Collisional relaxation of multipole moments in 42P potassium atoms.

Piotr. Skalinski

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THIS DISSERTATION HAS BEEN MICROFILMED EXACTLY AS RECEIVED.
COLLISIONAL RELAXATION OF MULTIPOLE MOMENTS
IN $4^2P$ POTASSIUM ATOMS

by

PIOTR SKALINSKI

A Dissertation
Submitted to the Faculty of Graduate Studies through the Department of Physics in Partial Fulfilment of the requirements for the Degree of Doctor of Philosophy at The University of Windsor

Windsor, Ontario, Canada
1982
ABSTRACT

\[ m_J \] mixing in \( 4^2P_\frac{1}{2} \) and \( 4^2P_{3/2} \) potassium atoms, as well as atomic multipole relaxation induced in K-K and K-Ar collisions, were investigated by methods of atomic fluorescence spectroscopy. Investigations of collisional depolarization of resonance fluorescence together with interferometric analysis of fluorescent spectra were employed to obtain decay rates for the atomic multipole moments.

The total cross sections for disorientation (\( \sigma^{(1)} \)) of \( 4^2P_\frac{1}{2} \) potassium atoms and disorientation (\( \sigma^{(1)} \)) and disalignment (\( \sigma^{(2)} \)) of \( 4^2P_{3/2} \) potassium atoms induced in resonant collisions with the ground state atoms, have been determined using a modified Zeeman scanning method. Potassium vapor at densities of the order of \( 10^{11} \text{ cm}^{-3} \), contained in a fluorescence cell located in a kilogauss variable magnetic field, was irradiated with circularly polarized 766.5 nm (or 769.9 nm) resonance radiation emitted from a discharge lamp located in a constant field of 5.4 kG. Scans of the variable field permitted selective excitation of single Zeeman components in the absorbing vapor. The \( \sigma^+ \) and \( \sigma^- \) components of the resulting resonance fluorescence emitted parallel to the scanning field were monitored in relation to the vapor density, as were the \( \pi \) and \( \sigma \) components emitted in the perpendicular direction. As the vapor density increased, so did the frequency of the collisions which caused transfers among the Zeeman states in the vapor, and thus disorientation and disalignment.

The observed dependence of circular and linear depolarization of the fluorescence on the potassium density, yielded the following
cross sections (corrected for imprisonment of radiation):

\[ \Lambda_{3/2}^{(1)} = 10 \times 10^{-12} \text{ cm}^2 \]
\[ \Lambda_{3/2}^{(1)} = 9 \times 10^{-12} \text{ cm}^2 \]
\[ \Lambda_{3/2}^{(2)} = 11 \times 10^{-12} \text{ cm}^2 \]

In a subsequent experiment potassium vapor, pure or mixed with Ar, was placed in a kG magnetic field and irradiated with a single Zeeman component of 769.9 nm or 766.5 nm resonance radiation, causing the selective excitation of the \( ^2P_{1/2}, -1/2 \) or \( ^2P_{3/2}, -3/2 \) substate, respectively. Collisions of the excited atoms with ground-state K or Ar atoms caused \( m_J \) mixing in the excited state, which was monitored by analysis of the resulting fluorescent spectrum using a scanning Fabry-Perot interferometer. Intensity measurements on the fluorescent Zeeman components in relation to ground-state atomic densities yielded the following multipole relaxation cross sections \( \Lambda_j^{(L)} \):

K-K \( (10^{-12} \text{ cm}^2) \):
\[ \Lambda_{1/2}^{(1)} = 5.7 \pm 0.9 \]
\[ \Lambda_{3/2}^{(1)} = 8.1 \pm 1.4 \]
\[ \Lambda_{3/2}^{(2)} = 11.4 \pm 2.0 \]
\[ \Lambda_{3/2}^{(3)} = 9.8 \pm 1.5 \]

K-Ar \( (10^{-16} \text{ cm}^2) \):
\[ \Lambda_{1/2}^{(1)} = 65 \pm 10 \]
\[ \Lambda_{3/2}^{(1)} = 175 \pm 25 \]
\[ \Lambda_{3/2}^{(2)} = 230 \pm 35 \]
\[ \Lambda_{3/2}^{(3)} = 190 \pm 30 \]

The \( Q_j (m \leftrightarrow m') \) cross sections for \( m_j \) mixing were derived from the \( \Lambda_j^{(L)} \), as well as the cross sections for multipole decay, \( \sigma_j^{(L)} = \Lambda_j^{(L)} + \sigma_j^{(0)} \). The experimental results (corrected for radiation trapping) are in good agreement with those obtained in the depolarization studies, as well as with theoretical calculations.
ACKNOWLEDGEMENTS

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The success of the experiment described in this thesis was made possible to a considerable extent by the technical expertise of Master Glassblower, R. Campbell, who constructed the fluorescence cell, of Mr. B. Masse, Senior Electronics Technologist and Mr. W. Grewe, Superintendent of the Physics Machine Shop.
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I. INTRODUCTION

The study of radiation emitted from atoms subjected to collisions provides useful information not only about atomic structure, but also about the nature of the collisional interaction. An excited atom colliding with a ground-state neutral atom or molecule may be affected in a variety of ways, each of which manifests itself by a particular phenomenon. Elastic collisions leave an atom in its quantum state, but may cause broadening and shift of the spectral line, resulting from long-range interactions causing random changes in the phase of the vibrations of the atomic oscillator.

There is a variety of inelastic processes which may cause the atom to lose part or all of its excitation energy. Collisional excitation transfer within the atom or to its collision partner leads to the emission of sensitized fluorescence of different wavelength than that associated with the initial excited state. Quenching causes complete radiationless deexcitation, with the excitation energy taken up by the various available translational, vibrational and rotational degrees of freedom of the colliding partners. Such inelastic processes have been classified by Klein and Rosseland (1921) as collisions of the second kind, in contrast with the effects produced by electron-atom collisions 'of the first kind' discovered by Franck and Hertz.

Sensitized fluorescence and quenching of resonance radiation have been studied extensively in the 1920s and 1930s. Cario and Franck (1922) found that a mixture of mercury and
thallium vapors illuminated by Hg light emitted a number of thallium lines in addition to the (expected) original exciting line. Beutler and Josephy (1929) investigated mercury-sensitized fluorescence in sodium and demonstrated the importance of the energy resonance condition which had been formulated earlier by Franck (1929). According to "Franck's rule" the smaller the energy difference between two atomic states, the more probable the excitation transfer. This effect was brought out by Mrozowski (1932) in his experiments on He-induced collisional transfer between hyperfine structure sublevels of the Hg $^3P_1$ state, which was effected by as little as 0.1 torr of He.

Collisional excitation transfer (accompanied by the emission of sensitized fluorescence) was also found to occur between two levels of the same atom. Wood and Dunoyer (1914) and Wood and Mohler (1918) observed sensitized fluorescence in pure sodium and a sodium-inert gas mixture. Their experiments were followed by those of Lochte-Holtgreven (1928) and of Seiwerp (1956a) who calculated and measured the cross sections for collisional mixing between resonance fine-structure substates in sodium. In his investigations, Seiwerp was the first to correct his experimental observations for radiation trapping effects, developing a quantitative treatment (1956b) based on Holstein's (1947, 1951) theory.

