Abstract

Under typical discharge conditions, atoms or molecules excited by electrons have a unique velocity component along the plasma electric field direction. This component results in Doppler shifts that can be observed and measured by a high resolution Fourier transform spectrometer. We show theoretically that if the upper state of a given transition suffers radiation trapping, its Doppler shift will be reduced by a factor dependent upon the average number of trapping cycles.
a photon of that frequency experiences. We further show how the diminution of the Doppler shift can be related to the volume and the density of the trapping species. These results can be used to measure the unknown concentration of a trapping species provided a “standard” is available. A typical application of this technique would be the measurement of the concentration of a metastable discharge species, e.g., He, using the trapping of its known ground state density as a standard.
1 Introduction

In recent papers,[1, 2, 3] 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.[1] Since the ion’s final velocity and corresponding Doppler shift depend upon the duration of this acceleration, these shifts have proven[2] 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[3] and result from similarly accelerated electrons and their subsequent momentum transfer in the collisions that generate the excited emissive states.

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 atoms, e.g., He atoms in a discharge as studied experimentally in the following paper.[4] 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 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, we assume that no significant collisional effects occur in the excited state because of its short lifetime and/or low gas pressure. (This situation is experimentally realized in the following paper.) 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 atoms it allows the approach to thermal equilibrium for the unique \( z \) component of the translational velocity of the prepared atoms. A similar effect has been reported for the destruction of excited state polarization.[5] 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. Ergo each trapping cycle reduces the Doppler shift significantly but does not cause it to vanish.

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[6], the Hanle effect[7], pulsed optical technique[8], the pulsed magnetic technique[9], pulsed electron beam
technique[10] and the stepwise-excitation coincidence technique[11]. 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 measurement of the $\gamma$ value, providing an alternative way for dealing with a steady-state system. The $\gamma$ 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 $\gamma$ 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. In the following paper this result is applied to the determination of the absolute concentration of metastable $2^3S$ He in a 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.
2 Theory

There are several important steps in adequately describing the effect of radiation trapping of 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 $\beta(\overline{y})$, 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.

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.[1, 2, 3] Consider a two-level atomic gas system illustrated in Fig. 1(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 $\vec{k}_2$

$$\nu(2) = \nu_{21}^{0} + \frac{\vec{k}_2 \cdot \vec{u}_2}{c} \nu_{21}^{0}$$

(1)

where $\nu_{21}^{0}$ is the rest frequency for the transition. The last term in Eq. (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, (see Fig.2) the fractional Doppler shift, \( \Delta \nu / \nu_0^2 \), from the rest frequency is given by

\[
\frac{\Delta \nu (2)}{\nu_0^2} = \frac{\vec{k}_z \cdot \vec{u}_2}{c}
\]

(2)

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

\[
\left\langle \frac{\Delta \nu}{\nu_0^2} \right\rangle = \frac{\int_{-\infty}^{\infty} \left( \vec{k}_z \cdot \vec{u}_2 \right) f_2(\vec{u}_2) d\vec{u}_2}{c \int_{-\infty}^{\infty} f_2(\vec{u}_2) d\vec{u}_2}
\]

(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

\[
f_2(\vec{u}_2) = \left( \frac{M}{2\pi kT} \right)^{3/2} \exp \left\{ - \left[ u_{2x}^2 + u_{2y}^2 + (u_{2z} - u'_{Mz})^2 / \bar{u}^2 \right] \right\}
\]

(4)

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 \( \bar{u}^2 = \frac{2kT}{M} \) the averaged square of the thermal velocity. (In the present
analysis we assume that there is only one temperature and hence one $u^2$ 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[3]. Using Eq.(4) to integrate Eq.(3) one obtains

$$\left\langle \frac{\Delta \nu}{\nu_{21}^0} \right\rangle_0 = \frac{u_{Mz}'}{c}$$

