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DOPPLER SHIFTED FOURIER TRANSFORM EMISSION SPECTROSCOPY

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

By

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1995

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CHAPTER I

Introduction

1.1 Doppler Shifts and Ion Spectroscopy

The existence of a small, but detectable, Doppler shift \( \Delta \nu / \nu_0 \sim 10^{-6} \) associated with molecular ions produced in a DC glow discharges was first observed in 1975 by Woods et al.\[1\]. in their measurement of \( J=0-1 \) rotational microwave absorption frequency for HCO\(^{+}\). They found that the frequency exhibited a small systematic deviation from astrophysical measurements on the ions\[2\]. Based on simple gas phase mobility considerations\[62, 71\], the ion drift velocity, \( u_d \), in the axial electric field of the discharge was estimated to be about 1 km/sec, consistent with the measured shift, according to the well-known relation

\[
\frac{\Delta \nu}{\nu_0} = \frac{u_d}{c}
\]  

(1.1)

The shift was further confirmed and reliably measured after they reconstructed their spectrometer by employing symmetric electric electrodes in the discharge cell and a DC power supply that could be reversed in polarity\[3\]. Similar observations for several other ionic species have also been made by Delucia and co-workers\[4\]-\[7\].

Such kinds of observations are of course important from the standpoint of obtaining accurate rest frequencies for transitions. But more interestingly the results
demonstrate that by means of spectroscopy one can distinguish between an ion's non-random motion and its random thermal motion within the positive column of a discharge, which are respectively related to the Doppler shift and the linewidth respectively. Since neutral molecules (at least, ground state neutral molecules) usually have only thermal motions, an immediate application of the phenomenon is that the shifts can be used to distinguish between ionic and neutral spectra. Over the past decade, techniques based on this principle, known as velocity (or Doppler) modulation spectroscopy, have been extensively used in molecular ion spectroscopy and proven a powerful spectroscopic tool for selectively obtaining ionic spectra. Transition frequencies employing this method have been observed from the microwave through the infrared to the visible. The Saykally group at the University of California at Berkeley[8]-[10] is one of the major contributors to the development of the field. Rather than switching the polarity of a DC discharge, they used a radio frequency AC glow discharge and phase-synchronous demodulation of the infrared laser radiation absorption. The introduction of IR lasers as well as the improved data acquisition and processing electronics have greatly improved the method's sensitivity and have given rise to the capability of discriminating against the overwhelmingly more abundant neutral species that exist in a plasma. Similar schemes have been adopted by many other research groups around the world. Ion spectroscopy has benefited numerously from technical breakthrough based on the of Doppler shifts of ionic spectra.
1.2 Doppler Shifted Fourier Transform Spectroscopy

While laser-based velocity modulation spectroscopy provides high sensitivity and high resolution, its relatively narrow spectral coverage can be a problem. In many applications, wide spectral coverages is of importance. To overcome the limitation of laser spectroscopy with respect to the spectral coverage, Fourier Transform Spectroscopy (FTS) certainly provides an attractive alternative through its unique combination of wide spectral coverage, multiplex advantage and high resolution[11]-[16]. Additionally, FT spectrometers are usually very stable both mechanically and optically and also very easy to operate. These advantages have made FTS very useful for producing high resolution spectra of stable molecules and ions on an almost routine basis. It can provide a large amount of information within a relatively short time. Unfortunately, the much poorer sensitivity of FTS has severely limited its use for the spectroscopic study of molecular ions or radicals. The sensitivity limitation is fundamental to FTS, whose principle is based on light interference, for two main reasons. First, to generate a detectable interferogram within a limited time duration, a photon flux is required, which would cause a high threshold for signal detection. Secondly, due to the finite length of the sampled light wave trains the interferences among lines of different frequencies are inevitable. The later is particularly harmful for cases where weak lines are close in frequency to strong lines as severe distortion or even disappearance to those weak lines is possible. As is well known, it is very common that weak ionic lines overlap with strong neutral spectra whenever a plasma source is used.
Despite its limitations in sensitivity, FTS remains attractive to both research and industrial application because it offers features that are unmatchable by other techniques. As a matter of the fact, the improvement of the instrumentation of both spectrometers and sample sources has extended the capability of FTS. Several very reactive radical neutrals or ions have now been studied by FTS[17]-[22]. Since the purpose of the present thesis research is to deal with stable ions and neutrals rather than search for spectra of new ions or radicals, the sensitivity was not a great problem. We mainly take the advantage of the wide spectral coverage, high resolution and high stability of the FT spectrometer.

The combination of FTS and velocity modulation was first demonstrated by Martin and Guelachvili in 1990[23]. Using either the polarity-switching scheme of a DC discharge or phase modulation of a AC discharge they observed Doppler shifts for emission of ground state ArH* vibrational transitions. We have begun this thesis research by adopting the similar DC polarity-switching scheme to observe and measure Doppler shifts in emission spectra of excited species in plasmas using a high resolution Fourier transform spectrometer. However, our work has mainly dealt with the electronic state transitions in the visible frequency region rather than the traditional vibrational transitions in the infrared region studied by FTS.

Unlike most velocity modulation studies that are centered around searching for new ion spectra or demonstrating the capabilities of the method for doing so, we have devoted ourself to the study of Doppler shifts in plasma line emissions themselves as a phenomenon and their relationship to the basic atomic, molecular and photon physics
as well as to the discharge plasma physics. Doppler shifts are studied for a much wider variety of systems than in any previous research. The carriers of Doppler shifted spectra range from long-lived to short-lived ionic species to even neutral molecules and atoms. We have found it a very rich and interesting new area to explore both experimentally and theoretically.

1.3 Study of Doppler Shift as a Phenomenon

1.3.1 Doppler Shifts of Ionic Spectra

For the past decade or so most of the reported work involving Doppler shifts have been focused on study of ion spectroscopy rather than Doppler shifts themselves. More specifically, Doppler shifts were just used as labels to selectively obtain spectra of ions in a plasma. Towards this end, great success has been achieved through the research of years.

Much less attention has been paid to the understanding of the underlining physics of Doppler shifts that occur under various circumstances. This is because a majority of velocity modulation experiments were dealing the infrared laser absorption of ground state ions in plasmas. For ground state ions, the associated Doppler shifts reflect simply the stead drift velocities of the ions in gases where electric fields are present. The drift velocity, $u_d$, is given by

$$u_d = K\epsilon$$ (1.2)

where $K$ is the ion's mobility and $\epsilon$ the external electric field. Ion mobilities and plasma fields have been the traditional areas of ion transport and the plasma physics.
For more than a century there have been developed various experimental tools and a large accumulation of related data also[24]. The simple relation of Eq.(1.2) describes important aspects of ion's translational motion that cause the Doppler shifts in absorption spectra. Few new phenomenon or new mechanisms pertaining to the chemical and physical processes of ions in a discharge can be discovered solely through observations of Doppler shifts for ground state ions.

The situation is, however, quite different when studying Doppler shifts in emission spectra. For ions, lifetimes of the emitting excited states vary by several orders of the magnitude, resulting a drift velocity from near zero to virtually the steady values. For emitting ions with a very short lifetime, the relation of Eq.(1.2) is clearly invalid because the ions may never reach the steady drift velocity under a given field and pressure condition.

In such circumstance, the ion's drift velocity that is observed as a Doppler shift depends on not just the momentum transfer collisions as the case of ground state ions but many other factors and processes as well. They may include, as witnessed in our experiments, the ion's lifetime itself, the quenching of the excited state ions and the way that the excited ions are created. The involvement of these factors makes Doppler shift of ion emission differ from that of absorption spectra most remarkably. For emissions from different electronic excited states of the same ion in identical environment, the Doppler shifts may be distinctly different in terms of either the magnitudes or the behaviors towards the change of the discharge conditions. Therefore, Doppler shifts of excited ion emissions can carry new information that are unable to be carried by
ground state ions. For example, Doppler shifts for excited state ions are sometimes extremely sensitive to the mechanisms that produce the emissive ions. By analyzing the Doppler shift data one may establish the mechanisms of producing excited state ions in a plasma as we have done for excited Ar ions in a He discharge. The reason why those ions can provide such information is apparently because of their short lifetimes. By the time an excited ion emits a photon it still 'remember' completely or partially the history of how it was created and will 'write' it on the emitted photon as a Doppler shift. The ground state ions in a plasma may also be created by various mechanisms. However, their effectively infinite lifetime washes away any 'memories' of their creation.

Despite their limited role as a probe of chemical and physical process in plasmas, Doppler shifts of ground state ions as an alternative probe have certain advantages over the traditional drift-tube based techniques for determining ion's mobilities or plasma fields. Haese, Pan and Oka at the University of Chicago have measured Doppler shifts in the fundamental and hot bands of ArH+ produced in a He discharge[26]. Combining the Doppler shift data with measurements of the electric field by inserting wire probes into the plasma, the ion's mobility were obtained. In their experiment, large Doppler shifts that are comparable to the linewidth were observed and the resulting mobilities were found to agree nicely with classical measurements of ArH+ mobilities in He based on drift tube data. Alternatively, Radunsky and Saykaley[25] have determined the axial electric field of the positive column of a He/N2 glow discharge from the Doppler shifts in the absorption spectra of ground
state $N_2^+$ in discharges and the known mobility values of ground state $N_2^+$. Apparently, the Doppler shifted stereoscopy measurement for electric field has the advantage over the traditional Langmuir probes in term that the measurement does not alter the plasma itself.

Recent experiment of Hirohazu Hori et al. is among few that deal with excited ions. By measuring Doppler shifts in laser absorption spectra, they have determined mobilities of excited Ca$^+$ and Cd$^+$ and compared them with the known mobility values of the corresponding ground state ions[27].

1.3.2 Doppler Shifts in Neutral Emission Spectra

This is essentially a new area in the field of the Doppler shifted spectroscopy. For the first time, we have observed Doppler shifts in emission spectra of neutral molecules and atoms. It appears that a similar phenomenon, velocity modulation in the IR absorption spectra, has been observed by Oka and co-workers[28, 29]. However, no detailed description of their observation has been reported. In the following, we will introduce this subject, in a most conceptual way, by giving the physical pictures of those newly observed phenomena.

Doppler Shift in Neutral Molecule's Emissions

A Doppler shift can be viewed as a measure of the non-random motion of the particles that carry the spectrum. Unless neutral molecules possess some degree of orderly
motion in a non-flowing gas, a Doppler shift should not be expected to appear in their spectra. It is indeed hard to imagine that neutral molecules in a gas (at rest) can have, on an average scale, a non-random motion. However, one shouldn't take it as granted that such situation will never come into existence.

It seems safe to assume that, even in the presence of an electric field, the motion of neutral molecules in a gas is totally random, i.e., without any preferential direction in velocity space. This is true if the gas contains only neutral particles. Care must be taken when both neutral and charged particles are present in a gas such as a discharge plasma, which is a mixture of neutral species, ions, electrons and photons. In such a case, for certain component of neutral particle's velocity, usually the one along the direction of the electric field, the ensemble average may become non-zero, i.e., the neutrals show some orderly motion. This orderly motion is, as proved in our experiment and theory, still created by the electric field, however, now indirectly through the intermediary of charged particles that collide with the neutral molecules. Charged particles always possess a non-zero average momentum component because they drift in the direction of the field in the gas. During collisions the charged particles pass this component, either partially or totally, to the neutral molecules, the latter, as a result, possess a non-zero average velocity component.

The next question is, of course, if this component is detectable under usual conditions, for example, in a glow discharge plasma. The answer is yes at least for a particular group of molecules in the gas, i.e., the molecules in short-lived excited states. In the plasma in our experiment, the excited neutral molecules are produced
by electrons impact on the ground state molecules and then emit photons after (on average) $\tau_e$ seconds, with $\tau_e$ the radiative lifetime of the excited states. If $\tau_e$ is shorter than the molecule-molecule collision time ($\tau_c$), i.e.,

$$\tau_e < \tau_c \quad (1.3)$$

the excited state molecules will 'remember' exactly the initial 'push' from the exciting electrons and move with the initial momentum transferred from the electrons as well as that inherited from their parent ground state molecules. This transferred momentum component may show up as a Doppler shift in the emission from the excited molecules.

Indeed such shift has been, for the first time, clearly observed in our experiments for several neutral molecules and atoms in discharges. For light molecules like H$_2$, the shift is large enough ($\Delta \nu \approx 0.02 \text{ cm}^{-1}$ at $\nu_0 \approx 20000 \text{ cm}^{-1}$, corresponding a non-zero velocity component of 300 m/s. Surprisingly big!) to be reliably measured. As expected, the Doppler shift shows many characteristics that are totally different from the Doppler shifts of positive ions, reflecting its different origin from that of Doppler shifts of ion spectra.

Ergo, the basic physical picture for the Doppler shift in a neutral molecule's emission is quite simple and clear. It has allowed us to establish a theory for quantitative description of the phenomenon. The theory has explained all the experimental results by predicting the dependence of observed Doppler shift on various factors, including, the properties of the molecules themselves, the details of electron-molecule interaction and parameters and processes that are presented in a discharge plasma.
Apparently, the investigation of the Doppler shift in neutral emission is of considerable interest as the phenomenon itself is a new one, and more importantly, it may carry information that may be difficult to be obtained by any other mean. The understanding of the underlying physics may make it possible for it to serve as new probes for many chemical and physical processes in a discharge.

On the other hand, the observation of Doppler shifts in neutral emissions has also inspired us to think of and look for some related new phenomena. Such successful example will be introduced below.

**Radiation Trapping and Doppler shifts**

In principle, there might also be a non-zero averaged velocity component associated with ground state molecules as long as there are charged particles and collisions between the charged particles and ground state molecules. However, for weakly ionized plasmas, such a component, if exists, will be extremely small because the density of charged particles is lower by many orders of magnitude than that of ground state molecules, therefore, the randomizing effect of molecule-molecule collisions always dominates. Basically, the motion of ground state molecules or atoms in weakly ionized plasmas can be considered to be completely random.

At this point it is clear that as far as velocity distributions are concerned within the discharge there are, at least, two groups of molecules, the excited state ones with a non-zero average velocity component and the ground state ones with a totally random velocity distribution. For the Doppler shift to be observable, molecules of different
groups should not interact each other so that the existence of one group does not affect the velocity distribution of the other's. For this to be true, the condition of (1.3) must be satisfied. Otherwise, inter-group interaction may occur via collisions between molecules of different groups, and the result will be the disappearance of the preferential velocity direction for the excited molecules because the density of the ground state atoms is larger than that of the excited ones by many orders of magnitude. This is reason that Doppler shift in neutral emission can only be observed for short-lived excited molecules or atoms.

It is clear that (1.3) is a necessary condition for keeping the two groups from interacting each other. Usually it is also a sufficient condition (sufficient perhaps for all the molecular cases and most of atomic cases). However, the condition may become insufficient for an atomic gas system where the atom's excited state is optically connected to the ground state. If the density of the ground state atoms is high enough, which is often the case in experiments, so called radiation trapping may occur, a process in which a resonance photon emitted by an individual atom is absorbed by another atom in the gas, thereby raising the latter to the excited state to reemit another resonance photon. It may take a number of such absorbing-remitting cycles for a photon to eventually escape out of the gas.

Under such circumstances, the two groups of atoms, the excited ones and the ground state ones, are no longer independent but are connected by photons. Specifically, for each trapping cycle, the two groups exchange atoms, i.e., a ground state atom becomes an excited state atom and vica versa, which, as far as the net result
concerned, is equivalent to the exchange of each other's velocity vectors for the two atoms. Since there is no correlation between the orientation of photons and velocity vectors, the two exchanged vectors are different. Therefore, the result of many of such exchange will be the changes of the velocity distributions of both groups. Due to the huge difference in size for the two groups, the change for the ground state atoms will be completely negligible, but for the excited state atoms, it will be the randomization of the velocity distribution, which increases rapidly with the number of exchanges. Such randomization will, of course, lead to the reduction of the absolute value of the non-zero velocity component and so of the corresponding Doppler shift.

The above conclusion means that radiation trapping can be detected by measuring the reduction of the Doppler shift of emission from neutral atoms. This is just what we have found in our theoretical study and as well as in our experiment.

Since radiation trapping happens to emissions selectively, the determination of the reduction can be done by comparing the Doppler shifts of emissions with and without the influence of radiation trapping. Such measurements have been made in our experiment for a He gas in a plasma.

It has no doubt that radiation trapping is solely an interaction between resonance photons and relevant atoms in a gas. Such interaction is apparently independent of the host environment where atoms and photons are present. Because of this, it is possible to compare two trapping systems for a given volume and, as demonstrated in our experiment, this comparison leads to the determination of the density of one state from the other. Finally it is very interesting to note that the approaching of the
statistical equilibrium between two systems can be caused by photons rather than atom-atom collisions.

1.4 The Outline of the Thesis

The introduction section (Chapter I) is an overview of the development and the current perspectives of Doppler shifted spectroscopy both as a spectroscopic tool and as a probe for chemical and physical processes in a discharge plasma. An emphasis has been given to the introducing, in a most conceptual way, the new developments arising from this thesis research for Doppler shifted emissions of both ions and neutral molecules. Chapter II details the apparatus and techniques that are used in the experiments throughout this research. Chapters III and IV deal with Doppler shifts of ion emissions using N$_2^+$ and Ar$^+$ as examples to describe the state-specific Doppler shifts, including the mechanisms for the producing of the shifts themselves and the related application for probing processes in a discharge plasma. Chapter V describes the experimental observation of Doppler shifts in emissions of neutral molecules in a discharge and the theory that explains the experimental results. Finally, Chapter VI is devoted to the radiation trapping effect on Doppler shift of neutral emissions, by developing the theory that underlies this phenomenon and describing the experimental observation as well as demonstrating a practical application of the effect.
CHAPTER II
Detailed Experimental Techniques

As has been mentioned earlier, the experiments for this thesis research have been confined to dealing with the Doppler shifts in emission spectra using the positive column of a DC glow discharge as a source. The principle of the experiment is quite simple. Doppler shifts of either ionic or neutral spectra are determined by comparing positions of lines in two spectra obtained at opposite discharge polarities (i.e., $\Delta \nu = \frac{1}{2}$ half the distance between positions of the two oppositely shifted lines). Clearly the two spectra that are used for the comparison must be obtained at all otherwise identical conditions except for the polarities. To guarantee this is the most important step for obtaining reliable data in the experiment. Therefore, it is one of the major concerns in setting up the experimental apparatus as well as in taking spectra through the experiment. Fig.1 shows the experimental arrangement. It consists of basically the following four parts.

2.1 Discharge Cell

The discharge cell is a U-shaped gas flow tube made of glass. The tube has an internal diameter of 0.8 cm and two sidearm tubes with two electrodes made of stainless steel
Figure 1: Experimental arrangement
at the ends. Each side arm tube and the horizontal tube are about 14 cm long. The middle length of 8 cm of the horizontal tube that contains the positive column of the glow discharge is used as the emission source. The long sidearms is used to avoid any sheath effect on the positive column at the source position. Gas is introduced through a small hole located in the center of horizontal tube and pumped out through the two side arm tubes. The layout of the whole cell structure and the gas flow system are geometrically symmetric about the center of the horizontal tube so that the otherwise discharge conditions of the positive column remain unchanged when the polarity of the applied discharge voltage is reversed. The whole gas system can be pre-evacuated to a background pressure below $10^{-3}$ torr. Before taking spectra, a continuous discharge running for certain time duration is needed to stabilize the system thermally and to passivate the surface of the discharge cell as well.