During subsequent years, a large number of experiments were carried out on collision-induced fine structure mixing and quenching of resonance radiation (Krause, 1975), with the results
generally behaving in accordance with Franck's rule. More recently, there has been widespread interest in collisional transfer between the higher (Rydberg) states in alkali atoms, which are being studied using methods of "classical" fluorescence spectroscopy, laser spectroscopy and atomic beams (e.g. Kleppner, 1978).

Collisions of excited atoms may result not only in excitation transfer between fine structure or ffs states, but they also frequently cause atomic depolarization and depolarization of the atomic fluorescence. Atomic polarization can be created by exciting the atoms with polarized resonance radiation. This causes some magnetic Zeeman sublevels to become preferentially populated and a bulk dipole, quadrupole or higher moment to be established in the vapor. At very low vapor densities and in the absence of collisions, the fluorescence emitted in the decay of the excited and polarized atoms is polarized in the same sense as the original exciting radiation. If before decaying the atoms are subjected to collisions, this causes depolarization of the atoms and of the fluorescence. Studies of such depolarization in relation to the density of the collision partner yield information about the character of the interactions as they affect the decay of the various multipole moments. Numerous experimental and theoretical studies of depolarization phenomena have been reported (Baylis, 1978). Experiments dealing with depolarization of excited atoms may be divided into two general groups: those carried out at zero external magnetic field or at
low fields at which the atomic hyperfine structure is preserved and the nucleus remains coupled to the atomic electrons, and experiments performed in high magnetic fields sufficient to decouple the nucleus, produce a Paschen-Back effect of the hfs and cause a separation of the Zeeman sublevels exceeding the Doppler width.

Disorientation (dipole relaxation) of \(^{2P}_{\frac{1}{2}}\) alkali atoms in zero magnetic field induced by noble gas collisions has been studied by Niewitecka et al. (1974) and Niewitecka and Krause (1975) for Na and K. The Hanle effect—magnetic depolarization in low fields—has been employed by Lewis, Wheeler and Wilson (1977) to study similar disorientation of potassium \(^{2P}\) states. Gallagher and Lewis (1974) measured cross sections for disorientation and disalignment of the Rb resonance states through resonant collisions with ground-state Rb atoms, by monitoring collisional broadening of Hanle signals, and Burgmans (1979) employed the same technique to the sodium resonance states. The cross sections for the resonant collisions are, on the whole, several orders of magnitude larger than for collisions with noble gases, since relatively long-range dipole-dipole interaction is involved in the former case, whereas only van der Waals forces are involved in the latter. Depolarization cross sections measured in the presence of hfs must be corrected for the effects of nuclear spin which, although decoupled during the actual collision, becomes immediately recoupled and diminishes the observed effect since it itself does not participate in the depolarization
process because the average collision time ($\approx 10^{-12}$s) is much shorter than the hfs period ($\approx 10^{-8}$s). The effect of nuclear spin inertia in Hanle experiments has been treated by Bulos and Happer (1971), and in zero-field depolarization experiments by Franz and Sooriamoorthy (1973), and all cross sections measured in the presence of hfs are now corrected appropriately.

There has been a rather smaller number of experiments carried out at higher magnetic fields, with the nucleus decoupled. In virtually all of these the depolarization was induced by noble gas collisions. Thus Elbel et al. (1974) studied $^2P_{3/2}$ disalignment in Na, Kamke (1975) investigated disorientation and disalignment in Rb and Guiry and Krause (1972, 1976) used modified Zeeman scanning techniques to measure disorientation and disalignment cross sections in Cs.

Depolarization of $^2P_{3/2}$ and $^2P_{3/2}$ potassium atoms through noble gas collisions in magnetic fields of several kG was investigated by Berdowski and Krause (1968) and Berdowski, Shiner and Krause (1971), who used a modified Zeeman scanning method to populate selected $^2P$ Zeeman substates and monitored circular and linear depolarization of the emitted resonance radiation. In this way they were able to measure the cross sections for relaxation of the dipole and quadrupole moments, though not the octupole since, in order to detect the octupole, it is necessary to resolve the individual Zeeman components in the fluorescent light. Such spectroscopic analysis was employed by Gay and Schneider who measured cross sections for transfer between the
$^{3}_{2}P_{3/2,\pm 3/2}$ Zeeman components in sodium and for multipole relaxation induced in collisions with noble gases (1978) and ground-state Na atoms (1979). Most recently, Boggy and Franz (1982) also determined cross sections for $J,m_J \leftrightarrow J',m_{J'}$ transfers within the $4^2P$ potassium doublet, caused by collisions with He, Ne and Kr.

The polarization in the vapor of an alkali metal and its collisional relaxation can be treated using the density matrix formalism (Baylis, 1978; Fano, 1957). In 1965 Omont (1965), Dyakonov (1965) and Dyakonov and Perel (1965a, 1965b) showed how an expansion of the density matrix in terms of irreducible tensor operators can be used to describe a population distribution among excited Zeeman substates and the resulting bulk polarization. The relaxation of the electromagnetic multipole moments which directly correspond to the terms of the expansion can be monitored by analysis of the atomic fluorescent spectrum.

The specific problem of collisional depolarization of $2^P$ alkali atoms by noble gas collisions has been attacked in various ways and using a variety of approximations to simplify the calculations. Of particular importance are methods involving the straight-line path approximation and the impact approximation which assumes the average collision time to be much shorter than the time between collisions, the hfs period and the lifetime of the excited state. The density matrix formalism was employed by Okunevich and Perel (1970) who investigated the relaxation of the density matrix resulting from collisions of the excited
alkali atoms with noble gases and obtained relative relaxation rates for dipole, quadrupole and octupole moments in a $J = 3/2$ state with coupled nuclear spin. This treatment was further pursued by Rebane and Rebane (1972, 1973) who considered separately the collisional relaxation of the electronic moments and I-J recoupling. At the same time a rather different approach was taken by Nikitin and his group (Gordeev et al. 1971) who postulated a model involving molecular coupling between the colliding alkali and noble gas atoms and the participation of Coriolis interaction in the depolarization process. This theory was extended by Rojeff and Suzor (1974) who applied it to alkali atoms with large fine-structure splitting (Rb and Cs).

The most recent theoretical calculations directly applicable to experimental situations in large magnetic fields were performed by Lewis and Wheeler (1977) and Lewis, Wheeler and Wilson (1977), who allowed for the effects of nuclear spin and calculated cross sections for multipole relaxation in $4^2P$ potassium atoms, induced by collisions with noble gases. An equally useful theory dealing with resonant alkali-alkali collisions was developed by Carrington, Stacey and Cooper (1973) who calculated decay rates for all the multipole moments on the basis of dipole-dipole interaction and using an impact approximation.