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 $\vec{u}_2$ may be absorbed by one of the surrounding atoms in the lower state 1 in Fig.1(a). The resonance condition requires that the absorbing atom’s component of the velocity, $\vec{u}_1$, along $\vec{k}_2$ must equal that of the initial atom, i.e.,

$$\vec{u}_1 \cdot \vec{k}_2 = \vec{u}_2 \cdot \vec{k}_2$$

(In writing Eq. (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

$$\nu(1) = \nu_{21}^0 + \frac{\vec{k}_1 \cdot \vec{u}_1}{c} \nu_{21}^0$$
Since the detector still lies along the z axis, for the photon to be observed \( k_1 = k_z \), and the Doppler shift of the detected photon will be

\[
\frac{\Delta \nu(1)}{\nu_{21}^0} = \frac{k_z \cdot \vec{u}_1}{c}
\]  

(8)

To obtain the observed fractional Doppler shift after one trapping cycle, it is necessary to average Eq.(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 \( \vec{k}_2 \), \( \vec{u}_1 \) is restricted to only certain allowed values by Eq. (6). For a single trapping cycle, the observable Doppler shift corresponding to the average over all three variables is denoted by \( \left\langle \frac{\Delta \nu}{\nu_{21}^0} \right\rangle_1 \).

We can write the average of Eq.(8) over \( \vec{u}_1, \vec{u}_2, \) and \( \vec{k}_2 \) as

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

(9)

where the first integral over \( \vec{u}_1 \) is restricted to the surface, \( S \), in velocity space proscribed by Eq.(6) while the integrals over \( \vec{u}_2 \) and \( \vec{k}_2 \) are unrestricted.

To perform the restricted integration over \( \vec{u}_1 \), we can use Eq.(6) to write

\[
\vec{u}_1 = \vec{u}_2 + \vec{\rho}
\]  

(10)

where \( \vec{\rho} \) is an arbitrary vector lying on the surface \( S \) to which \( \vec{k}_2 \) is perpendicular. These relationships are clearly shown in Fig. (2). Substituting for
\( \vec{u}_1 \) in Eq.(9) we have

\[
\left\langle \frac{\Delta \nu}{\nu_{21}^2} \right\rangle_1 = \frac{\int \int_S k_z \cdot (\vec{u}_2 + \vec{\rho}) \ f_1 (\vec{u}_1) \ f_2 (\vec{u}_2) \ f_k (\vec{k}_2) \ d \vec{u}_1 \ d \vec{u}_2 \ d \vec{k}_2}{c \int \int_S f_1 (\vec{u}_1) \ f_2 (\vec{u}_2) \ f_k (\vec{k}_2) \ d \vec{u}_1 \ d \vec{u}_2 \ d \vec{k}_2} =
\]

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

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

\[
\vec{\rho} = (\rho_{x'}, \rho_{y'}, 0) \quad (12)
\]

\[
\vec{z} = (R_{13}, R_{23}, R_{33})
\]

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

where \(K\) is a normalization constant. In writing Eq.(12), we have used the fact that \(\vec{\rho}\) lies on the surface \(S\). In Eq.(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.(14) follows from the Boltzmann distribution of velocities.

Both the numerator and the denominator can now be integrated analytically with respect to \(\vec{u}_1\) with the result,

\[
\int_S (\vec{k}_z \cdot \vec{\rho}) f_1 (\vec{u}_1) \ d \vec{u}_1 = \int_{-\infty}^{\infty} K (R_{13}\rho_{x'} + R_{23}\rho_{y'}) \times
\]

10
\[
\exp - \left\{ \left[ (\rho x' + u_{x'})^2 + (\rho y' + u_{y'})^2 + u_{z'}^2 \right] / \overline{u^2} \right\} \, d\rho x' d\rho y' \\
= -K \pi \overline{u^2} (R_{13}u_{x'} + R_{23}u_{y'}) \exp - \left( u_{z'}^2 / \overline{u^2} \right)
\]

and

\[
\int_S f_1 (\overline{u_1}) \, d\overline{u_1} \\
= K \int_{-\infty}^{\infty} \exp - \left\{ \left[ (\rho x' + u_{x'})^2 + (\rho y' + u_{y'})^2 + u_{z'}^2 \right] / \overline{u^2} \right\} \, d\rho x' d\rho y' \\
= K \pi \overline{u^2} \exp - \left( u_{z'}^2 / \overline{u^2} \right)
\]