For the experiments of emissions of neutral molecules $\text{H}_2$, $\text{He}$ and others, a modified cell has been used, which, as shown in Fig.2, has a 3-cm long tube at the center with a reduced diameter of 0.2 cm instead of 0.8 cm for the rest. The new design allows a higher current density at the center position where lights are collected, therefore strengthen the spectral signal. To prevent overheating the outside surface of the small tube is wind cooled by compressed air.

While the small diameter cell increases the emission signals, it also enhances the electric field considerably. This has been clearly verified for $\text{He}$ discharge in pur experiment. Under same gas conditions, e.g. 10 mtorr $\text{N}_2$ in 0.5 torr $\text{He}$, the axial electric field in the positive column is found to be 14.2 V/cm for the 2 mm diameter
tube, compared to 6.4 V/cm for the 8 mm one. The field is enhanced by a factor of two or so.

Such enhancement is mainly due to the higher rate of loss of electrons and ions at the wall due to recombinations for a tube with a reduced diameter. Electrons in the positive diffuse much more rapidly than the heavier ions. As a result, there are electrons accumulated on the wall. This net negative charge on the wall forms a radial potential gradient with its force line pointing to the wall, which will prevent further accumulation of electrons on the wall, however, pull the positive ions in the discharge to the wall (such process is known also as ambipolar diffusion). When the ions arrive on the wall they will be quickly neutralized by the excess negative charges. Apparently the larger the gradient the higher the rate the ions arrive at the wall. A smaller tube diameter corresponds a larger a larger gradient, therefore,
a higher ion loss rate. When the positive column losses an ion, it must create a new one to maintain the neutrality as well as the current constant. New ions are created by ionizations by electron’s impacts on the neutral molecules in the discharge. A high ion loss rate demands a high ionization rate, which requires a large number of energetic electrons because of the ionization potential for electrons to overcome. The energy of those electrons can only be provided by the electric field. As a result, the electric field is enhanced in a small tube.

As the magnitudes of Doppler shifts for both ionic and neutral emissions are proportional to that of the axial electric field, larger Doppler shifts have been observed using the smaller discharge tube.

### 2.2 Collecting Optics

A framed CaF window, which acts also as an aperture, is placed at the end of the horizontal tube, about 7 cm from the center so that a small collecting solid angle with respect to the center is obtained. The small solid angle guarantees only lights that propagate nearly parallel to the horizontal axis to be collected. The emission lights from the center part of the cell is collected and collimated by lens $f_1$ (f=40 cm) and then focused by lens $f_2$ onto the entrance aperture of the spectrometer. $f_2$ is chosen to have a diameter of 5 cm and a focal length of 25 cm to properly focus the collimated light as well as to match the f-number of the spectrometer. The axes of all the optical elements including that of the discharge tube coincide with the optical axis of the
spectrometer. The is checked using a He-Ne laser beam passing through the centers of all the internal and external optical elements, from the detector of the spectrometer to the emission source point. An object-image checking procedure is employed to ensure that the plasma column at the center of the discharge tube is correctly imaged to the spectrometer. In the procedure a small bright object (usually a illuminated sharply-edged triangle) is placed at the center of the tube and adjust the horizontal position of the discharge tube till a clear image is seen on the entrance plane of the spectrometer.

2.3 DC Power Supply and the Controller

A high DC voltage is applied to the discharge cell through the two sidearm electrodes to maintain the glow discharge. Between the DC power supply and the electrodes and in series there are a large resistor and a switcher that can switch polarity of the discharge voltage. The resistor (R=40kΩ) is used to give the RC circuit a large time constant so as to maintain a stable discharge. The discharge current, ranging typically between 20 mA and 50 mA, is monitored constantly during experiments. A total voltage from 1 kV to 2 kV is required to run the discharge, dependent on types of gas mixtures and discharge pressures.

Switching the polarity of the discharge can be done either automatically with the electronic switcher or by changing the connection manually. In the automatic operation mode, the switcher is controlled by the Bruker spectrometer computer. At the end of each data acquisition cycle, the computer sends a TTL pulse to the
switcher to switch the discharge polarity. Interferograms corresponding to opposite
discharge polarities are stored separately to yield to two spectra that have opposite
signs of Doppler shifts. This method has the advantage that two spectra are obtained
simultaneously so that the effect of time fluctuation of discharge may be minimized.

The electronic switcher works well for types of gases or at discharge pressures
that are easy to ignite the discharge. However, for certain gases and gas conditions,
the switcher may fail to restart the discharge after its interrupting of circuit during
switching. At these circumstances, switching need to be done manually. In the man­
ual mode, two spectra of opposite polarities are taken one after the other. Since both
the discharge and the spectrometer are highly stable, little difference in quality has
been seen for spectra obtained by the two methods. Both methods are very reliable
regarding to obtaining spectra at identical discharge conditions at different polarities.

2.4 Fourier Transform Spectrometer

A commercial Bruker IFS 120 HR Fourier transform spectrometer is used throughout
the experiments to obtain the spectra. The spectrometer is designed to offer a very
high resolution(\(\sim 0.02\) cm\(^{-1}\) at maximum) and a wide spectral coverage from 200
cm\(^{-1}\) to 3000 cm\(^{-1}\). These potentials, especially, the capability of high resolution,
however, have not been fully utilized in the experiments since they are basically
carried out in the visible or near IR region and with a glow discharge(at a pressure
of a few torr or less) of room temperature or higher as the light source. Under our
source conditions, Doppler broadening is always dominating. For the purpose of obtaining approximately the possible minimum linewidth, we only need to choose an instrumental resolutions (in cm$^{-1}$) that are considerably less than Doppler linewidth. A resolution of 0.02 cm$^{-1}$ was used through the experiment. Both experimental tests and numerical calculations indicate that this value gives a negligible instrumental broadening contribution. While a higher instrumental resolution may have little help for the quality of the spectra, it would force to us to narrow the spectral coverage because of the maximum capacity a file size. A wide spectral coverage for a particular scan is sometimes very desirable when comparing the shifts of different transitions as we have done through the experiment. Balance must be considered between resolution and spectral coverage.

As a detector, either a photon multiple tube or a silicon diode is used for visible light or the near IR. And accordingly, beamsplitters of coating quartz and CaF are used for the two frequency regions respectively. All the spectra have been obtained by using both narrow optical band filters and electronic filters. The filters cut off the unwanted frequencies and are very critical to the quality of spectra. The whole system is very stable both mechanically and optically and its operation has been on a very routine basis.
CHAPTER III

Doppler Shifts of $N_2^+$ Emissions in a He Discharge

3.1 Introduction

The transport properties of ions in a gas in presence of an electric field is a subject of great and prolonged interest[24]. It is at the heart of the understanding of weakly ionized plasmas, such as those used for electronic device processing and novel material synthesis[30]. It is important in some lasers[31] and in ion-molecule reactions like those that occur in the upper atmosphere[32]. It is also of great importance to the spectroscopic detection of ions because of the wide-spread use of the velocity-modulation technique in infrared absorption spectroscopy[8].

The majority of our information on ion transport has been obtained from drift-tube measurements. Traditionally these involved physical sampling, in a time-resolved manner, of the ions and suffered from the need for careful compensation for perturbations on the ion's velocity by the sampling process. Recent efforts by Leone's group[33, 34] and others[35, 36],[26] have largely removed the problem of perturbations by measuring velocities via the Doppler shifts and widths of ion absorption lines, using a laser-based spectroscopic technique.
Other workers[37, 38] have applied lasers to measure the Stark effects of spectral transitions to deduce electric fields. Indeed, almost all recent work on Doppler shifts of ion lines or other techniques to measure electric fields have used laser spectroscopy except for the seminal paper of Martin and Guelachvili[23]. They pioneered the coupling of Fourier transform emission spectroscopy (FTE) with Doppler modulation. By using the technique, they have obtained the Doppler modulated spectra for the IR emissions of ArH^+. The FTE approach has the fundamental advantage of providing much more general frequency coverage than dose laser spectroscopy, albeit at the expense of reduced sensitivity.

A common stand for all these previous studies, whether based on the traditional drift-tube technique or on the recent IR absorptions and emissions, is that they were dealing with either the ground state ions or ions with a very long lifetime (much longer than the ion-molecule collision time). For those ions, the observed drift velocity, \( u_d \), (or equivalently, the Doppler shifts, \( \Delta \nu/\nu_0 \)), is always the steady drift velocity and related to the ion’s mobility \( K \) and the external electric field \( E \) as

\[
    u_d = K E \quad \text{or} \quad \frac{\Delta \nu}{\nu_0} = \frac{u_d}{c} = \frac{KE}{c}
\]

Eq.(3.1) indicates that \( E \) causes the drifting of the ions while \( K \), which is inversely proportional to the momentum-changing cross section, represents the resistance of the drift of the ions due to the gas molecules. These two opposite effects on the drift motion are inseparable for ground state ions in a gas. The determining of one of them by the measurement of ion’s drift motion must be based on the known other as demonstrated in many previous works.
The experiments described in this chapter, while employing the FTE method proposed by Martin and Guelachvili for the measurement of the Doppler shifts of ion's emission spectra, have extended the spectroscopic application of the technique to electronic, rather than the traditional vibrational, transitions.

Such extension is not merely extending the frequency coverage of the technique. It brings some new considerations for the motion of ions in a gas. Electronically excited states have a much shorter lifetime compared with the ions in their ground electronic states. The short lifetime may prevent ions making enough collisions with the gas molecules to reach their steady drift velocities. At the extreme case as the B state \( N_2^+ \) in a gas of low pressure, the ions may experience no collisions and the observed drift velocity (or Doppler shift) is solely determined by the free acceleration of ions in the field. Under such circumstance, the effects of \( K \) (i.e., collisions) and \( \mathcal{E} \) on transport of ions in a gas are completely decoupled, and the Doppler shifts are reduced to the measure of the electric field of the plasma only.

In addition to the lifetime effect, an electronically excited state may also be quenched in a ion-molecule collision. All these new effects make Eq. (3.1) no longer appropriate for describing the motion of short-lived excited ions in a gas. We have formulated a general theory for the observed drift velocity for ions with a finite lifetime. Experimentally we have selected two bands systems of \( N_2^+ \), the \( \text{B}^2\Sigma_u^+ - \text{X}^2\Sigma_g^+ \) and \( \text{A}^2\Pi_u - \text{X}^2\Sigma_g^+ \), for detailed study and presentation here. By analyzing and understanding the results from this model system, we hope to lay the foundation for using FTE both as a general spectroscopic tool and as an innovative plasma diagnostic.
3.2 Experiment

The experimental arrangement is shown in Fig.1 and the corresponding details about the apparatus and the procedure for obtaining the Doppler shifts have been discussed in chapter 2. In the present experiment, the excited state \( \text{N}_2^+ \) ions are produced in a \( \text{N}_2/\text{He} \) DC glow discharge in a U-type gas flow tube. The discharge current is monitored and maintained at 20 mA. Typically, a voltage of 1 kV is needed to maintain the discharge. The partial pressure of \( \text{N}_2 \) is kept at 10 mtorr throughout the experiment. A stable discharge can be obtained for total pressure from 0.05 to 6 torr. A photomultiplier tube is used to detect the B-X emission while a Si diode detects the A-X emission. An excellent signal to noise ratio is achieved for the B-X emission spectra over the entire pressure region. However, the intensity of the A-X is much weaker and the spectra became too noisy to measure the Doppler shifts when the He pressure was above 3 torr.

3.3 Theory

Since ions in the discharge drift in the direction of the electric field, Doppler shifts are expected in their emission spectra. If we defined \( u_z(t) \) as the \( z \)-axis (the input axis of the spectrometer) component of the velocity of an ion \( t \) seconds after it was created, then the observed Doppler shift, \( \Delta \nu/\nu_0 \), of the ion's emission line from its rest frequency,
\( n_0 \), is just

\[
\frac{\Delta \nu}{\nu_0} = \frac{\langle u_z \rangle}{c}
\]  

(3.2)

where \( \langle u_z \rangle \) is the ensemble average of \( u_z(t) \). The symbol \( \langle u_z \rangle \) denotes the time average of \( u_z(t) \) for various times at which the excited state ion emits a photon.

For an excited ionic state we must consider collisions that quench the state as well as change the ion's velocity (For our purpose, a quenching collision is defined as one which does not leave the ion in a quantum state whose emission is detected by the spectrometer). The time, \( t_q \), at which an ion is quenched can be written as

\[
t_q = \frac{\lambda_q}{V}
\]  

(3.3)

where \( V \) is the relative velocity between ions and buffer gas molecules. When the ion's drift velocity is much less than the thermal velocity of molecules and ions, as is the case under our experimental conditions, \( V \) can be considered to depend solely on the thermal motion of particles, which is, of course, independent of time and the external field.

The mean free path for quenching, \( \lambda_q \), can be expressed as

\[
\frac{1}{\lambda_q} = \sum_i Q_q(i)N_i + \frac{\gamma_f}{V}
\]  

(3.4)

where the sum runs over the neutral species present and may be approximated by a single term in a strong excess of buffer gas. \( Q_q(i) \) and \( N_i \) are, respectively, the quenching cross section and the concentration of species \( i \). The last term in Eq.(3.4) comes from the ion-wall quenching, which is characterized by \( \gamma_f \), the rate of the arrival of ions at the wall.
We can now construct the time average of drift velocity, $\langle u_z \rangle$, by weighing the velocity function $u_z(t)$ by the probability for emission $P(t)$ to the time, $t_q$, when the ion is quenched

$$\langle u_z \rangle = \frac{\int_0^{t_q} u_z(t)P(t)dt}{\int_0^{t_q} P(t)dt}$$  \hspace{1cm} (3.5)$$

where $P(t)$ has the usual form

$$P(t) = \frac{1}{\tau} \exp\left(-\frac{t}{\tau}\right)$$  \hspace{1cm} (3.6)$$

with $\tau$ the radiative lifetime of the emissive state. The ensemble averaged velocity along the axial field, $u_z(t)$ is considered to have the form

$$u_z(t) = \frac{eE}{MT}\left[1 - \exp(-\Gamma t)\right]$$  \hspace{1cm} (3.7)$$

where $E$ is the axial plasma electric field, $M$ the mass of the ion, and $\Gamma$ the rate for velocity-changing of ion-molecule collisions. Equation (3.7) is the result of applying the familiar Stokes's law of resistance to our problem of an ion cloud moving in a buffer gas in the presence of an electric field. In doing this, we have considered the ensemble average drift velocity as the velocity of the center mass of the ion cloud, and that the resistance for the cloud comes from ion-molecule collisions. The model of Eq.(3.7) was also used by Hori et al[35], in describing excited atomic ions moving in a gas. By definition $\Gamma$ is related to the mobility $K$ by

$$\Gamma = \frac{e}{MK} = \frac{e}{M} \sum \frac{\chi_i}{K_i}$$  \hspace{1cm} (3.8)$$
where $\chi_i$ is the mole fraction of species $i$ and $K_i$ the ion's mobility in the $i$th pure component of a mixture. The second equality in Eq.(3.8) follows the well-known Blanc law[39].

The integral in Eq.(3.5) can be performed analytically and give the Doppler shift as function of molecular constant, gas dynamic parameters and the external plasma field

$$\frac{\Delta \nu}{\nu_0} = \frac{<u_z>}{c} = \frac{eE}{MTc} \left[ 1 - \frac{1}{1 + \Gamma \tau} \frac{1 - \exp\left(-\frac{\lambda}{\nu\tau} - \frac{\Gamma\lambda}{\nu\tau}\right)}{1 - \exp\left(-\frac{\lambda}{\nu\tau}\right)} \right]$$  \hspace{1cm} (3.9)

This is the basic equation that will be used to interpret our experimental data.

Eq(3.9) can be easily seen to have the correct limiting forms under various circumstances. For example, at the limit, $\tau \to \infty$ and $\lambda \to \infty$, appropriate for ground state ions, $<u_z>$ becomes

$$<u_z> = \frac{eE}{MT} = E K$$  \hspace{1cm} (3.10)

which is just the usual formula for the drift velocity of ions in an external field.

At the no-collision limit ($\tau \to 0$, or $N \to 0$, or both), Eq.(3.9) yields

$$<u_z> = \frac{eE}{M \tau}$$  \hspace{1cm} (3.11)

which is just the velocity that the ion gained through free acceleration ($eE/M$) over its lifetime. Eq.(3.11) gives a very simple relation between the Doppler shift and the electric field. It will be found to be very useful for analyzing out data from the short-lived state of $N_2^+$. 
3.4 Results and Analysis

3.4.1 Doppler Modulated Emission Spectra

Fig.3 shows part of the R branch of the $B^2\Sigma_u^+ (v=0) - X^2\Sigma_g^+ (v=1)$ band of $N_2^+$. The top two spectra were taken at opposite discharge voltage polarities and the third trace is their difference spectrum. In the difference spectrum all the neutral emission lines disappear while the ion lines remain and show a "first derivative" type line shape. The cancellation of the neutral transition is due to the fact that the motion of the neutral molecules is not affected by the electric field, and therefore, their transitions, unlike ionic transitions, are not subject to velocity modulation. This example provides a good demonstration that Doppler modulation is a useful method for discriminating between ionic and neutral transitions in Fourier transform emission spectroscopy studies. Similar results have also been obtained for a number of molecular ions such as $N_2^+$, $O_2^+$, $CO_2^+$, and $N_2O^+$.

A pair of typically shifted lines are shown in an expanded view in Fig.4. The red-shifted and blue-shifted $R(10)$ line of $B^2\Sigma_u^+ (v=0) - X^2\Sigma_g^+ (v=1)$ transition of $N_2^+$ are plotted together. The Doppler shift $\Delta \nu$ is defined as half of the distance between the centers of the two oppositely shifted lines.

3.4.2 $B^2\Sigma_u^+ - X^2\Sigma_g^+$

3.4.3 The Electric Field

Fig.5 shows the measured dependence of the Doppler shift, $\Delta \nu/\nu_0$, on the He buffer gas pressure for $B^2\Sigma_u^+ (v=0) - X^2\Sigma_g^+ (v=1)$ transition of $N_2^+$. The measurement has
Figure 3: Emission spectra of $\text{N}_2$ and $\text{N}_2^+$ ions. Traces (a) and (b) are taken under the same conditions except for the polarities of the discharge. Each trace contains both ionic and neutral transition of B-X (0,1) band of $\text{N}_2^+$ and the C-B (1,5) band of $\text{N}_2$. The ion lines in the two spectra are oppositely Doppler shifted while the neutral lines are unshifted. Trace (c) is the difference spectrum of (a) and (b), in which all the neutral transitions are cancelled while the ion transition remain and display a line shape of ‘first derivative’ type.
Figure 4: The red-shifted and blue-shifted R(10) lines (with resolved spin-rotational components) of the B-X (0,1) of N$_2^+$. The Doppler shift ($\Delta \nu$) is defined as half the distance between the two oppositely shifted lines.
been performed on several rotational lines of the band. However, no dependence of Doppler shift on rotational level is perceived.

