rotational temperature as a function of field strength. Previous experiments conducted on this apparatus \(^{25}\) did characterize the rotational temperature of \(N_2^+\), but under much poorer signal-to-noise conditions; the idea here was to look for possible non-Boltzmann rotational distribution behavior that may have been missed in the first work.
A floating programmable "high voltage" power supply was constructed (schematic in JILA electronics shop) to permit these voltages to be swept under digital-to-analog computer control. Typical results are shown in Figs. 3.14 and Fig. 3.15 for the production conditions detailed in Fig. 2.3. Fig. 3.14 shows scans of the charge separation voltage across 5 rings for various fixed drift voltages; Fig. 3.15 shows scans of the drift voltage across forty rings for various fixed charge separation voltages. The truly bizarre structures shown in Fig. 3.15 are completely reproducible. Additionally, experiments of this sort were performed with the "good" production conditions of Fig. 2.4. While the structures shown in the figure is less pronounced with these latter production conditions, they are still present. Since this investigator does not understand what these plots mean right now, they are presented just for archive purposes. This investigator's best conjecture is that the changes in the tube voltages are altering the plasma conditions in the source region over time. These changes occur on a time scale slower than the change in tube voltages, so the plots represent a convolution of the ion source's "memory". Since these effect are not understood, no rotational temperature experiments were attempted with this technique.

F. Discussion & theory

A discussion of experimental results is given in this section, with comparisons both to existing transport property literature and, in particular, to the previous studies of Bastian\textsuperscript{5} that employed both LIF and arrival-time techniques to measure CO\textsuperscript{+} mobilities in He. Figure 3.16 shows a summary of these previous results. A considerable discrepancy is apparent between the LIF and arrival-time values (both
LIF intensity at linecenter as a function of $V_{CS}$ for various fixed drift voltages

- $V_{\text{drift}} = 0.0$ V (0 Td)
- $V_{\text{drift}} = 9.79$ V (1.5 Td)
- $V_{\text{drift}} = 19.6$ V (3.0 Td)
- $V_{\text{drift}} = 39.1$ V (6.0 Td)
- $V_{\text{drift}} = 58.7$ V (9.0 Td)
- $V_{\text{drift}} = 78.3$ V (12 Td)
- $V_{\text{drift}} = 97.9$ V (15 Td)

**Fig. 3.14:** Results of charge-separation voltage scanning experiments.
LIF intensity at linecenter as a function of $V_{\text{drift}}$ for various fixed charge-separation voltages

Fig. 3.15: Results of drift voltage scanning experiments.
Fig. 3.16: Comparison of reduced mobilities of CO⁺ drifting in He as a function of E/N, for various tube pressures, as determined by pulsed field arrival time (AT) and LIF techniques.
obtained on a modified version of this apparatus) that is well outside of the measurement error bars. Additionally, at approximately 4.5 Td, the LIF mobilities rise rapidly with field strength, changing by almost 4 cm$^2$ V$^{-1}$ s$^{-1}$ over a field range of only about 3 Td. This unusual structure seems too "sharp" and is difficult to reconcile with conventional interpretations of mobility as a physical property that reflects an average of collision processes governed by the ion-neutral interaction potential.

As a starting point, an approximate comparison between the CO$^+$-He and N$_2^+$-He interaction potentials can be made. In order to investigate other seemingly anomalous results in a vibrationally-state selected CO$^+$-He mobility study, Bastian carried out a limited set of ab initio calculations for CO$^+$-He as a function of CO$^+$ bond length.$^5$ Only the collinear geometry was considered, but energies were calculated for the approach of both the C and O ends. We can obtain an approximate comparison with N$_2^+$-He for the collinear approach by averaging the equilibrium bond distance CO$^+$-He energies and comparing them with the N$_2^+$-He interaction potential for $\theta = 0$, as shown in Fig. 1.1. A comparison plot of these values indicates that, within the uncertainty of the CO$^+$-He calculation (hampered primarily by missing values at critical separation distances), the two interaction potentials appear identical. This observation, along with the isoelectronic structure of the two molecules and the equal ion-buffer reduced masses, would suggest that the transport properties of the two systems should be identical for room temperature measurements.

The mobilities of both CO$^+$ and N$_2^+$ drifted in helium at room temperature have been previously measured by a variety of non-state-specific techniques. An early
drift-tube study of the arrival-time mobilities of \( N_2^+ \) in He with a pulsed ion source was performed by Johnsen \textit{et al.} Measurements over the range of about 8 to 50 Td yielded a \( N_2^+ \)-He reduced mobility extrapolated to zero field (i.e., \( K_0(0) \)) of approximately \( 19 \pm 2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \). A more comprehensive set of measurements of a number of ion mobilities in He, including \( N_2^+ \), was performed by McFarland \textit{et al.} on the original NOAA drift apparatus using the pulsed-field arrival time technique. These measurements yielded an extrapolated zero-field reduced mobility of \( K_0(0) = 21.0 \pm 1.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \). The \( N_2^+ \)-He mobilities over the range 8 to 90 Td from this study are shown in Fig. 3.17(a); the low-field values are also plotted in Fig. 3.6 for comparison with the \( R_1(15) \) LIF data. A comprehensive drift-tube study of arrival-time mobilities of many species of atmospheric interest was performed by Lindinger and Albritton on this same apparatus; however, \( N_2^+ \) (oddly enough) was not studied at that time. \( \text{CO}^+ \)-He mobilities were measured in this study and are plotted in Fig. 3.16 for comparison to the previous \( \text{CO}^+ \)-He LIF mobility data of Bastian. The NOAA mobility measurements on \( N_2^+ \)-He and \( \text{CO}^+ \)-He are the ones tabulated in standard reference tables and are generally considered to be the accepted values. A more recent determination of the mobility of a number of atmospheric ions, including \( N_2^+ \) in helium, by Fhadil \textit{et al.} using the technique of cylindrical electrostatic energy analysis yield mobility values in excellent agreement with the NOAA studies. This convergence of measurements from entirely different techniques strongly suggests the correctness of these values.
Fig 3.17: Literature values of $N_2^+$ and $CO^+$ mobilities at room temperature, in various buffer gases. a) $N_2^+$-He arrival-time mobilities from McFarland et al. (Ref. 27); b) $N_2^+$ and $CO^+$ SIDT mobilities in Ne and Ar, from Ref. 32.
Additional mobility measurements have been made on both $N_2^+$ and $CO^+$ with other buffer gases and at other temperatures. The mobilities of $N_2^+$ and $CO^+$ were measured in neon and argon at room temperature by Kondo and Moruzzi using a selected-ion drift tube (SIDT).\textsuperscript{32} Their data are shown in Fig. 3.17 (b); note in particular the close agreement between the mobilities of the two species in both buffer gases. More recently, the mobilities of $N_2^+$ and $CO^+$ were measured in He at 4.35 K by Sanderson \textit{et al.}\textsuperscript{33} using the pulsed-field arrival time technique and compared to the polarization limit. This mobility, $K_{pol}$, is the theoretical value for a pure $r^{-4}$ induced-dipole potential in the limit that $E/N$ and $T \rightarrow 0$. $K_{pol}$ can be shown to be given by\textsuperscript{4}

$$K_{pol} = \frac{13.853}{\sqrt{\alpha \mu}} \text{ as } E/N, \ T \rightarrow 0$$

(3.33)

where $\alpha$ is the buffer gas polarizability in $\text{Å}^3$, and $\mu$ is the ion-neutral reduced mass in g mole$^{-1}$. For $N_2^+$-He or $CO^+$-He, with $\alpha_{He} = 0.205 \ \text{Å}^3$ and $\mu = 3.5$ g mole$^{-1}$, this gives a $K_{pol}$ of 16.35 cm$^2$ V$^{-1}$ s$^{-1}$. Sanderson \textit{et al.} compare their mobilities at various field strengths to the room temperature measurements discussed above by plotting these values as a function of effective temperature, given by

$$\frac{3}{2} k_B T_{\text{eff}} = \frac{3}{2} k_B T + \frac{1}{2} M v_d^2 \quad \text{or} \quad T_{\text{eff}} = T + \frac{1}{3 k_B} v_d^2$$

(3.34)

where $M$ is the mass of the buffer gas. For high ($> 300$ K) effective temperatures, the $T = 4.35$ K measurements agree well with previous measurements. For sufficiently
low $T_{\text{eff}}$, the mobilities of both species dip below the polarization limit and have qualitatively the same behavior. However, the mobility of CO$^+$ was found to plateau significantly below the polarization limit at $T_{\text{eff}} < 100\,\text{K}$. This result was ascribed to more facile CO$^+$-He collisional excitation, due to the $\Delta j=\pm 1$ heteronuclear collisional selection rule, as well as possible orbiting resonances at these low effective temperatures.

For room temperature measurements ($T_{\text{eff}} > 300\,\text{K}$), however, the mobility of both species in He would be expected to be significantly above the polarization limit for low-field values.$^{28,34}$ For ion-neutral systems with small interaction potential wells, $K_0(0)$ in general would be anticipated to lie considerably above $K_{\text{pol}}$, with $K_0$ decreasing gradually with increasing $E/N$, with an approximate $(E/N)^{-1/2}$ roll-off behavior.$^{13}$ Qualitatively, this is because at $T_{\text{eff}} \approx 300\,\text{K}$, the ions are already sampling the repulsive part of the interaction potential. A rise in mobility to a maximum at intermediate field strength would be expected in more polarizable buffer gases with deeper potential wells; indeed, the data of Fig. 3.17 show these maxima for both CO$^+$ and N$_2^+$ drifted in Ne. The N$_2^+$-He LIF measurements shown in Fig. 3.6 exhibit this qualitative behavior; the basically flat mobility curve in the range of 1.5 to 16 Td suggests that predominantly repulsive scattering is occurring. What appears unusual about the CO$^+$-He LIF mobility results is that they lie considerably closer to $K_{\text{pol}}$ for small fields and then increase with increasing $E/N$. 
A more quantitative description of the low-field mobility behavior of either species can be made by employing two-temperature theory to obtain approximate mobility values for non-zero $E/N$. The canonical expression for reduced mobility in two-temperature theory is

\[ K_0 = \frac{3e}{16N_0} \left( \frac{2\pi}{\mu k_B T_{\text{eff}}} \right)^{1/2} \frac{1}{\Omega^{(1,1)}(T_{\text{eff}})} = 9.89 \times 10^3 \frac{1}{\sqrt{T_{\text{eff}}} \Omega^{(1,1)}(T_{\text{eff}})} \]  

(3.35)

for $N_2^+$-He or $CO^+$-He, where the collision integral $\Omega^{(1,1)}$ depends on the specific form of the ion-neutral interaction potential and is a function of the effective temperature given by Eq. (3.34). Approximate collision integral values for $N_2^+$-He are obtained by fitting the "angle-averaged" potential (i.e., $\theta = 45$ degrees in Fig. 1.1) to standard $(n, 6, 4)$ atomic ion potential forms and then looking up tabulated collision integral values for these standard forms. The best fit of the Miller et al. $N_2^+$-He $\theta = 45$ degree potential to this form is given with the repulsive $r^n$ term set to $n = 8$, and $\gamma$, which weights the relative strength of the $r^{-6}$ and $r^{-4}$ attractive terms, set to 1.0 (i.e., a pure $r^{-6}$ attractive potential). The Miller et al. potential parameters for the position and depth of the well minimum are $r_m = 5.841598 \ a_0$ and $\epsilon = -139.367388 \ \text{cm}^{-1}$, respectively. This simple form mimics the $\theta = 45$ degree $ab \ initio$ potential surprisingly well in the critical region $r = 3$ to $13 \ a_0$. The tabulated collision integral $\Omega^{(1,1)}$ values for this form in the effective temperature range of 281 to 501 K are interpolated with a simple decaying exponential plus constant background. Effective temperatures are matched to $E/N$ values by the experimentally obtained drift
velocities, as shown in Fig. 3.5. The resulting "theoretical" mobilities for the field range 1.5 to 16 Td are shown in Fig. 3.6. Note in particular that the predicted mobility is in reasonable agreement with the LIF values and remains essentially constant in this field region, rolling off slightly for E/N > 12 Td.