This thesis describes an experimental study of collisional depolarization of potassium $4^2P_{1/2}$ and $4^2P_{3/2}$ atoms through collisions with ground-state potassium and argon atoms, taking place in kilogauss magnetic fields. A modified Zeeman scanning,
method developed in this laboratory (Berdowski and Krause, 1968; Berdowski et al. 1971) was used to populate selected \(^2\!P\) Zeeman substates and the relaxation of the dipole, quadrupole and octupole moments was monitored through the analysis of the emitted fluorescence. Two basic kinds of experiments were carried out, differing from one another by the analysis to which the fluorescence was subjected. In the first series of experiments the circular and linear depolarization of the fluorescence was monitored in relation to the density of the collision partners (ground-state K atoms), yielding disorientation and disalignment cross sections. Subsequently the individual Zeeman components in the fluorescent spectrum were resolved with a scanning interferometer, which permitted the determination of cross sections for Zeeman mixing and for relaxation of dipole, quadrupole and octupole moments induced in collisions with ground-state Ar and K atoms. This constitutes the first determination of a complete set of such cross sections for alkali-alkali resonant collisions; they are directly comparable with theoretical calculations with which there is a gratifying measure of agreement. There is equally satisfactory accord in the K-Ar cross sections and in comparisons with experimental data pertaining to similar systems.
II. THEORETICAL

1. General Formulation

The method by which light emitted from an r.f. potassium discharge may be used to selectively populate Zeeman sublevels of \(4^2P_{\frac{3}{2}}\) or \(4^2P_{\frac{3}{2}}\) potassium resonance states, has been described previously (Berdowski et al. 1971). Collisions with atoms of an added buffer gas or with ground state potassium atoms tend to equalize the Zeeman state populations:

\[
K(4^2P_{\frac{3}{2},m}) + X \leftrightarrow K(4^2P_{\frac{3}{2},m'}) + X \\
K(4^2P_{\frac{3}{2},m}) + X \leftrightarrow K(4^2P_{\frac{3}{2},m'}) + X
\]

where \(X\) is a ground state atom and \(m\) or \(m'\), the \(m_j\) Zeeman substates; may have values \(3/2, \frac{1}{2}, -\frac{1}{2}, -3/2\). Continuous optical excitation results in a steady state which involves spontaneous decay to the ground state as well as collisional transfers between the Zeeman substates and which may be represented by the following rate equations:

\[
\frac{dN_m}{dt} = -\frac{N_m}{\tau} - N_m \sum_{m' \neq m} Z(m \rightarrow m') + \sum_{m' \neq m} N_m Z(m \rightarrow m') + S_m = 0
\]

where \(Z\) are the frequencies of collisions per excited atom, corresponding to transfers between the optically populated state \(m\) and the other states \(m'\). \(N_m\) and \(N_m\), are the population densities of the Zeeman substates, \(S_m\) are the densities of atoms
excited per second to state $m$ and $\tau = 2.77 \times 10^{-8}$ s is the mean lifetime of the $4^2P$ state (Copley and Krause, 1969). The $m_J$ mixing cross sections may be defined analogously with the gas-kinetic cross section.

$$Z(m \rightarrow m') = N Q(m \rightarrow m')v$$

(4)

where $N$ is the density of the ground-state collision partners, $v = (8kT/mM)^{1/2}$ is the average relative speed of the colliding atoms and $M$ is their reduced mass. Equations (1)-(3) take no account of collisional $^2P_{\frac{1}{2}} \rightarrow ^2P_{\frac{3}{2}}$ fine-structure mixing or quenching to the ground state.

The rate equations (3) can be directly related to the experimental observations by representing the densities of the atoms as components of an $q$-dimensional vector $\mathbf{N} = (N_1, N_2, \ldots, N_q)$ (Baylis, 1979). The excitation term in (3) is correspondingly represented by $\mathbf{S} = (S_1, S_2, \ldots, S_q)$. For the $^2P_{\frac{1}{2}}$ state $q = 2$ and for the $^2P_{\frac{3}{2}}$ state $q = 4$. The time evolution of the density vector $\mathbf{N}$ may be described by

$$\frac{d\mathbf{N}}{dt} = \frac{1}{\tau} (\mathbf{N} - \gamma \mathbf{N} + \mathbf{S})$$

(5)

where $\tau$ is the mean lifetime of the $4^2P$ state and $\gamma$ represents the relaxation matrix representing the collisional processes of the $4^2P_{\frac{1}{2}}$ or $4^2P_{\frac{3}{2}}$ state.

$\gamma_{mm'}$ ($m \neq m'$) is the rate at which an atom in state $|m\rangle$ is collisionally transferred to state $|m'\rangle$. When the energy separation between the sublevels $|m\rangle$ is much smaller than $kT$, $\gamma_{mm'} = \gamma_{m'm}$. In a steady state involving continuous optical
excitation, spontaneous decay to the ground state and collisional transfers between the Zeeman substates

$$\frac{dN}{dt} = 0$$  \hspace{1cm} (6)

To solve (5) and (6) one can take advantage of the rotational invariance of the matrix $\hat{V}$ in 3-dimensional space, due to collisional isotropy, while the vectors $\hat{N}$ and $\hat{S}$ are expanded as linear combinations of the spherical basis vectors $\hat{T}(L)$. The vectors $\hat{T}(L)$ are examples of irreducible tensor operators, so called because of their transformation properties under rotations. The importance of these operators derives from the fact that many dynamical variables of physical interest can be expressed in this form. For example, the $2^L$-th electromagnetic multipole moment is an irreducible tensor operator of order $L$. Thus the density vector expanded in the $\hat{T}(L)$ basis takes the form of the sum of the various multipole moments, each having direct physical meaning.

$$\hat{N} = \sum_{L = 0}^{q} (\hat{T}(L))^\dagger \hat{T}(L) =$$

$$= n(0)^T(0) + n(1)^T(1) + \cdots + n(q)^T(q).$$  \hspace{1cm} (7)

where $n(L)$ represents the $2^L$-th multipole moment of $\hat{N}$. For $L = 0$, $n(0)$ represents the monopole or "occupation" component of $\hat{N}$, $n(1)$ (for $L = 1$) is proportional to the magnetic dipole density and is known as the orientation component of $\hat{N}$. The quadrupole moment (alignment) corresponds to $L = 2$, and for $L = 3$ $n(3)$ represents the octupole moment.
Equations (3) can be transformed through this expansion into an equivalent set of equations, each of which includes only one characteristic relaxation time:

\[ \dot{n}_J^{(L)} = -\frac{1}{\tau} n_J^{(L)} - \gamma_J^{(L)} n_J^{(L)} + s_J^{(L)} \]  \hspace{1cm} (8)

where \( s_J^{(L)} = \hat{T}(L) \cdot S \). Equation (8) has a general solution

\[ n_J^{(L)}(t) = n_J^{(L)}(\infty) + \left[ n_J^{(L)}(0) - n_J^{(L)}(\infty) \right] \exp \left[ -\left(\frac{1}{\tau} + \gamma_J^{(L)}\right)t \right] \]  \hspace{1cm} (9)

whose steady state value is

\[ n_J^{(L)}(\infty) = \frac{s_J^{(L)}}{1 + \gamma_J^{(L)} \tau} \]  \hspace{1cm} (10)

For the case of isotropic collisions, the time-evolution of an ensemble of atoms, each having \( 2J + 1 \) substates, is described by \( 2J + 1 \) relaxation constants. Thus there are two relaxation constants for the \( ^2P_{\frac{3}{2}} \) state and four relaxation constants are required for the complete description of the \( ^2P_{3/2} \) state. In the absence of collisional depopulation \( \gamma_J^{(0)} = 0 \) and \( n_J^{(0)} = \tau s_J^{(0)} \).