To complete the simplification of Eq.(11), we express the dot product \((\overrightarrow{k_z} \cdot \overrightarrow{u_2})\) in the primed coordinate system

\[
\left( \overrightarrow{k_z} \cdot \overrightarrow{u_2} \right) = R_{13}u_{x'} + R_{23}u_{y'} + R_{33}u_{z'}
\]

Substituting Eqs.(15-17) in Eq.(11) yields

\[
< \Delta \nu > _1^{\nu_{21}} = \frac{\int \int R_{33}u_{z'} \exp - \left( u_{z'}^2 / \overline{u^2} \right) f_2 \left( \overrightarrow{u_2} \right) f_k \left( \overrightarrow{k_2} \right) \, d \overrightarrow{u_2} d \overrightarrow{k_2}}{c \int \int \exp - \left( u_{z'}^2 / \overline{u^2} \right) f_2 \left( \overrightarrow{u_2} \right) f_k \left( \overrightarrow{k_2} \right) \, d \overrightarrow{u_2} d \overrightarrow{k_2}}
\]

or

\[
< \Delta \nu > _1^{\nu_{21}} = \frac{\int \int (\overrightarrow{k_z} \cdot \overrightarrow{u_2}) (\overrightarrow{k_z} \cdot \overrightarrow{u_2}) \exp - \left[ \left( \overrightarrow{k_z} \cdot \overrightarrow{u_2} \right)^2 / \overline{u^2} \right] f \left( \overrightarrow{u_2} \right) f_k \left( \overrightarrow{k_2} \right) \, d \overrightarrow{u_2} d \overrightarrow{k_2}}{c \int \int \exp - \left[ \left( \overrightarrow{k_z} \cdot \overrightarrow{u_2} \right)^2 / \overline{u^2} \right] f \left( \overrightarrow{u_2} \right) d \overrightarrow{k_2}}
\]

where in Eq.(19) we have expressed \(R_{33}\) and \(u_{z'}\) in terms of the dot products \((\overrightarrow{k_z} \cdot \overrightarrow{k_z})\) and \((\overrightarrow{k_z} \cdot \overrightarrow{u_2})\) respectively.

Eq.(19) admits of a relatively straightforward physical interpretation.

The factor \((\overrightarrow{k_z} \cdot \overrightarrow{u_2})/c\) 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)), the final non-zero Doppler shift depends upon the projection $\left(\vec{k}_2 \cdot \vec{k}_z\right)$ 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.(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 distribution 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.(19), we express $f_2(\vec{u}_2)$, via Eq.(4), and integrate over $\vec{u}_2$ yielding

$$\frac{\langle \Delta \nu \rangle}{\nu_{21}^0} = \left(\frac{u'_{mz}}{2c}\right) \frac{\int \left(\vec{k}_2 \cdot \vec{k}_z\right)^2 \exp \left(-\frac{(\vec{k}_2 \cdot \vec{k}_z)^2 u'_{mz}^2}{2u^2}\right) f(\vec{k}_2)d\vec{k}_2}{\int \exp \left(-\frac{(\vec{k}_2 \cdot \vec{k}_z)^2 u'_{mz}^2}{2u^2}\right) f(\vec{k}_2)d\vec{k}_2}$$

(20)

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

\[
\frac{\langle \Delta \nu \rangle}{\nu_{21}^0} = \left( \frac{u'_{Mz}}{2c} \right) \int_0^{2\pi} \int_0^{\pi} \cos^2 \theta \exp\left( -\frac{\cos^2 \theta \, u'_z^2}{2u^2} \right) d\phi \sin \theta d\theta
\]

In writing Eq.(21), we have used the following relationships (see Fig. 2) 