The above calculation is approximate and only strictly applicable to atomic ion systems. Transport theories for polyatomic ions have been formulated by Viehland et al.\textsuperscript{1} and Koutelos and Mason.\textsuperscript{37} Explicit expressions for the mobility and translational temperatures are given in these works that formally resemble the expressions for the two- and three-temperature atomic theories.\textsuperscript{4} Unfortunately, these expressions depend on the evaluation of much more complicated collision integrals. Limited calculations have been performed for molecular ion systems of interest, and no general tabulations exist. However, recently, Liu and Dickinson\textsuperscript{38} calculated generalized cross sections for N\textsubscript{2}\textsuperscript{+}-He that, in principle, can be used to describe either transport properties such as thermal conductivity or rotational alignment. They find good agreement between quantum close-coupled and classical trajectory calculations at high (\(E_r > 400\) cm\textsuperscript{-1}) energies, suggesting that the simpler classical mechanical approach of Viehland\textsuperscript{39} could be employed to study systems such as CO\textsuperscript{+}-He or N\textsubscript{2}\textsuperscript{+}-He. It should be noted that, in general, the introduction of an additional internal temperature \(T_i\) is needed to characterize the internal energy distribution of molecular ions. However, for the case of molecules drifting in an atomic buffer gas, detailed balance requires that \(T_i = T_{\text{eff}},^1\) which is one of the reasons the above approximate calculation works reasonably well.
The J-state dependent mobility effects shown in Figs. 3.7 and 3.8 are small, but consistent with behavior reported in other systems. Several investigators have previously looked for quantum state dependencies of molecular ion transport properties. Haese et al. report a slight enhancement of mobility with vibrational state for ArH drifted in He, as studied in a DC glow discharge with infrared absorption techniques. The more recent vibrationally state-selected measurements of Bastian on CO-He performed on this apparatus find CO+(v' = 2) to be significantly more mobile than CO+(v' = 0). However, the inherent difficulties in controlling the ion production chemistry that form vibrationally-excited species in a drift tube or discharge make these results considerably more ambiguous than they might appear. These difficulties are circumvented for J-state dependent transport property investigations of molecular ions in their ground electronic and vibrational states, due to the rapid thermalization of rotational levels. Several studies have investigated possible J-dependent transport properties. Hong and Miller report no rotational line dependence of the N2 Doppler shifts studied with Fourier transform emission spectroscopy, but the resolution of their instrument is considerably poorer than the present work. Borysow and Phelps studied N2 Doppler shifts in a positive column pulsed discharge of N2 and He by single-frequency laser absorption techniques on bands in the Meinel (A-X) system. They report no dependence of N2 drift velocities on rotational state up to N = 20 in either N2 or He; however, their measurement uncertainties are ± 7%. Bastian et al. also reported a small but
persistent difference in the mobilities between J=3.5 and J=13.5 of CO\(^+\left(v''=0\right)\) in He, the higher-J state being slightly more mobile above 9 Td.

The interpretation previously given for the CO\(^+\) results involves simple rotational distribution and energy gap scaling laws arguments.\(^5\) The probability of rotational-to-translational energy transfer in a single ion-neutral collision is assumed to be proportional to a Boltzmann factor

\[
P_{R \rightarrow T} \propto \exp\left(\frac{-\Delta E_{jj'}}{k_B T}\right), \quad \text{with} \quad k_B T = 207 \text{ cm}^{-1} \quad \text{at} \quad T = 298 \text{ K} \tag{3.36}
\]

where \(\Delta E_{jj'}\) is the energy gap between adjacent rotational levels in the manifold. Lower rotational states have more facile T-R or R-T energy exchange as they undergo inelastic collisions more frequently. At higher rotational levels, it becomes increasingly less probable to undergo T-R exchange in a single collision; higher J-states tend to scatter elastically and preserve their rotational energy, thus behaving more “atom-like”. Note in particular that the \(\Delta j = \pm 2\) collisional selection rule for \(N_2^+\), which leads to the effective doubling of the rotational constant, would be anticipated to make these J-dependent transport property effects more pronounced in \(N_2^+\) than in CO\(^+\).

There are far fewer central moment measurements in the literature for comparison. A much less dramatic translational temperature difference was observed for J=3.5 and 4.5 in the CO\(^+\)-He system by Bastian. Additionally, both the attractive and repulsive Maxwell model failed to give a good prediction of the measured
temperature. Here, we will use two-temperature theory to produce approximate translational temperatures. The appropriate expressions are\(^5\)

\[
T_{\parallel} = T + \frac{5m - (2m - M) A^{*} M}{5m + 3M A^{*}} \frac{M}{k_B} v_d^2
\]

\[
T_{\perp} = T + \frac{(m + M) A^{*} M}{5m + 3M A^{*}} \frac{M}{k_B} v_d^2
\]

where \(m\) and \(M\) are the ion and buffer masses, and \(A^{*} = \frac{\Omega^{(2,2)}}{\Omega^{(1,1)}}\) is the ratio of two collision integrals. We can use the model potential parameters discussed above to look up \(A^{*}\) values for this range of effective temperatures. Because \(A^{*}\) is a ratio, it is a weak function of \(T_{\text{eff}}\) and equal to 1.11 for this range. The temperatures predicted by this theory are plotted in Fig. 3.10 for comparison with the experimental data. The agreement is much closer than for the Maxwell model in comparison to \(\text{CO}^+\)-He.

Since \(\text{CO}^+\) is a system with no nuclear spin, there is no underlying hyperfine structure and previous investigators have always fitted the line shapes to a symmetric Gaussian. No observation of fit residual pattern like those show in Fig. 3.11 have been reported.

**G. Conclusions**

The reasonable agreement ultimately reached between the \(N_2^+\)-He LIF mobilities studied here and other mobility techniques suggests that nothing is fundamentally flawed in our understanding of transport properties or the LIF technique. Fortunately or unfortunately, the method is one of great sensitivity that is capable of revealing a great deal of information. One fundamental problem with the single-frequency LIF technique however, is the rather severe limitation on field range due to signal-to-noise. The investigator is likely to yield to the temptation to search
for production conditions that increase signal, at the peril of perhaps introducing space-charge effects.

A fairly conclusive demonstration is given of a small but definite increase in the mobility of $N_2^+$ with increasing rotational state from $J=13.5$ to $J=22.5$. A significant difference of over 100 K has been confirmed between the parallel and perpendicular temperatures of a single rotational line measured at the highest field strength (16 Td). Furthermore, a small degree of positive skewness is confirmed for the parallel VCDF’s, which may be the first report of such an effect in a molecular ion system. Future work will attempt to extract numerical skewness parameters and attempt a more comprehensive comparison between the experimental results and theory.
References for Chapter III


CHAPTER IV

COLLISION-INDUCED ROTATIONAL ALIGNMENT OF N₂⁺ DRIFTED IN He

A. Introduction

Collision-induced rotational alignment can be produced whenever there exist anisotropies both in the interaction potential and relative velocity vector distribution of the colliding partners. The phenomenon has been observed often in supersonic jet expansions, in which the latter anisotropy is created by the velocity slip of the seed and carrier in the expansion. For example, substantial degrees of alignment are reported for sodium dimer expanded in sodium,¹ for I₂ seeded in Ar, He, and H₂²,³ and for the expansion of CO₂ seeded in Ar, He, and H₂.⁴ All of the aforementioned studies incorporate some form of optical detection of the alignment, either laser-induced fluorescence or infrared absorption. Additionally, all of these studies find a general propensity for the rotational angular momentum vectors to be aligned perpendicular to the jet expansion direction.

However, only a few studies to date have incorporated some distinct form of selection of the velocity component along the jet expansion axis. The most notable is the work of Aquilanti and colleagues in experiments performed on a supersonic jet expansion coupled to a molecular beam velocity-selector and Stern-Gerlach apparatus. A dramatic correlation between velocity subgroup and alignment has been demonstrated on both neutral O₂⁵,⁶ and neutral N₂⁷ expanded in various carrier gases.
In the most extreme case of \( \text{O}_2 \) expanded in He, the polarization varied from essentially zero in the low-velocity tail of the beam to greater than 80% in the high-velocity tail. More recently, Wodtke and colleagues, using the technique of quantum-state specific metastable time-of-flight spectroscopy, studied two rotational states, \( J = 4 \) and 6, of CO expanded in He, and found velocity alignment correlations that, \( \text{prima facie} \), appear to contradict the work of Aquilanti.\(^8,9\) Unfortunately, both of these investigators cite the work presented here to buttress their arguments, placing this investigator in a decidedly uncomfortable position. Additionally, all of these observations have been on neutral-neutral systems.

The external electric field of a drift tube also creates an anisotropic distribution of relative velocities and thus, the possibility of alignment. The first observation of collision-induced rotational alignment in an ion-neutral system was reported by Dressler et al.\(^ {10} \) in a much earlier incarnation of the drift-tube apparatus used in the present work. The \( \text{N}_2^+ (v'' = 0) \) ions drifted in He were studied by polarized LIF with a broadband Nd:YAG pumped dye laser. By probing perpendicular to the tube axis at 14 Td (corresponding to an average center-of-mass collision energy of 52 meV), Dressler et al. measured fully velocity-averaged polarization coefficients for two rotational states, \( N''=4 \) and \( N''=10 \). They found a corresponding \( A_{\theta}^{(2)} \) quadrupole alignment parameter of \(-0.11 \pm 0.05\) for both states, the sign and magnitude indicating a significant preference for the rotational angular momentum vectors to be aligned perpendicular to the drift field, as discussed further in Sec. IV.B below.
This early drift-tube study subsequently motivated theoretical work by Follmeg, Rosmus, Werner, and colleagues. In a series of three papers, a ground-state \textit{ab initio} $N_2^+$-He interaction potential was calculated\textsuperscript{11} (as discussed in Sec. I.B), and both quantum close-coupled (CC)\textsuperscript{12} and classical-trajectory\textsuperscript{13} scattering calculations were performed with this potential surface, using as a framework a steady-state kinetics or master equation formalism and semi-empirical relative velocity vector distribution previously developed by Meyer and Leone.\textsuperscript{14} This theoretical work produced qualitative but not quantitative agreement with the experimentally-determined alignment parameters. Specifically, the theoretical CC $A^{(2)}_0$ values were found to be -0.010 and -0.034 for the N$''$ = 4 and 10 states, respectively, smaller in absolute value than the experimental parameters by factors of 11 and 3. A better agreement could be reached by adjusting the second coefficient of the Legendre moment expansion of the relative velocity vector distribution, underscoring the importance of the precise degree of anisotropy in the distribution of relative velocity vectors as well as in the interaction potential for determining the resultant steady-state alignment. The steady-state fully-velocity averaged theory is summarized in Sec. IV.F below, and the reasons why this theory is not appropriate for the current experiment are discussed.

Unfortunately, this first $N_2^+$-He experiment had several shortcomings. In particular, the low duty cycle of the pulsed laser resulted in inherently poor signal-to-background; to obtain adequate signal, the dye laser had to be run with sufficient power to saturate the transitions, introducing further complications to the data
Additionally, the broad linewidth of the laser (approximately 0.9 cm$^{-1}$) meant that the first experiment was incapable of resolving velocity-subgroup alignment, or any details about the underlying velocity component distributions. The current single-frequency version of the experiment circumvents both of these shortcomings and represents the "state of the art" of drift-tube alignment experiments. Because, to the best of this investigator's knowledge, only one other JILA thesis has investigated collision-induced rotational alignment, a more extensive treatment of background material is presented in Secs. IV.B and C. Section IV.D discusses results of two different types of alignment experiments, and Sec. IV.E covers diagnostic experiments conducted. A discussion of the underlying dynamics is given in Secs. IV.F. Section IV.G wraps up with an conclusion.

B. Descriptive theory

The brief overview of the descriptive theory of the detection of rotational alignment is given in this section. Section IV.B.1 covers the phenomenon at an elementary level, with simple qualitative descriptions and observations. Section IV.B.2 treats classical rigid-rotor theory, while Sec. IV.B.3 outlines the quantum theory. Section IV.B.4 discusses extensions and approximations to the quantum theory that are particularly relevant for this work.