This result together with Eq. (10) yields an expression

\[ \tau \gamma_J^{(L)} = \left( \frac{n_J^{(0)}}{n_J^{(L)}} \right) \left( \frac{s_J^{(L)}}{s_J^{(0)}} \right) - 1 \]  \hspace{1cm} (11)

from which it is possible to calculate \( \gamma_J^{(L)} \) and the cross sections \( \sigma_J^{(L)} \) for collisional relaxation of the multipole moments, since

\[ \gamma_J^{(L)} = N \sigma_J^{(L)} v \]  \hspace{1cm} (12)

According to the generally accepted definition (Baylis, 1979),
the total cross sections \( \sigma_{J}^{(L)} \) for the collisional decay of the multipole moments may be represented as

\[
\sigma_{J}^{(L)} = \Lambda_{J}^{(L)} + \sigma_{J}^{(0)}
\]  

(13)

where, in this case, \( \sigma_{J}^{(0)} \) is the cross section for \( J + J' \) fine-structure mixing.

By monitoring the populations of the individual Zeeman substates in relation to the buffer gas pressure, it is possible to obtain cross sections \( Q_{J}(m \leftrightarrow m') \) for transfers between them and also the multipole relaxation cross sections \( \Lambda_{J}^{(L)} \) which are related as follows to each other (Berdowski et al. 1971).

For the \( 4^{2}P_{\frac{3}{2}} \) state:

\[
Q_{3/2}(\frac{3}{2} \leftrightarrow -\frac{1}{2}) = (\frac{1}{20}) \Lambda_{3/2}^{(1)}
\]

(14)

For the \( 4^{2}P_{\frac{1}{2}} \) state:

\[
Q_{3/2}(\frac{3}{2} \leftrightarrow \frac{1}{2}) = (1/20) \Lambda_{3/2}^{(1)} - (\frac{1}{4}) \Lambda_{3/2}^{(2)} + (9/20) \Lambda_{3/2}^{(3)}
\]

(15)

\[
Q_{3/2}(3/2 \leftrightarrow 1/2) = (3/20) \Lambda_{3/2}^{(1)} + (\frac{1}{4}) \Lambda_{3/2}^{(2)} + (3/20) \Lambda_{3/2}^{(3)}
\]

(16)

\[
Q_{3/2}(3/2 \leftrightarrow -1/2) = (3/20) \Lambda_{3/2}^{(1)} - (\frac{1}{4}) \Lambda_{3/2}^{(2)} - (3/20) \Lambda_{3/2}^{(3)}
\]

(17)

\[
Q_{3/2}(3/2 \leftrightarrow -3/2) = (9/20) \Lambda_{3/2}^{(1)} - (\frac{1}{4}) \Lambda_{3/2}^{(2)} + (1/20) \Lambda_{3/2}^{(3)}
\]

(18)

Because the Zeeman splitting is much smaller than \( kT \) and because of the spherical symmetry of isotropic collisions the \( m_{J} \) mixing cross sections are symmetric as follows:

\[
Q(m \leftrightarrow m') = Q(-m \leftrightarrow -m')
\]

(19)

It can be seen that if the populations of the Zeeman sublevels
can be determined in relation to the buffer gas density, it is possible to obtain the cross sections for transfer between the individual Zeeman substates as well as for relaxation of all the multipole moments.

2. **Application of Density Matrix Formalism to Collisional Dipole Relaxation in the $^{4}P_{\frac{3}{2}}$ State**

The optical transitions between the $^{2}S_{\frac{1}{2}}$ and $^{2}P_{\frac{3}{2}}$ Zeeman substates, and the collisional $m_J$ mixing in the $^{2}P_{\frac{3}{2}}$ state are depicted in Fig. 1. The optical excitation is effected by $\sigma^-$ circularly polarized resonance radiation (769.9 nm) and the fluorescence consists of the $\sigma^-$ component emitted in the decay of the optically excited state and the $\sigma^+$ component arising from the collisionally populated $m_J = +\frac{3}{2}$ state. The $\pi$-polarized components are not shown in the diagram since they were not observed in these experiments.

For the $^{4}P_{\frac{3}{2}}$ state, the density and source vectors are $\mathbf{N} = (N_{\frac{3}{2}}, N_{-\frac{3}{2}})$ and $\mathbf{S} = (S_{\frac{3}{2}}, S_{-\frac{3}{2}})$, respectively, where the subscripts refer to the $m_J = \frac{3}{2}$ and $-\frac{3}{2}$ Zeeman substates. The "spherical" basis vectors are

$$\hat{T}(0) = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}, \quad \hat{T}(1) = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

(20)

The multipole densities $n^{(L)}$, expressed in terms of $N_n$, are directly obtainable from Eq. (7).

$$n_{\frac{3}{2}}^{(0)} = \frac{1}{\sqrt{2}} (N_{\frac{3}{2}} + N_{-\frac{3}{2}})$$

$$n_{\frac{3}{2}}^{(1)} = \frac{1}{\sqrt{2}} (N_{\frac{3}{2}} - N_{-\frac{3}{2}})$$

(21)
By analogy the "source" vectors are

\[ s_{\frac{1}{2}}^{(0)} = \frac{1}{\sqrt{2}} \left( S_{\frac{1}{2}}^{+} + S_{\frac{1}{2}}^{-} \right) \]  

\[ s_{\frac{1}{2}}^{(1)} = \frac{1}{\sqrt{2}} \left( S_{\frac{1}{2}}^{+} - S_{\frac{1}{2}}^{-} \right) \]  

(22)

Substitution of Eqs. (21) and (22) into (11) gives

\[ \tau_{Y(1)}^{\frac{1}{2}} = \frac{N_{\frac{1}{2}} + N_{-\frac{1}{2}}}{N_{\frac{1}{2}} - N_{-\frac{1}{2}}} \times \frac{S_{\frac{1}{2}} - S_{-\frac{1}{2}}}{S_{\frac{1}{2}} + S_{-\frac{1}{2}}} - 1 \]  

(23)

Since, under the excitation conditions shown in Fig. 1

\[ s_{\frac{1}{2}}^{(0)} = s_{\frac{1}{2}}^{(1)} = \frac{1}{\sqrt{2}} S_{\frac{1}{2}} \]  

(24)

Eq. (20) is reduced to

\[ \tau_{Y(1)}^{\frac{1}{2}} = \frac{N_{\frac{1}{2}} + N_{-\frac{1}{2}}}{N_{\frac{1}{2}} - N_{-\frac{1}{2}}} - 1 \]  

(25)

which, in conjunction with Eq. (12), yields the following expression for the dipole relaxation cross section \( \Lambda_{\frac{1}{2}}^{(1)} \).

\[ \Lambda_{\frac{1}{2}}^{(1)} = \frac{1}{Nv\tau} \left( \frac{1 + \frac{N_{-\frac{1}{2}}}{N_{\frac{1}{2}}} - 1}{1 - \frac{N_{-\frac{1}{2}}}{N_{\frac{1}{2}}} - 1} \right) \]  

(26)

The intensities of the Zeeman components are related to the populations through the appropriate Einstein A coefficients.