To analyze our data, we first need to determine the electric field of the positive column of the discharge. An accurate experimental determination of a discharge electric field is usually a difficult problem. However, for the case of short-lived B state \( N_2^+(\tau=63 \text{ ns}) \), averaged from the results given by Refs[41]-[44]) and at low discharge pressure, the problem becomes particularly simple. Under these conditions, the collision-free path is too long for the short-lived ions to suffer a collision before emitting a photon. Under this no-collision limit, the drift velocity is given by Eq.(3.11) and we have

\[
\mathcal{E}_D = \frac{M c \Delta \nu}{\epsilon r \nu_0} = 1.38 \times 10^7 \frac{\Delta \nu}{\nu_0} \text{(V/cm)} \tag{3.12}
\]

which allows us to determine the electric field from the measured Doppler shift \( \Delta \nu/\nu_0 \).

The electric field calculated from Eq.(3.12) is plotted in Fig.6.

A simple estimation based on the lifetime and the dynamic parameters of the gas mixture, such as \( \lambda \) and \( V \), suggests the Eq.(3.12) is valid up to a pressure of about 1 torr. For pressure above 1 torr, ion-molecule collisions typically occur before radiation and hence Eq.(3.12) is not valid anymore. We therefore assume that the \( \mathcal{E}_D \) at low pressure (<1 torr) represents the true discharge field while \( \mathcal{E}_D \) obtained from Eq.(3.12) at high pressure does not.

To estimate the electric field for the higher pressure region, the usual method of probes was used. Two wire electrodes were inserted into the plasma and the voltage across them was measured. The result, \( \mathcal{E}_P \), is also shown in Fig.6. It was found
Figure 5: The measured Doppler shift ($\Delta \nu/\nu_0$) as a function of the He pressure for B-X(0,1) transition of $N_2^+$. 
Figure 6: Plasma electric field determined vs pressure. $E_D$ is the electric field calculated from Eq.(3.12) using the measured Doppler shift data from the B-X transition of $N_2^+$, and $E_P$ the electric field determined from the probe measurement. At low pressure, they are remarkably similar in pressure dependence except for an offset of $\sim 1.5$ V/cm. $E_C$ is derived by subtracting 1.5 V/cm from $E_P$ and taken to be the true discharge field (see text). The asterisks are the electric field measurements from Ref.[25] for a discharge very similar to ours.
that, in the low pressure region, the dependence of $E_D$ and that of $E_P$ are remarkably similar but show a 1.5 V/cm offset (see Fig.6). This 1.5 V/cm difference is presumably caused by various factors, such as sheath effect, asymmetry of the electrodes, etc., since limited efforts have been made to minimize such effects. We assume that the offset is constant throughout the entire pressure region. The corrected field for all pressure is thus obtained by subtracting 1.5 V/cm from $E_P$ as is shown in Fig.6 (the curve $E_C$).

Radunsky and Saykally[25] have measured the electric field of a He glow discharge similar to ours for the pressure region of 3-11 torr by velocity modulation IR laser absorption spectroscopy. As Fig.6 shows, our result for the electric field is in good agreement with theirs.

### 3.4.4 Fitting to the Model

Once the discharge electric field is known, we are able to normalize the Doppler shift by the field to obtain information about ion dynamic in the discharge. The normalized Doppler shift, $\Delta \nu/(\nu_0E)$, which is independent of the field, is plotted in Fig.7. From Fig.7 we see that, as expected, $\Delta \nu/(\nu E)$ is fairly a constant at low pressure (<1 torr) and then start decreasing at higher pressures where the ions begin suffering collisions. The fitting of experimental points with Eq.(3.9) is also shown in Fig.7. Because of their short lifetime, B state N$_j^+$ ions can only travel a very short distance before they radiate. In other words, the motion of each short-lived ion in the discharge tube is rather localized. Therefore, any wall effect is negligible. Likewise, N$_j^+$—N$_2$ collisions
Figure 7: The normalized Doppler shift, $\Delta \nu / (\nu E)$, for the B-X (0,1) transition of $N_2^+$. It remains quite constant in the low pressure region (no-collision zone), and decreases with increasing pressure. The solid line is a fit to the Eq.(3.9).
are negligible due to the low pressure N₂. Under these conditions, both Eq.(3.4) and Eq.(3.8) reduce to single term, i.e., only N₂⁺-He collisions needs to be considered. The fitting has resulted in the following parameters

\[ K_{He} = 35 \pm 20 \, \text{cm}^2/\text{Vs}, \quad \text{and} \quad Q_q = 5.6 \pm 0.8 \, \text{Å}^2 \]  \hfill (3.13)

The large uncertainty in \( K_{He} \) is because \( \Delta \nu / (\nu_0 E) \) is very insensitive to the mobility \( K_{He} \). This is the special nature for the short-lived B state ions. A mobility is a quantity that describes the steady motion of ions in a gas in presence of an electric field. It reflects the balance between the ion's acceleration by the field and the drag due to the collisions over a long time period. It can be best determined by sampling ions that have a steady drift velocity because these ions have repeatedly gone through many collisions and their steady velocity correctly reflects the average effect of collisions and so does the mobility determined from it. For B state N₂⁺ in our experiment, even at the highest pressure, the ions are far from reaching the steady velocity. Under our experimental conditions, the ions experience only a few or no collisions during the lifetime. The mobility given by Eq.(3.13) was actually the prediction of the ion's steady motion based the observation of ions that are still in the process acceleration in the gas. A large uncertainty is therefore inevitable. The important and interesting implication of the Doppler shift data of the B-X emission is their measure of the acceleration of the ions by the field. At low pressure collisionless condition, such acceleration is unperturbed so that the magnitude of the field may be deduced from that of the Doppler shift as described above.

No other measurements on the N₂⁺(B²Σ⁺)⁻He quenching cross section have been
reported thus far. Katayama[46] and his co-workers have measured the cross section for the v' = 4 and v' = 3 levels of A^2Π_g state of N_2^+, giving Q_y(A) = 1.5 and 0.6 Å², respectively. Our measured cross section for v' = 0 of the B state is somewhat greater than these two values. A possible explanation for this is that the B^2Σ_u^+ state is nested within both the higher vibrational levels of the ground X^2Σ_g^+ state and also those of the A^2Π_g state. The higher density of levels near v' = 0 level of the B state may facilitate quenching.

3.4.5 A^2Π_u-X^2Σ_u^+ Transition

Fig. 8 shows the normalized Doppler shift Δν/(ν₀E) for A^2Π_u(v = 1)-X^2Σ_u^+(v = 0) emission of N_2^+, and for comparison, the Δν/(ν₀E) data for B-X of N_2^+ transition as well. The two sets of data were obtained under the same discharge condition. However, it is very interesting to note that the Doppler shift for the A-X transition is, at least, several times greater than that for the B-X transition at any given pressure. Such a large difference is apparently due to the difference in lifetime of the two states (9.7 μs for the A state[47] vs 63 ns for the B state). Ions with short radiative lifetimes decay too quickly to gain a high drift velocity from the field, and thus, have a small Doppler shift. The situation for ions with long radiative lifetime is just the opposite.

Unlike the case for the B state of N_2^+ where ion-molecule collisions occur only at high pressure (>1 torr), ion-molecule collisions modify the Doppler shift at all pressure
Figure 8: The normalized Doppler shift for the A-X (1,0) transition and that for the B-X (0,1) transition. The Doppler shift for the A-X transition is much larger. The solid lines A-D are the fit curves for the following assumption: A, only $N_2^+$-He velocity changing collisions are considered; B, $N_2^+$-He quenching collisions included; C, $N_2^+$-$N_2$ collisions included; and D, wall quenching included.
used in our experiment for the A state of N$_2^+$. In addition to N$_2^+$-He collisions, N$_2^+$-N$_2$ collisions need to be considered because of the constant 10 mtorr of N$_2$ in the discharge. To take N$_2^+$-N$_2$ collisions into account, we treat the buffer gas as a mixture of He and N$_2$. Furthermore, we ignore the quenching of the excited A state of N$_2^+$ because the quenching cross section are much smaller than the cross section for N$_2^+$-N$_2$ velocity-changing collisions. The value of $Q_V$ for both A and B states are quite similar to the ground state values. If we assume the same is true for N$_2^+$-N$_2$ collisions, we can avoid introducing another unknown parameter into our fit. Under these considerations and according to Eqs.(3.8) and (3.9), the effect of N$_2^+$-N$_2$ collisions can be included by a correction term in $\Gamma$, i.e.,

$$\Gamma = \Gamma_{He} \left( 1 + \frac{P_{N_2} K_{He}}{P_{He} K_{N_2}} \right)$$ (3.14)

where $P_i$ is the partial pressure of gas species $i$. We take, respectively, 1.86 cm$^2$V/s$^4$ and 19 cm$^2$V/s, the well established values of mobilities, for $K_{N_2}$ and $K_{He}$ in Eq.(3.14). As the correction term in Eq.(3.14) is proportional to $P_{N_2}/P_{He}$, the effect of N$_2^+$-N$_2$ collisions on the Doppler shifts is important only at low He pressure.

Another process that affects the Doppler shift at low He pressure for the long-lived ions is ion-wall collisions due to the radial diffusion of ions. The wall effect is described by the last term in Eq.(3.4), $\gamma_I/V$. For a cylindrical discharge tube, $\gamma_I$ has the form

$$\gamma_I = \frac{D_a}{P_{He}} \left( \frac{T}{273} \right)^2 \left( \frac{2.405}{R} \right)^2$$ (3.15)

where $R$ is the radius of the discharge tube, $T(=400)$ the temperature of the buffer gas, and $D_a(=900$ cm$^2$torr/s$)$ the ambipolar diffusion coefficient reduced to 1 torr.
at 273K. As \( \gamma_I \) is proportional to \( 1/P_{He} \), the wall effect is not significant unless the He pressure is low.

Fitting of the theoretical model to the experimental data have been done and is shown in Fig.8. From the curves in Fig.8 one can see the effect on the Doppler shift of the individual processes of collisions with He, N\(_2\) and the wall. Note that the corrections of N\(_2^+\)-N\(_2\) collisions and ion-wall quenching have greatly improved the fit in the low pressure region but have little effect in the higher pressure region. The cross section for N\(_2^+\)-He collision determined from the fit are

\[
K_{He} = 14.4 \pm 1.7 \text{cm}^2/\text{Vs}
\]

and

\[
Q_q(A) = 0.7 \pm 0.2 \text{ A}^2
\]

for the \( v' = 1 \) level of the A state.

### 3.5 Conclusion

The potential of Doppler shifted Fourier transform emission spectroscopy as both a plasma diagnostic and a spectroscopic tool has been demonstrated for the B-X and A-X electronic transitions of N\(_2^+\). As Fig.3 shows, ionic emissions can be extracted from a spectral region strongly congested by lines from a neutral carrier.

As a diagnostic, we have shown that the axial plasma electric field can be determined from the Doppler shifts of emissions of short-lived ions. Our results are consistent with previous measurements, but as a technique can probably be more
generally applied. In addition, we have shown the capability to probe the transport of ions in a plasma and the quenching of the excited states of $\text{N}_2^+$ by collisions.
4.1 Introduction

Argon ion emissions have long been of considerable interest, principally because of the importance of the Ar$^+$ laser[51, 52]. There has also been a good deal of fundamental work[56]-[60]concerning emissions from the upper lasing levels, 3p$^4$4p$^1$, of Ar$^+$ in a discharge of mixtures of He and Ar. The mechanisms for the excitation to the emitting levels are central problem. Despite the abundance of work there is still no consensus over the details of the excitation mechanisms for various levels.

Most of those mechanism studies so far have been accomplished by measuring the intensities of emissions from the Ar$^+$ excited states towards the change of the discharge conditions, for instance, by measuring for the discharge current dependence of the emission intensity to determine the role of the electrons, or by adding quenching gases to determine the effect of metastable He on the intensity[53]-[55]. These experiments have yielded some useful information, however, hardly given unambiguous answers to the problem because a discharge is a very complicate system and the change of one component may causes the changes of many others, and hence the predication of the
net effect may be very difficult. For example, adding a foreign gas to a discharge will quench the metastable He, and in mean while, also reduce the electron temperature in the discharge. If the emitting states are produced by reactions with both He* and electrons, difficulty may be found in distinguishing the individual roles responsible for the change of the emission intensity. Such kind of difficulty is quite often encountered in previous experiments.

The method of Doppler shifted emission spectroscopy offers a totally new alternative for solving the excitation mechanism problems, in which, the information about the excitation mechanisms is obten from the magnitudes of Doppler shifts of the emissions instead of emission intensities. Doppler shifts are the measure of the ion's drift velocities. Information about formations of excited ions can be drawn directly from the Doppler shift measurement because the excited ions created by different mechanisms sometimes show very different drift velocities in the discharge and the difference can be easily detected in the Doppler shifts in the emission spectra. For excited 3p^44p^1Ar^+ with a typical lifetime of 10 ns in a discharge of 2 torr He, for example, at the time the ions emit a photon, the drift velocity will be about 660 m/s or 24 m/s depending on whether they are formed from the ground state Ar^+ or by one-step from the ground state neutral Ar atoms. The difference is large enough for unambiguously identifying the mechanisms.

In this chapter we will describes in detail the application of the Doppler shifted emission spectroscopy to the study of excited Ar^+ formation mechanisms.
4.2 Experimental

The ion emission source is the positive column of a Ar/He DC glow discharge. Throughout the experiment, the partial pressure of Ar is kept at 20 mtorr and the discharge current are monitored and maintained at 20 mA. All the spectra are taken at a spectrometer resolution of .02 cm$^{-1}$ so that the line width is Doppler limited. Narrow band-pass optical filters centering at 480nm, 490nm and 510nm are used to accommodate various transition frequencies.

4.3 Result and Discussion

We have performed two kinds of Doppler Shifted emission experiments. In the first set we compared the Doppler shifts at constant discharge conditions, pressure, current, etc., for various emission lines from the 3p$^4$p$^1$ levels of Ar$^+$ (see Fig.9). There are the levels involved in the lasing action of commercial Ar$^+$ laser. In a second set of experiments, we have measured the Doppler shifts of these lines as a function of gas pressure.

4.3.1 Doppler Shifts of Various Emission lines

We have observed and measured the Doppler shifts of a number of 4p-4s Ar$^+$ emission lines at a discharge pressure of 2 torr. We show the results of these measurements in Fig.10. The measured Doppler shifts clearly divide into two groups, one 'large' and another 'small', the latter group's Doppler shifts being more than an order of
The energy levels of Ar$^+$

Figure 9: The simplified energy level diagram of the Ar ion. E* represent the energy of the $2^2S$ He metastable state.
Figure 10: The observed Doppler shifts plotted versus the excitation energies of the upper emissive levels. Each data point was obtained from the Doppler shift measurement of the indicated transition. The numbers in the brackets are the excitation energies in eV of the upper states. The dashed line at $E^*=19.82$ eV divides the transitions with 'large' and 'small' Doppler shifts.
magnitude smaller than the former's. Within the groups any variation in Doppler shifts is well within experimental error.

As Fig.10 clearly shows, there is a strong correlation between the size of the Doppler shift and the energy of the emitting state. All transitions with large Doppler shifts have emitting states of lower energy than any of the emitting states associated with small Doppler shifts. It therefore seems appropriate to refer to the emitting 4p states with small Doppler shifts Doppler shifts as 'high'(energy) states with the remaining states with large Doppler shifts 'low'(energy) states. As Fig.10 shows, the transition between high and low 4p states occurs very abruptly, within 0.1 eV.

In an empirical sense, we clearly have two kinds of ions, high and low 4p ones. It is of interest to consider the possible mechanisms for production of emission from the 4p levels and see whether they might give large or small Doppler shifts. Generally speaking, we can divide the mechanisms into 'neutral' or 'ion' excitation categories.

The neutral mechanisms include:

\[ \text{Ar}^{1}S_{0}(p) + e \rightarrow \text{Ar}^{+}(4p) + 2e \]  \hspace{1cm} (4.1a)

and

\[ \text{Ar}^{*}(4^{3}P_{2,0}) + \text{He}^{+} \rightarrow \text{Ar}^{+}(4p) + \text{He} \]  \hspace{1cm} (4.1b)

Process (4.1a), the direct electron impact excitation of \text{Ar}^{+}(4p), will always be present, if there is a sufficient density of sufficiently energetic electrons. Reaction (4.1b), between metastable Ar neutrals and He ions, has sufficient excitation energy (20.38 or 20.55 eV depending upon the Ar metastable fine structure levels) to populate some but not all the high 4p levels of \text{Ar}^{+}. Masaharu et al\[58\] has suggested
that this process is responsible for their observed high 4p Ar\(^+\) emission lines in a He afterglow.

Alternatively a ground state Ar ion process for excitation of the Ar\(^+\) 4p levels is possible

\[ \text{Ar}^+ (^2P_{3/2}) + \text{He}^* \rightarrow \text{Ar}^+ (4p) + \text{He} + e \]  
\[ \text{Ar}^+ (^2P_{1/2}) + \text{He}^* \rightarrow \text{Ar}^+ (4p) + \text{He} + e \]  

(4.2a)  
(4.2b)

The significance of reaction (4.2a) can be appreciated by reference to Fig.9 where the He\(^*\) excitation energy \(E^* = 19.82\) eV is indicated. Reference to both Figs.9 and 10 shows that \(E^*\) lies precisely in the <0.1 eV gap between the highest low energy 4p level and the lowest high energy 4p level.

Process (4.2b) extends the available energy for 4p Ar\(^+\) excitation by 0.2 eV. Solanki et al. assumed that the high 4p Ar\(^+\) (with \(E = 19.87-19.97\) eV) in their hollow-cathode He discharge were formed via process (4.2b). A similar assumption was adopted by Mezei et al.[57, 58] for 4p\(^2\)P\(_{3/2}\) state Ar ions (with \(E = 19.87\) eV), which gave rise to the laser oscillation in their He-Ar discharge cavity.

Processes (4.1) and (4.2) would be expected to give very different Doppler shifts. In process (4.1) the ion only has a period comparable to its radiative lifetime to be freely accelerated by the discharge electric field. Under these circumstances the Doppler shift, \(\Delta\nu/\nu_0\), is given by

\[ \frac{\Delta\nu}{\nu_0} = \frac{e\mathcal{E}}{Mc^2} \]  

(4.3)

where \(e\), \(M\), and \(c\) have their usual meaning, and \(\mathcal{E}\) is the axial electric field in the discharge, which is about 10 V/cm at 2 torr He.
we can either estimate the Doppler shift from the state’s radiative lifetime or use the measured shift to determine $\tau$. Using the latter approach, we obtain $\tau = 11$ ns compared to the reported $\tau$ value of 8.5 ns. However, it is well known that electron impact is nonselective in its excitation and cascading from other excited ionic states is possible. Such cascading is well known in $\text{Ar}^+$ emission and based upon previous experimental results a 30% increase in the apparent lifetime is not surprising[61].

We note that mechanism (4.2a) is energetically incapable of populating the high 4p levels. Furthermore, we do not believe either mechanism (4.1b) or (4.2b) is very significant in their population. For example, process (4.1b) cannot energetically populate the $4p^2F_{7/2}$ level (with $E = 21.14$ eV) but its emission to the $3d^5D_{5/2}$ level is as strong as that from the other high 4p levels. Other authors[59, 60] have also discounted the importance of this mechanism.

Finally, as we shall see below, any process involving excitation of a ground state $\text{Ar}^+$ would be expected to give rise a transition with a large Doppler shift which is not observed for any of the high 4p levels. Thus we conclude mechanism (4.2a) is the dominant process for excitation of the high 4p levels, based upon energetics, intensities and Doppler shifts. Clearly then, process (4.2a) is the dominant excitation mechanism for the low 4p states in our discharge.