1. Qualitative & heuristic arguments

A cartoon diagram of the basic geometry of the canonical LIF probe-measurement scheme used in this work is shown in Fig. 4.1. The drift field is along the laboratory Z-axis, and the fluorescence detector is placed along the Y-axis. The two laser probe directions employed are shown: the coaxial probe direction along the
Fig. 4.1: Cartoon diagram of LIF probe-detection scheme.
field or symmetry axis ($\hat{k}_{\text{laser}} \parallel Z$) and the perpendicular probe direction ($\hat{k}_{\text{laser}} \parallel X$).

The laser polarization vector $\hat{e}_A$ for either of these probe directions is fixed parallel to the detection axis.

Classically, a diatomic molecule can be modeled as a rigid rotor with its rotational angular momentum $\mathbf{J}$ always fixed perpendicular to the internuclear axis, as shown in the inset of Fig. 4.1. The rotor axis has three mutually orthogonal planes of rotation in the lab frame: the X-Y, Y-Z, and X-Z planes. Because of the cylindrical symmetry of the drift tube, the latter two planes are physically equivalent. Hence, there are two distinct senses of molecular rotation: the X-Y plane of rotation with $\mathbf{J} \parallel Z_{\text{lab}}$, referred to here as “pinwheels”, and the Y-Z plane with $\mathbf{J} \perp Z_{\text{lab}}$, referred to as “frisbees”. The essence of any collision-induced alignment experiment is to formulate a scheme of distinguishing between these two types of rotation. In a LIF experiment, this information is obtained by knowing how the absorption and emission dipole moments are tied to the molecular framework, i.e., how the molecule is “built”. For the particular system studied here, we are concerned with $\Sigma - \Sigma$ or parallel transitions, which means the induced electric dipole moment $\hat{\mu}$ lies along the internuclear axis, in the plane of rotation of the molecule.

For the probe scheme shown in Fig. 4.1, the laser picks out both the X-Y and Y-Z planes of rotation with dot-product efficiency $\hat{\mu} \cdot \hat{e}_A$. The fluorescence polarizer then distinguishes between these two senses by selectively attenuating either the pinwheel (X-Y) or frisbee (Y-Z) emission with dot-product efficiency $\hat{\mu} \cdot \hat{e}_D$. Placing the polarizer so that its transmission axis $\hat{e}_D$ is along $Z$ preferentially selects the
frisbee fluorescence, of intensity $I_Z$ or $I_{\parallel}$; rotating the polarizer 90 degrees so that $\hat{e}_D$ is along X selects the pinwheel fluorescence, of intensity $I_X$ or $I_{\perp}$. Then the basic experimental parameter for probing with vertically polarized light is the linear polarization coefficient

$$P = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}}$$  \hspace{1cm} (4.1)

reported in this work as a percentage ($P \times 100\%$).

A very simple physical picture of collision-induced rotational alignment is given by the model first suggested by Gorter, who pointed out that the hard-ellipsoidal collisional cross section of a rotating molecule is orientation dependent and, for linear molecules, is minimized when the angular momentum vectors $J$ are aligned perpendicular to the flow direction. Thus, one would expect to observe a propensity for more frisbee-like than pinwheel-like molecules in a drift tube experiment. Since frisbees are associated with fluorescence intensity $I_{\parallel}$ and pinwheels associated with intensity $I_{\perp}$, this simple model would in general predict positive polarization coefficients to be observed in any collision-induced alignment experiment.

Figures 4.2 (a) and (b) are cartoons of the corresponding $m_J$ distribution picture for the simple rigid-rotor model. In the isotropic case (no alignment), all projections of $J$ onto $Z_{lab}$ are equally likely. For the expected case of preferential population of frisbee-like planes of rotation, the polarization coefficients are positive, $m_J = 0$ is more likely than $m_J = J$, and the $m_J$ distribution is bowed down. The
Isotropic distribution of $m_J$ values:

Alignment: anisotropic symmetric distribution of $m_J$ values:

\[ P(\chi_A = 90^\circ) = \frac{I_{||} - I_L}{I_{||} + I_L} \]

To first approximation, can think of sign of $P(90^\circ)$ as determining overall "bow" of $m_J$ distribution and quadrupole alignment parameter $A_0^{(2)}$

\[ P(90^\circ) > 0: A_0^{(2)} < 0 \quad \text{and} \quad P(90^\circ) < 0: A_0^{(2)} > 0 \]

**Fig 4.2**: Cartoon $m_J$ distribution picture. (a) isotropic and aligned distributions for $J=3$ case (b) qualitative meaning of polarization coefficients and alignment parameters in terms of "bow" of $m_J$ distributions.
converse holds for preferential population of the pinwheel-like plane of rotation: the polarization coefficients are negative and the $m_J$ distribution is bowed up. In the dominant moment approximation discussed below, only the leading nonisotropic term, the quadrupole alignment parameter $A_0^{(2)}$, is retained. With this approximation, and the measurement scheme just outlined, the linear polarization coefficients have a very simple interpretation, as illustrated in Fig. 4.2 (b). A polarization coefficient of zero indicates no rotational alignment, while positive (negative) polarization coefficients are associated with negative (positive) quadrupole alignment parameters, which in turn indicate a preference for population of the frisbee (pinwheel) planes of rotation.

One of the primary advantages of the geometry of the above scheme is that in principle, the measurements should be free of isotropic polarization, which in general can be defined as the presence of a predictably nonzero polarization signal even in the complete absence of molecular alignment. Isotropic polarization is discussed more quantitatively in the following sections; however there is a simple symmetry heuristic argument that can be used to predict whether or not a measurement scheme will exhibit isotropic polarization. As can be seen from Fig. 4.1, the vector $\hat{e}_D$ always remains perpendicular to $\hat{e}_A$ for either the $I_\parallel$ or $I_\perp$ measurement. As discussed below, isotropic polarization will always be modulated as $P_2(\cos\chi_{AD})$, where $\chi_{AD}$ is the angle between $\hat{e}_A$ and $\hat{e}_D$. For the chosen geometry, however, this angle is fixed to 90 degrees no matter how $\hat{e}_D$ is rotated, which suggests that no modulation in fluorescence intensity should be observed as $\hat{e}_D$ is rotated. If a different measurement
scheme had been chosen—for example, one in which horizontally polarized light was used, then the angle $\chi_{AD}$ will change depending on how $\hat{e}_D$ is rotated, and the fluorescence signal will modulate. Loosely, this is because there is a geometric coincidence between the $\hat{e}_A$ and $\hat{e}_D$ vectors that permits efficient detection of the dipole emission.

2. Simple classical theory

The simple classical rigid rotor model of the previous section is extended to produce a $J$-independent LIF intensity expression for the two laser probe directions, as a function of the orientation of the two polarization vectors $\hat{e}_A$ and $\hat{e}_D$. The treatment here is quite similar to models previously developed by Sinha et al.\textsuperscript{1} and Sanders et al.,\textsuperscript{18} but explicitly addresses the coaxial probe geometry. Additionally, resulting expressions are found which correspond to the quantum treatment outlined below in Sect. IV.B.3 in the high-$J$ limit. High-$J$ limit expressions are frequently used in the analysis of experiments where large angular momentum quantum numbers are encountered. This treatment is particularly convenient because no angular momentum recoupling terms need be calculated.

In this model, the transition moment $\hat{\mu}$ is treated as a classical electric dipole, tied to the geometry of the molecule. Only $\Sigma - \Sigma$ (parallel) transitions, with $\hat{\mu}$ lying along the internuclear axis are considered here. The absorption and emission dot products $\hat{\mu} \cdot \hat{e}_A$ and $\hat{\mu} \cdot \hat{e}_D$ still contain the essential geometrical information about the alignment of the molecules. But now, the resulting LIF intensity is treated as a
function of the two angles that can be conveniently controlled in a polarized LIF experiment, $\chi_A$ and $\chi_D$, as illustrated in Fig. 4.3.

The fluorescence intensity expression as a function of $(\chi_A, \chi_D)$ is produced by averaging over the distribution of angular momentum vectors according to

$$I_{LIF}(\chi_A, \chi_D; \hat{k}_{laser}) = K \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin \theta \, n(\theta) \left( \langle (\hat{\epsilon}_A \cdot \hat{\mu}_{lab})^2 \rangle \langle (\hat{\epsilon}_D \cdot \hat{\mu}_{lab})^2 \rangle \right)$$

(4.2)

where $K$ is an arbitrary rescaling constant, $(\theta, \phi)$ are the polar angles of $\mathbf{J}$ with respect to $Z_{lab}$, and $\hat{\mu}_{lab}$ is the transition moment of the molecule transformed into the lab frame by the appropriate rotation matrix. The absorption dot product in the integrand depends implicitly on the laser probe direction $\hat{k}_{laser}$.

In the high-$J$ limit, $\mathbf{J}$ is treated classically as a continuous vector and is allowed any continuous projection along the coordinate axes. Thus, $n(\theta)$ is the expansion of molecular orientations along the symmetry axis in terms of even Legendre moments,

$$n(\theta) = a_0 + a_2 P_2(\cos \theta) + a_4 P_4(\cos \theta) + \ldots$$

(4.3)

where $\theta$ is the angle between $\mathbf{J}$ and $Z_{lab}$. The $\langle \rangle$'s in Eq. (4.2) denote an average of the fast molecular rotation of the dipole axis. Because the classical molecular period of rotation, $T_{rot}$, is much smaller than the average fluorescence lifetime ($T_{rot}$ is approximately 0.52 ps for $J = 15$, corresponding to about 120,000 rotations per fluorescence lifetime), the dot products corresponding to photon absorption and emission are averaged separately (incoherently), assuming no phase correlation.
Fig. 4.3: Schematic of "two-angle" LIF geometry for alignment experiment.
between these processes; i.e., many molecular rotations are assumed to take place between absorption and emission.

The $a_2$ and $a_4$ terms are the alignment parameters of the ensemble. The expansion of Eq. (4.3) is in Legendre polynomials $P_k(\cos \theta)$ instead of spherical harmonics $Y_{k,q}(\theta, \phi)$ because of the cylindrical symmetry of the experiment about the external electric field. Since the ensemble is invariant to rotations about $Z_{lab}$, the $\phi$ dependence is ignorable. Only even moments appear because we are concerned with an aligned ("double-headed arrows") as opposed to an oriented ("single-headed arrows") ensemble. Physically, this is due to the interaction potential being sensitive only to the angle the $N^+_2$ internuclear axis makes with the $N^+_2$-He collision axis.

Although, mathematically, the expansion of Eq. (4.3) continues past $k = 4$, in a 1+1 LIF experiment (1 photon in absorption, 1 photon in emission), it is only possible to obtain the $k = 2$ and $k = 4$ terms of this expansion. Qualitatively, this can be seen from inspection of Eq. (4.2). Loosely, each $\hat{e} \cdot \hat{\mu}$ dot product in the integral has a $\cos^2 \theta$ or $P_2(\cos \theta)$ "character". The product of these two terms can give an expression with at most $\cos^4 \theta$ or $P_4(\cos \theta)$ character. By the orthogonality of Legendre polynomials, any expansion term of $n(\theta)$ past $k = 4$ will vanish in the integral over $\theta$. In words, each probe or fluorescence photon carries "one moment's worth" of information about the ensemble. Thus, in a one-photon absorption experiment, it is only physically possible to obtain the second moment of the $m_j$ distribution. The $a_2$ and $a_4$ parameters describe the relative amounts of $P_2(\cos \theta)$ and $P_4(\cos \theta)$ needed to
characterize the underlying $m_j$ distribution. For a bowed-down $m_j$ distribution as shown in Fig. 4.2, $a_2$ is negative simply because mathematically, $+P_2(\cos \theta)$ functions happen to bow up.