For \( 4^2P_{\frac{1}{2}} \rightarrow 4^2S_{\frac{1}{2}} \) transitions

\[ \Lambda_{\pi} : \Lambda_{\sigma} = 2 : 4 \]  

(27)

where \( \Lambda_{\pi} \) and \( \Lambda_{\sigma} \) are the transition probabilities for the decays
Fig. 1 Radiative and collisional transitions between the Zeeman sublevels of the ground state and $4^2P_1$ resonance state in potassium. Single collision conditions are assumed.
of the $^{2}p_{\frac{1}{2}, \frac{3}{2}}$ substates by emission of $\pi$ and $\sigma^{\pm}$ polarized radiation, respectively. The total intensity of radiation emitted in the decay of a Zeeman sublevel is

$$N_{\pm} (A_{\pi} + A_{\sigma}) = N_{\pm} A_{\sigma} \left( \frac{A_{\pi}}{A_{\sigma}} + 1 \right) = 3/2 N_{\pm} A_{\sigma} = 3/2 I_{\pm}$$

(28)

where $I_{\pm}$ is the intensity of the $\sigma^{+}$ or $\sigma^{-}$ polarized components. Accordingly,

$$\frac{N_{-\frac{1}{2}}}{N_{+\frac{1}{2}}} = \frac{N_{-\frac{1}{2}} (A_{\pi} + A_{\sigma})}{N_{+\frac{1}{2}} (A_{\pi} + A_{\sigma})} = \frac{I_{-\frac{1}{2}}}{I_{+\frac{1}{2}}}$$

and Eq. (26) may now be expressed in terms of the fluorescent intensities.

$$\Lambda_{\frac{1}{2}}^{(1)} = \frac{1}{N\nu} \left( \frac{1 + \frac{I_{-\frac{1}{2}}}{I_{+\frac{1}{2}}} \frac{I_{+\frac{1}{2}}}{I_{-\frac{1}{2}}} - 1}{1 - \frac{I_{-\frac{1}{2}}}{I_{+\frac{1}{2}}} \frac{I_{+\frac{1}{2}}}{I_{-\frac{1}{2}}} - 1} \right)$$

(30)

All the quantities in Eq. (30) are directly measurable. $N$ may be measured with a pressure gauge or determined from temperature-vapor pressure relations, $\nu$ is a function of temperature and $\nu$ is known.

Equation (30) can be used to obtain $\gamma_{\frac{1}{2}}^{(1)}$ and $\Lambda_{\frac{1}{2}}^{(1)}$ by two separate means. The fluorescent intensities $I_{\frac{1}{2}}$ and $I_{-\frac{1}{2}}$ can be determined directly by resolving the Zeeman components in the fluorescent light and substituted in the equation. They can also be derived from the degrees of circular polarization of the
fluorescence. For purposes of polarization spectroscopy, it is useful to define the degree of circular polarization.

\[ p = \frac{I_{o^+} - I_{o^-}}{I_{o^+} + I_{o^-}} = \frac{I_{+\frac{3}{2}} - I_{-\frac{1}{2}}}{I_{+\frac{3}{2}} + I_{-\frac{1}{2}}} \]  

(31)

In the absence of depolarizing collisions (at \( N = 0 \)) \( p = P_0 \) where

\[ P_0 = \frac{S_{\frac{3}{2}} - S_{-\frac{1}{2}}}{S_{\frac{3}{2}} + S_{-\frac{1}{2}}} \]  

(32)

Substitution of Eqs. (31) and (32) into (23) yields

\[ \tau_{V_3}^{(1)} = \frac{P_0}{p} - 1. \]  

(33)

3. Application of Density Matrix Formalism to Collisional Dipole, Quadrupole and Octupole Relaxation in the \( 4^2P_{3/2} \) State

The optical transitions between the \( 4^2S_{\frac{1}{2}} \) and \( 4^2P_{3/2} \) Zeeman substates, and the collisional \( m_J \) mixing in the \( 4^2P_{3/2} \) state are depicted in Fig. 2.

The \( m_J = -3/2 \) Zeeman sublevel is selectively populated by absorption of \( \sigma^- \)-polarized radiation using the Zeeman scanning technique described in Chapter IV. As the result of collisional transfer (\( m_J \) mixing), the fluorescence also contains Zeeman components arising from the other collisionally populated Zeeman sublevels. As before, the \( \pi \) =polarized fluorescent components are not shown.

The basis vectors for \( 4^2P_{3/2} \) state are
\[ \hat{T}(0) = \frac{1}{2} \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}; \hat{T}(1) = \frac{1}{2\sqrt{5}} \begin{pmatrix} 3 \\ 1 \\ -1 \end{pmatrix}; \hat{T}(2) = \frac{1}{2} \begin{pmatrix} 1 \\ -1 \\ 1 \end{pmatrix}; \hat{T}(3) = \frac{1}{2\sqrt{5}} \begin{pmatrix} 1 \\ -3 \\ 3 \end{pmatrix} \]

(34)

The corresponding multipole densities are obtained from Eqs. (7) and (34).

\[ L = 0: \eta_{3/2}^{(0)} = \frac{1}{2}(N_{3/2} + N_{1/2} + N_{-1/2} + N_{-3/2}) \]

\[ L = 1: \eta_{3/2}^{(1)} = \frac{1}{2\sqrt{5}}(3N_{3/2} + N_{1/2} - N_{-1/2} - 3N_{-3/2}) \]

\[ L = 2: \eta_{3/2}^{(2)} = \frac{1}{2}(N_{3/2} - N_{1/2} - N_{-1/2} + N_{-3/2}) \]

\[ L = 3: \eta_{3/2}^{(3)} = \frac{1}{2\sqrt{5}}(N_{3/2} - 3N_{1/2} + 3N_{-1/2} - N_{-3/2}) \]

(35)

When only the \( m_J = -3/2 \) Zeeman sublevel is optically populated, the source vectors are

\[ s_{3/2}^{(0)} = \frac{1}{2} s_{3/2} \]

\[ s_{3/2}^{(1)} = \frac{3}{2\sqrt{5}} s_{3/2} \]

\[ s_{3/2}^{(2)} = \frac{1}{2} s_{3/2} \]

\[ s_{3/2}^{(3)} = \frac{1}{2\sqrt{5}} s_{3/2} \]

(36)

As in the case of the \( 4^2P_{3/2} \) state, collisional depolarization of the \( 4^2P_{3/2} \) state can be studied using methods of polarization spectroscopy or by resolving the individual Zeeman components in the fluorescent light. However, only the latter method yields all three relaxation rates \( \gamma_{3/2}^{(1)} \), \( \gamma_{3/2}^{(2)} \) and \( \gamma_{3/2}^{(3)} \). Polarization measurements provide the means to detect only collisional
disorientation and disalignment.