The dominant role of mechanism (4.2a) in forming low $4p^1 \text{Ar}^+$ has been recognized by several previous authors[56][58]-[60]. The present experiment provides a novel and unambiguous confirmation of this mechanism. As discussed above, various mechanisms for excitation of the high 4p levels had been proposed, perhaps because
of the ambiguousness of previous data. The present experiment provides definitive evidence for electron impact as the dominant mechanism exciting high 4p levels in a Ar/He glow discharge.

4.3.2 Pressure Dependence of Intensity and Doppler Shifts

The measurement in the previous section were all performed at fixed Ar pressure (20 mtorr) and He pressure of 2 torr. It is of considerable interest to see how both the intensities of the emission lines and their Doppler shifts vary as a function of He pressure with fixed Ar content (20 mtorr) and discharge current. For these studies two emission lines, 4s2P3/2-4p2P1/2 (ν0=20981.1 cm⁻¹) and 4s2P5/2-4p2P5/2 (ν0=20801.5 cm⁻¹) were chosen to represent respectively the high and low 4p levels. The two 4p states are separated by only 0.64 eV and have comparable radiative lifetimes with transitions having comparable branching ratios.

The results of our observation are plotted in Fig. 11 (intensities) and Fig. 12 (Doppler shifts). As can be seen, the intensities and Doppler shifts are both constant with respect to pressure for the high 4p state. These results are consistent with mechanism (4.1a), direct electron excitation of neutral Ar. The pressure of He at constant current would not be expected to affect the probability for direct electron excitation. Likewise the Doppler shift would be unaffected unless the He pressure become high enough for excited Ar⁺ to suffer collisions before emission, which given the short radiative lifetime is unlikely even at the highest He pressure used.
Figure 11: The emission intensities of the high and low 4p states as a function of He pressure.
Figure 12: The Doppler shifts of the high and low 4p states as a function of He pressure. The solid line is the prediction (see text) of the Doppler shift for the low 4p levels as a function of He pressure.
Fig. 11 shows however a roughly linear dependence of the low 4p states' emission intensities on He pressure. Again, this is consistent with the proposed excitation by He* impact on Ar+. The concentration of He* would in this region be proportional to total He pressure.

This leaves only the rather complicated pressure dependence of the Doppler shifts of the low 4p level, as illustrated in Fig. 12, to be explained. To formulate this explanation it must be remembered that both excitation mechanisms (4.1a) and (4.2a) for populating the low 4p states, although we concluded that at 2 torr and above process (4.2a), i.e. Ar+ excited by He* dominates. However, Fig. 11 shows that at low pressure both mechanisms give comparable contributions. Thus to describe the whole pressure region one can write for the observed Doppler shift, normalized by the electric field $E$, as

$$\frac{\Delta \nu}{\nu_0} = \left(\frac{\Delta \nu}{\nu_0 E}\right)_1 \frac{I_1}{I_1 + I_2} + \left(\frac{\Delta \nu}{\nu_0 E}\right)_2 \frac{I_2}{I_1 + I_2}$$ (4.4)

where the 1 and 2 subscripts refer to the contribution respectively of mechanisms (1a) and (2a). Because of the similarity of the two 4p states considered, we assume that $I_1$ and $(\Delta \nu/\nu_0 E)_1$ for the low 4p level are the same as the measured values for the high 4p level where only mechanism (4.1a) can contribute. We can assume that the pressure dependence of $E$ in the discharge is the same as we experimentally determined is for same He discharge with 20 mtorr of N2 present.

To obtain a value of $(\Delta \nu/\nu_0 E)_2$ we shall assume that this value is determined by the drift velocity of ground state Ar+. This assumption is justified by the fact that drift velocities of Ar+ in different electronic state should be similar and the ion spends
more than most of its time in its ground state. We can then write

\[
\left( \frac{\Delta \nu}{\nu_0 \mathcal{E}} \right)_2 = \frac{K}{C}
\]

(4.5)

where \( K \) is the mobility of ground state \( \text{Ar}^+ \) in the \( \text{Ar}/\text{He} \) mixture. \( K \) can be expressed in terms of the known mobilities at 300 K of \( \text{Ar}^+ \) in pure \( \text{He}, K_{\text{He}}, \) and pure \( \text{Ar}, K_{\text{Ar}}, \)

and the partial pressures, \( P_i \), of the gases

\[
K = \frac{760 K_{\text{He}} 300}{P_{\text{He}} T} \left( 1 + \frac{P_{\text{Ar}} K_{\text{He}}}{P_{\text{He}} K_{\text{Ar}}} \right)^{-1}
\]

(4.6)

To determine the temperature of the discharge gas we have measured some emission lines of neutral He. From their Doppler width we find a value of \( T \) of 410±20K. Combining Eqs.(4.5) and (4.6) to give \( \left( \Delta \nu/\nu_0 \mathcal{E} \right)_2 \) and taking the experimental values for \( \left( \Delta \nu/\nu_0 \mathcal{E} \right)_1 \) and the intensities from Fig.11 we obtain the solid curve in Fig.12. as the figure shows the agreement between the predication and the experimental observation is most satisfactory.

4.4 Conclusion

The experimental result of the measurements of the Doppler shifts as well as the pressure dependence of the emission intensities for \( \text{Ar}^+ \) emissions has provided probably the most complete and direct evidence for the mechanisms of forming the 4p state \( \text{Ar}^+ \) ions in a \( \text{He} \) discharge. It has been identified from our experimental result that the single-step electron impact on an neutral \( \text{Ar} \) is the reaction producing high 4p \( \text{Ar}^+ \) ions and the \( \text{He}^*+\text{Ar}^+ \) excitation is dominantly responsible for producing the low 4p \( \text{Ar}^+ \) ions. Our observation and analysis have confirmed some of conclusions from the
previous experiments, and more importantly, have further clarified the mechanism, especially for the formation of the high 4p Ar ions.

The Doppler shifted Fourier transform emission (DSFTE) spectroscopy is the first time used for studying the ion formation mechanism in a discharge and has been proven as an effective one. As one can see, Doppler shifts of ion emissions reveal the ion motions on a time scale from few nano seconds to virtually infinite. The motion of ions is usually affected by factors such as, the external electric field, ion mobilities, ion losses, destructions of excited states, the excited state lifetime, and ion formation mechanisms. Under many circumstance, only a few or maybe just one of them are effective enough that are needed to be considered. By analyzing the Doppler shift data, information related these factors can be obtained as we have done in present work and the one described in chapter III. The potential of the method is clearly visible and promising.
CHAPTER V

Doppler Shifts of Neutral Emissions

5.1 Introduction

In the last two chapters we have begun to explore the possibility of Doppler shifted Fourier Spectroscopy (DSFTS) as a technique for probing the physical and chemical processes occurring in plasmas and discharges. Basically we have used the high stability and resolution of FTS to measure the Doppler shifts of ion emissions as the polarity of a discharge is reversed. The magnitudes of the shifts have proved to be a sensitive probe of the ion’s formation mechanisms or some discharge parameters such as the electric field.

In the present experiments we have applied the same experimental technique. However in this case we have monitored the emissions from excited states of neutral H$_2$ and its isotopomers. We find that these lines are also Doppler shifted and that these shifts are correlated with discharge polarity and multiplicity of the emitting molecular state. It appears that a similar phenomenon, velocity modulated IR absorption spectra of H$_2$ in discharges, has been previously mentioned, however, no detailed descriptions of the effect have ever been reported.
In this chapter we describe our observations and develop a theoretical framework for their explanation. Interestingly we find that the Doppler shifts that we observed are sensitively related to the details of the electron-molecule collisions which generate the excited states from which emission is observed.

5.2 Experimental

The emission source is the positive column of the glow discharge of H₂ or H₂/D₂/HD mixture. The discharge current is maintained at 50 mA throughout the experiments. For the present experiment, a tube with a diameter of 2 mm instead of 8 mm is used for the source positive column. This modification allows a higher current density at the source position and hence greatly strengthens the emission signal. And equally importantly, the reducing of the diameter enhances considerably the electric field in the positive column. As a result, larger Doppler shifts can be obtained.

The rest of experimental setup and the procedure for obtaining Doppler shifted emission spectra are similar as described for the ionic emission experiments previously. All the spectra were taken at a instrumental resolution of 0.02 cm⁻¹ and with narrow bandpass optical filters. As the cases for ion emissions, the Doppler shift is defined as the half of the distance between the centers of the two oppositely shifted lines. At all the discharge gas conditions, intense H₂ emission lines have been observed. However, the singlet emissions are usually seen stronger than the triplet emissions.
5.3 Experimental Results

It is customary to consider the theory underlying a phenomenon before considering the experimental results. However, in this case, surprising experimental results motivated our understanding of the theory so it seems appropriate to summarize our novel experimental observations first.

As noted in Section 5.1, previous studies of ours involving polarity switched discharges, reported the Doppler shifts of the spectral lines of ionic species. In the case of Hg emission from a discharge there is little or no reason to expect either direct or indirect ion involvement. Ergo, it was a somewhat unexpected observation when we detected discharge-polarity-dependent shifts in the Hg emission lines.

Such spectral shifts are shown in Fig.13 for two excited state emissions of Hg while Fig.14 shows that the shifts scale inversely with the mass of the isotopomer. Two more qualitative observations can be made. The shifts, while distinctly observable, are smaller than those previously measured for long-lived atomic and molecular cation emission. Furthermore, the correlation with discharge polarity is opposite to that of the cations, i.e., it corresponds to the Doppler shift of a negatively charged particle.

We have in addition made two quantitative observations. One of these observations is summarized in Table I where the shifts, $\Delta \nu/\nu_0$, of a number of emitting states are summarized for the same discharge conditions.
Figure 13: Doppler shifts of two closely-lying $H_2$ emission lines: $R(0)$ of $2p^1\Sigma_u^+(v=1)-3d^1\Sigma_g^+(v=0)$ and $P(3)$ of $2s^2\Sigma_g^+(v=0)-4p^3\Sigma_u^+(v=0)$. Note that the triplet emission line has a larger shift than the singlet line. The spectrum was taken at 0.6 torr pure $H_2$. 
Figure 14: Doppler shifts (\( \Delta = \Delta \nu / \nu_0 \)) of emissions of hydrogen isotopomers, \( H_2 \), HD and \( D_2 \). The ratio for the three shifts is 1:0.71(4):0.49(4), which is equivalent within error to \( 1/M_{H_2}:1/M_{HD}:1/M_{D_2}(1:0.67:0.50) \). The spectrum was taken at a total pressure of 0.6 torr of an equal mixture of \( H_2 \), HD and \( D_2 \).
Table 1: Doppler Shifts of H₂ Emissions

<table>
<thead>
<tr>
<th>ν₀ (cm⁻¹)³</th>
<th>Δν/ν₀ x 10⁶</th>
<th>upper state</th>
<th>ε (eV)³</th>
</tr>
</thead>
<tbody>
<tr>
<td>13446.10</td>
<td>.97(4)</td>
<td>3p³Π_u</td>
<td>15.11</td>
</tr>
<tr>
<td>18445.40</td>
<td>.96(4)</td>
<td>3p³Π_u</td>
<td>14.41</td>
</tr>
<tr>
<td>20285.01</td>
<td>.98(4)</td>
<td>4p³Σ⁺_u</td>
<td>14.35</td>
</tr>
<tr>
<td>22223.38</td>
<td>.96(4)</td>
<td>4p³Π_u</td>
<td>14.75</td>
</tr>
<tr>
<td>22225.36</td>
<td>.97(4)</td>
<td>4d³Σ⁺_g</td>
<td>14.84</td>
</tr>
<tr>
<td>22431.04</td>
<td>.99(4)</td>
<td>4p³Σ⁺_u</td>
<td>14.35</td>
</tr>
<tr>
<td>13582.58</td>
<td>.64(4)</td>
<td>3p¹Π_g</td>
<td>14.00</td>
</tr>
<tr>
<td>18539.83</td>
<td>.65(4)</td>
<td>4d¹Π_g</td>
<td>14.58</td>
</tr>
<tr>
<td>20283.96</td>
<td>.64(4)</td>
<td>3d¹Σ⁺_g</td>
<td>13.86</td>
</tr>
<tr>
<td>20515.42</td>
<td>.65(4)</td>
<td>3d¹Π_g</td>
<td>13.89</td>
</tr>
<tr>
<td>21350.84</td>
<td>.66(4)</td>
<td>3d¹Π_g</td>
<td>13.90</td>
</tr>
<tr>
<td>22813.27</td>
<td>.66(4)</td>
<td>3s¹Σ⁺_g</td>
<td>14.00</td>
</tr>
</tbody>
</table>

a. In a 0.6 torr H₂ discharge with 50 mA current

b. Rest frequency of transitions

c. Threshold excitation energy of upper states
One can see that there is no obvious correlation with emitting state energy (over the limited range studied). Rather the shifts fall into two distinct groups: one for triplet and one for singlet excited states. Within each group $\Delta \nu_0$ is the same within experimental error.

The other quantitative observation is shown in Fig. 15. This figure plots the ratio of the shift of a emitting singlet state to that of an emitting triplet state as a function of discharge pressure. Clearly, this ratio is fairly strongly pressure dependent.

5.4 Theory

Either in ionic emissions or in neutral emissions, Doppler shift is the measure of non-random motion of the emissive particles. Neutral $\text{H}_2$ bear neither charges nor dipole moment. Their motions are not directly affected by the electric field in the discharge. One has to relate the observed non-random motion of neutral $\text{H}_2$ to charged particles in the discharge. The sign of the Doppler shifts has completely ruled out the possibility of any involvement of positive ions. As to negative charge carriers, in a $\text{H}_2$ discharge, it is no doubt that electrons are the only species of any abundance. Hence, we begin the developing of the theory with the assumption that the Doppler shifts observed for $\text{H}_2$ emission lines derive from momentum transferred from the electron-molecule collisions that produced the excited states. Since the observed emitting states are short-lived (typically $\tau \approx 30$ ns or less), any momentum transferred upon excitation should be unperturbed by any collisions before the state emits. This
Figure 15: The measured $\Delta_1/\Delta_3$ (solid dots) as a function of (a) the discharge pressure (pure hydrogen) and (b) the discharge electron temperature vs the theoretical predication of Eq.(5.20). The two lines chosen for the measurement are $R(0)$ of $2p^1\Sigma_u^+(v=1)-3d^1\Sigma_g^+(v=0)$ and $P(3)$ of $2s^3\Sigma_g^+(v=0)-4p^3\Sigma_u^+(v=0)$, which are shown in Fig.13. The electron temperature and the pressure are related by the Eq.(5.21).
means that no molecule-molecule collisions are involved and we need only to consider electron-molecule collisions in the theory.

5.4.1 Momentum Transfer of Electron-Molecule Collisions

Fig.16 depicts an electron-molecule collision event in a molecule-fixed collision frame whose $z'$-axis coincides with the velocity vector of the incident electron. The space-
fixed z axis at an angle \( \theta \) with respect to \( z' \), coincides with the axial of plasma electric field of the discharge (Because of cylindrical symmetry about \( z \), we can take the azimuthal angle at any value, and we chose zero).

In the molecule-fixed coordinate system, it is straightforward to write the equations expressing conservation of momentum in the \( z' \) and \( x' \) directions and conservation of total energy, respectively

\[
m u_e = m u'_e \cos \beta + M u'_M \cos \alpha \quad (5.1a)
\]

\[
u'_e \sin \beta + M u'_M \sin \alpha = 0 \quad (5.1b)
\]

\[
\frac{1}{2} m u^2_e = \frac{1}{2} m u^2'_e + \frac{1}{2} M u^2'_M + \varepsilon \quad (5.1c)
\]

where as usual, \( m \) and \( M \) denote the electronic and the molecular masses respectively. Velocities are denoted by \( u \)'s (with primes after collision) and \( \varepsilon \) is the threshold excitation energy of the emitting state.

These equations can be solved in the approximation, \( 1 + \frac{m}{M} \approx 1 \), to yield the resulting molecular velocity components,

\[
u'_{Mz'} = u'_M \cos \alpha = \frac{m}{M} u_e \left[ 1 - \left( 1 - \frac{\varepsilon}{E} \right)^{1/2} \cos \beta \right] \quad (5.2a)
\]

\[
u'_{Mx'} = u'_M \sin \alpha = \frac{m}{M} u_e \left( 1 - \frac{\varepsilon}{E} \right)^{1/2} \sin \beta \quad (5.2b)
\]

where \( E \) is the collision energy, which we take to be \( E = \frac{1}{2} m u^2_e \) since the \( \text{H}_2 \) molecule can be considered initially at rest in the collision frame.

If we now rotate the vector \( u'_M \) into the space-fixed coordinate system we find for the component, \( u'_{Mz'}(E, \theta, \beta) \) along the \( z \)-axis in the lab frame (the only term affecting
the observed Doppler shifts), the following expression

$$u'_{Mz}(E, \theta, \beta) = \frac{m}{M} \left[ 1 - \left( \frac{1 - \frac{e}{E}}{1/2} \cos \beta \right) (u_{ex} + u_{ex} \tan \alpha) \right]$$ \hspace{1cm} (5.3)

Eq.(5.3) describes the momentum transfer for a single collision by presenting the relation between the momentum of an incident electron and the momentum received by the molecule during the collision. To obtain the observed Doppler shift, we need to average this expression over several distribution functions such as the electron velocity distribution in the space-fixed system, the distribution of the scattering angle $\beta$ and the e-molecule excitation function as well. An average can be calculated according to the standard procedure

$$\langle \lambda \rangle = \int \lambda f(\lambda) \, d\lambda \hspace{1cm} (5.4)$$

where $f(\lambda)$ is the normalized distribution function for the quantity $\lambda$.

First we average over the distribution function for the scattering angle $\beta$, which is different for excitations to the singlet and triplet states. We take experimentally measured differential cross sections [64, 65] and numerically perform the integrations of these functions multiplied by $\cos \beta$. We find

$$\langle \cos \beta \rangle_3 = -0.03 \hspace{1cm} (5.5a)$$

$$\langle \cos \beta \rangle_1 = .91 \hspace{1cm} (5.5b)$$

The first value is consistent with the fact that the triplet excitation is basically an electron exchange process with a nearly isotropic distribution for the scattered electron. On the other hand the differential scattering cross section for singlet excitation is strongly peaked for small angle scattering, i.e., $\beta \approx 0$. 

Next is the averaging of (5.3) over the orientations of electron's velocity for a given electron energy \( E(=\mu_0^2/2) \). In the present case that electron's drift velocity is much smaller than its thermal velocity, a reasonable approximation for the required distribution functions can be obtained

\[
f\left(u_{ex}, u_{ey}, u_{ez}\right) = \left(\frac{m}{2\pi kT_e}\right)^{3/2} \exp\left\{\frac{\left[ u_{ex}^2 + u_{ey}^2 + \left( u_{ez} - u_d^e \right)^2 \right]}{2mkT_e} \right\}
\]

(5.6)

where \( u_d^e \) is the drift velocity, which, as will be seen, is a function of electron energy \( E \), and \( T_e \) is the electron temperature of the plasma. In writing (5.6) we have regarded the motion of electrons in a discharge as a thermal motion superposed by a small drifting motion in the z-axis direction. Using (5.4) an (5.6) to do the average over the orientations of electron's velocity, those angle-depended terms in (5.3) become

\[
\langle u_x \rangle = \langle u_y \rangle = 0
\]

(5.7a)

and

\[
\langle u_z \rangle = u_d^e(E)
\]

(5.7b)

With (5.6) and (5.7) we can now write

\[
\langle u'_{Mz} \rangle_i = \frac{m}{M} u_d^e(E) T_i(E)
\]

(5.8)

where

\[
T_i(E) = \left[ 1 - \langle \cos \beta \rangle_i \left( 1 - \frac{\varepsilon}{E} \right)^{1/2} \right]
\]

(5.9)

called momentum transfer factor, and \( i = 1 \) or 3 denoting either an excitation to a singlet or triplet state. Eq.(5.8) gives the net velocity component that molecules obtain through collisions with electrons of energy \( E \). The component is proportional to
\( u_e^d(E) \), the drift velocity of electrons at a given energy of \( E(=m_u^2/2) \). \( u_e^d(E) \) is an important quantity and will be discussed in the following section.