A straightforward but somewhat tedious calculation\(^\text{20}\) produces the result for the coaxial probe geometry as

$$\begin{align*}
I_{LIF}(\chi_A, \chi_D; k_{\text{laser}} \parallel Z) &= \\
&= \frac{4\pi}{9} K \left[ a_0 \left\{ 1 + \frac{3}{20} \left( -\frac{2}{3} P_2(\cos \chi_D) + \sin^2 \chi_D \cos 2\chi_A \right) \right\} \\
&\quad + \left( \frac{2}{5} a_2 \right) \frac{1}{28} \left\{ 7 - 16 P_2(\cos \chi_D) - 3 \sin^2 \chi_D \cos 2\chi_A \right\} \\
&\quad + \left( \frac{1}{9} a_4 \right) \frac{9}{140} \left\{ -4 P_2(\cos \chi_D) + \sin^2 \chi_D \cos 2\chi_A \right\} \right]
\end{align*}$$

and for the perpendicular probe geometry,

$$\begin{align*}
I_{LIF}(\chi_A, \chi_D; k_{\text{laser}} \parallel X) &= \\
&= \frac{4\pi}{9} K \left[ a_0 \left\{ 1 + \frac{3}{20} \left( \frac{4}{3} P_2(\cos \chi_D) P_2(\cos \chi_A) - \sin^2 \chi_D \sin^2 \chi_A \right) \right\} \\
&\quad + \left( \frac{2}{5} a_2 \right) \left\{ -\frac{1}{2} P_2(\cos \chi_D) - \frac{1}{2} P_2(\cos \chi_D) \\
&\quad \quad + \frac{3}{28} \left( \frac{4}{3} P_2(\cos \chi_D) P_2(\cos \chi_A) + \sin^2 \chi_D \sin^2 \chi_A \right) \right\} \\
&\quad + \left( \frac{1}{9} a_4 \right) \frac{9}{140} \left\{ 8 P_2(\cos \chi_D) P_2(\cos \chi_A) - \sin^2 \chi_D \sin^2 \chi_A \right\} \right]
\end{align*}$$

These two expressions correspond to Eq. (21) of Ref. 21, with the replacements:

$$A_0^{(0)} = 1 \quad A_0^{(2)} = \frac{2}{5} a_2 \quad A_0^{(4)} = \frac{1}{9} a_4 \quad \text{(4.5)}$$
It should be noted that even in the $J \to \infty$ limit, it is necessary to choose the correct absorption and emission branches consistent with the geometry of the molecule (i.e., $P \uparrow$ or $R \uparrow$, $P \downarrow$ or $R \downarrow$ for this case) in order to obtain this correspondence.

In this “two-angle” experiment in which both $(\chi_A, \chi_D)$ can be varied, the basic experimental parameter is modified from Eq. (4.1) to become

$$P(\chi_A) = \frac{I_{LIF}(\chi_A, \chi_D = 0^0) - I_{LIF}(\chi_A, \chi_D = 90^0)}{I_{LIF}(\chi_A, \chi_D = 0^0) + I_{LIF}(\chi_A, \chi_D = 90^0)}$$  \hspace{1cm} (4.6)$$

with $\chi_A = 90^0$ corresponding to vertically-polarized light for either probe direction. It should be mentioned that the polarization coefficients as defined here differ from some literature, in which the polarization vector of the probe beam is taken as the quantization axis. In the latter designation, $I_\parallel$ and $I_\perp$ denote fluorescence polarized parallel and perpendicular to $\hat{e}_A$, which is only in agreement with the definitions of this work for the perpendicular laser probe $P(\chi_A = 0^0)$.

Figures 4.4 (a) and (b) shows plots of Eqs. (4.4) both for the case of no alignment ($a_2 = a_4 = 0$) and for a significant degree of alignment representative of the parameters observed in this experiment. It is useful to think of the two-angle experiment as producing fluorescence surfaces as in the figure that are modulated by the alignment parameters of the ensemble. Note that even for the isotropic case, the LIF surfaces are in general not flat, i.e., there exists isotropic polarization. However, note that there is a “valley” along $\chi_A = 90$ degrees in these plots for either probe direction, corresponding to the measurement scheme used here. For an isotropic distribution, this valley is perfectly flat, indicating that true polarization coefficients
Fig. 4.4: Isotropic and aligned fluorescence intensity plots for the two probe directions.
\[ P(\chi_A = 90^\circ) \] will vanish for either probe direction. For horizontally polarized light, this model gives a value for isotropic \( P(\chi_A = 0^\circ) \)'s for the (coaxial/perpendicular) probe geometry of \((-/+ \ 1/7 = (-/+ \ 14.3%)\), a well-known result in the high-J limit. Figure 4.4 also illustrates why a measurement scheme frequently employed in absorption and TOF experiments, namely the modulation of the laser polarization angle by a photo-elastic modulator (PEM) or other device, will not work for a right-angle detection LIF experiment. One will detect a large change in fluorescence intensity (isotropic polarization) simply due to geometric factors, while the true alignment signal due to nonzero alignment will be a small signal on top of this.

3. Quantum theory

The model of the previous section does not account for the quantization of angular momentum nor does it conserve the angular momentum of the absorbed and emitted photons. A proper quantum-mechanical treatment of detection and characterization of molecular alignment via LIF has been previously developed in detail in two papers by Greene and Zare.\(^{21,23}\) The resulting LIF intensity expression for a known \((J_i, J_e, J_f)\) initial, excited, and final state pump-fluoresce transition as a function of the two angles \((\chi_D, \chi_A)\) shown in Fig. 4.3 is

\[
I_{\text{LIF}}(\chi_D, \chi_A; \hat{k}_{\text{laser}}) = CS \sum_{k_D, k_A} e(k_D, k_A, k; \hat{k}_{\text{laser}}) \omega(k_D, k_A, k; J_i, J_e, J_f) A_0^{(k)} \tag{4.7}
\]

where the various terms in Eq. (4.7) are defined below. Conceptually, this expression is produced from an expression analogous to Eq. (4.2) above. The absorption and
emission dot products are now replaced by amplitudes \( \langle J_e m_e | \hat{e}_A \cdot \hat{\mu} | J_i m_i \rangle \) and 
\( \langle J_f m_f | \hat{e}_D \cdot \hat{\mu} | J_e m_e \rangle \). The unknown ground-state distribution of molecular alignments 
\( f(m_i) \) is still being averaged over; however, because of the coherent sum over the indistinguishable intermediate states \( m_i \) and the incoherent sum over final states \( m_f \), the math needed to disentangle this dynamical information from the geometrical factors becomes considerably more complicated.\(^{21}\)

The various terms in Eq. (4.7) correspond to the various aspects of this model that must be accounted for. The rescaling constant \( C \) contains the experimental dependencies on ion number density, laser power, and fluorescence detection efficiency. The isotropic line strength factor \( S \) varies as the product of two dipole reduced matrix elements \( \left| \langle J_f | t^{(1)} \| J_e \rangle \langle J_e | t^{(1)} \| J_i \rangle \right|^2 \). These two factors, which are important for extracting actual alignment parameters from experimental data, are discussed in greater detail in Sec. IV.B.4 below. The \( \varepsilon(k_D, k_A, k; k_{laser}) \) are polarization tensor elements dependent on the values of the photon multipole moments \( k \) and completely specified by the LIF geometry, and can be shown to be identical to those in Eqs. (4.4) above. The \( \omega(k_d, k_a, k; J_i, J_e, J_f) \) are angular momentum recoupling factors dependent on both the photon multipoles and the specific pump-fluoresce transition. Explicit expressions for both the polarization tensor elements and the angular momentum recoupling factors are tabulated in Ref. 21 and will not be repeated here. The angular momentum recoupling factors can be
calculated in a number of ways, including by Mathematica. An angular momentum
calculator program written in object Pascal for the MS Windows environment is given
in Appendix C that will calculate numerical values for these factors directly.

The \( A_0^{(k)} \) are the unknown alignment parameters of the system. In general, the
alignment parameters \( A_q^{(k)} \) are related by a rescaling factor to the ensemble average of
the spherical tensor operators \( J_q^{(k)} \). The cylindrical symmetry of the experiment forces
all moments with \( q \neq 0 \) to vanish, while the reflection symmetry requires all odd \( k \)
moments to be zero. Additionally, the 1+1 photon LIF scheme constrains the photon
multipole moments \( k_D \) and \( k_A \) to have only the values 0 or 2. Thus, Eq. (4.7) contains
only two unknowns: \( A_0^{(2)} \) and \( A_0^{(4)} \), the quadrupole and hexadecapole alignment
parameters, respectively. The \( A_0^{(0)} \) parameter is identically equal to 1 and is usually
grouped with the \( C \) prefactor and taken as a measure of total population. In general,
the limits on the nonisotropic parameters are

\[
-1 \leq A_0^{(2)} \leq +2 \quad \text{and} \quad -\frac{3}{7} \leq A_0^{(4)} \leq +1, \quad (4.8)
\]

although the extreme values are rarely encountered in collision-induced rotational
alignment experiments, and these parameters are not truly independent at these
limiting values.

An approximate \( m_J \) distribution may be found from these alignment
parameters. In general, the \( m_J \) distribution can be found from the state multipole
expansion of the density matrix.\(^{24} \) In this particular experiment, the density matrix is
diagonal because for a cylindrically symmetric system, no coherences are possible.
The state multipoles are proportional to the alignment parameters $A_{0}^{(k)}$ such that the density matrix may be expanded as:

$$\rho_{MM}^{J} = \sum_{k} (-1)^{J-M} \left( \frac{2k+1}{c(k)} \frac{[J(J+1)]^{k/2}}{\langle J | J^{(k)} | J \rangle} \begin{pmatrix} J & J & k \\ M & -M & 0 \end{pmatrix} A_{0}^{(k)} \right)$$

where the expression in parentheses is a Wigner 3-j symbol. For even $k$, the rescaling constants $c(k)$ and reduced matrix elements $\langle J | J^{(k)} | J \rangle$ are:

$$c(0) = 1 \quad c(2) = \sqrt{6} \quad c(4) = \frac{35}{8}$$

$$\langle J | J^{(0)} | J \rangle = \sqrt{2J+1} \quad \langle J | J^{(2)} | J \rangle = \sqrt{\frac{J(J+1)(2J-1)(2J+1)(2J+3)}{6}}$$

$$\langle J | J^{(4)} | J \rangle = \sqrt{\frac{(J-1)J(J+1)(J+2)(2J-3)(2J-1)(2J+1)(2J+3)(2J+5)}{70}}$$

The diagonal elements of the density matrix give the probability $p(J,m_J)$ of finding a molecule with angular momentum $J$ in a given $m_J$ state. Thus, an approximate measure of the resulting $m_J$ distributions can then be produced from the $k = 0$ and $k = 2$ terms of Eq. (4.9); explicitly, these first two terms give:

$$p(J,m_J) = \rho_{MM}^{J} = \frac{1}{2J+1} + 5 \frac{3(m_J)^2 - J(J+1)}{(2J+3)(2J+1)(2J-1)} A_{0}^{(2)}$$

This expression is used to produce $m_J$ distributions for the experimental data below.

4. Extensions to quantum theory

As is the usual practice in LIF experiments of this nature, particularly those with inherently low signal-to-background, all fluorescence branches from the upper electronic state are collected unresolved. This fluorescence is weighted by both the appropriate intrinsic branch-weighting (Hön-London) factors and the transmission of...
any frequency-selective elements through which the fluorescence passes. As discussed in Sec. II.D, both the $P$ and $R$ fluorescence branches are collected here, but the interference filters favor the $P$-branch over the $R$-branch by a factor that is approximately 9:1, depending on the particular transition probed.