(a) *Derivation of disorientation and disalignment cross sections from optical polarization measurements*

The degrees of circular and linear polarization $P$ and $P'$, respectively, are defined in the usual manner.

\[ P = \frac{I_{\sigma^+} - I_{\sigma^-}}{I_{\sigma^+} + I_{\sigma^-}}; \quad P' = \frac{I_{\sigma} - I_{\pi}}{I_{\sigma} + I_{\pi}} \]  \hspace{1cm} (37)

where $I_{\sigma^+}$ and $I_{\sigma^-}$ represent the total intensities of circularly polarized fluorescent light emitted in the decay of all the Zeeman substates, parallel or antiparallel to the magnetic field, as may be seen in Fig. 2.

\[ I_{\sigma^\pm} = I_{3/2}^{\pm} + I_{1/2}^{\pm} \]  \hspace{1cm} (38)

The intensities of the fluorescent Zeeman components observed perpendicularly to the field are

\[ I_{\sigma} = \frac{2}{5}(I_{\sigma^+} + I_{\sigma^-}) \]  \hspace{1cm} (39)

and

\[ I_{\pi} = I_{3/2}^\pi + I_{1/2}^\pi \]  \hspace{1cm} (40)

where $I_{3/2}^\pm$ are the intensities of linearly polarized fluorescent $\pi$ components arising from the Zeeman sublevels $m_j = \pm \frac{3}{2}$. The intensities of the various components can be expressed in terms of the multipole densities defined by Eqs. (35).

\[ I_{\sigma^\pm} = A \left[ n_{3/2}^{(0)} + \frac{1}{4} n_{3/2}^{(2)} \pm \frac{\sqrt{5}}{2} n_{3/2}^{(1)} \right] \]  \hspace{1cm} (41)

\[ I_{\sigma} = A \left[ n_{3/2}^{(0)} + \frac{1}{4} n_{3/2}^{(2)} \right] \]  \hspace{1cm} (42)
Fig. 2  Radiative and collisional transitions between the Zeeman sublevels of the ground state and $4^2P_{3/2}$ resonance state in potassium. Single collision conditions are assumed.
Fig. 2
\[ I_\pi = A \left[ n_{3/2}^{(0)} - n_{3/2}^{(2)} \right] \]  

where \( A = \frac{1}{3} A' = A_\sigma = \frac{1}{3} A_\pi \) and \( A'_\sigma : A_\sigma : A_\pi = 6:2:4 \), where \( A_\sigma \) and \( A_\pi \) are the transition probabilities for the decays of the \( ^2P_{3/2, \pm 1/2} \) substates, taking place by emission of \( \sigma^\pm \) and \( \pi \)-polarized radiation, respectively, and \( A'_\sigma \) is the corresponding transition probability for the \( ^2P_{3/2, \pm 3/2} \) substates.

Substitution of Eqs. (41)-(43) into (37) leads to the following expressions for the degrees of circular and linear polarization in terms of the dipole and quadrupole moment densities

\[ p = \frac{\sqrt{5} n_{3/2}^{(1)}}{2n_{3/2}^{(0)} + n_{3/2}^{(2)}} \]  

\[ p' = \frac{3 n_{3/2}^{(2)}}{4n_{3/2}^{(0)} - n_{3/2}^{(2)}} \]  

Equations (44) and (45) in conjunction with (9) establish the connections between the degrees of polarization and the rates of collisional disorientation and disalignment

\[ p = \frac{\sqrt{5} S_{3/2}^{(1)}}{2 S_{3/2}^{(0)}} \left( 1 + \gamma_{3/2}^{(2) \cdot \tau} \right) \]  

\[ p' = \frac{3 S_{3/2}^{(2)}}{4 \frac{S_{3/2}^{(0)}}{S_{3/2}^{(2)}} + \gamma_{3/2}^{(2) \cdot \tau}} \]
Since, as shown in Fig. 2, only the \( m_J = -3/2 \) state is optically populated, the relations (36) between the \( s_{3/2}^{(L)} \) may be used to simplify Eqs. (46) and (47), yielding finally:

\[
P = \frac{3(1 + \gamma_{3/2}^{(2)} \cdot \tau)}{(1 + \gamma_{3/2}^{(1)} \cdot \tau)(3 + 2\gamma_{3/2}^{(2)} \cdot \tau)}
\]

(48)

\[
P' = \frac{1}{(1 + \gamma_{3/2}^{(2)} \cdot \tau - \frac{1}{3} \gamma_{3/2}^{(2)})}
\]

(49)

(b) **Derivation of multipole relaxation cross sections from Zeeman spectra**

Substitutions of Eqs. (35) and (36) into (11) produce, in conjunction with Eq. (12), the following expressions for the cross sections \( \Lambda_{3/2}^{(L)} \)

\[
\Lambda_{3/2}^{(1)} = \frac{1}{N_{\nu \tau}} \left( \frac{3(N_{3/2}^{+} N_{+}^{+} + N_{-}^{-} N_{-3/2}^{+} + N_{-3/2}^{-})}{3N_{3/2}^{+} N_{+}^{+} - N_{+}^{-} N_{-3/2}^{+} - 3N_{-3/2}^{-}} - 1 \right)
\]

(50)

\[
\Lambda_{3/2}^{(2)} = \frac{1}{N_{\nu \tau}} \left( \frac{N_{3/2}^{+} N_{+}^{+} + N_{-}^{-} N_{-3/2}^{+} + N_{-3/2}^{-}}{N_{3/2}^{+} N_{+}^{+} - N_{+}^{-} N_{-3/2}^{+} - N_{-3/2}^{-}} - 1 \right)
\]

(51)

\[
\Lambda_{3/2}^{(3)} = \frac{1}{N_{\nu \tau}} \left( \frac{N_{3/2}^{+} N_{+}^{+} + N_{-}^{-} N_{-3/2}^{+} + N_{-3/2}^{-}}{N_{3/2}^{+} N_{+}^{+} - 3N_{+}^{-} N_{-3/2}^{+} - N_{-3/2}^{-}} - 1 \right)
\]

(52)

The populations of the Zeeman substates are derived from the intensities of the Zeeman components in the fluorescent spectrum, bearing in mind that the fluorescence is circularly polarized and is observed in the direction parallel to the magnetic field.
Under these circumstances, the intensity of the polarized fluorescent radiation emitted in the decay of the $^2P_{3/2, \pm 3/2}$ substate is proportional to its population, while the $\sigma^+$ intensity arising from the $^2P_{3/2, \pm 1/2}$ substate is proportional to one-third its population. The total fluorescent intensity $I_{\pm \frac{1}{2}}^{tot}$ arising from the $^2P_{3/2, \pm \frac{1}{2}}$ substate is

$$I_{\pm \frac{1}{2}}^{tot} = N_{\pm \frac{1}{2}} (A_{\pi} + A_{\sigma}) = 3N_{\pm \frac{1}{2}} A_{\sigma}$$  \hspace{1cm} (53)$$

The intensity of the fluorescence emitted in the decay of the $^2P_{3/2, \pm 3/2}$ substate is

$$I_{\pm \frac{3}{2}} = N_{\pm \frac{3}{2}} A_{\sigma}$$  \hspace{1cm} (54)$$

Hence,

$$N_{\pm \frac{1}{2}} = \frac{1}{3} \frac{I_{\pm \frac{1}{2}}^{tot}}{A_{\sigma}} \hspace{1cm} N_{\pm \frac{3}{2}} = \frac{I_{\pm \frac{3}{2}}}{A_{\sigma}}$$  \hspace{1cm} (55)$$