### 5.4.2 Electron’s Drift Velocity

To obtain the expression for \( u_e^d(E) \), we first use the definition to relate \( u_e^d(E) \) to \( w \), the average drift velocity of electrons in a discharge

\[
w = \int_0^\infty u_e^d(u_e)f_B(u_e)du_e
\]  

(5.10)

where

\[
f_B(u_e) = 4\pi \left( \frac{m}{2\pi kT_e} \right)^{3/2} u_e^2 e^{-\frac{u_e^2}{2m/kT_e}}
\]  

(5.11)

is the normalized Boltzman distribution function. The physical meaning of \( w \) as well as the methods for its measurement have been well established previously.

Based on the Maxwell-Boltzman transport equation for electrons in a gas in presence of external electric field \( \mathcal{E} \), the averaged drift velocity can also be calculated by

\[
w = -\frac{4\pi e \mathcal{E}}{3mN} \int_0^\infty \frac{u_e^2 \sigma_m(u_e)df_0}{du_e} du
\]  

(5.12)

where \( N \) is gas density, \( \sigma_m(u_e) \) the momentum transfer cross section for electron-molecule collisions, and the function \( f_0(u_e) \) has the form

\[
f_0(u_e) = \left( \frac{m}{2\pi kT_e} \right)^{3/2} e^{-\frac{(m\mathcal{E})^2}{2kT_e}}
\]  

(5.13)

Eq. (5.13) is valid when electron’s thermal velocity is much larger than its drift velocity, which is the case under our experimental conditions.
Putting (5.13) into (5.12) we obtain

\[
w = \int_0^\infty \frac{eE u_e}{3 N \sigma_m kT_e} \frac{4\pi m}{2\pi kT_e} \gamma_p u_e e^{-\frac{u_e^2}{2m kT_e}} du_e
\]

(5.14)

or

\[
w = \int_0^\infty \frac{eE u_e}{3 N \sigma_m kT_e} f_B(u_e) du_e
\]

(5.15)

Comparing (15) with (10), we obtain \( u^d_e(E) \) as a function of electron energy \( E \) and other discharge parameters as

\[
u^d_e(E) = \frac{eE}{3N \sigma_m(u_e) kT_e} = \left( \frac{2}{m} \right)^{1/2} \frac{eE}{3N \sigma_m(E) kT_e} E^{1/2}
\]

(5.16)

Eq.(5.16) is simple but interesting and needs some discussions.

1) Like the drift velocity of ions, \( u^d_e(E) \) is proportional to \( E \) and inversely proportional to \( 1/(N \sigma_m) \), indicating that the electric field makes electrons to drift while gas molecules slow them down by electron-molecule collisions. The registration of \( \sigma_m \), rather than the total collision cross section, in the Eq.(16) assures that only those collisions that change the electron’s momentum will effect the drift velocity, \( u^d_e(E) \).

\( \sigma_m(E) \) is related to the total differential cross section, \( \sigma_t(E, \theta, \varphi) \), as

\[
\sigma_m(E) = \int_0^\infty \sigma_t(E, \theta, \varphi)(1 - \cos \theta) d\Omega
\]

(5.17)

where \( \theta \) and \( \varphi \) are scattering angles. At high energy, the \( \theta \) angle becomes small and so does \( \sigma_m(E) \). A decrease in \( \sigma_m(E) \) will, according to Eq.(5.1), increase \( u^d_e(E) \).

2) \( u^d_e(E) \) is inversely proportional to the electron temperature \( T_e \), which represents electron’s thermal motion. It is always the case that the electron’s thermal velocity \( u_e = (2kT_e/m)^{1/2} \) is much larger than either molecular thermal velocity or
the electron's drift velocity. The electron's thermal motion, therefore, controls the frequency of electron-molecule collisions. The larger the $u_e$, the higher the collision frequency and the smaller the electron's drift velocity. This is the reason for the inverse law with regards to $T_e$. Usually electron temperatures of molecular gas discharges are lower than that of noble gas discharges because the electrons are slowed down more effectively by inelastic collisions in molecular gases. As a result, the electron's drift velocities are higher in molecular gases discharges than in noble gas discharges and so are the Doppler shifts of neutral emissions. This has experimentally been verified as we have observed a large difference between Doppler shifts of He emissions in H$_2$ and in He discharges.

3) $u_e^2(E)$ is proportional to $E^{1/2}$, the square root of electron's energy. This correlation between $u_e^2(E)$ and $E$ is very interesting yet very reasonable. For example, at a given moment, if an electron has a high energy $E$, it means that during certain time right before this specific moment, the electron has suffered fewer collisions than those lower energy electrons have so that it can accumulate its energy gained from the electric field. While it accumulating the total energy, the electron also accumulates the drift velocity gained from the field. As a result, $u_e^2(E)$ and $E$ are related as Eq.(5.16).
5.4.3 The Observed Doppler Shift

The Doppler shift that is caused by the collisions with electrons of energy $E$ is

$$\frac{\Delta \nu}{\nu_0} = \frac{u_e(E)}{c}$$ (5.17)

To obtain the observed Doppler shift, we need to average this expression over the probability, $F(E)$, that a photon was observed as a result of a collision between a molecule and an electron of energy $E$. We take the probability as proportional to the cross section for excitation, $\sigma_i(E)$, and the number of electrons available at energy $E$, whose distribution of electron energies as Maxwellian. Therefore

$$F(E) = \sigma_i(E) \frac{2}{\sqrt{\pi} E^{3/2}} e^{-\frac{E}{E_T}}$$ (5.18)

Thus we obtain the result that the observed Doppler shift for emission from state $i$ can be expressed

$$\left(\frac{\Delta \nu}{\nu}\right)_i = \frac{\langle u_{Mz} \rangle_i}{c} = \frac{m}{Mc} \frac{\int_0^\infty u_i^4(E) F_i(E) [1 - \langle \cos \beta \rangle_i (1 - \frac{E}{E_T})^{1/2}] dE}{\int_0^\infty F_i(E) dE}$$ (5.19)

Eq.(5.19) relates Doppler shift to electron’s drift velocity as well as the momentum transfer between electrons and molecules. It provides a basis on which the interpretation of the experimental result may be attempted. Using Eq.(5.19) and Eq.(5.16) we obtain the expression for $\Delta_1/\Delta_3 (\Delta=\Delta \nu/\nu_0)$, the ratio of singlet shift to triplet shift

$$\frac{\Delta_1}{\Delta_3} = \frac{\int_0^\infty \frac{\sigma_1 E}{\sigma_m} e^{-E/E_T} [1 - \langle \cos \beta \rangle_1 (1 - \frac{E}{E_T})^{1/2}] dE}{\int_0^\infty \frac{\sigma_2 E}{\sigma_m} e^{-E/E_T} [1 - \langle \cos \beta \rangle_2 (1 - \frac{E}{E_T})^{1/2}] dE} \times \frac{\int_0^\infty \sigma_3 E^{1/2} e^{-E/E_T} dE}{\int_0^\infty \sigma_1 E^{1/2} e^{-E/E_T} dE}$$ (5.20)

Eq.(5.20) is useful because it doesn’t contain the unknown $E/N$ and may be calculated numerically. The electron temperature, $E_T=K_T$, in the discharge can be determined
by the following equation\[69\]

$$\frac{e^{V/V_0}}{(\frac{V}{E})^{1/2} + 2(\frac{E}{V})^{1/2}} = a^2 R^2 P^2$$

(5.21)

where

\( V \) = Ionization Potential of H\(_2\)

\( P \) = Gas pressure in torr

\( R \) = radius of the discharge tube in cm

and the \( a \) is an empirical constant; for H\(_2\) \( a^2 = 2.14 \times 10^3 \)

To obtain \( \sigma_i \) we return to previous experimental data. While experimental electron impact excitation cross sections are not available for all the observed states, we note that for states of comparable excitation threshold energy, \( \varepsilon_i \), the experimental curves can be well represented by the following empirical equation

$$\sigma_i = \begin{cases} 0 & E < \varepsilon_i \\ \frac{1-e^{-\frac{\varepsilon_i}{b_i}}}{1-e^{-\varepsilon_i}} & E \geq \varepsilon_i \end{cases}$$

(5.22)

where \( b_i \) is a constant that can be determined by simulating the experimental curve with Eq.(5.22). The denominator in Eq.(5.22) is introduced for normalization. In Fig.17 we show that the simulation by Eq.(5.22) is in good agreement with the available experimental data[65, 66].

The momentum transfer cross section \( \sigma_m \) is available from previous experiments. Fig.18 is its reconstruction from the data provided by previous experiments.
Figure 17: Simulation of the experimental excitation cross sections by Eq.(12). The normalized experimental points (solid dots) are reconstructed from ref[66] for the triplet excitation and ref[65] for singlet excitation. The parameters that enter into Eq.(5.22) are respectively $b_3=18.1\text{eV}$, $b_1=79.0\text{eV}$ and $\varepsilon=14.0\text{eV}$. 
Figure 18: The experimental momentum transfer cross section and its simulation. The experimental points (solid dots) are reconstructed from refs [67] and [68] and simulated by the function \( \sigma_m(E) = (16/E + 400/E^2) \times 10^{-16} \text{cm}^2 \).
5.5 Discussion

There are several experimental observations that need to be understood theoretically. The first and simplest result is the relation of the Doppler shifts among isotopomers as shown in Fig. 14. Eq. (5.19) of section IV predicts an inverse molecular mass dependence, or \( \text{H}_2: \text{HD}: \text{D}_2 = 1.00:0.67:0.50 \) which compares well with the experimental ratio from Fig. 14 of 1.00:0.71(4):0.49(4). This is apparently the result of the conservation of momentum in electron-molecule collisions.

A second and much more stringent test of our understanding of the phenomenon is given by Fig. 15 where the ratio of singlet/triplet Doppler shifts, \( \Delta_1/\Delta_3 \), is plotted vs pressure or electron temperature, the latter two quantities being related by Eq. (5.21). As can be seen from Fig. 15, there is an excellent quantitative agreement between the experimental observations and the curves generated from Eq. (5.22). This result is more remarkable since no parameters were fitted to achieve this agreement. All the factors entering into Eq. (5.22) were determined from previous investigations.

While the quantitative agreement is important, it is useful to understand the qualitative reason behind the variation of \( \Delta_1/\Delta_3 \) with \( kT_e \). This ratio departs from unity the most under the conditions when the electron temperature is highest. The principle, but not quantitatively sufficient, explanation for this non-unity ratio comes from the transfer function \( T_e \) (given by Eq. (5.9) and shown in Fig. 19). As Fig. 19 shows, as the energy of electron increases, the percentage transfer of the electron momentum to triplet hydrogen remains constantly high, but decreases dramatically for singlet hydrogen. Fig. 17 shows that high energy electrons remain efficient for excitation of
Figure 19: Plots of the momentum transfer factor $T_s(E)$ as a function of electron energy for singlet-singlet excitation and for singlet-triplet excitation.
the singlet states. As $kT_e$ rises, more high energy electrons with small $T_e$ become available for excitations of the singlet states and reduce their average Doppler shift.

The final point that requires discussion is the magnitude of the observed Doppler shift. We can evaluate Eq. (5.19) for a triplet $\text{H}_2$ excitation. Under typical discharge condition ($P=0.6$ torr and $400K$ gas temperature), we have $N=1.44 \times 10^{16}$ molecule/cm$^3$, and from Eq. (5.22), $kT_e=4.93$ eV. We can then express, via Eq. (5.22), the plasma field in term of the absolute Doppler shift,

$$\mathcal{E} = 2.08(\Delta \nu/\nu_0)_3 \times 10^7 = 20.4 \text{ V/cm}$$

(5.23)

This $\mathcal{E}$ value seems rather large, but is supported by its independent measurement via the Doppler shift of the B-X emission of $\text{N}_2^+$. By adding 40 mtorr $\text{N}_2$ gas into the 0.6 torr $\text{H}_2$ discharge, we were able to obtain the B-X emission spectrum of $\text{N}_2^+$ and its Doppler shift, $(\Delta \nu/\nu_0)_+$. As described previously, $\mathcal{E}$ can be determined by the following equation

$$\mathcal{E} = \frac{Mc}{er} \left( \frac{\Delta \nu}{\nu_0} \right)_+$$

(5.24)

where $M$ is the mass of $\text{N}_2^+$ and $r(=63$ ns) the lifetime of the emissive B state of $\text{N}_2^+$. The measured $(\Delta \nu/\nu_0)_+$ is $1.36 \times 10^{-6}$ and Eq. (5.24) therefore leads to

$$\mathcal{E} = 18.9 \text{ V/cm}$$

(5.25)

Under these discharge conditions, the value of $\mathcal{E}$ from the $\text{H}_2$ neutral Doppler shift is $19.8$ V/cm. Given the uncertainties in the measured $\sigma$'s etc. entering into $\mathcal{E}$, the equivalent values must have uncertainties of $10\sim15\%$. Thus the $\mathcal{E}$'s measured from $\text{H}_2$ and $\text{N}_2^+$ Doppler shifts are clearly consistent.
The high electric field in the discharge suggested by either Eq. (5.23) or Eq. (5.25) is due partially to the small diameter of the discharge tube. It is well known [70] that the electric field will be enhanced if a small diameter discharge tube is used. The method of Eq. (5.24) has allowed an experimental investigation of the discharge tube size effect. We also studied a He discharge because its discharge electric field is known from previous experiment for a 8 mm diameter tube. Under the gas condition of 10 mtorr N₂ in a 0.5 torr He, the electric field was found to be 14.2 V/cm, compared to 6.4 V/cm in the 8 mm tube and under the same gas conditions.

5.6 Conclusion

Overall there seems to be almost remarkable agreement between the observed Doppler shifts and our predictions based upon a large number of previously measured electron-H₂ collision properties. As Eq. (5.1) shows, the Doppler shift is determined by an energy average over three parameters, u₂(E), \( T_\parallel(E) \) and \( F_\parallel(E) \). The latter two functions depend primarily upon excitation cross sections and scattering angles, which, at least for H₂-e⁻ collisions, seems to have been well determined previously. Thus in the present case the Doppler shift really reduces to a measurement of the electron drift velocity, \( u_d(E) \), for those electrons energetic enough to excite the observed emission.

In turn \( u_d(E) \) depends fundamentally upon the acceleration provided by the electric field \( \mathcal{E} \), and the drag caused by H₂ collisions as measured by the momentum changing cross section \( \sigma_m(E) \). Again we find pleasing consistency between our present
experiment and previous work. Taking $\sigma_m(E)$ from earlier work, we obtain the same value for $\mathcal{E}$ as that determined by free acceleration of $N_2^+$. Alternatively, we could use the $\mathcal{E}$ from the $N_2^+$ measurement and determine $\sigma_m(E)$ which would be consistent with previous measurements.

Overall we have demonstrated the ability to experimentally observe and measure Doppler shifts of neutral H$_2$ caused by momentum transfer from electron collisions. We have also demonstrated that in a system where the electron-molecule collisions are well understood as those in H$_2$ the experiment yields a reliable value of the plasma electric field. In less understood systems, independent measurement of the electric field, e.g. via $N_2^+$, may yield new information on the details of electron-molecule collisions.
CHAPTER VI

Determination of Concentration via the Diminution of Doppler Shifts by Radiation Trapping

6.1 Introduction

In the last three chapters, we have shown that quite small Doppler shifts can be accurately measured using the technique of Doppler Shifted Fourier Transform Spectroscopy (DSFTS). We have applied this technique to study the motion of ions and neutrals along the direction of the weak axial plasma electric field of the positive column of a DC discharge. We have used the high stability and resolution of FTS to measure small Doppler shifts of atomic and molecular emissions as the polarity of the discharge is reversed. The Doppler shifts of the emission of the ions are directly attributable to their acceleration along the field direction.[72] Since the ion's final velocity and corresponding Doppler shift depend upon the duration of this acceleration, these shifts have proven[73] to be a sensitive diagnostic of ionic creation and destruction mechanisms. Doppler shifts in the emission of light neutral atoms and molecules have also been recently observed[74] and result from similarly accelerated electrons and their subsequent momentum transfer in the collisions that generate the excited emissive states.
In this chapter, we will consider exclusively the emission from neutral He atoms. In a departure from our previous work, we will not discuss in detail the production of the emissive states rather we simply treat these states as “prepared” from a random ensemble of He atoms. This prepared sample is unique in two respects. It is internally electronically excited and it has a unique velocity component along the field direction (defined as z) created by the momentum transfer in the collision. We use the former property, with its photon emission of characteristic Doppler shift, as a means of monitoring the latter quantity.

Under some experimental conditions the unique velocity component would be randomized by collisions with other He atoms either in the excited state or after the atom has decayed to its ground state where it can no longer be monitored by our approach. In the present case, no significant collisional effects occur in the excited state because of its relatively short lifetime and the low gas pressure. Rather, the randomizing of the velocity of excited state atoms occurs because of the phenomenon of radiation trapping. Because the absorption/re-emission process causes the initially prepared state to communicate with the “bath” of He atoms it allows the approach to thermal equilibrium for the translational velocity of the prepared atoms. A similar effect has been reported for the destruction of excited state polarization.[75] Basically photons with characteristic Doppler shifts are emitted from atoms initially excited by electron-atom collisions with concomitant momentum transfer. In the trapping process, these photons are absorbed by atoms with partially randomized velocity vectors. However, the memory of the unique component of the velocity of the initial
atom is not completely eradicated in a single trapping cycle. Rather each trapping cycle reduces the Doppler shift by a numerical factor that we calculate.

Given this result, the observed Doppler shift depends upon the average number of trapping cycles, $\bar{\gamma}$. The determination of $\bar{\gamma}$ has often been the goal of radiation trapping investigations using various techniques such as the optical double-resonance method[76], the Hanle effect[77], pulsed optical technique[78], the pulsed magnetic technique[79], pulsed electron beam technique[80] and the stepwise-excitation coincidence technique[81]. For most of these techniques, radiation trapping is detected by monitoring the emission in a time-resolved manner, utilizing the fact that radiation trapping prolongs the lifetime of the emissive atoms. The Doppler shift method presently described, however, allows a direct measurement of the $\bar{\gamma}$ value, providing an alternative way for dealing with a steady-state system. The $\bar{\gamma}$ value depends only on the medium's absorption coefficient, a parameter determined by the number of trapping atoms and the oscillator strength of the transition.

Since oscillator strengths are often well known for atomic transitions, a measurement of $\bar{\gamma}$ from the observed Doppler shift can determine the medium's absorption coefficient. We show that under fairly widely applicable conditions that there is a simple relationship between the medium's absorption coefficient and the density of the trapping species.