The mathematical treatment of the branch-weighting is straightforward. A fluorescence intensity expression in the form of Eq. (4.7) can be written for each fluorescence branch. Assuming no $J$-scrambling collisions in the upper excited state, the total observed fluorescence intensity is just the sum of these two intensities

$$I_{\text{Total}} = I_{P\downarrow} + I_{R\downarrow},$$

where

$$I_{P\downarrow} = C_{P\downarrow}S_{P\downarrow} \sum_k A_0^{(k)} \varepsilon(k) \omega(k; J_{P\downarrow}),$$

$$I_{R\downarrow} = C_{R\downarrow}S_{R\downarrow} \sum_k A_0^{(k)} \varepsilon(k) \omega(k; J_{R\downarrow})$$

(4.12)

where the shorthand notation $\varepsilon(k_D, k_A, k; \bar{k}_{\text{laser}}) = \varepsilon(k)$ and $\omega(k_D, k_A, k; J_i, J_e, J_f) = \omega(k; J)$ has been employed for the arguments of the polarization tensor elements and angular momentum coupling factors. If we take the rescaling constant $C$ and line strength factor $S$ in Eq. (4.7) as

$$C = K[n_{ion}][I_{laser}^{i\rightarrow e} (\bar{\nu}_{e\rightarrow f})^3 T_{\text{filter}} (\bar{\nu}_{e\rightarrow f})^3], \quad S = \left| \left< J_f \parallel r_1 \parallel J_e \right> \left< J_e \parallel r_1 \parallel J_i \right> \right|^2$$

(4.13)

where $K$ is an apparatus proportionality constant, $[n_{ion}]$ is the local ion number density in the LIF region, $I_{laser}^{i\rightarrow e}$ is the laser irradiance, $\bar{\nu}_{e\rightarrow f}$ is the fluorescence transition frequency, and $T_{\text{filter}}$ the transmission of the interference filter at this frequency. The cubed dependence on the fluorescence frequency comes from the Breit formula and is ultimately related to the frequency dependencies of the Einstein A
and B coefficients. The product $CS$ for the $P$-branch fluorescence can then be written as

$$C_{P\perp}S_{P\perp} = K [n_{ion}][I_{i\rightarrow e}] \langle J_e \parallel r^{(1)} \parallel J_i \rangle^2 \times \left( \tilde{u}_{e\rightarrow f}^P \right) T_{\text{filter}} \left( \tilde{u}_{e\rightarrow f}^P \right) \langle J_f \parallel r^{(1)} \parallel J_e \rangle^2$$

(4.14)

with an analogous expression for the $R$-branch. Noting that the first line of Eq. (4.14) just depends on factors related to the pump ($i \rightarrow e$) step, which is common to both branches, we can redefine the proportionality constant $C$ as

$$C = K [n_{ion}][I_{i\rightarrow e}] \langle J_e \parallel r^{(1)} \parallel J_i \rangle^2$$

(4.15)

and define effective line strength factors $S_P$ and $S_R$

$$S_P = \left( \tilde{u}_{e\rightarrow f}^P \right) T_{\text{filter}} \left( \tilde{u}_{e\rightarrow f}^P \right) \langle J_f \parallel r^{(1)} \parallel J_e \rangle^2$$

$$S_R = \left( \tilde{u}_{e\rightarrow f}^R \right) T_{\text{filter}} \left( \tilde{u}_{e\rightarrow f}^R \right) \langle J_f \parallel r^{(1)} \parallel J_e \rangle^2$$

(4.16)

such that the total branch-weighted fluorescence is given by

$$I_{\text{Total}} = C S_P \sum_k A_0^{(k)} \epsilon(\vec{k}) \omega(\vec{k}; \vec{J}_{P\perp}) + C S_R \sum_k A_0^{(k)} \epsilon(\vec{k}) \omega(\vec{k}; \vec{J}_{R\perp})$$

(4.17)

with the branch-weighting given by the effective line strength factors in Eq. (4.16).

The fluorescence branch-weighting is just an experimental complication and no approximations have been made. However, as is often done in alignment experiments, the measured polarizations are converted into quadrupole alignment parameters $A_0^{(2)}$ in the approximation that the hexadecapole alignment parameter $A_0^{(4)}$ is negligible (i.e., set to zero in Eq. (4.7) or (4.17)). Pragmatically, this is necessary because only one experimental unknown can be extracted from a linear
polarization coefficient of the form of Eq. (4.6). Physically, for the relatively high
(J>9) rotor states studied in this work, it would be expected that $A_0^{(2)} > A_0^{(4)}$. This
intuition is supported by the CC calculations of Follmeg on $N_2^+$-He.12 These
calculations show that the $K=4$ tensor cross sections (discussed below), which are
associated with the hexadecapole parameter, are at least an order of magnitude
smaller than the $K=2$ tensor cross sections associated with the quadrupole parameter
for all states studied. Thus, we believe for this particular set of experiments that the
dominant moment approximation is a very good one.

Given this approximation, it is straightforward to produce an explicit formula
for quadrupole alignment parameters as a function of measured polarizations. The
assumption is made throughout that a point fluorescence source is being imaged, the
probe-detection geometry is perfectly rectilinear, and the angles $(\chi_D, \chi_A)$ are
perfectly matched to the apparatus geometry. We note in passing that none of these
assumptions are realized in the practice of this experiment! Setting $A_0^{(4)}$ identically
equal to zero in Eq. (4.7) yields the result

$$A_0^{(2)} = \frac{\left\{D_\parallel^{(0)} + D_\perp^{(0)}\right\} P}{\left\{D_\parallel^{(2)} - D_\perp^{(2)}\right\} - \left\{D_\parallel^{(2)} + D_\perp^{(2)}\right\} P} \quad (4.18)$$

with the definitions:

$$D_\parallel^{(0)} = \varepsilon_\parallel(0,0,0) \omega(0,0,0; J) + \varepsilon_\parallel(2,2,0) \omega(2,2,0; J)$$
$$D_\parallel^{(2)} = \varepsilon_\parallel(2,0,2) \omega(2,0,2; J) + \varepsilon_\parallel(0,2,2) \omega(0,2,2; J) + \varepsilon_\parallel(2,2,2) \omega(2,2,2; J) \quad (4.19)$$

where the subscript on the polarization tensor elements denotes the setting of the
fluorescence polarizer angle $\chi_D$ either parallel or perpendicular to the drift tube axis.
The $D_{\perp}^{(k)}$ terms are defined analogously. Eq. (4.18) is the one-branch fluorescence expression in the dominant moment approximation. For weighted fluorescence branches, each term in braces in Eq. (4.18) appears twice, once for each fluorescence branch, and is weighted by the effective line strength factors of Eq. (4.16). This two-branch expression is the formula used below to calculate $A_0^{(2)}$'s from corrected polarizations.

Another experimental complication is spin depolarization. As discussed in Sec. II.G, $N_2^+$ possesses nonspatial angular momentum vectors associated with the unpaired electronic spin $S$ and coupled nuclear spins $I$; these spins lead to a degradation or depolarization of the degree of observed alignment of the total orbital angular momentum $N$. This is because the addition of the electronic and nuclear spins to the total orbital angular momentum means that both $N$ and $J$ precess about $F$, which remains space-fixed in the lab frame. The spins interact very weakly with the scattering potential, so they do not become aligned in collisions with the He buffer.

However, it is possible to correct the alignment parameters for the spin depolarizations. There are several conventional formulas in the literature. Here, we correct for the depolarization of the nuclear spins only to obtain the true alignment of $J$. Specifically, each quadrupole alignment moment derived from a measured polarization according to Eq. (4.18) is corrected as:

$$p(2)_{\text{actual}} = p(2)_{\text{observed}}$$

with the correction factor $g^{(2)}$ given by: 21
\[ \bar{g}^{(2)} = \sum_{F_i} \frac{(2F_i+1)^2}{2I+1} \begin{bmatrix} F_i & F_i & 2 \\ J_i & J_i & I \end{bmatrix}^2 \]  

(4.21)

where the expression in braces is a Wigner six-j symbol and the sum is over all unresolved hyperfine levels. Since the LIF measurements are time-unresolved (cw) and since the linewidth of the laser is sufficiently narrow that coherent excitation of the unresolved hyperfine levels is not possible, this correction is applied to the LIF absorption step only. The \( \bar{g}^{(2)} \) factors approach unity fairly rapidly with increasing \( J \), as would be anticipated from the vector model. For the \( R_1(15) \) transition, Eq. (4.21) gives \( \bar{g}^{(2)} = 0.984 \), and the lowest \( J \)-state probed here, \( J=9.5 \), has \( \bar{g}^{(2)} = 0.960 \). Thus, this correction is essentially negligible at the level of detail of the current measurements. We do note that for sub-Doppler probing, there is an argument that Eq. (4.21) should be modified to include a factor \( w(F_i) \) in the summation that weights each term in the sum by the relative strength of each sub-Doppler hyperfine component at the given detuning. However, this approach was not explored.

C. Experimental & analysis techniques

As made clear in Sec. IV.B.3 above, in principle the two unknown alignment parameters \( A_0^{(2)} \) and \( A_0^{(4)} \) could be determined by measuring the LIF intensity at a grid of different angles \( (\chi_A, \chi_D) \) and then performing a linear least-squares fit. Additionally, if one is primarily interested in determining the dominant quadrupole alignment parameter, data in principle could be taken at the set of special angles \( (\chi_A, \chi_D) \) that force the geometrical coefficient \( \varepsilon(k_D = 2, k_A = 2, k = 4; k_{laser}) \) of the
\( A_0^{(4)} \) term to zero. This so-called “magic line” experiment\(^{21} \) yields a fluorescence measurement that is perfectly free of contributions from hexadecapole alignment.

Unfortunately, in experimental practice matters are not so tidy. Although this grid approach is explored below in Sec. IV.D, we believe this is not the most robust method for acquiring data on this experiment. There are several important pragmatic difficulties. For one, both long and short term fluctuations in ion density and ring dye laser power make comparison of polarization curves with more than a few points difficult. Additionally, for an arbitrary choice of angles \((\chi_A, \chi_D)\), a significant component of the polarized fluorescence will be due to isotropic polarization. However, the largest problem is that there remain unresolved systematics in the experiment. The spurious polarization systematics, discussed in Sec. IV.E, make a precise determination of the absolute value of alignment parameters very difficult. In practice, we found the best data were always obtained by comparing relative values of \( P(\chi_A = 90^0) \)'s as a function of laser detuning.

There are several advantages to this approach. As discussed above in Sec. IV.B, this scheme is in principle free of isotropic polarization contributions. Also, the linear polarization coefficients have a very simple interpretation: a true \( P(\chi_A = 90^0) \) of zero indicates no rotational alignment, while true positive (negative) polarization coefficients are associated with negative (positive) quadrupole alignment parameters, which in turn indicate a preference for the rotational angular momentum vectors to be aligned perpendicular (parallel) to the field axis. Only two angles of measurement are needed to obtain a data point, which greatly speeds the data acquisition, and the 0 and
90 degree polarizer settings measure the extremes of the fluorescence polarization, permitting the general trends of the experiment to be mapped out quickly. Additionally, long-term fluctuations in ion density and laser power tend to be canceled out by rapid, comparative $0^\circ/90^\circ$ measurements. The primary disadvantage of this method is that the higher-order hexadecapole moment $A_0^{(4)}$ must be neglected (i.e., set to zero) in order to obtain an $A_0^{(2)}$ quadrupole moment for each polarization coefficient, as discussed in Sec. IV.B.4 above. However, an approach frequently employed here is to ignore these underlying alignment parameters and treat the measured polarizations on a purely phenomenological level. Indeed, it can be argued that since there are unresolved systematics, the measured polarizations should be regarded as the fundamental entities, and only relative comparisons between these polarizations are valid. For the relatively high $J$ states studied here, this is a very reasonable approximation.

The mechanics of acquiring sub-Doppler polarization data are now discussed. The "atom" of data collection is the counting trial, which is a measurement of polarized LIF acquired at a specific laser detuning, with a specific fixed setting of polarizer angles $(\chi_A, \chi_D)$ for a given interval of time. For the above scheme, two trials with $\chi_A = 90^\circ$ and $\chi_D$ set sequentially to 0 and 90 degrees are needed to measure a $P(90^\circ)$. The trials are acquired at sub-Doppler laser detunings referred to in general as markers, even though, as discussed below, there may not be a physical marker at the chosen detuning. Trials are assembled together into sequences, which are designed to yield a certain number of polarization coefficients (or more generally,
polarization curves) for each marker. Sequences are run for one or more iterations before the trial data is written out to disk. Calibration files used to determine marker positioning are taken before and sometimes after the sub-Doppler data acquisition.