\( (\vec{k}_2 \cdot \vec{k}_z) = \cos \theta \), 

\( k_2 = (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta) \), 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

\[
\frac{\langle \Delta \nu \rangle}{\nu_{21}^0} = \left( \frac{u'_{Mz}}{2c} \right) \int_0^{\pi} \exp\left( -\frac{\xi^2 u'_z^2}{2u^2} \right) d\xi = \frac{u'_{Mz}}{6c} \left[ 1 - \frac{2}{15} \left( \frac{u'_{Mz}}{\pi} \right)^2 + \ldots \right]
\]

In arriving at the second equality in Eq.(22) we have expanded all the exponential functions in terms of a series in the factor, \( (u'_{Mz} / \pi) \), 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 and hereafter, we denote \( \sqrt{u^2} \) by \( \pi \). 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

\[
\frac{\langle \Delta \nu \rangle}{\nu_{21}^0} = \frac{1}{6} \frac{u'_{Mz}}{c} = \beta(1) \frac{\langle \Delta \nu \rangle}{\nu_{21}^0}
\]

The diminution factor \( \beta(1) \) of \( \left( \frac{1}{6} \right) \) can be seen to arise physically from two sources. A factor of \( \left( \frac{1}{3} \right) \) results from the angular average of \( \cos^2 \theta \) over the
surface of a sphere while the remaining factor \((\frac{1}{2})\) comes from the probability of photons with different Doppler shifts to be differentially trapped.

### 2.2 The Observed Diminution Factor, \(\bar{\beta}\)

In most DSFTS experiments, including the one described in the following paper,[4] we will have a Doppler broadened line with profile \(f_g(\nu, \nu_0', \sigma_g)\) where

\[
f_g(\nu, \nu_0', \sigma_g) = A_g e^{-\frac{(\nu - \nu_0')^2}{2\sigma_g^2}}
\]

where \(\nu_0'\) is the line center, \(A_g\) its normalization constant and \(2\sigma_g \sqrt{\ln(4)}\) is the FWHM of the line.

It then follows that the shape \(F(\nu, \nu_{12}^0, \sigma_g)\) of the radiation trapped transition between states 1 and 2 can be written as

\[
F(\nu, \nu_{12}^0, \sigma_g) = \sum_y f_g(\nu, \nu_0'(y), \sigma_g) P(y)
\]

where

\[
\nu_0'(y) = \nu_{12}^0 \left[ 1 \pm \left\langle \frac{\Delta \nu}{\nu_{12}^0} \right\rangle_y \right]
\]

and we have assumed reasonably that \(\sigma_g\) is independent of the number of trapping cycles \(y\) and \(P(y)\) is the probability that a molecule is trapped \(y\) times.

There are clearly two interesting physical limits for \(F(\nu, \nu_{12}^0, \sigma_g)\). The simplest case is for the untrapped Doppler shift to be much greater than linewidth, i.e., \(\left\langle \frac{\Delta \nu}{\nu_{12}^0} \right\rangle_0 \Delta \nu_{12}^0 \gg \sigma_g\). In this case we would expect a series of distinct Doppler shifted lines starting at \(\nu_{12}^0 \left[ 1 \pm \left\langle \frac{\Delta \nu}{\nu_{12}^0} \right\rangle_0 \right]\) for \(y = 0, \beta(y = 0) = 1, \ldots \).
and finally converging to \( \nu_{12}^0 \) for large \( y \), with their relative intensities determined by \( P(y) \). The analysis of experimental data in this case to determine \( P(y) \) or \( \beta(y) \) should be straightforward.

Unfortunately the second case of the linewidth being greater than the Doppler shift, i.e., \( \sigma_y \gg \left< \frac{\Delta \nu}{\nu_{12}} \right>^0 \nu_{12}^0 \), is a more likely practical situation (see the succeeding work) and represents a more complicated case for analysis. However, for essentially all practical experiments falling near this limit, some observations about \( P(y) \) and \( \beta(y) \) can be made that greatly limit the sum in Eq. (25). (These approximations may also be valid for many situations near the large Doppler shift limit, except in the case where radiation trapping is also extreme.)