While this relationship contains often-difficult-to-determine geometric information it is possible to eliminate this potential unknown in the determination of the relative density of two trapping species in the same volume. We apply this result
to determine the absolute concentration of metastable $^2S$ He in the discharge from the easily measurable ground state density. This approach does not require that the chemical identity of the species be the same for the densities of the two states being ratioed. This technique therefore offers the possibility of a fairly general diagnostic of the concentrations of metastable, excited state and reactive ground state species, if they are responsible for observable radiation trapping.

6.2 Theory

There are several important steps in adequately describing the effect of radiation trapping on Doppler shifts. We break our analysis into the following steps. (A) First, we calculate the diminution factor $\beta(1)$ of the Doppler shift for a single absorption/re-emission cycle of a two-level system. (B) We then relate $\beta(1)$ to the observed diminution factor $\overline{\beta}$, which we show equals $\beta\left(\overline{y}\right)$, where $\overline{y}$ is the average number of trapping cycles for the system. (C) Under fairly general conditions, $\overline{\beta}$ is related to the number density of the trapping state. (D) Finally, we justify the application of the two-level model to a multi-level experimental system.

6.2.1 Doppler Shift Diminution by a Single Trapping Cycle

It is useful to briefly review the calculation of the Doppler shift in the absence of radiation trapping, a subject treated in more detail elsewhere. Consider a two-level atomic gas system illustrated in Fig. 20(a) with states 1 and 2 and corresponding
velocities. The photon emitted from level 2 will have the frequency, \( \nu(2) \), if it is viewed in the direction of \( \vec{k}_2 \)

\[
\nu(2) = \nu_{21}^{\theta} + \frac{\vec{k}_2 \cdot \vec{u}_2}{c} \nu_{21}^{\theta} \tag{6.1}
\]

where \( \nu_{21}^{\theta} \) is the rest frequency for the transition. The last term in Eq. (6.1) represents the frequency shift due to the Doppler effect; \( \vec{k}_2 \) is the unit vector representing the propagation direction of the photon from the atom moving with velocity, \( \vec{u}_2 \).

When there is no radiation trapping, the photon emitted by the atom escapes the gas volume immediately upon emission. For a detector on the z axis, the fractional Doppler shift, \( \Delta \nu / \nu_{21}^{\theta} \), from the rest frequency is given by

\[
\frac{\Delta \nu(2)}{\nu_{21}^{\theta}} = \frac{\vec{k}_z \cdot \vec{u}_2}{c} \tag{6.2}
\]

where \( \vec{k}_z \) is the unit vector along the \( z \) direction. The observed Doppler shift is the average of Eq. (6.2) over \( f_2(\vec{u}_2) \), the velocity distribution function of the emitting atoms (atoms in state 2)

\[
\left\langle \frac{\Delta \nu}{\nu_{21}^{\theta}} \right\rangle = \frac{\int_{-\infty}^{\infty} \left( \vec{k}_z \cdot \vec{u}_2 \right) f_2(\vec{u}_2) d \vec{u}_2}{c \int_{-\infty}^{\infty} f_2(\vec{u}_2) d \vec{u}_2} \tag{6.3}
\]

If the velocity distribution were random, the averaged \( z \)-component of \( \vec{u}_2 \) would be zero causing the Doppler shift to vanish. However, when the excited state atoms are produced by collisions with electrons accelerated along the discharge axis (also along \( z \)) and suffer no collisions prior to emission, \( f_2(\vec{u}_2) \) can be taken as
Figure 20: Illustration for (a) a two-level and (b) a three-level system with radiation trapping between 1 and 2.
where \( k \) is the Boltzmann constant, \( T \) is the gas temperature, \( M \) the mass of the gas atoms, \( u'_{Mz} \) the (non-zero) averaged \( z \) component of atom's velocity and \( \overline{u^2} = \frac{kT}{M} \) the averaged square of the thermal velocity. (In the present analysis we assume that there is only one temperature and hence one \( \overline{u^2} \) for a given species of atom, independent of the state.) The relationship of \( u'_{Mz} \) with the parameters defining the motion of electrons in the discharge has been discussed previously.

Using Eq. (6.4) to integrate Eq. (6.3) one obtains

\[
\left\langle \frac{\Delta \nu}{\nu_{21}} \right\rangle _0 = \frac{u'_{Mz}}{c}
\]

the Doppler shift without radiation trapping, with the subscript 0 denoting zero trapping cycles. We now consider the case of a single radiation trapping cycle. A photon initially emitted from an atom of velocity \( \overrightarrow{u}_2 \) may be absorbed by one of the surrounding atoms in the lower state 1 in Fig. 20(a). The resonance condition requires that the absorbing atom's component of the velocity, \( \overrightarrow{u}_1 \), along \( \overrightarrow{k}_2 \) must equal that of the initial atom, i.e.,

\[
\overrightarrow{u}_1 \cdot \overrightarrow{k}_2 = \overrightarrow{u}_2 \cdot \overrightarrow{k}_2
\]

(In writing Eq. (6.6) we have assumed an infinitely narrow natural absorption linewidth. According to Appendix A, this is a very good assumption under our, and likely many other, experimental conditions.) Once the second atom absorbs the
initial photon, it is promoted to the excited state 2 and subsequently emits a photon in the $\vec{k}_1$ direction. The frequency, $\nu(1)$, of the emitted photon will be

$$\nu(1) = \nu_{21}^0 + \frac{\vec{k}_1 \cdot \vec{u}_1}{c} \nu_{21}^0$$

(6.7)

Since the detector still lies along the $z$ axis, for the photon to be observed $\vec{k}_1 = \vec{k}_2$, and the Doppler shift of the detected photon will be

$$\frac{\Delta \nu(1)}{\nu_{21}^0} = \frac{\vec{k}_2 \cdot \vec{u}_1}{c}$$

(6.8)

To obtain the observed fractional Doppler shift after one trapping cycle, it is necessary to average Eq.(6.8) over three quantities, the velocity, $\vec{u}_2$, of the atom which initiates the cycle, the propagation direction, $\vec{k}_2$, of the initial photon, and $\vec{u}_1$ the velocity of the absorbing atom. There is no restriction on the properties, $\vec{u}_2$ and $\vec{k}_2$, associated with the first atom and its emitted photon, but for a given $\vec{u}_2$ and $\vec{k}_1$, $\vec{u}_1$ is restricted to only certain allowed values by Eq. (6.6). For a single trapping cycle, the observable Doppler shift corresponding to the average over all three variables is denoted by $\langle \frac{\Delta \nu}{\nu_{21}^0} \rangle_1$.

We can write the average of Eq.(6.8) over $\vec{u}_1$, $\vec{u}_2$, and $\vec{k}_2$ as

$$\langle \frac{\Delta \nu}{\nu_{21}^0} \rangle_1 = \frac{\int \int_S \left( \vec{k}_2 \cdot \vec{u}_1 \right) f_1(\vec{u}_1) f_2(\vec{u}_2) f_k(\vec{k}_2) d\vec{u}_1 d\vec{u}_2 d\vec{k}_2}{c \int \int_S f_1(\vec{u}_1) f_2(\vec{u}_2) f_k(\vec{k}_2) d\vec{u}_1 d\vec{u}_2 d\vec{k}_2}$$

(6.9)

where the first integral over $\vec{u}_1$ is restricted to the surface, $S$, in velocity space prescribed by Eq.(6.6) while the integrals over $\vec{u}_2$ and $\vec{k}_2$ are unrestricted.
To perform the restricted integration over $\mathbf{u}_1$, we can use Eq.(6.6) to write

$$\mathbf{u}_1 = \mathbf{u}_2 + \mathbf{\rho}$$  \hspace{1cm} (6.10)

where $\mathbf{\rho}$ is an arbitrary vector lying on the surface $S$ to which $\mathbf{k}_2$ is perpendicular. These relationships are clearly shown in Fig.21.

Substituting for $\mathbf{u}_1$ in Eq.(6.9) we have

$$
\langle \Delta \nu \rangle_{21} = \frac{\int \int_S \mathbf{k}_2 \cdot (\mathbf{u}_2 + \mathbf{\rho}) f_1 (\mathbf{u}_1) f_2 (\mathbf{u}_2) f_k (\mathbf{k}_2) d \mathbf{u}_1 d \mathbf{u}_2 d \mathbf{k}_2}{c \int \int_S f_1 (\mathbf{u}_1) f_2 (\mathbf{u}_2) f_k (\mathbf{k}_2) d \mathbf{u}_1 d \mathbf{u}_2 d \mathbf{k}_2} = \left( \frac{\Delta \nu}{\nu_{21}} \right)_{1} \hspace{1cm} (6.11)
$$

$$
\int \int_S \left[ (\mathbf{k}_2 \cdot \mathbf{u}_2) + (\mathbf{k}_z \cdot \mathbf{\rho}) \right] f_1 (\mathbf{u}_1) f_2 (\mathbf{u}_2) f_k (\mathbf{k}_2) d \mathbf{u}_2 d \mathbf{\rho} = \int \int_S f_1 (\mathbf{u}_1) f_2 (\mathbf{u}_2) f_k (\mathbf{k}_2) d \mathbf{u}_1 d \mathbf{u}_2 d \mathbf{k}_2
$$

The integral over $\mathbf{u}_1$ is easiest to perform if we transform to a coordinate system $(x', y', z')$ where $z'$ coincides with $\mathbf{k}_2$ and $x'$ and $y'$ lie on $S$. In the primed coordinate system

$$\mathbf{\rho} = (\rho_{x'}, \rho_{y'}, 0)$$  \hspace{1cm} (6.12)

$$\mathbf{z} = (R_{13}, R_{23}, R_{33})$$  \hspace{1cm} (6.13)

$$f_1 (\mathbf{u}_1) = f (\mathbf{u}_2 + \mathbf{\rho}) = K \exp \left\{ - \left[ (\rho_{x'} + u_{2x'})^2 + (\rho_{y'} + u_{2y'})^2 + u_{2z'}^2 / u_{2z}^2 \right] \right\}$$  \hspace{1cm} (6.14)

where $K$ is a normalization constant. In writing Eq.(6.12), we have used the fact that $\mathbf{\rho}$ lies on the surface $S$. In Eq.(6.13), the $R_{ij}$'s are the elements of the transformation matrix which relates the $(x, y, z)$ and $(x', y', z')$ coordinate systems. Eq.(6.14) follows from the Boltzmann distribution of velocities.
Figure 21: Schematic diagram showing the geometric relationships among the various velocities and photon propagation vectors. The detector is assumed to be on the z axis.
Both the numerator and the denominator can now be integrated analytically with respect to $\vec{u}_1$ with the result,

$$
\int_S (\vec{k}_z \cdot \vec{p}) f_1 (\vec{u}_1) d \vec{u}_1 = \int_{-\infty}^{\infty} K \left( R_{23} \rho_{22'} + R_{23} \rho_{22'} \right) \times 
$$

$$
\exp - \left\{ \left[ (\rho_{22'} + u_{22'})^2 + (\rho_{22'} + u_{22'})^2 + u_{22'}^2 \right] / \vec{u}_1^2 \right\} d\rho_{22'} d\rho_{22'} \quad (6.15)$$

$$
= -K \pi \vec{u}_1^2 (R_{13} u_{22'} + R_{23} u_{22'}) \exp - \left( u_{22'}^2 / \vec{u}_1^2 \right)
$$

and

$$
\int_S f_1 (\vec{u}_1) d \vec{u}_1
$$

$$
= K \int_{-\infty}^{\infty} \exp - \left\{ \left[ (\rho_{22'} + u_{22'})^2 + (\rho_{22'} + u_{22'})^2 + u_{22'}^2 \right] / \vec{u}_1^2 \right\} d\rho_{22'} d\rho_{22'} \quad (6.16)
$$

$$
= K \pi \vec{u}_1^2 \exp - \left( u_{22'}^2 / \vec{u}_1^2 \right)
$$

To complete the simplification of Eq.(6.11), we express the dot product $\left( \vec{k}_z \cdot \vec{u}_2 \right)$ in the primed coordinate system

$$
\left( \vec{k}_z \cdot \vec{u}_2 \right) = R_{13} u_{22'} + R_{23} u_{22'} + R_{33} u_{22'}
$$

(6.17)

Substituting Eqs.(6.15-6.17) in Eq.(6.11) yields

$$
\langle \Delta \nu / \nu_{21} \rangle_1 = \frac{\int \int R_{33} u_{22'} \exp - \left( u_{22'}^2 / \vec{u}_1^2 \right) f_2 (\vec{u}_2) f_k (\vec{k}_2) d \vec{u}_2 d \vec{k}_2}{c \int \int \exp - \left( u_{22'}^2 / \vec{u}_1^2 \right) f_2 (\vec{u}_2) f_k (\vec{k}_2) d \vec{u}_2 d \vec{k}_2} \quad (6.17)
$$

or

$$
\langle \Delta \nu / \nu_{21} \rangle_1 = \frac{\int \int \left( \vec{k}_2 \cdot \vec{u}_2 \right) \left( \vec{k}_2 \cdot \vec{u}_2 \right) \exp - \left[ \left( \vec{k}_2 \cdot \vec{u}_2 \right)^2 / \vec{u}_1^2 \right] f (\vec{u}_2) f_k (\vec{k}_2) d \vec{u}_2 d \vec{k}_2}{c \int \int \exp - \left[ \left( \vec{k}_2 \cdot \vec{u}_2 \right)^2 / \vec{u}_1^2 \right] f (\vec{u}_2) d \vec{u}_2} \quad (6.19)}
where in Eq.(6.19) we have expressed $R_{33}$ and $u_{2z'}$ in terms of the dot products $\left( \vec{k}_2 \cdot \vec{k}_{2'} \right)$ and $\left( \vec{k}_2 \cdot \vec{u}_2 \right)$ respectively.

Eq.(6.19) admits of a relatively straightforward physical interpretation. The factor $(\vec{k}_2 \cdot \vec{u}_2)/c$ is just the fractional Doppler shift of the first photon emitted along the direction $\vec{k}_2$. Since the only non-random component of velocity of the second atom lies along $\vec{k}_2$ (due to Eq.(6.6)), the final non-zero Doppler shift depends upon the projection $\left( \vec{k}_2 \cdot \vec{k}_2 \right)$ of $\vec{k}_2$ along the detector axis ($z$), for only photons finally emitted along $z$ can be observed.

The appearance of the exponential factor in the numerator of Eq.(6.19) results from the fact that the probability that the initial photon is trapped is dependent upon the relative orientation of the emitting atom's velocity vector $\vec{u}_2$ and its photon propagation direction $\vec{k}_2$. (The denominator just provides normalization of this probability function.) This probability distribution is again proportional to the Maxwell Boltzmann distribution which specifies the number of atoms available with a given velocity $\vec{u}_1$. For example, if $\vec{k}_2$ and $\vec{u}_2$ are parallel, the photon suffers the maximum Doppler shift, but then only atoms towards the wings of the Maxwell-Boltzmann have velocities appropriate for absorption. Only the $\vec{k}_2$ component of the velocity distribution survives in the expression, because it is only in this direction that distribution will be non-random and contribute a non-zero Doppler shift after averaging over $\vec{u}_1$.

To perform the averaging implicit in Eq.(6.19), we express $f_2(u_2)$, via Eq.(6.4),
and integrate over \( \overrightarrow{u}_2 \) yielding

\[
\left\langle \frac{\Delta \nu}{\nu_{21}} \right\rangle_1 = \left( \frac{u_{mx}'}{2c} \right) \frac{\int (\overrightarrow{k}_2 \cdot \overrightarrow{k}_2) \exp \left( \frac{(\overrightarrow{k}_2 \cdot \overrightarrow{k}_2)^2 u_{mx}^2}{2u^2} \right) f(\overrightarrow{k}_2) d\overrightarrow{k}_2}{\int \exp \left( \frac{(\overrightarrow{k}_2 \cdot \overrightarrow{k}_2)^2 u_{mx}^2}{2u^2} \right) f(\overrightarrow{k}_2) d\overrightarrow{k}_2}
\]

(6.20)

Now the average over \( \overrightarrow{k}_2 \) can be performed by expressing its isotropic angular dis­tributor function i.e., \( f(\overrightarrow{k}_2) = \text{const} \), and performing the integration over all angles. Explicitly,

\[
\left\langle \frac{\Delta \nu}{\nu_{21}} \right\rangle_1 = \left( \frac{u_{mx}'}{2c} \right) \frac{\int_0^{2\pi} \int_0^\pi \cos^2 \theta \exp \left( \frac{\cos^2 \theta u_{mx}^2}{2u^2} \right) d\phi \sin \theta d\theta}{\int_0^{2\pi} \int_0^\pi \exp \left( \frac{\cos^2 \theta u_{mx}^2}{2u^2} \right) d\phi \sin \theta d\theta}
\]

(6.21)

In writing Eq.(6.21), we have used the following relationships (see Fig. 21) \( (\overrightarrow{k}_2 \cdot \overrightarrow{k}_2) = \cos \theta \), \( \overrightarrow{k}_2 = (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta) \), and the differential solid angle element \( d\Omega = d\phi \sin \theta d\theta \).

Performing the integral over \( \phi \), substituting \( \xi = \cos \theta \), and expanding the exponential yields

\[
\left\langle \frac{\Delta \nu}{\nu_{21}} \right\rangle_1 = \frac{u_{mx}'}{2c} \frac{\int_1^1 \xi^2 \exp \left( \frac{\xi u_{mx}^2}{2u^2} \right) d\xi}{\int_1^1 \exp \left( \frac{\xi u_{mx}^2}{2u^2} \right) d\xi} = \frac{u_{mx}'}{6c} \left[ 1 + \frac{2}{15} \left( \frac{u_{mx}'}{u} \right)^2 + \cdots \right]
\]

(6.22)

In arriving at the second equality in Eq.(6.22) we have expanded all the exponential functions in terms of a series in the factor, \( (u_{mx}' / u) \), which is equal to the ratio of the Doppler shift to the linewidth, which is about \( 10^{-1} \) or less under our experimental conditions. In the above, we denote \( \sqrt{u^2} \) by \( u \). The second term in the expansion is
thus negligibly small ($\sim 10^{-3}$) as are terms of higher order. Therefore the Doppler shift for photons undergoing one absorbing-remitting trapping cycle is given by

$$\left\langle \frac{\Delta \nu}{\nu_{21}} \right\rangle_1 = \frac{1}{6} \frac{u_{im}}{c} \beta(1) \left\langle \frac{\Delta \nu}{\nu_{21}} \right\rangle_0 \quad (6.23)$$

The diminution factor $\beta(1)$ of $\left\langle \frac{\Delta \nu}{\nu_{21}} \right\rangle$ can be seen to arise physically from two sources. A factor of $\left(\frac{1}{2}\right)$ results from the angular average of $\cos^2 \theta$ over the surface of a sphere while the remaining factor $\left(\frac{1}{8}\right)$ comes from the increased probability of photons with small Doppler shifts to be trapped.