The choice of the best sequences for a given situation was determined by experience. In principle, the sequences can be of arbitrary length and complexity, involving many sub-Doppler markers with trial lengths of varying time duration. In practice, it was found best to keep things as simple as possible. The trial counting intervals were kept short to insure good time correlation between successive measurements. The longest trials used for any sub-Doppler experiment were 20 s. Additionally, although not necessary (and indeed, not optimal), the trials were the same length throughout the sequence. The sequences were kept fairly short to insure that the ring dye laser did not drift significantly in frequency or mode-hop; the longest sequences used consisted of 29 trials. In a single sequence, data were acquired at only one, two or three positions (referred to as signal or “A” markers) on a given Doppler profile, as well as one background position (“B” marker) at least 3.7 GHz (typically considerably more) from line center. The 2A/B and 3A/B sequences were employed about line center to interleave low-frequency and high-frequency trials, and to insure equivalent counting statistics for each marker. The 1A/B sequences were either used to acquire data in the wings of the line profiles or for diagnostic checks at line center.

Table 4.1 is an example of a 29-trial, 3A/B sequence which yields four polarization coefficients for each marker, for each iteration. In practice, it was found essential to “mix up” the trials and sequences to insure that one particular polarizer setting or marker is not being systematically favored. In particular, sequences must be
Table 4.1: Example of actual data collection sequence used for sub-Doppler alignment experiments. This is a “3A/B” sequence consisting of three signal (A) markers (numbered 0, 1, 2) and a background (B) marker (3). The 270 degree trials are treated as equivalent to 90 degrees and are taken to reduce wear on the rotation stage. The “mirror” sequence consists of just exchanging the 0 and 90 degree trials.

<table>
<thead>
<tr>
<th>Trial #</th>
<th>A Marker 0 $\chi_D$</th>
<th>A Marker 1 $\chi_D$</th>
<th>A Marker 2 $\chi_D$</th>
<th>B Marker 3 $\chi_D$</th>
<th>Trial Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td></td>
<td></td>
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<td>Total polarized LIF signal</td>
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<tr>
<td>2</td>
<td>90</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>3</td>
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<td></td>
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<td></td>
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<td>270</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>0</td>
<td></td>
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</tr>
<tr>
<td>7</td>
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<td>0</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>8</td>
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<td>270</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td></td>
<td></td>
<td>90</td>
<td></td>
<td></td>
</tr>
<tr>
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<td></td>
<td></td>
<td>90</td>
<td>0</td>
<td>LIF effective background</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>90</td>
<td>LIF effective background</td>
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<td>12</td>
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<td></td>
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<td>0</td>
<td>Total polarized LIF signal</td>
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<td>29</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>PMT dark count</td>
</tr>
</tbody>
</table>

Table 4.1: Example of actual data collection sequence used for sub-Doppler alignment experiments. This is a “3A/B” sequence consisting of three signal (A) markers (numbered 0, 1, 2) and a background (B) marker (3). The 270 degree trials are treated as equivalent to 90 degrees and are taken to reduce wear on the rotation stage. The “mirror” sequence consists of just exchanging the 0 and 90 degree trials.
arranged so that there are equal numbers of pairs of first, 0 degree, then 90 degree (0/90) measurements and 90/0 measurements. Additionally, "mirror" sequences are run in which the order of the 0/90 and 90/0 trials pairs are interchanged. These measures are necessary primarily because of the overall downward slope of the LIF signal with time, due to both losses in both laser power and ion density. Alternations in the polarization coefficients can often be seen which will correlate with this systematic.

Two techniques were used to position the ring dye laser in frequency space. The simplest method was just to designate positions by their digital-to-analog (D/A) setting. These so-called "software" frequency signal markers were set symmetrically about the onscreen A cursor in the data acquisition program (Eta-Spex) by a preselected digital-to-analog delta value; the B marker was set at the B cursor position. In the sub-Doppler trials, the ring laser was slewed at a preset rate to these D/A positions. Although more uncertain than hardware positioning, this technique was often good enough for acquiring diagnostic or plasma data, where the relative detuning from line center was not particularly critical. The second method was to use the 0.375 GHz free spectral range transmission peaks of the 20 cm ULE cavity as frequency markers, as discussed in Sec. II.C.2 above. The spacing of these "hardware" markers turns out to be quite appropriate for this experiment.

The relative detuning from line center was determined by taking an unpolarized calibration file immediately before the trial data. However, for the data acquired with the stepper motor rotation stage in the latter part of this work, a slightly different analysis technique was used. Because the polarizer was fixed in the stage
and could not be removed, a second unpolarized PMT channel was added to the bottom of the apparatus to allow for a better fit of the unpolarized calibration scan. Calibration files were taken both immediately before and after the trial data. The detunings were determined by fitting these unpolarized PMT signals to a 3-parameter Gaussian and then determining the average frequency marker position relative to line center. Frequency error bars could then be assigned by taking the difference between these positions.

For each trial, data from three 16-bit microcomputer-controlled counters are acquired. One counter accumulates the polarized fluorescence PMT signal. A second counter integrates a measure of “local” ring dye laser power during the trial, obtained from the normalization photodiode of the cavity-side lock system; a third counter records a count of laser unlock/lock transitions during the trial for diagnostic purposes. Both of these technical details are discussed in more depth in Sec. II.C. As discussed in Sec. II.E, the counters are hardware-gated by a crystal-locked trial gate generated by another counter. The counters are sampled at either 0.5 s or 1.0 s intervals, depending on gate width, and an average and sample standard deviation are calculated from these samples before they are discarded. A large standard deviation in the counting rate of either the PMT or ring dye laser power signal is usually an indication that something has gone amiss during the trial.

Acquisition program (Eta-Spex) output of typical trial data for a 2A/B sequence is shown in Table 4.2. Three sub-tables are contained in the output. The marker table, indexed by marker number, contains information about where the sub-Doppler markers fall in frequency space. The trial information table, indexed by trial
Table 4.2: Example of program data output. Three sub-tables are shown: the marker table, the trial information table, and the trial data table, and are discussed in the text.

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<tr>
<th>Marker #</th>
<th>Initial</th>
<th>Equivalent</th>
<th>D/A Position</th>
</tr>
</thead>
<tbody>
<tr>
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<td>108</td>
<td>3235</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>218</td>
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</tr>
<tr>
<td>2</td>
<td>21</td>
<td>470</td>
<td>339</td>
</tr>
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<table>
<thead>
<tr>
<th>Trial #</th>
<th>Xd</th>
<th>Xa</th>
<th>Gate Width (ms)</th>
<th>Sample T (ms)</th>
<th>Marker #</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>90</td>
<td>16000</td>
<td>1000</td>
<td>0</td>
<td>Pol LIF + Pol SLL bk + FA bk + PMT bk</td>
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<td>90</td>
<td>90</td>
<td>16000</td>
<td>1000</td>
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<table>
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<th>Trial #</th>
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Elapsed time for sequence iteration = 648 sec
number, stores the information needed to carry out the sub-Doppler trials, and contains the marker number as a pointer to the marker table. The trial data table, indexed by the trial number, contains the actual data acquired during the sequence. The data from the three counters appears in columnar form. Under each counter heading is the total counts accumulated during the trial, average counting rate per sample interval, and the sample standard deviation (note that there are only two independent pieces of information here). Although the actual sequences used for this particular set of experiments were quite simple, it should be emphasized that the programming of an arbitrarily complex sequence is possible with this technique. The trial information tables for the various sequences are data structures stored as program look-up tables that can be easily changed. Often “programming” of a new sequence was done on the fly and the program recompiled while the experiment was running. Since the stepper motor-driven rotation stage and hardware marker positioning are completely under computer control, much of the clerical work of data acquisition is almost completely automated.

Table 4.3 illustrates the calculation of corrected polarization coefficients from trial data. This table, which is appended by the acquisition program to the data files, contains the analysis of the same data shown in Table 4.2. Two corrections are always applied to the raw polarization data. An effective background, measured at the “B” marker, is subtracted from the total accounts accumulated during the LIF trial. The three contributors to this effective background are residual scattered laser light, unquenched flowing afterglow fluorescence, and PMT dark counts, the latter being the dominant component at typically 200 counts s\(^{-1}\). Flowing afterglow fluorescence
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**Table 4.3:** Example of program data analysis output, illustrating the analysis of the data shown in Table 4.2. The final background & laser-power corrected polarization coefficients are shown in bold.
is quenched by the neutral N$_2$ flow to approximately 40 counts s$^{-1}$ or less. Scattered laser light is held to typically less than 20 counts s$^{-1}$ (120 counts s$^{-1}$) for coaxial (perpendicular) probe. Note that careful beam transport, aided by the two prealigned counterpropagating HeNe lasers, is absolutely essential to minimize this background contribution. After background subtraction, the ring dye laser power dependence of the resulting LIF signal is corrected by simple division of the accumulated trial counts in the laser power channel. Diagnostic data indicate that the LIF signal remains linear with laser power up to the absolute maximum of 50 mW at the baffle arm entrances. A linear polarization coefficient is then calculated from the background and laser-power-corrected LIF signals as per Eq. (4.6). These calculation steps are shown explicitly in Table 4.3. Polarization coefficients are calculated from raw data and background-corrected-only data for diagnostic purposes; note that the laser power correction is typically small. Since these two corrections are always applied to the data, these are referred to as “uncorrected” polarization coefficients, meaning that no additional systematic corrections of any sort have been applied.

**D. Results**

Two sets of alignment data are presented in this section, acquired in the fall of '95 and the spring of '98. The fall '95 data have been previously published$^{27}$ and are discussed in Sec. IV.D.1. For a variety of reasons, it was felt necessary to perform the experiment again. These first data were taken with the production conditions in Fig. 2.3, which were subsequently found to lead to a significant zero-field axial ion velocity systematic, as discussed in Sec. III.E. There was some residual concern that
this systematic would invalidate the alignment results. Additionally, the polarization systematics in this first experiment were not adequately resolved. In particular, there was concern that the manual rotation stage PMT stack employed in the first work was introducing systematic errors. Most importantly, several other experiments have since been conducted by other groups suggesting that this particular experiment is perhaps a key link to understanding partially velocity-selected collision-induced rotational alignment. Thus a second set of experiments in the spring of '98 were conducted, focusing on possible rotational state effects. Results are presented in Sec. IV.D.2.

1. Field dependence of alignment for single rotational line

The basic experimental idea was to examine partial velocity-selected alignment for a single high-lying rotational state, \( R_1(N=15) \), for the two probe directions and several field strengths. Figures 4.5 (a) and (b) display these results for the three field strengths examined. All of this data were taken with the manual rotation stage PMT stack and the “software” sub-Doppler positioning scheme. There are several significant qualitative features to be explained in these data. For perpendicular probe at a fixed field strength, the polarization coefficients are essentially equal across the Doppler profile and the degree of polarization increases somewhat with increasing field strength. For coaxial probe at a fixed, non-zero field strength, the degree of polarization increases monotonically across the Doppler profile, and the slope of this increase appears to increase as well with field strength, as can be seen in Fig. 4.5 (b). Additionally, inspection of Fig. 4.5 will reveal that data points taken at the same laser detuning (i.e., absolute frequency) but at different field strengths do not in general have the same alignment.
Fig. 4.5 (a): Perpendicular probe polarization results for $R_1(15)$. The corrected polarizations are shown at the approximate sub-Doppler detunings at which they were acquired.
Fig. 4.5 (b): coaxial probe polarization results for $R_1(15)$. The corrected polarizations are shown at the approximate sub-Doppler detunings at which they were acquired.
It is important to keep in mind that the single-frequency LIF technique used in this experiment measures velocity vector projections along the laser propagation direction \( \hat{k}_{\text{laser}} \); ions that have laboratory velocity components along \( \hat{k}_{\text{laser}} \) in resonance with the laser frequency can absorb a photon, fluoresce, and, when in the LIF imaging region of the apparatus, be detected. As discussed in Chapter III, the result of probing in a particular direction is a steady-state velocity component distribution function, which is a projection of the complete ion velocity distribution function. If we assume that the components of the complete velocity distribution function are either completely uncorrelated or very weakly correlated and thus separable, the perpendicular and coaxial laser probe data provide two orthogonal “slices” of this distribution function. Probing perpendicular (parallel) to the drift-tube axis at a particular frequency effectively constrains the laboratory velocity component of the fluorescing molecules along \( \hat{k}_{\text{laser}} \), while the components transverse to \( \hat{k}_{\text{laser}} \) can vary over all possible values with a distribution given by the parallel (perpendicular) velocity component distribution. Thus, a specific probe direction gives an effective average over the other, orthogonal component.