It is clear that if the probability of trapping for a photon were independent of the number of earlier trapping cycles, then we could write for \( y \geq 1 \)

\[
P(y) = Q^y (1 - Q)
\]  

(27)

In the above \( P(y) \) is the probability \((Q^y)\) that the photon is trapped \( y \) times and then escapes with likelihood \((1 - Q)\). \( Q \) is of course the fractional probability that the photon of wavelength of interest is absorbed in the gas volume. It follows that

\[
P(0) = 1 - \sum_{y \geq 1} P(y),
\]  

(28)

In the present case, this independence is not quite true since the probability for trapping increases slightly as the unique \( z \)-component of its velocity
approaches equilibrium. However, for small to moderate values of $\langle \Delta \nu / \nu_{12} \rangle_0$ and/or not extreme radiation trapping, i.e., $P(1) \ll 1$, we expect the above equations to be good approximations.

In particular for independent trapping cycles we would expect that

$$\beta(y) = \left(\frac{1}{6}\right)^y = e^{-y \ln 6} \quad (29)$$

Again the independence condition is not quite fulfilled since the photons of each cycle are emitted from a slightly different distribution of atoms with unique $z$ velocity components. However, since $\sigma_g \gg \langle \Delta \nu / \nu_{12} \rangle_0 \nu_{12}^0$, we expect this variation to be small and Eq. 29 to approximately hold.

For the specific experiments reported in the succeeding paper, and probably most other experiments, the radiation trapping will be such that $P(1) \ll 1$. In that case because of the approximate exponential dependence of both $P(y)$ and $\beta(y)$ on $y$, only the first two or at most three terms ($y = 0, 1, 2$) of Eq. (25) will be important. This result follows from the fact that not only does the intensity of the multiply trapped lines became very small, but so do their differential Doppler shift.

In the Doppler broadening dominated case, $\sigma_g \gg \langle \Delta \nu / \nu_{12} \rangle_0 \nu_{12}^0$, experimentally the best one can do is measure the shift in the maximum of $F(\nu, \nu_{12}^0, \sigma_g)$ as a function of the average number of cycles $\overline{y}$. By an expansion of the exponentials in Eqs. (24) and (25) for $(\nu - \nu_0)^2 / 2 \sigma_g^2 \ll 1$ it is somewhat tedious but straightforward to show that the resultant (average) shift, $\langle \Delta \nu / \nu_{12} \rangle_{\overline{y}}$, is given by

$$\langle \Delta \nu / \nu_{12} \rangle_{\overline{y}} = \beta \left( \langle \Delta \nu / \nu_{12} \rangle_0 \right)_0 = \beta \langle \overline{y} \rangle \left( \langle \Delta \nu / \nu_{12} \rangle \right)_0 \quad (30)$$
where

\[
\bar{\beta} = \sum_y \beta(y) P(y)
\]  

and the last equality must hold for the approximation of independent trapping cycles.

### 2.3 Relation of \( \bar{\beta} \) to System’s Physical Properties

It is necessary to relate \( \Psi \) 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. 1 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,

\[
\Psi = \frac{\tau_e - \tau_2}{\tau_2} = \frac{\tau_e}{\tau_2} - 1 \quad (\tau_e \geq \tau_2)
\]

(32)

According to Holstein[12], in the presence of radiation trapping, \( \tau_e \) is also the eigenvalue of the following integral equation

\[
\left( 1 - \frac{\tau_2}{\tau_e} \right) n_2(\vec{r}) = \int_{\Gamma} G_{12}(\vec{r}, \vec{r'}) n_2(\vec{r'}) d\vec{r'} \quad (\tau_e \geq \tau_2)
\]

(33)