Substitution of relations (54) and (55) into Eqs. (50)-(52) leads to the following expressions for the cross sections $\Lambda_{3/2}^{(L)}$ in terms of the measured intensities of the Zeeman components.

$$\Lambda_{3/2}^{(1)} = \frac{1}{N_{\pi} \tau} \left( \frac{1 + 3 \frac{I_{\frac{1}{2}}}{I_{-\frac{1}{2}}} + 3 \frac{I_{-\frac{1}{2}}}{I_{-\frac{1}{2}}} + \frac{I_{3/2}}{I_{-3/2}}}{1 + \frac{I_{\frac{1}{2}}}{I_{-\frac{1}{2}}} - \frac{I_{-\frac{1}{2}}}{I_{-\frac{1}{2}}} - \frac{I_{3/2}}{I_{-3/2}}} \right)$$  \hspace{1cm} (56)$$

$$\Lambda_{3/2}^{(2)} = \frac{1}{N_{\pi} \tau} \left( \frac{1 + 3 \frac{I_{\frac{1}{2}}}{I_{-\frac{1}{2}}} + 3 \frac{I_{-\frac{1}{2}}}{I_{-\frac{1}{2}}} + \frac{I_{3/2}}{I_{-3/2}}}{1 + \frac{I_{\frac{1}{2}}}{I_{-\frac{1}{2}}} - \frac{I_{-\frac{1}{2}}}{I_{-\frac{1}{2}}} - \frac{I_{3/2}}{I_{-3/2}}} \right)$$  \hspace{1cm} (57)$$
\[ \lambda^{(3)}_{3/2} = \frac{1}{N \tau} \left( \frac{1 + 3 \frac{I_{3/2}^+}{I_{-3/2}^-} + 3 \frac{I_{-3/2}^-}{I_{-3/2}^-} + \frac{I_{3/2}^+}{I_{-3/2}^-}}{1 - 9 \frac{I_{3/2}^+}{I_{-3/2}^-} + 9 \frac{I_{-3/2}^-}{I_{-3/2}^-} - 1} \right) \]  

(58)

4. **Simplifications in the Treatment of Zeeman Spectroscopic Data obtained under Single Collision Conditions**

When the densities \( N \) of the ground-state collision partners are sufficiently low that the time between collisions is longer than the lifetime of the excited state, all transfer rates are negligible except those leading directly from the optically populated state \( m \) to the other states \( m' \). Then the rate equations for the steady-state equilibrium population of a collisionally populated state \( m' \) become:

\[ \frac{dN_{m'}}{dt} = -\frac{N_{m'}}{\tau} + Z(m \rightarrow m') N_m = 0 \]  

(59)

which, with the aid of Eq. (4), leads to the expressions

\[ Q(m \rightarrow m') = \frac{N_{m'}}{N_m} \cdot \frac{1}{N \tau} \]  

(60)

In the present case \( m = -3/2 \) and \( m' = 3/2, \frac{3}{2}, -\frac{3}{2} \); consequently, Eq. (60) taken together with (55) produces the following expression for \( Q(m \rightarrow m') \), applicable to "single collision" conditions.

\[ Q_{3/2}(-3/2 \rightarrow 3/2) = \frac{1}{N \tau} \cdot \frac{I_{3/2}}{I_{-3/2}} \]  

(61)
\[ Q_{3/2}(-3/2 \rightarrow \text{even}) = \frac{1}{NvT} \cdot 3 \frac{I_{\text{even}}}{I_{-3/2}} \]  

(62)

\[ Q_{3/2}(-3/2 \rightarrow \text{odd}) = \frac{1}{NvT} \cdot 3 \frac{I_{\text{odd}}}{I_{-3/2}} \]  

(63)

By similar reasoning it is possible to derive the corresponding expression for the \( m_J \) mixing cross section under single collision conditions in the \( 4^2P_{3/2} \) state.

\[ Q_{\text{odd}}(-3/2 \rightarrow \text{odd}) = \frac{1}{NvT} \cdot \frac{I_{\text{odd}}}{I_{-3/2}} \]  

(64)

The relations between the Zeeman mixing cross sections \( Q_J(m \rightarrow m') \) and the multipole relaxation cross sections \( q_j^{(L)} \) are given by Eqs. (12)-(18).
III. EXPERIMENTAL

1. Description of the Apparatus

Two separate experiments were carried out employing different methods for the analysis of the fluorescent light. In the first, for which the experimental arrangement is shown in Fig. 3, and in which the fluorescent light was analysed for circular and linear polarization, I determined the cross sections for disorientation in the $^2P_1$ state, and for disorientation and disalignment in the $^2P_{3/2}$ state. In the second experiment, for which the block diagram is shown in Fig. 4, the Zeeman spectrum was resolved and yielded the appropriate cross sections for dipole, quadrupole and octupole decay.

In both experiments a potassium spectral lamp, placed in a uniform magnetic field of 5.4 kG, provided the resonance radiation used to excite the fluorescence. The $\sigma$-polarized light emitted parallel to the field was passed through an interference filter, quarter-wave plate and linear polarizer, and was brought to a focus inside the fluorescence cell containing potassium vapor and located in a 0-10 kG variable magnetic field. The resulting fluorescence was observed at right angles to the direction of excitation and after analysis was detected with an ITT FW-118 photomultiplier tube whose signal was amplified with a Keithley Picoammeter and registered with an X-Y plotter.

(a) The light source

The light source was provided by an r.f. electrodeless discharge described elsewhere (Berdowski et al. 1967). The
Fig. 3 Arrangement of the apparatus for polarization spectroscopy. S, light source; C, fluorescence cell; F, interference filter; P, HN-7 polaroid; L, lenses; A, amplifier; G, gaussmeter; B₁ and B₂, magnetic fields.
Fig. 4 Arrangement of the apparatus for Zeeman spectroscopy. L, source of exciting light; F, interference filter; P, HN-7 polaroid; M, electromagnets; F-P, interferometer; A, amplifier, RG, ramp generator - both connected to an X-Y plotter.
Fig. 4
cylindrical pyrex bulb was 2.5 cm long and 2.5 cm in diameter, with plane windows sealing both ends and with a 2.5 cm long side-arm placed midway between the ends of the cylinder, which contained about 1/3 g potassium. The lamp was placed in a coil of an r.f. generator with its side-arm protruding between the turns of the coil and located in a small oven which controlled the potassium vapor pressure in the lamp. The rim of the exit window was painted with Aquadag to decrease scattered light reflected from the walls of the tube and to ensure that only light emitted along the field would reach the fluorescence cell. A semi-transparent mirror placed in front of the lamp reflected a small portion (about 10%) of the exciting light to a photodiode preceded by an interference filter, whose output was monitored on a strip-chart recorder to control the intensity of the exciting light. Short-term stability (within one experimental run) was better than one percent.

(b) The fluorescence cell and the oven

The pyrex fluorescence cell was 6 cm long and 2.5 cm in diameter, and was equipped with a side-arm 4 cm long and 1.5 cm in diameter, which contained an excess of metallic potassium. The cell was mounted in an oven consisting of two compartments: one containing the body of the cell in which a constant temperature was maintained by means of an electronic temperature controller, and the other containing the side-arm in which a precisely controlled temperature in the range 320-390 K was produced by a copper coil through which silicon oil (Dow Corning
Fluid 202) was circulated from an ultrathermostat. Temperatures were measured using several thermocouples attached at various points on the fluorescence cell and side-arm. In order to prevent condensation on the cell windows, the main oven was always kept at about 35 K above the temperature of the side-arm, causing a 1.5 K temperature gradient along the side-arm. However, metallic potassium occupied the lowest part of the side-arm where the temperature was lowest and the gradient (if any) was estimated to be smaller than the variation in the temperature ($\pm 0.25$ K) as maintained by the ultrathermostat.