A simple qualitative explanation of the features in Fig. 4.5 can be given, using the arguments above. The anisotropy of the relative velocity vector distribution is most pronounced in the field direction. The perpendicular probe polarizations always average over these anisotropies. If the velocity distribution function is separable, these data will then be insensitive to the particular velocity vector component selected by the laser and will be an effective average over the field direction. This would imply no variation across the Doppler profile for perpendicular probe and a fixed field strength;
as the field strength is increased, the field direction anisotropy increases, and the perpendicular polarizations increase as well. Likewise, the coaxial probe polarizations average over the radial or perpendicular velocity components, but now each data point represents a velocity slice taken along the direction of greatest anisotropy. For a fixed field strength, as the laser is scanned from the low to the high-velocity tail of a coaxial Doppler profile, the relative velocity vector distribution becomes increasingly more directed, as reflected by the increasing coaxial polarizations with increasing laser frequency. Again, the degree of anisotropy increases with increasing field strength, so the slope of the polarizations will increase. The polarizations of data points taken at the same laser frequency but at different field strengths will in general not be equal. Although these points have in common the scalar magnitude of the velocity component $v_i$ along $\hat{k}_{laser}$ selected out by the laser, these slices are drawn from different velocity distribution functions with different vector properties; the alignment is not solely dependent on this scalar component. Note in particular that if the observed alignment did somehow depend on the magnitude of $v_i$ alone, then it would be possible to observe alignment in the high- or low-velocity tail of a zero-field Doppler profile, contrary to both intuition and ample experimental evidence.

To obtain an approximate $m_J$ distribution picture, the polarization coefficients were corrected and converted into quadrupole alignment parameters (Sec. IV.B.4). A more thorough discussion of the cause of the systematics present in these measurements is given in Sec. IV.E. Pragmatically, what was done for these measurements is as follows. A set of diagnostic measurements was performed for
each probe geometry; a more extensive set was performed for coaxial than for perpendicular probe. One check involved removing the polarizer from the PMT stack and performing 0/90 degree stack rotations, as if polarization coefficients were being measured. Comparison of these “polarizations” with true polarization measurements taken by locking the PMT stack to one position and manually rotating just the polarizer indicates that the rotation of the entire PMT stack introduces a small degree of variation, which is believed due to small geometrical modulations of the effective detector solid angle as the PMT stack rotations are performed. Coaxial “polarization” measurements taken under plasma conditions at line center with no polarizer in the stack yield a coefficient x 100% of -1.59 ± 0.07. From each pair of these 0/90 degree isotropic measurements, a geometrical correction factor $f$ can be calculated

$$f = \frac{I_{0^\circ \text{measured isotropic}}}{I_{90^\circ \text{measured isotropic}}} = 0.969 \pm 0.004, \quad (4.22)$$

which can then be used to multiplicatively correct the 90 degree background and laser-power corrected LIF intensities for the actual polarization measurements as

$$P(90^\circ)_{f\text{-corrected}} = \frac{I_{0^\circ \text{measured}} - f I_{90^\circ \text{measured}}}{I_{0^\circ \text{measured}} + f I_{90^\circ \text{measured}}}. \quad (4.23)$$

However, there was an additional unidentified source of spurious polarization in this first experiment. Coaxial laser probe plasma measurements made with the rotation stage locked at 0 degrees and with just the polarizer itself manually rotated to 0/90 degrees yield a polarization coefficient x 100% of -1.98 ± 0.07, indicating that the geometrical modulation is not the only systematic present. Although not a completely satisfactory treatment, this offset was merely subtracted from the
polarizations corrected via Eq. (4.23) to obtain a set of corrected polarizations, as shown in Fig. 4.5. Obtaining a more consistent method of correcting for systematics in the polarization measurements was one of the primary motivations for building the stepper-motor-driven PMT stack discussed in Sec. II.D.

These corrected polarizations can be converted into $A_0^{(2)}$ alignment parameters using the relations in Sec. IV.B.4. An approximate $m_J$ distribution picture for the various sub-Doppler "slices" can then be obtained from Eq. (4.11) above. The $m_J$ distributions for the 16 Td coaxial data are shown in Fig. 4.6.

2. Rotational quantum state dependence of alignment

All the data in the above section were acquired on a single rotational state. However, there is considerable interest in examining whether different rotational states will exhibit significantly different alignments. The focus of the experiment discussed in this section was on exploring possible relative differences between sub-Doppler polarizations acquired on different rotational lines, taken under otherwise identical conditions. As in Sec. III.D.1, measurements were confined to a single field strength—12 Td—and the parallel probe direction.

Figure 4.7 displays the "raw" data from this set of experiments. Coaxial probe linear polarization coefficients were measured for a total of five rotational lines (four para lines, one ortho) for a variety of laser detunings, all at a fixed field strength of 12.0 Td. The $R_1(N'' = 17)$ transition is not accessible by any combination of ring dye laser birefringent filter/thin etalon/intracavity Brewster plate tunings and thus could not be measured. Additionally, the poor signal-to-background levels of the $R_1(19)$
Fig. 4.6: Corresponding $m_j$ distributions derived from the 16 Td coaxial probe corrected polarization coefficients, as numbered in the top panel.
Fig. 4.7: Raw polarization data from rotational state alignment experiment. The sub-Doppler polarizations at shown at the detunings at which they were acquired, relative to the line center of the respective transition. The "hardware marker" method was used to position the laser in frequency space; thus the frequency uncertainty is well-represented by the size of the symbols on the plot. The range of the means of the coaxial probe plasma measurements, shown in Fig. 4.8 (a), is indicated by the dotted lines; these lines are taken as the empirically-determined "line of isotropy" for this experiment.
transition prohibited acquisition of sub-Doppler polarization data on the wings of the transition; the $R_1(20)$ line in the ortho manifold was "substituted" for $R_1(19)$ in order to acquire high-$J$ wing data. The decrease in spacing between the spin-rotation doublets with decreasing $N$" prevented acquisition of lower $J$-state data because the low-velocity tail of the $J_1$ branch will overlap the high-velocity tail of the $J_2$ branch, leading to ambiguities in data interpretation. The uncorrected (i.e., background and laser-power-corrected only) polarizations are shown at the relative detunings from the respective line centers at which they were acquired, as determined from a single Gaussian fit to the unpolarized PMT calibration scan. The "hardware marker" method was used to position the ring laser in frequency; the uncertainty in frequency positioning is well-represented by the size of symbols in the figure. The stepper motor driven rotation stage was used exclusively for this experiment. All of these data were taken under completely identical laser polarization and fluorescence detection optics. Several of the points in Fig. 4.7 on a given rotational line were acquired on different days, providing excellent corroborating evidence of the reproducibility of the data set.

Because of the unresolved systematics, a very pragmatic approach was taken to determine the "zero" of alignment for each transition. A plasma (all fields off) measurement was made for each of the rotational states at line center to determine what uncorrected polarization corresponds to no alignment. These data are presented in Fig. 4.8 a). Note that the uncorrected plasma polarizations are reasonably independent of $J$-state, within error bars, as one would anticipate if the systematic is primarily due to geometrical imaging, as discussed below. Shown in Fig. 4.8 b) are the results of a vertical-matching diagnostic experiment, performed to assess the
Fig. 4.8: Systematic plasma polarization checks. a) coaxial plasma polarization coefficients as a function of rotational state, measured at line center.
b) $\chi_A$ vertical-matching check, performed on $R_1(15)$ at line center.
matching of the laser polarization axis "vertical" with the fluorescence detection axis. The Glan setting of 86 degrees was the minimum of these polarizations; all data shown here were taken with this setting.

The range of plasma polarizations for all rotational lines measured is shown by the dotted lines in Fig. 4.7. Note that the "slope" of the polarizations for each rotational line in the figure appears to be the same for all measured rotor states. However, there is a dramatic difference in the "offset" of these lines that is well outside the measurement error bars. The lines shift downward with decreasing J such that for J = 9.5 and 11.5, the low-velocity tail polarizations are considerably below the empirically-determined "line of isotropy". If the interpretation of these data is correct, the alignment parameter $A_{0}^{(2)}$ is changing sign from positive (i.e., m$_{J}$ distribution bowed up) in the low-velocity tail to significantly negative (m$_{J}$ distribution bowed down) in the high-velocity tail. As discussed in more depth below, we believe that the slopes of the polarizations are related to the change in the relative velocity vector distribution across the Doppler profile. The polarization slopes are the same because all of these states have virtually identical relative vector distributions at 12 Td. The offset of the lines is related to tensor cross section information. These offsets are pronounced because this experiment essentially measures partially-integrated differential cross sections due to the partial velocity selection obtained by measuring polarizations as a function of one component of the ion laboratory velocity. Although not entirely satisfactory, we make the simplest data correction possible to the polarizations by just subtracting off the average plasma polarization for each
respective rotational line. These corrected polarizations are shown in Fig. 4.9, along
with an additional x-axis that gives the approximate value of the laser-selected
velocity component along the tube axis, relative to the mean buffer gas velocity.

E. Possible systematics

For any collision-induced alignment experiment, it is essential to have a set of
conditions that are known to produce no alignment. These conditions essentially
define the "zero" of alignment and allow one to detect and (hopefully) correct for any
systematics present. A very important systematic check for this particular experiment
for either probe geometry is performed by recording sub-Doppler polarization
measurements with both the charge-separation and drift fields off. As discussed in
Chapt. III, the N₂⁺ molecules in the resulting plasma experience no field and therefore
their velocity distribution should be strictly Maxwell-Boltzmann, with a resulting
linewidth characterized by the temperature of the buffer gas. The relative velocity
vectors \( \mathbf{g} \) of the N²⁺-He pair are isotropically distributed and no alignment is possible.

In principle then, all zero-field P(90°)'s for either probe geometry and at any laser
frequency should vanish. Unfortunately, these measurements are not entirely free of
spurious polarization, which results in non-zero fluorescence polarization coefficients
even in the complete absence of molecular alignment. For this experiment, spurious
polarization acts as the major systematic error that affects the accuracy of the
alignment parameters calculated from the measured polarization coefficients.

In this experiment, exhaustive checks were performed to determine the cause
of this systematic. Frequently-cited causes of spurious polarization, such as stress-
induced birefringence on the laser entrance windows or LIF windows, or glancing-
J-state dependent linear polarizations: coaxial laser probe at 12 Td, identical conditions throughout

Fig. 4.9: Polarizations of Fig. 4.7, with simple subtractive correction made to each point.
angle polarizing reflections off of metallic surfaces were ruled out. One trend noted quite early was that the coaxial laser probe polarizations at plasma line center tend always to be negative, while perpendicular laser probe polarizations tend to be positive. This trend became extremely pronounced once the stepper motor-driven rotation stage was employed. It is now believed that the non-zero polarizations are primarily geometrical in nature. What is being imaged in this experiment is a bar of fluorescence over a finite, irregularly-shaped solid angle. Changing the probe direction changes the orientation of the bar, thus changing the sign but not the magnitude of the observed polarization. An attempt was made to model this supposition by starting with the generalized expressions for polarization tensor elements.\textsuperscript{21} These elements are functions of two sets of Euler angles. By treating a point fluorescence source and integrating over the set of angles corresponding to variations either along or perpendicular to the tube axis, qualitative correspondence was obtained with the trends observed in the experiment. However, the range of solid angle needed to obtain quantitative correspondence is considerably greater than any of the effective apertures employed. Future work is planned on modeling this problem more comprehensively.