Using Eq.(32), one can rewrite Eq.(33) in terms of \( \Psi \)

\[
\left( 1 - \frac{1}{\Psi + 1} \right) n_2(\vec{r}) = \int_{\Gamma} G_{12}(\vec{r}, \vec{r'}) n_2(\vec{r'}) d\vec{r'}
\]

(34)

In Eqs.(33) and (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[12]

\[
G_{12}(\vec{r}, \vec{r}') = G_{12}(R) = -\frac{1}{4\pi R^2} \frac{\partial T_{12}}{\partial R}, \quad R = |\vec{r} - \vec{r}'| \tag{35}
\]

where

\[
T_{12}(R) = \frac{1}{\pi^{1/2}} \int_{-\infty}^{\infty} e^{-x^2} \exp \left(-K_{12} R e^{-x^2}\right) dx \quad \tag{36}
\]

with \( x \) a dummy variable of integration. The absorption coefficient, \( K_{12} \), at the center of the frequency transition is defined by

\[
K_{12} = \frac{\lambda_{21}^3 N_1 g_2 k_{21}}{8\pi^{3/2} u_1 g_1} \tag{37}
\]

In Eq.(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.(22)) and density respectively of the absorbing atoms. The quantity, \( k_{21} \), is the rate at which level 2 radiatively decays via the (1-2) transition; for a 2-level system it is equal to \( \tau_2^{-1} \), the radiative lifetime of level 2. If one assumes that \( N_1 \) is not a function of \( R \), then it can be treated as a well-defined experimental quantity.

It is clear from Eqs.(35-37) 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 \( K_{12} = K'_{12} \), or

\[
\frac{\lambda_{21}^3 g_2 N_1 k_{21}}{u_1 g_1} = \frac{\lambda_{21}^3 g_2' N_1' k_{21}'}{u_1' g_1'} \tag{38}
\]
Usually one has \( \overline{u_1} = u_1 \) if the two transitions belong to atoms of the same type. Therefore, Eq.(38) reduces to

\[
\frac{\lambda_{21}^2 g_2 N_{1k_{21}}}{g_1} = \frac{\lambda_{21}^2 g'_2 N'_{1k'_{21}}}{g'_1}
\]

for a two level system.

Eq.(38) or Eq.(39) is simple but very useful because it allows the determination of the population of one state from another. For using Eq.(38), the two transitions, (2-1) and (2-1)', can be completely independent as long as their \( \overline{y} \) 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 sources with equivalent trapping volumes. An obvious application of the principle 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.

### 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. 1(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 transi-
tion (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.(33), which defines the effective lifetime, \( \tau_e \), of
the excited state. Holstein has obtained Eq.(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.1(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

\[
\frac{\partial n_2(\vec{r},t)}{\partial t} = -k_{21}n_2(\vec{r},t) - k_{23}n_2(\vec{r},t) + k_{21} \int G_{12}(\vec{r},\vec{r'})n_2(\vec{r'},t)d\vec{r'} \quad (40)
\]

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 \( n_2 \) due to the photons that are
trapped in the volume. As Holstein[12] pointed out, Eq.(40) has a solution
of the following type
\[ n_2(\vec{r}, t) = n_2(\vec{r})e^{-\frac{t}{\tau_e}} \]  
(41)

where \( \tau_e \) is the effective lifetime of the excited state 2. Inserting Eq.(41) into Eq.(40), we find that \( \tau_e \) and \( n_2(\vec{r}) \) satisfy the eigenvalue equation,

\[
[1 - \frac{1}{\tau_e (k_{21} + k_{23})}]n_2(\vec{r}) = \frac{k_{21}}{k_{21} + k_{23}} \int G_{12}(\vec{r}, \vec{r}')n_2(\vec{r}')d\vec{r}'
\]  
(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.(42) becomes approximately

\[
[1 - \frac{1}{\tau_e k_{21}}]n_2(\vec{r}) = \left[1 - \frac{\tau_2}{\tau_e}\right]n_2(\vec{r}) = \int G_{12}(\vec{r}, \vec{r}')n_2(\vec{r}')d\vec{r}'
\]  
(43)

where \( \tau_2 \approx k_{21}^{-1} \). Eq. (43) is just the same as Eq. (33) for a two-level system, which means that under our experimental conditions a three-level system can be treated to a good approximation just as a two-level system.