6.2.2 The Observed Diminution Factor, $\overline{\beta}$

If we consider an arbitrary number, $y$, of trapping cycles it is clear that each cycle is independent and identical so that

$$\left\langle \frac{\Delta \nu}{\nu_{21}} \right\rangle_y = \beta(y) \left\langle \frac{\Delta \nu}{\nu_{21}} \right\rangle_0 = \left(\frac{1}{6}\right)^y \left\langle \frac{\Delta \nu}{\nu_{21}} \right\rangle_0 \quad (6.24)$$

or that

$$\beta(y) = \left(\frac{1}{6}\right)^y = e^{-y \ln 6} \quad (6.25)$$

If we want the observed or average value, $\bar{\beta}$, for the ensemble we have

$$\bar{\beta} = \int \left(\frac{1}{6}\right)^y f(y) \, dy = \int e^{-y \ln 6} f(y) \, dy \quad (6.26)$$

where $f(y)$ is the distribution function for the number of trapping cycles, $y$. If we now use a power series expansion of the exponential, we obtain

$$\bar{\beta} = 1 - y \ln 6 + \frac{1}{2!} (y^2) (\ln 6)^2 - \frac{1}{3!} (y^3) (\ln 6)^3 + ... \quad (6.27)$$
where

$$\overline{(y^n)} = \int y^n f(y) \, dy \quad (6.28)$$

We note that if we write $\bar{\beta} \equiv \beta(\bar{y})$ we have

$$\bar{\beta} \equiv \left(\frac{1}{6}\right)^{\bar{y}} = e^{-\bar{y} \ln 6} = 1 - \bar{y} \ln 6 + \frac{1}{2!} (\bar{y})^2 (\ln 6)^2 - \frac{1}{3!} (\bar{y})^3 (\ln 6)^3 + \ldots \quad (6.29)$$

Eq.(6.27) is equivalent to Eq.(6.29) if for all $n$

$$\sum_{n=1}^{\infty} (n!)^{-1} \left[\overline{(y^n)} - (\bar{y})^n\right] = 0 \quad (6.30)$$

Eq.(6.30) is usually a good physical approximation for a quantity like $\beta$ and we adapt Eq.(6.29) as the definition of $\bar{\beta}$. This gives us the result that the observed Doppler shift, denoted $\left\langle \frac{\Delta \nu}{\nu_{12}} \right\rangle_{\bar{y}}$, can be written

$$\left\langle \frac{\Delta \nu}{\nu_{12}} \right\rangle_{\bar{y}} = \bar{\beta} \left\langle \frac{\Delta \nu}{\nu_{12}} \right\rangle_0 = \beta \left(\bar{y}\right) \left\langle \frac{\Delta \nu}{\nu_{12}} \right\rangle_0 \quad (6.31)$$

### 6.2.3 Relation of $\bar{\beta}$ to System’s Physical Properties

It is necessary to relate $\bar{y}$ to other physical characteristics of the system. It is well-known that radiation trapping prolongs the lifetime of the excited state. Let $\tau_2$ be the radiative lifetime of level 2 in Fig. 20 and $\tau_e$ be the observed, effective lifetime, $\tau_e$, of the system in the presence of trapping. We prove in Appendix B, the intuitive relationship,

$$\bar{y} = \frac{\tau_e - \tau_2}{\tau_2} = \frac{\tau_e}{\tau_2} - 1 \quad (\tau_e \geq \tau_2) \quad (6.32)$$
According to Holstein[82], in the presence of radiation trapping, $\tau_e$ is also the eigenvalue of the following integral equation

$$\left(1 - \frac{\tau_e}{\tau_0}\right) n_2(\vec{r}) = \int_{\Gamma} G_{12}(\vec{r}, \vec{r}') n_2(\vec{r}') d\vec{r}' \quad (\tau_e \geq \tau_0) \tag{6.33}$$

Using Eq.(6.32), one can rewrite Eq.(6.33) in terms of $\bar{y}$

$$\left(1 - \frac{1}{\bar{y} + 1}\right) n_2(\vec{r}) = \int_{\Gamma} G_{12}(\vec{r}, \vec{r}') n_2(\vec{r}') d\vec{r}' \tag{6.34}$$

In Eqs.(6.33) and (6.34), $\Gamma$ is the volume in which the radiation is trapped which depends on the geometry of the light source (in our case, the discharge cell); $n_2(\vec{r})$ is the density of atoms in the excited state 2; and $G_{12}(\vec{r}, \vec{r}') d\vec{r}$ is the probability that a photon emitted at $\vec{r}'$ is absorbed in the volume element $d\vec{r}$ at the position $\vec{r}$. When Doppler broadening dominates, which is the case for our experiment and many others, $G_{12}(\vec{r}, \vec{r}')$ has the form[82]

$$G_{12}(\vec{r}, \vec{r}') = G_{12}(R) = \frac{1}{4\pi R^2} \frac{\partial T_{12}}{\partial R}, \quad R = |\vec{r} - \vec{r}'| \tag{6.35}$$

where

$$T_{12}(R) = \frac{1}{\pi^{1/2}} \int_{-\infty}^{\infty} e^{-x^2} \exp \left(-K_{12} R e^{-x^2}\right) dx \tag{6.36}$$

The absorption coefficient, $K_{12}$, at the center of the frequency transition is defined by

$$K_{12} = \frac{\lambda_{21}^3 N_1 g_2 k_{21}}{8\pi^{3/2} u_1 u_2} \tag{6.37}$$

In Eq.(6.37), $\lambda_{21}$ is the transition wavelength, $g_i$ the degeneracy of state $i$, $u_1$ and $N_1$ the thermal velocity (as defined after Eq.(6.22)) and density respectively of the absorbing atoms. If one assumes that $N_1$ is not a function of $R$, then it can be
treated as a well-defined experimental quantity. In Appendix C, we show that to a good approximation $N_1$ should be constant over our trapping volume.

It is clear from Eqs. (6.34-6.37) that for the eigenvalues, $\bar{y}$ and $\bar{y}'$, for two atomic or molecular transitions present in the same trapping volume to be equal, it is required that

$$K_{12} = K'_{12}, \quad \text{or} \quad \frac{\lambda_{21}^3 g_2 N_{1k_{21}}}{u_1 g_1} = \frac{\lambda_{21}^3 g_2' N'_{1k_{21}}}{u_1' g_1'} \quad (6.38)$$

Usually one has $u_1 = u_1'$ if the two transitions belong to atoms of the same type. Therefore, Eq. (6.38) reduces to

$$\frac{\lambda_{21}^3 g_2 N_{1k_{21}}}{g_1} = \frac{\lambda_{21}^3 g_2' N'_{1k_{21}}}{g_1'} \quad (6.39)$$

Eq. (6.38) or Eq. (6.39) is simple but very useful because it allows the determination of the population of one state from another. For using Eq. (6.38), the two transitions, (2-1) and (2-1)', can be completely independent as long as their $\bar{y}$ values are obtained from the same trapping volume. It is not important whether (2-1) and (2-1)' are two transitions of the same atom or transitions of two, chemically distinct atoms as long as they are observed experimentally from the sources with equivalent trapping volumes. An obvious application of the principle, which we have used in our experiment, is to determine excited metastable state densities from easily measured ground state ones. Alternately, ground state populations of transient reactive atoms could also be obtained from the ground state population of unreactive ones.
6.2.4 The Three-Level System

Thus far the discussion has treated the simplest case of a two level system, with the trapping of radiation between the levels being monitored by the reduction of the Doppler shift on that same transition. Fig.20(b) represents a more complicated situation in which radiation trapping occurs on the (1-2) transition but its effects are monitored via the Doppler shift of the (2-3) transition. The three level system has considerable application. For example, radiation trapping often occurs on the resonance transition between the ground and first excited state. However, for most of the lighter atoms, the resonance transition lies well into the vacuum UV where small Doppler shifts in emission are very difficult to observe and measure. However, the transition (2-3) usually lies in an easily accessible spectral range and so its Doppler shift can be measured readily.

It is clearly understood that even though the transition (2-3) is untrapped its Doppler shift may still be affected by the radiation trapping on the (1-2) transition, for the latter serves to randomize the velocity vector of the atoms in the state before they can emit a photon on the (2-3) transition.

The problem of a 3-level (or by implication an n-level) system can be dealt with by generalizing Eq.(6.33), which defines the effective lifetime, \( \tau_e \), of the excited state. Holstein has obtained Eq.(6.33) from the law of conservation of particles within a given element inside the trapping volume. Now consider the three-level system shown in Fig.20(b) and let \( n_2(\vec{r}, t) \) be the density of the atoms of the excited state 2 in the place \( \vec{r} \) and at time \( t \). The law of conservation of particles for the volume element
requires
\[ \frac{\partial n_2(\vec{r}, t)}{\partial t} = -k_{21}n_2(\vec{r}, t) - k_{23}n_2(\vec{r}, t) + k_{21} \int \frac{G_{12}(\vec{r}, \vec{r}')n_2(\vec{r}', t)d\vec{r}'}{r} \]  
(6.40)

where \( G_{12}(\vec{r}, \vec{r}')d\vec{r}' \) is again the probability that a photon emitted at \( \vec{r} \) is absorbed in a volume element \( d\vec{r}' \) around point \( \vec{r}' \). The first two terms on the right side represent the decrease in excited atoms due to radiative decay through transition \((2-1)\) and \((2-3)\), with rates \( k_{21} \) and \( k_{23} \) respectively, while the third term represents the increase in number of \( n_2 \) due to the photons that are trapped in the volume. As Holstein pointed out, Eq.(6.40) has a solution of the following type

\[ n_2(\vec{r}, t) = n_2(\vec{r})e^{-\frac{t}{\tau_e}} \]  
(6.41)

where \( \tau_e \) is the effective lifetime of the excited state 2. Inserting Eq.(6.41) into Eq.(6.40), we find that \( \tau_e \) and \( n_2(\vec{r}) \) satisfy the eigenvalue equation,

\[ [1 - \frac{1}{\tau_e} \frac{1}{(k_{21} + k_{22})}]n_2(\vec{r}) = \frac{k_{21}}{k_{21} + k_{22}} \int \frac{G_{12}(\vec{r}, \vec{r}')n_2(\vec{r}')d\vec{r}'}{r} \]  
(6.42)

As one can see, \( \tau_e \) now depends not only on the absorption coefficient \( K \) (because \( G \) contains \( K \)) but also on \( k_{21} \) and \( k_{23} \).

Generally, this dependence is quite complicated. However often \( k_{21} \gg k_{23} \), as is our experimental case and Eq.(6.42) becomes

\[ [1 - \frac{1}{\tau_e k_{21}}]n_2(\vec{r}) = [1 - \frac{\tau_2}{\tau_e}]n_2(\vec{r}) = \int \frac{G_{12}(\vec{r}, \vec{r}')n_2(\vec{r}')d\vec{r}'}{r} \]  
(6.43)

where \( \tau_2 = k_{21}^{-1} \). Eq.(6.43) is just the same as Eq.(6.33) for a two-level system, which means that under condition, \( k_{21} \gg k_{23} \), a three-level system can be treated just as a two-level system.
6.3 Experimental

Radiation trapping is typically observed only in atomic gases or vapors, because an atomic system can provide a sufficient population in a single state, either a ground or metastable state, for a large enough absorption coefficient $K$. In our experimental study of radiation trapping affecting Doppler shifts of neutral emissions, we have chosen He gas. As described previously[74], Doppler shifts exist in emissions of neutral molecules or atoms in a glow discharge. The shift is caused by the momentum transfer during electron-molecule collisions that produce the emissive excited state. Specifically, the emitting excited atoms obtain, as result of collisions with electrons, a non-zero $z$ component of velocity along the plasma electric field direction, which is then translated into an observable Doppler shift in the emission. The details of the experimental observations and the theoretical explanation of Doppler shifts of neutral emissions have been published previously[74]. Obviously light atoms or molecules have the largest Doppler shifts, and that motivates our choice of He atoms for the study. The experimental arrangement and procedures for observing and measuring Doppler shifts for He emissions are basically the same as our previous work for the $\text{H}_2$ molecule[74]. A Bruker IFS-120HR Fourier transform spectrometer is used to collect and record the emission from the positive column of a DC glow discharge in a He/$\text{H}_2$ gas mixture. The discharge cell is illustrated in Fig. 22. Its positive column acting as the emission source is a small bore tube with an axis coincident with the spectrometer’s input axis, allowing only photons traveling parallel to the plasma field direction to be collected. The experimental setup permits us to obtain paired spectra
Figure 22: The detail shape of the discharge light source.
with opposite discharge polarities but with otherwise identical discharge conditions. Doppler shifts are then determined by comparing the position of lines in the two spectra ($\Delta \nu = \text{half the distance between the two oppositely shifted lines}$). Throughout the experiment, the discharge current was maintained at 50 mA (corresponding to a current density of $1.6 \text{ A/cm}^2$), while a spectrometer resolution of $0.02 \text{ cm}^{-1}$ and an entrance aperture with a diameter of 0.8 mm were used.

### 6.4 Experimental Results

#### 6.4.1 Ground State Radiation Trapping

In a He gas system the ground state has the highest population, therefore radiation trapping would be expected to occur between the ground state and excited states that are optically connected to it. Fig.23(a) illustrates the transitions that we choose for observing radiation trapping and its reduction of the Doppler shift. The states include the ground state, $1^1S_0$, and the emitting upper levels, $4^1D_2$, $3^1P_1$ and $2^1S_0$. The $3^1P_1$ state is optically connected to both the ground and the $2^1S_0$ state. This constitutes a three-level system with radiation trapping occurring on the $3^1P_1-1^1S_0$ transition which results in a reduction of the Doppler shift of the $3^1P_1-2^1S_0$ emission. Fortunately, the radiative lifetime is 1.77 ns for $3^1P_1-1^1S_0$ and 70 ns for $3^1P_1-2^1S_0$, satisfying the condition $k_{21} \gg k_{23}$, very well. The emission of $3^1P_1-1^1S_0$ is in the VUV frequency region (53.7 nm), which is unreachable with our spectrometer, while the $3^1P_1-2^1S_0$ transition lies in the easily accessible visible region (501.6 nm). These
Figure 23: He atom energy levels involved in transitions observed in the experiments:
(a) ground state trapping (b) metastable state trapping
transitions provide a good example of how a three-level system provides convenience for the experimental study of radiation trapping. Experimentally, we measured the Doppler shifts of the \(3^1P_1-2^1S_0\) He emission, and for comparison, the shift of the \(4^1D_2-2^1P_1\) emission, whose Doppler shift is undiminished by any radiation trapping. The two emission wavelengths (501.6 nm vs. 492.2 nm) are close enough that they can easily be obtained under identical discharge conditions.

The measurement was accomplished for discharges of \(H_2/He\) mixtures with the \(H_2\) pressure fixed at 0.2 torr while varying the He partial pressure from 2-50 mtorr. Although the \(2^1S_0\) state is also a metastable state, at these He partial pressures the density of the \(2^1S_0\) state is extremely low and radiation trapping on the \(3^1P_1-2^1S_0\) transition is negligible. Fig.24 The measured Doppler shifts of \(3^1P_1-2^1S_0\) (trapping) and \(4^1D_2-2^1P_1\) (no trapping) as function of He partial pressure in 0.2 torr \(H_2\) discharge. gives the results of our measurements, showing that while the Doppler shift of the \(4^1D_2-2^1P_1\) transition remains almost constant, that of \(3^1P_1-2^1S_0\) transition decreases rapidly with increasing He partial pressure, i.e., with radiation trapping as the \(1^1S_0\) density increases.

### 6.4.2 Metastable State Trapping

Under discharge conditions where the density of metastable \(He(2^3S_1)\) is appreciable, radiation trapping on the transitions between the metastable state \(2^3S_1\) and more highly excited triplet states is also observable. We have chosen, as shown in Fig.23(b), the emissions \(2^3P_0-2^3S_1\) and \(3^3S_1-2^3P_0\) for observation. In this case, we have a simple
Figure 24: The measured Doppler shifts of $3^1P_1 - 2^1S_0$ (trapping) and $4^1D_2 - 2^1P_1$ (no trapping) as function of He partial pressure in 0.2 torr H$_2$ discharge.
two-level system with radiation trapping between $2^3P_0$ and $2^3S_1$ and a reduction of the Doppler shift of the same transition. The Doppler shift of $3^3S_1-2^3P_0$ transition, which is not affected by the trapping, serves as a reference. The two lines again have wavelengths, respectively, of 1083 nm and 7065 nm, in proximate spectral regions.

The measurements at a discharge pressure of 0.4 torr pure He show markedly different Doppler shifts as shown in Fig.25. As H$_2$ is added to the discharge (up to 80%). The difference of the Doppler shifts for the two transitions diminish, as the He $2^3S_1$ metastable state is quenched by H$_2$.

### 6.5 Analysis and Discussion

Figs. 5 and 6 illustrate clearly the difference in Doppler shift between excited states decaying without radiation trapping and ones trapped respectively by ground and metastable state He populations. From these curves, it is straightforward to obtain $\beta(\bar{y})$ values via Eq.(6.24) by simply ratioing the observed Doppler shifts,

$$\bar{\beta} = \beta(\bar{y}) = \frac{<\nu_{(12)}>_{\bar{y}}}{<\nu_{(12)'}>_{0}}$$

(6.44)

For ground state trapping, illustrated in Fig.24, transition (1-2) corresponds to $3^1P_1-2^1S_0$, and the untrapped (1-2)' transition is $4^1D-2^1P$. For metastable state trapping the (1-2) transition is $2^3P_0-2^3S_1$ and the untrapped (1-2)' transition is $3^3S_1-2^3P_0$. These $\beta(\bar{y})$ values are plotted as a function of discharge conditions for ground and metastable state trapping in Figs.26 and Fig.27 respectively. Also plotted in these
Figure 25: The measured Doppler shifts of $^{2}\text{P}_0-^{2}\text{S}_1$ (trapping) and $^{3}\text{S}_1-^{2}\text{P}_0$ (no trapping) as functions of percentage of $\text{H}_2$ of the total pressure (with $\text{He}$ pressure=0.4 torr)
figures are $\bar{y}$ values obtained from $\bar{\beta}$ via Eq. (6.25), i.e.,

$$\bar{y} = -\frac{\ln \bar{\beta}}{\ln 6} \quad (6.45)$$

Fig. 26 gives $\bar{\beta}$ (or $\bar{y}$) values as a function of absolute (ground state) He concentration in the discharge which we have measured with a capacitance manometer. We can therefore invoke Eq. (6.39) to write

$$\bar{N}_1 = \left(\frac{\lambda_{21}}{\lambda_{21}'}\right)^3 \left(\frac{k_{21}}{k_{21}'}\right) \left(\frac{g_2g_1'}{g_1g_2'}\right) \bar{N}_1 \quad (6.46)$$

In the above $\bar{N}_1$ is the $2^3S$ metastable population which gives the same $\bar{\beta}$ value (Fig. 27) the same as that (Fig. 26) for a particular measured ground state He concentration $N_i$. In the above

$$\left(\frac{\lambda_{21}}{\lambda_{21}'}\right) = \left(\frac{53.7nm}{1082.9nm}\right) \quad (6.47)$$

$$\left(\frac{k_{21}}{k_{21}'}\right) = \left(\frac{98ns}{1.77ns}\right) \quad (6.48)$$

$$\left(\frac{g_2g_1'}{g_1g_2'}\right) = \left(\frac{3 \cdot 3}{1 \cdot 1}\right) \quad (6.49)$$

The yields the numerical relationship

$$\bar{N}_1 = 6.08\bar{N}_1 \times 10^{-2} \quad (6.50)$$

for equal $\bar{\beta}$. Using this result it is easy to calculate from the data in Fig.26 a unique metastable concentration $\bar{N}_1$ for each $\bar{\beta}$ in Fig.27. In Fig. 28, we plot the resulting metastable He density vs percent H$_2$ in the discharge.
Figure 26: The diminution factor, \( \bar{\beta} \) (stars), and the average number (solid circles) of trapping cycles, \( \bar{\gamma} \), for the \( 3^1P_1-2^1S_0 \) transition as functions of He partial pressure in a 0.2 torr \( \text{H}_2 \) discharge.
Figure 27: The $\bar{\beta}$ (stars) and $\bar{y}$ (solid circles) values for the $2^3P_0-2^3S_1$ transition as functions of percentage of $H_2$ with a He pressure of 0.4 torr.
Figure 28: The absolute density of He*(2S) as a function of percentage of H₂ with a He pressure of 0.4 torr determined from Eq.(6.46).
There is not a great deal of other data with which to compare our present results. From Fig. 9 we see that in the 0.4 torr pure He discharge, the density of He\(^{2^5S_1}\) is at its maximum of \(10 \times 10^{12}\) cm\(^{-3}\). This value is comparable to the corresponding theoretical value (\(~10 \times 10^{12}\) cm\(^{-3}\)) given by Hardy et al\[83\]. However, it is about a factor of \(3\) larger than the value obtained by Browne and Dunn\[84\] using atomic absorption under similar discharge conditions (0.5 torr He in a 3 mm diameter tube with a discharge current density of 1.6 A/cm\(^2\)).