\textbf{F. Discussion & dynamics theory}

A steady-state set of equations that describes the population of the state multipoles $T_j^k$ has been previously derived, first by Meyer \textit{et al.}\textsuperscript{14} and subsequently rederived by Follmeg \textit{et al.}\textsuperscript{12} The equations are:
\[
\sum_{j_f, K_f, \lambda} \left( \lambda + \frac{1}{2} \right) T^K_{j_f} \int_0^\infty dg \ g^3 \ \chi_{j_f}^{K_f}(g) \ \chi_{j_f}^{K_f}(g) = \\
\sum_{j_f, K_f, \lambda} (-)^{2j_f} \left( \lambda + \frac{1}{2} \right) \sqrt{[K_i][K_f][j_f][\lambda]} \times
\]

\[
\left( \begin{array}{ccc} K_i & K_f & \lambda \\ 0 & 0 & 0 \end{array} \right) \left( \begin{array}{ccc} K_i & K_f & \lambda \\ j_i & j_i & j_i \end{array} \right) T^K_{j_i} \int_0^\infty dg \ g^3 \ \chi_{j_i}^{K_i}(g) \ \chi_{j_i}^{K_i}(g)
\]

where \([X] = 2X + 1, \{\ldots\}\) and \{\ldots\} are the Wigner 3-j & 6-j symbols and \(g\) is the relative speed of the ion-neutral pair. The quantities \(\lambda f_j^K(g)\) and \(\lambda \sigma_{j_i}^{K_i}(g)\) are the \(\lambda\)th coefficients in the expansion of the relative velocity vector distribution and tensor cross sections in Legendre moments, respectively, and are discussed in greater detail below. The \(T^K_j\) are the state multipoles in which the density matrix \(\rho_{mm}^j\) can be expressed in the standard expansion\(^24\)

\[
\rho_{mm}^j = \sum_K (-1)^{j-m} \sqrt{2K+1} \left( \begin{array}{ccc} j & j & K \\ m & -m & 0 \end{array} \right) T^K_j
\]

The \(T^K_j\)'s are related to the experimentally obtainable alignment parameters \(A_0^{(K)}\) by rescaling factors, given explicitly below.

In both the work of Meyer and Follmeg, a velocity-dependent form of the density matrix expansion of Eq. (4.25) is used:

\[
\rho_{mm}^j(v) = \sum_K (-1)^{j-m} \sqrt{2K+1} \left( \begin{array}{ccc} j & j & K \\ m & -m & 0 \end{array} \right) f_j^K(v) T^K_j
\]

where the velocity form factors \(f_j^K(v)\) are supposed to contain all of the velocity dependence of the state multipoles \(T^K_j\). However, in both works it is subsequently assumed that all \(K>0\) velocity form factors are equal to the \(K=0\) term that essentially
describes the ion velocity distribution function (independent of alignment). This function just factors out of the density matrix expansion and the $K$ index becomes ignorable. Equation (4.24) can then be written in slightly revised notation by just dropping the $K_i$ superscript on the $f$'s as:

$$
\sum_{j_f, K_i, \lambda} \left( \lambda + \frac{1}{2} \right) T_{j_f}^{K_i} \int_0^\infty dg \ g^3 \lambda f_{j_f}(g) \lambda \sigma_{j_f \rightarrow j_i}^{K_i K_f}(g) =
\sum_{j_f, K_i, \lambda} (-)^{2j_i} \left( \lambda + \frac{1}{2} \right) \sqrt{[K_i][K_f][j_f][\lambda]} \times
\left( \begin{array}{ccc} K_i & K_f & \lambda \\ 0 & 0 & 0 \end{array} \right) \left( \begin{array}{ccc} K_i & K_f & \lambda \\ j_i & j_i & j_i \end{array} \right) T_{j_f}^{K_i} \int_0^\infty dg \ g^3 \lambda f_{j_f}(g) \lambda \sigma_{j_f \rightarrow j_i}^{\lambda 0}(g) 
$$

(4.27)

As pointed out in both works, this means that the velocity distribution function is assumed to be the same for each rotor state, so the $j$ indices in Eq. (4.27) are redundant as well. These assumptions were made for both experimental & theoretical reasons. Experimentally, there were no good measurements of rotor-state dependent velocity distributions; theoretically, there was no good development on what these $K$-dependent velocity form factors should be. The apparent removal of velocity dependence from the density matrix expansion seems paradoxical, since as the experiment has evolved, we became explicitly concerned with the dependence or correlation of alignment parameters with one component of velocity, and all this information appears to be gone.

Although not solved explicitly by Meyer, and discussed briefly by Follmech, it should be pointed out that Eq. (4.27) describes a practical, working set of equations that can be solved for the state multipoles of any rotor state, given velocity distribution functions and tensor cross sections for each rotor state, the two
ingredients that are the real physical content of these equations. The structure of these
equations is discussed in more detail in the thesis of Follmeg. Equation (4.27) can
be written in matrix form as:

\[ A \tilde{T} = B \tilde{T} \]  \hspace{1cm} (4.28)

where matrix \( A \) is associated with the right hand ("depopulation") side of Eq. (4.27),
and \( B \) with the left hand ("population") side. It should be pointed out that the key to
understanding the matrix structure of this equation is recognizing that \( j_i \) and \( K_f \) are
free indices, i.e., Eq. (4.27) must be true for any choice of \( j_i \) and \( K_f \). There is an
analogy to a much simpler set of kinetic or master equations that describe just the
populations of each state, which allows the structure of \( A \) and \( B \) to be easily seen. As
discussed by Follmeg, Eq. (4.28) can then be solved for the solution vector \( \tilde{T} \) as:

\[ B^{-1}A \tilde{T} = \tilde{T} \]  \hspace{1cm} (4.29)

an eigenvector equation. The solution vector \( \tilde{T} \) is the eigenvector of matrix \( B^{-1}A \)
associated with the eigenvalue 1 and can be found numerically. The elements \( T_j^K \) of
the solution vector can then be related to the experimentally-obtainable alignment
parameters \( A_0^{(K)} \) through the relation:

\[ T_j^K = \frac{\sqrt{2K+1}}{\langle j || J_j^{(K)} || j \rangle} \langle J_j^{(K)} \rangle \]  \hspace{1cm} (4.30)

where the \( \langle J_j^{(K)} \rangle \) are ensemble averages of the spherical tensor operators.\(^{29}\)
Explicitly, for the \( K=2 \) and 4 quadrupole & hexadecapole alignment parameters, the
relations are:
with the reduced matrix elements given by Eq. (4.10) above. As discussed by Follmeg,\textsuperscript{12} to match up a numerically-calculated $\bar{T}$ vector with experimentally-obtained alignment parameters via Eq. (4.27), the $\bar{T}$ vector must be normalized such that the trace of each $j$th sub-block of the density matrix equals 1, i.e., the $T_j^K$'s must satisfy:

$$\sum_m \rho_{nm}^j = \sum_m \sum_K (-1)^{j-m} \sqrt{2K+1} \binom{j}{m} \binom{j}{m} T_j^K = 1 \quad (4.32)$$

Unfortunately, the formalism developed for the original broadband experiment is not appropriate for this experiment, in which one laboratory component of ion velocity is essentially completely specified by the single-frequency LIF technique. Equation (4.24) above was derived starting from a statement of detailed balance at steady-state for each rotor state $|j,m_1\rangle$:

$$\sum_{j_f} \sum_{m_f} k_{j,j_f,m_f} \langle j_f m_f | j m_1 \rangle = \sum_{j_f} \sum_{m_f} k_{j,j_f,m_f} \langle j_f m_f | j m_1 \rangle \quad (4.33)$$

where the $k$'s are fully-velocity averaged state-to-state rate constants:

$$k_{j,j_f,m_f} = \int_{-\infty}^{+\infty} d^3 v_1 \int_{-\infty}^{+\infty} d^3 v_2 f_1(v_1) \rho_{m_1 m_2}^{j_1} (v_2) \left\langle g | \sigma_{j,m_1 \rightarrow j_f,m_f} (g) \right\rangle \quad (4.34)$$

The buffer gas coordinates in Eq. (4.34) are denoted with "1" subscripts, and the ion molecule coordinates are denoted with "2" subscripts. Note that Eq. (4.34) already contains integral state-to-state cross sections. For the case here, it is necessary to start with a detailed balance equation that involves differential cross sections, and attempt
to integrate these over center-of-mass coordinates to obtain integral cross sections.

The starting equations might be:

\[
\sum_{j_f} \sum_{m_f} \int d^3v_1 \int d^2\hat{v}_2 f_1(v_1) \rho^{j_f}_{m_f} (v_2) \left| v_{2i} - v_1 \right| \frac{d\sigma}{d\Omega_{j_m \rightarrow j_f m_f}} (g_i, \Theta_f) 
\]

(4.35)

with \( g_i = v_{2i} - v_1 \), \( g_f = v_{2f} - v_1 \) and \( \Theta_f \) the angle between \( v_{2i} \) and \( v_{2f} \). This set of equations is completely analogous to the starting point of the fully-velocity averaged equations, except that another index has been added, the velocity vector \( v_{2i} \). The left and right-hand sides of Eq. (4.35) describe the depopulation and population of the lab velocity-labeled rotor state \( \left| j_i m_i \right\rangle (v_{2i}) \). On the left hand side, the integrands can be rearranged to obtain an integral cross section fairly easily as:

\[
\int d^2\hat{v}_2 f_2 \frac{d\sigma}{d\Omega_{j_i m_i \rightarrow j_f m_f}} = \sigma_{j_i m_i \rightarrow j_f m_f} (g_i) 
\]

(4.36)

(the “hat” notation denotes an angular integral). In words, this is because we are just concerned with the depopulation of a particular chosen vector \( v_{2i} \) into all possible final vectors. However, the right hand side, problems are encountered as the center-of-mass velocity \( G \) cannot be easily integrated out of the population differential cross section. This is because, loosely, one needs to integrate over all final lab velocity vectors \( v_{2f} \) in a “funny way” to get the particular \( v_{2i} \) chosen. This complication makes it much harder to “integrate out” to an integral cross section that could in principle be calculated by some formalism. This is because the differential cross sections that depend on relative velocity must be integrated in such a way as to meet
the "constraint" imposed by completely specifying one vector component in the lab frame. Additionally, because this is not a single-collision experiment, there is no concept of "before" and "after" or initial and final. All that can be known is that the molecules observed were in a particular quantum state and have one completely specified component of velocity.

G. Conclusions

It has been demonstrated that LIF rotational alignment experiments involving charged species in a drift tube or plasma environment are possible. A fairly powerful methodology for measuring alignment parameters by single-frequency polarized LIF has been detailed. For \( \text{N}_2^+ \) drifted in He, a strong correlation is found between the degree of rotational alignment for a single rotational line and the velocity subgroup when probed parallel to the tube axis. Furthermore, a dramatic difference in velocity-selected alignment as a function of rotational state is observed when probing coaxially for a fixed field strength (12 Td). The slopes of these polarization curves are believed related to the relative velocity distribution of the ion-buffer pair; the offsets are believed to be giving tensor cross section information. Additionally, it appears that, for sufficiently low rotational state, the quadrupole alignment parameter is changing sign across the Doppler profile, behavior that has not been observed in an alignment experiment before, to the best of this investigator's knowledge. There is evidence presented here that supports the hypothesis that velocity-subgroup alignment is the "generic" behavior of any gas phase system in which there is some sort of anisotropic (non-Maxwell-Boltzmann) velocity distribution.
References for Chapter IV


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APPENDIX A

Contains various electronics circuits constructed by this investigator in the course of experiments:

A.1 Simple analog divider circuit.

A.2 Simple window detector circuit.

A.3 Stepper motor driver for rotation stage ("Steppingstein").
Fig. A.1: Simple analog divider circuits, used in conjunction with 0.375 GHZ FSR cavity and laser power photodiode.
Fig. A.2: Simple window detector used for detecting unlock/lock transitions on reference cavity
Fig. A.3: Stepper motor driver for rotation stage (1 of 2)
Fig. A.3: Stepper motor driver for rotation stage (2 of 2)