3 Conclusion

An application of the results of this paper is a new approach for measuring atomic or molecular densities remotely by measuring precisely the Doppler shift of atomic or molecular emission being trapped by these species. Numerous examples exist where this could be a valuable technique. These examples include Doppler-shifted sources in interstellar space, where the only available
information is carried by their radiative emissions. Closer to home are laboratory and industrial plasmas wherein the densities of reactive species is critical but difficult to measure.

In the succeeding paper, we investigate experimentally the photons emitted by a D.C. discharge in He. We find that excited He atoms emit Doppler-shifted radiation along the discharge axis due to momentum exchange with the electrons that excited them. This Doppler shifted radiation can be trapped by ground state He atoms or metastable 2s 3S1 He atoms. By comparing conditions such that the probability for trapping by the two states is equal, Eq. (38) allows us to determine the metastable He density from the ground state density which is easily measured via the total He pressure in the cell.

It should be possible to measure the concentration of many metastable, or other discharge-produced, species by applying this technique. Such measurements are probably most useful when applied to plasmas for which other techniques, e.g., self-absorption, cannot be used for various reasons such as restricted geometries, remoteness, etc.

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When a finite natural linewidth is considered, it is not necessary that the vector \( \vec{\rho} \) in Eq.(10) be exactly perpendicular to \( \vec{k}_2 \) (\( \vec{\rho} \cdot \vec{k}_2 = 0 \)) and lie on the surface \( S \) shown in Fig.2. Rather, \( \vec{\rho} \) satisfies

\[
\vec{\rho} \cdot \vec{k}_2 = a, \quad -\Delta u_n < a < \Delta u_n
\]  

(44)

where \( a \) is a number between \(-\Delta u_n\) and \(\Delta u_n\) as indicated in Eq.(44) and \(\Delta u_n\), which is the velocity variation region corresponding to natural linewidth, is given by

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

(45)

with \(\lambda_{21}\) the transition wavelength and \(\tau_2\) the natural lifetime of the upper state of a two-level system. Equation (44) defines a volume, \( W \), in which the allowed \( \vec{\rho} \) 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.(11) through (16) must be replaced by the volume \( W \), and accordingly, \( \vec{\rho} \) in Eq.(12) becomes

\[
\vec{\rho} \rightarrow \vec{\rho}' = (\rho'_x, \rho'_y, \rho'_z); \quad -\infty < \rho'_x, \rho'_y < \infty; \quad -\Delta u_n < \rho'_z < \Delta u_n
\]  

(46)

Using the above modification to recompute Eqs.(11) through (22), one can find the Doppler shift of Eq.(22) under the assumption of a finite linewidth as

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

(47)
For the transitions in our experiment, the ratio $\frac{\Delta u_n}{\pi}$, which is, according to Eq. (45), given by

$$\frac{\Delta u_n}{\pi} = \frac{\lambda_{21}}{2\pi r_2} \sqrt{\frac{M}{2kT}}$$

(48)

is of the order of $10^{-3}$. Therefore, these correction terms in Eq. (47) are vanishingly small and the finite natural linewidth has virtually no effect on the result.
For a given system (with a given gas density and geometry of the trapping volume) consisting of three-level atoms, as in Fig. 1(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

$$P_1 = \frac{k_{21}}{k_{21} + k_{23}}$$

$$P_2 = \frac{k_{23}}{k_{21} + k_{23}}$$

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 2. This atom may emit a photon at time $t_1 > 0$ with a probability $P(t_1)$