6.6 Conclusions

We have demonstrated both experimentally and theoretically that radiation trapping by a bath of thermal atoms can lead to a diminution of the Doppler shift of a group of atoms prepared with a unique velocity component. Theoretically, we have shown that each trapping cycle diminishes the Doppler shift by a factor of \(\left(\frac{1}{6}\right)\). Further, we have shown how the observed diminution can be directly related to the number of trapping cycles, independent of whether one monitors the light of the trapped transition or photons of other wavelengths originating from the trapped state.

We have shown how the diminution factor \(\bar{\beta}\) allows us to calculate the relative density of two trapping states. We have applied this result to measure the density of metastable \(2^3S_1\) He from the known density of group \(1^1S_0\) He. In principle this application could be extended to measure the density of various transient atomic species, so long as they give rise to radiation trapping.
APPENDIX A

Effect of Natural Linewidth

When a finite natural linewidth is considered, it is not necessary that the vector $\vec{p}$ in Eq.(6.10) be exactly perpendicular to $k_2$ ($\vec{p} \cdot k_2 = 0$) and lie on the surface $S$ shown in Fig.21. Rather, $\vec{p}$ satisfies

$$\vec{p} \cdot k_2 = a , \quad -\Delta u_n < a < \Delta u_n$$

where $a$ is a number between $-\Delta u_n$ and $\Delta u_n$ as indicated in (A1) and $\Delta u_n$, which is the velocity variation region corresponding to natural linewidth, is given by

$$\Delta u_n = \frac{\lambda_{21}}{2\pi \tau_2}$$

with $\lambda_{21}$ the transition wavelength and $\tau_2$ the natural lifetime of the upper state. Equation (A1) defines a volume, $W$, in which the allowed $\vec{p}$ lies. In the primed coordinate system where we will carry out the velocity integrations, $W$ is the volume between the planes of $\rho'_z = -\Delta u_n$ and $\rho'_z = \Delta u_n$.

Now the surface $S$ that appears in Eqs.(6.11) through (6.16) must be replaced by the volume $W$, and accordingly, $\vec{p}$ in Eq.(6.12) becomes

$$\vec{p} \rightarrow \vec{p}' = (\rho'_x, \rho'_y, \rho'_z) ; \quad -\infty < \rho'_x, \rho'_y < \infty; \quad -\Delta u_n < \rho'_z < \Delta u_n$$
Using the above modification to recompute Eqs. (6.14) through (6.22), one can find the Doppler shift of (6.22) under the assumption of a finite linewidth

\[
\left< \frac{\Delta \nu}{\nu_{21}} \right>_1 = \frac{u_{Mz}}{6c} \left[ 1 - \frac{4}{3} \left( \frac{\Delta u_n}{u} \right)^2 + \cdots \right] \left[ 1 + \frac{2}{15} \left( \frac{u_{Mz}}{u} \right)^2 + \cdots \right]
\] (A4)

For the transitions in our experiment, the ratio \( \frac{\Delta u_n}{u} \), which is, according to (A2),
given by

\[
\frac{\Delta u_n}{u} = \frac{\lambda_{21}}{2\pi\tau_2} \sqrt{\frac{M}{2kT}}
\] (A5)

is of the order of \(10^{-3}\). Therefore, these correction terms in (A4) are vanishingly small and the finite natural linewidth has virtually no effect on the result.
APPENDIX B

A Rigorous Derivation of the $\bar{\gamma}$-$\tau_c$ Relation for a Three-level System

For a given system (for a given gas density and the geometry of the trapping volume) consisting of three-level atoms, as in Fig. 20(b) we introduce $Q$ as the probability that a resonance (1-2) photon is absorbed by the gas, with $(1-Q)$ the probability that the photon escapes the volume. Furthermore we introduce $P_1$ as the probability that an excited atom (in state 2) decays through the (2-1) transition and $P_2$ the (2-3) transition. We have

$$P_1 = \frac{k_{21}}{k_{21} + k_{23}} \quad \text{(B1a)}$$
$$P_2 = \frac{k_{23}}{k_{21} + k_{23}} \quad \text{(B1b)}$$

where $k_{21}$ and $k_{23}$ are the radiative decay rates of transitions of (2-1) and (2-3) respectively.

Now consider an individual atom born at $t=0$ into its excited upper state. This atom may emit a photon at time $t_1 > 0$ with a probability $P(t_1)$

$$P(t_1) = \frac{1}{\tau_2} e^{-t_1/\tau_2} \quad \text{(B2)}$$

where $\tau_2 = (k_{21} + k_{23})^{-1}$ is the atom’s radiative lifetime. For this atom to live a time $t_1$, the photon must not be trapped by the gas on the (2-1) transition or the atom
must emit on the untrapped (2-3) channel. One can find the probability for each related event that consists of the process that lets the atom have a lifetime of $t_1$:

The total probability the atom lives a time $t_1$ is the sum of the probability of each event,

$$p(t_1, 0) = \frac{1}{\tau_2} e^{-t_1/\tau_2} (1 - Q) P_1 + \frac{1}{\tau_2} e^{-t_1/\tau_2} P_2$$

where the 0 explicitly indicates no trapping cycles occur.

Now consider the probability an atom decays after $t_1 + t_2$ second with one trapping cycle. This even can occur in two ways:

1. A (2-1) photon is emitted and reabsorbed at $t_1$, followed by emission and escape $t_2$ second after $t_1$

Alternatively

2. A (2-1) photon is emitted and reabsorbed at $t_1$ followed by a (2-3) emitted $t_2$ second after $t_1$

Both 1 and 2 processes lead the result that the atom has a lifetime of $t_1 + t_2$ and is trapped for once. The corresponding total probability for the result is

$$p(t_1 + t_2, 1) = \frac{1}{\tau_2} e^{-t_1/\tau_2} Q P_1 \frac{1}{\tau_2} e^{-t_2/\tau_2} P_1 (1 - Q) +$$

$$+ \frac{1}{\tau_2} e^{-t_1/\tau_2} Q P_1 \frac{1}{\tau_2} e^{-t_2/\tau_2} P_2$$

$$= \frac{1}{\tau_2} e^{-(t_1 + t_2)/\tau_2} P_1 Q[(1 - Q) P_1 + P_2]$$

Extending this logic, one can easily find the expression for the probability for the atom undergoing $n$ emission-absorption cycles, which happen sequentially at $t=t_1$,
\begin{align*}
\sum_{n=0}^{\infty} \int_{0}^{\infty} \cdots \int_{0}^{\infty} p(t_1 + t_2 \cdots t_{n+1}, n) dt_1 \cdots dt_{n+1} &= 1 \\
\tau_{e} &= \sum_{n=0}^{\infty} \int_{0}^{\infty} \cdots \int_{0}^{\infty} (t_1 + t_2 \cdots t_{n+1}) p(t_1 + t_2 \cdots t_{n+1}, n) dt_1 \cdots dt_{n+1} \tag{B7}
\end{align*}

or

\begin{align*}
\tau_{e} &= \sum_{n=0}^{\infty} \int_{0}^{\infty} \cdots \int_{0}^{\infty} \frac{1}{\tau_2} e^{-\frac{(t_1 + t_2 \cdots t_{n+1})}{\tau_2}} P_1^n Q^n (1 - Q P_1) dt_1 \cdots dt_{n+1} \\
&= \sum_{n=0}^{\infty} (n+1) P_1^n Q^n (1 - Q P_1) = (1 - Q P_1) \frac{\partial}{\partial (Q P_1)} \sum_{n=0}^{\infty} (P_1 Q)^{n+1} \\
&= \frac{1}{1 - Q P_1} \tau_2 \\
\end{align*}

In the same way the average value of \( y, \bar{y} \), is given by

\begin{align*}
\bar{y} &= \sum_{n=0}^{\infty} \int_{0}^{\infty} \cdots \int_{0}^{\infty} n p(t_1 + t_2 \cdots t_{n+1}, n) dt_1 \cdots dt_{n+1} \\
\end{align*}

or

\begin{align*}
\bar{y} &= \sum_{n=0}^{\infty} \int_{0}^{\infty} \cdots \int_{0}^{\infty} \frac{n}{\tau_2} e^{-\frac{(t_1 + t_2 \cdots t_{n+1})}{\tau_2}} P_1^n Q^n (1 - Q P_1) dt_1 \cdots dt_{n+1} \\
&= \sum_{n=0}^{\infty} n P_1^n Q^n (1 - Q P_1) = Q P_1 (1 - Q P_1) \frac{\partial}{\partial (Q P_1)} \sum_{n=0}^{\infty} (P_1 Q)^{n} \\
&= \frac{Q P_1}{1 - Q P_1} \\
\end{align*}
Combining Eqs. (B8) and (B10) and eliminating $QP_1$, we obtain

$$\bar{y} = \frac{\tau_e}{\tau_2} - 1$$  \hspace{1cm} (B11)

where $\tau_2$ is the natural radiation lifetime of level 2. In terms of $k_{21}$ and $k_{23}$ we have

$$\tau_2 = \frac{1}{k_{21} + k_{23}}$$  \hspace{1cm} (B12)

When $k_{23} = 0$, it becomes a two level system. Following the same logic the result of Eq. (B11) can be shown to hold for an arbitrary n-level system with trapping on the transition (2-1).

From (B8) and the three-level system trapping equation, one can recognize that the probability $Q$ has the following meaning

$$Q = \int \int G_{12}(\vec{r}, \vec{r}') n(\vec{r'}) d\vec{r} d\vec{r}' / \int n(\vec{r}) d\vec{r}$$  \hspace{1cm} (B13)

Considering the definition of the $G$ function, (B13) is the expression one should expect.

By examining the physical meaning of Eq. (B7), one can find the probability that an escaped photon is a 2-1 resonance photon as

$$L_{21} = \sum_{n=0}^{\infty} \int_{0}^{\infty} \int \frac{1}{\tau_{n+1}} e^{-(t_1 + t_2 + \cdots + t_{n+1})/\tau_2} P_1^n Q^n (1 - Q)P_1 dt_1 \cdots dt_{n+1}$$

$$= \frac{(1 - Q)P_1}{1 - QP_1}$$  \hspace{1cm} (B14)

and the probability that an escaped photon is a 2-3 resonance photon as

$$L_{23} = \sum_{n=0}^{\infty} \int_{0}^{\infty} \int \frac{1}{\tau_{n+1}} e^{-(t_1 + t_2 + \cdots + t_{n+1})/\tau_2} P_1^n Q^n P_2 dt_1 \cdots dt_{n+1}$$

$$= \frac{P_2}{1 - QP_1}$$  \hspace{1cm} (B15)
Obviously, $L_{ij}$ is proportional to the measured emission intensity of transition i-j, $I_{ij}$, i.e.,

$$L_{21} \propto I_{21} \quad \text{and} \quad L_{21} \propto I_{21}$$  \hfill (B16)

Therefore

$$\frac{L_{21}}{L_{23}} = \frac{I_{21}}{I_{23}} = \frac{(1 - Q)P_1}{P_2}$$  \hfill (B17)

If we introduce $\gamma_\tilde{y}$ as the ratio of $I_{21}/I_{23}$ corresponding to $\tilde{y}$ trapping cycles, we have

$$\gamma_\tilde{y} = (1 - Q)\gamma_0$$  \hfill (B18)

where $\gamma_0$ is the ratio corresponding to $\tilde{y}=0$, which is equal to

$$\gamma_0 = \frac{P_1}{P_2} = \frac{k_{21}}{k_{23}}$$  \hfill (B19)

Using Eqs.(B12), (B18) and (B19), we can obtain

$$\tilde{y} = \frac{\gamma_0 - \gamma_\tilde{y}}{1 + \gamma_\tilde{y}}$$  \hfill (B20)

and

$$\gamma_\tilde{y} = \frac{\gamma_0 - \tilde{y}}{1 + \tilde{y}}$$  \hfill (B21)

Since for a given system $\gamma_0$ is known, Eq.(B20) indicates that the $y$ value of a three-level atom system can be determined by measuring the intensity ratio for two emission channels. As can be seen by Eq.(B21), the dependence of $\gamma_\tilde{y}$ on $\tilde{y}$ is quite sensitive. For instance, there will be at least a change of 50% for the ratio if $\tilde{y}=1$.

At the two-level system limit, $k_{21} \gg k_{23}$ and $\gamma_0 \gg \tilde{y}$,

$$k_{21} \gg k_{23} \quad \text{and} \quad \gamma_0 \gg \tilde{y}$$  \hfill (B22)
one has

$$\gamma \approx \frac{\gamma_0}{1 + \bar{y}} = \frac{\tau_2}{\tau_e} \gamma_0$$  \hspace{1cm} (B23)$$

It is obvious that at the condition (B22), the presence of radiation trapping has little effect on the emission intensity of 2-3 transition. Hence, the decrease in $\gamma$ is mainly due to the decrease of the 2-1 emission rate because of a longer effective lifetime (this can be seen as there appears the factor of $\tau_e$ in (B22)).
APPENDIX C

The Trapping Volume

The physical nature of the trapping volume $\Gamma$ has not been discussed in detail. It needs to be clearly defined in order to interpret the measured quantities $\beta$, $\bar{y}$, and $N_1$.

The situation is simple if the emission source is bounded, spatially uniform, and photons from any volume element within it are collected with an equal efficiency. Under such circumstance, $\Gamma$ is just identically the source volume. Although emission sources are often inhomogeneous and emissions from different parts are not collected necessarily with an equal efficiency. A general and rigorous treatment of the problem appears to be prohibitively complicated. Here we only consider the specific case approximate to the present experiment and possibly many others.

Suppose that the entire gas can be divided, in terms of emission intensity and light collection efficiency, into two sub-volumes, 1 and 2. We assign $I_1$ and $b_1$ for 1 and $I_2$ and $b_2$ for 2 as the relative emission intensities and collection efficiencies. Clearly each sub-volume is associated with its own trapping parameter $\bar{y}_i$ (i=1,2). If 1 and 2 are independent of each other, i.e., the existence of one volume does not affect the detection of the photons in the other volume, the measured $\bar{y}$ value should be

$$\bar{y} = \frac{I_1 b_1 V_1 \bar{y}_1 + I_2 b_2 V_2 \bar{y}_2}{I_1 b_1 V_1 + I_2 b_2 V_2} \quad \text{(C1)}$$
where $V_1$ and $V_2$ are the respective emission source volumes.

Often values 1 and 2 are not independent but exchange photons, i.e., a photon may go back and forth between two volumes for a number of times before it reach the detector. Each time the photon is in $i$, it is trapped for $y_i$ cycles. To include the exchange effect, (C1) needs be modified as

$$\bar{y} = \frac{I_1 b_1 V_1 \bar{y}_1 + I_2 b_2 V_2 \bar{y}_2 + \left[\xi I_1 b_1 V_1 \frac{V_2 \Sigma_1}{V_1 \Sigma_2} + \zeta I_2 b_2 V_2 \frac{V_1 \Sigma_2}{V_1 \Sigma_1}\right]\left(\bar{y}_1 + \bar{y}_2\right) + \cdots}{I_1 b_1 V_1 + I_2 b_2 V_2 + \xi I_1 b_1 V_1 \frac{V_2 \Sigma_1}{V_1 \Sigma_2} + \zeta I_2 b_2 V_2 \frac{V_1 \Sigma_2}{V_1 \Sigma_1}}$$

In Eq.(C2), $\xi$ and $\zeta$ are the probability of a photon emitted from one volume being trapped in the other. They are of order units. For two independent volumes, $\xi=0$ and $\zeta=0$ and Eq.(C2) reduces to Eq.(C1). $V_1$ and $V_2$ are defined as the exchanging volumes. Photons in $V'_1$ or $V'_2$ can participate in exchanges but are not necessarily detected. For a photon to be detected, it has to be in the source volume $V_1$ or $V_2$.

Let $V'_1 \geq V_1$ and $V'_2 \geq V_2$ while $\Sigma_1$ and $\Sigma_2$ are the surface areas associated with $V'_1$ and $V'_2$ and $\Sigma_{12}$ is the interfacial surface through which photons are interchanged. Terms accounting for the contributions from photons that are exchanged more than once are omitted from Eq.(C2). These terms are proportional to $(\Sigma_{12}/\Sigma_i)^n$ ($n \geq 2$) and presumably negligible for the present case.

Now we employ the above result to our experiment. Fig.3 shows the geometry of the discharge cell that contains the positive column of the discharge used in our experiment as the emission source. We define the constricted tube as subvolume 1 and the remainder as subvolume 2. Within each individual volume densities are considered to be uniform. $I_1$ is much higher than $I_2$ because the positive column at the center has a higher current density (by a factor of 16), a higher electric field (by probably a
factor of 2)\textsuperscript{[74]} and a higher electron temperature also. Under those conditions and given the fact that the emissive excited states are produced by electron impact, even for a conservative estimation, \( I_1 \gtrsim 10I_2 \). Additionally, we have aligned the collecting optics so that the collection efficiency as a function of source position has a maxima at the geometric center of the horizontal discharge tube and decreases off center. The collection efficiency curve has been estimated experimentally by measuring the variation of light caused by an object moving about the focal point of the collecting lens. On average \( b_1 \approx 4b_2 \). Since the size of the spectrometer’s entrance aperture \( (d=0.8\text{ mm}) \) is smaller than the size of the image of the cross section of discharge tube (the diameter of the image is roughly equal to \( f_1D/f_2=0.625D \), where \( D \) is the internal diameter of the discharge tube and \( f_1 \) and \( f_2 \) the focal lengths of the focusing and the collimating lens), \( V_1 \) and \( V_2 \) can be considered columns of a diameter of 1.28 (=0.8/0.625) mm with a length of 3 cm for the former and 5 cm for the latter. \( V_1' \) and \( V_2' \) are respectively the total volumes of 1 and 2 with the surfaces \( \Sigma_1 \) and \( \Sigma_2 \). The interface area \( \Sigma_{12} \) is twice the cross section of the small tube. Again for a conservative estimation, we put \( \xi = \zeta = 1 \).

With all the above information we obtain from Eq.(C2)

\[
\bar{y} = 0.96\bar{y}_1 + 0.04\bar{y}_2
\]  

(C3)

i.e., the measured \( \bar{y} \), and therefore \( \bar{\beta} \) and \( N_1 \), reflect to better than 5% the properties of the restricted positive column at the center of the discharge tube.
BIBLIOGRAPHY