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

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 easily write the probability for each event that allows the atom to 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 $t_1 + t_2$ sec with one trapping cycle. This can occur in two ways: a (2-1) photon is emitted and reabsorbed at $t_1$, followed by emission and escape $t_2$ sec after $t_1$. Alternatively, a (2-1) photon is emitted and reabsorbed at $t_1$ followed by a (2-3) photon emitted $t_2$ sec after $t_1$. Both events lead to the result that the atom has a lifetime of $t_1 + t_2$ and is trapped 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 $t=t_1$, $t=t_1+t_2$, $t=t_1+t_2 \cdots t_{n+1}$, as

$$p(t_1 + t_2 \cdots t_{n+1}, n) = \frac{1}{\tau_{n+1}} e^{-(t_1+t_2 \cdots t_{n+1})/\tau_2} P_1^n Q^n [(1 - Q) P_1 + P_2]$$

$$= \frac{1}{\tau_{n+1}} e^{-(t_1+t_2 \cdots t_{n+1})/\tau_2} P_1^n Q^n (1 - Q P_1)$$

It can be easily seen that Eq. (54) satisfies the condition

$$\sum_{n=0}^{\infty} \int_0^\infty \cdots \int_0^\infty p(t_1 + t_2 \cdots t_{n+1}, n) dt_1 \cdots dt_{n+1} = 1$$

(55)

Correspondingly the effective average lifetime of an atom is

$$\tau_e = \sum_{n=0}^{\infty} \int_0^\infty \cdots \int_0^\infty (t_1 + t_2 \cdots t_{n+1}) p(t_1 + t_2 \cdots t_{n+1}, n) dt_1 \cdots dt_{n+1}$$

(56)
or

\[ \tau_e = \sum_{n=0}^{\infty} \int_{0}^{\infty} \cdots \int_{0}^{\infty} (t_1 + t_2 \cdots t_{n+1}) \frac{1}{\tau_{n+1}} e^{-(t_1+t_2+\cdots t_{n+1})/\tau_2} P_1^n Q^n (1 - QP_1) dt_1 \cdots dt_{n+1} \]

\[ = \sum_{n=0}^{\infty} (n + 1) P_1^n Q^n (1 - QP_1) = (1 - QP_1) \frac{\partial}{\partial (QP_1)} \sum_{n=0}^{\infty} (QP_1)^n+1 \]

\[ = \frac{1}{1 - QP_1} \tau_2 \]

where in writing the final equality, we have used the formula for the sum of a geometric series when the quantity \( QP_1 < 1 \), as it must be for a probability.

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

\[ \overline{y} = \sum_{n=0}^{\infty} \int_{0}^{\infty} \cdots \int_{0}^{\infty} np(t_1 + t_2 \cdots t_{n+1}, n) dt_1 \cdots dt_{n+1} \]  

(58)

or

\[ \overline{y} = \sum_{n=0}^{\infty} \int_{0}^{\infty} \cdots \int_{0}^{\infty} n \frac{1}{\tau_{n+1}} e^{-(t_1+t_2+\cdots t_{n+1})/\tau_2} P_1^n Q^n (1 - QP_1) dt_1 \cdots dt_{n+1} \]

(59)

\[ = \sum_{n=0}^{\infty} n P_1^n Q^n (1 - QP_1) = QP_1 (1 - QP_1) \frac{\partial}{\partial (QP_1)} \sum_{n=0}^{\infty} (QP_1)^n \]

\[ = \frac{QP_1}{1 - QP_1} \]

Combining Eqs.(57) and (59) and eliminating \( QP_1 \), we obtain

\[ \overline{y} = \frac{\tau_e}{\tau_2} - 1 \]  

(60)

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

\[ \tau_2 = \frac{1}{k_{21} + k_{23}} \]  

(61)
When $k_{23}=0$, it becomes a two level system. Following the same logic the result of Eq.(60) can be shown to hold for an arbitrary $n$-level system with trapping on the transition (2-1).
Figure Captions

**Fig.1** Schematic diagram illustrating (a) a two-level and (b) a three-level system with radiation trapping.

**Fig.2** Schematic diagram showing the geometric relationships among the various velocity and photon propagation vectors. The detector is assumed to be on the z axis.
References