The cell was connected to a vacuum and gas-filling system by a folded capillary. The vacuum system was evacuated by an Edwards E02 diffusion pump filled with Dow Corning 705 silicon oil, backed by an ES50 rotary pump. This combination generated an ultimate vacuum better than $10^{-8}$ Torr.

The main body of the cell was coated with Aquadag to reduce stray scattered light. At the beginning of each experimental run, the temperature of the side-arm was lowered to "freeze out" the potassium vapor. The stray scattered light did not exceed 3% of the smallest measured fluorescent signals and its contribution to the measured fluorescent intensities was insignificant. The fluorescence was excited in the rectangular corner between the entrance and observation windows, so that the fluorescent light traversed a distance of about 0.3 cm in the vapor before emerging from the cell.

(c) The electromagnets

The two magnetic fields were produced by Magnion Mod. L-128A
12-inch water-cooled electromagnets with 4-inch gaps. The homogeneity of the field was better than 0.1% over the central region between the poles. The magnet in whose field the fluorescence cell was located had an aperture in one of the poles, permitting observation of the fluorescence in the direction parallel to the magnetic field. Two d.c. power supplies provided current for the magnets. An Electronic Measurements SCR Model 120-40 was used with the lamp magnet which was required to produce a field of about 5.4 kG, and an SCR Model 120-60 was used with the cell magnet which generated fields up to 10 kG.

(d) Optical components and detection system

As may be seen in Figs. 3 and 4, the arrangement of the exciting light beam was common to all the experiments since all required circularly polarized light for excitation of the fluorescence. The light from the lamp emitted along the magnetic field consisted of $\sigma^+$ and $\sigma^-$-polarized components of resonance radiation with a slight admixture of $\pi$ "impurity" caused by reflections from the walls of the lamp. The light was reflected by a right-angle prism and collimated by an f = 25 cm lens to an interference filter, a quarter-wave plate and linear polarizer (HN-7 polaroid). The $\lambda/4$ plates used in the circular polarizers and analysers produced polarized light circular to within 2.6% for the 766.5 nm radiation and 3.2% for the 769.9 nm radiation. The circular polarizer consisted of an $\lambda/4$ plate with its "fast and slow axes"
inclined at 90° and an HN-7 polaroid with its transmission axis bisecting the angle between the "fast and slow axes" of the quarter-wave plate. The component extracted in such a way was brought to focus in the rectangular corner of the fluorescence cell, between the front and side windows by an f = 7 cm lens. The fluorescence emerging from the cell along the magnetic field was collimated by an f = 8 cm lens placed in the pole aperture of the magnet; fluorescence perpendicular to the magnetic field was collected by a second similar lens and brought to the focus at the end of a light-guide, leading directly to the photomultiplier. There was no preferential attenuation of any polarized component by the light-guide.

The polarization spectrum of the fluorescence was monitored by an FW-118, 16 dynode ITT photomultiplier tube with an S-1 (Ag-O-Cs) photocathode which has a peak sensitivity in the 800 nm region. In order to reduce dark noise, the photomultiplier was cooled with liquid nitrogen which reduced background noise to less than 10^{-12} A. A Fluke Model 412-B high-voltage power supply operated at 1.6 kV, provided about 90 V per stage of a resistive divider chain. The signal from the photomultiplier was amplified by a Keithley 427 high speed current amplifier and recorded.

(e) The Fabry-Perot Interferometer

To resolve the fluorescent Zeeman spectrum, I used the Burleigh Model RC-140 Fabry-Perot interferometer, an instrument capable of extremely high spectral resolution, having a high
transmission (typically 70%) and spectrally tunable. The interferometer is fitted with two high-quality plane mirrors oriented parallel to each other. Since its performance depends critically on the relative position of the mirrors, its principal parts (the cavity rods and sleeves) are made of Super Invar whose thermal expansion coefficient $\alpha \geq 0.4 \times 10^{-6}/^\circ\text{C}$ is about five times lower than that of ordinary Invar. The alignment screws and mirror holders are made of Invar. The mirrors (flatness $\lambda/200$) were coated to have a reflectance of 96% in the range 740-920 nm. The radiation, whose spectrum is to be analysed, is scanned by moving one mirror along the interferometer axis without disturbing the parallelism of the mirrors. This is done by piezoelectric ceramic elements attached to one of the mirrors, which expand upon application of a potential difference. The PZT material used for this purpose offers good linearity and good hysteresis characteristics (the typical linearity was better than 1%). In order to ensure maximum stability of performance, the interferometer was located in a thermal enclosure (Burleigh RC-75) in which constant temperature (within $\pm 0.1^\circ\text{C}$) was maintained. High voltage to drive the piezoelectric elements was generated by a Burleigh RC-42 ramp generator. The ramp linearity was better than 0.25% at a ramp scanning time 200 s, which was used in most of the experimental runs. This scanning rate gave the best performance with respect to effecting a match with the time constant of the electrometer amplifier, whose damping control was adjusted to produce an undistorted trace of the spectrum with
an optimal signal-to-noise ratio. The alignment of the mirrors was achieved in two steps: a coarse adjustment by means of the alignment screws and fine adjustment with an electronically controlled output voltage from the ramp generator.

2. Experimental Procedures

(a) Polarization spectroscopy

This method was used to investigate circular and linear depolarization of the resonance radiation in relation to potassium vapor pressure. The purpose of the experiments was to obtain cross sections for disorientation of \(^{2}\text{P}_{3/2}\) atoms, and disorientation and disalignment of \(^{2}\text{P}_{3/2}\) atoms, induced in resonant collisions with \(^{2}\text{S}_{1/2}\) ground state atoms. The cross section \(\Lambda_{3/2}^{(1)}\) for \(^{2}\text{P}_{3/2}\) disorientation was obtained from fluorescence observed along the direction of the magnetic field surrounding the fluorescence cell. In order, however, to measure \(\Lambda_{3/2}^{(1)}\) and \(\Lambda_{3/2}^{(2)}\), it was necessary to observe the fluorescence arising from the decay of the \(^{2}\text{P}_{3/2}\) state both along and perpendicularly to the magnetic field. The experimental arrangement is shown in Fig. 3. The fluorescence emitted parallel to the field (and perpendicularly to the direction of excitation) was passed through an aperture in the pole piece of the magnet and through a circular analyser which separated the \(\sigma^+\) and \(\sigma^-\) components of the 769.9 nm or 766.5 nm resonance radiation, and was detected with the photomultiplier tube. In the case of the 766.5 nm component the fluorescent light emitted perpendicularly to the field (and to
the direction of excitation) was passed through a sheet of HN 7 polaroid to separate the $\sigma$ and $\pi$ components, and was conducted by a light-guide to the phototube. The amplified photomultiplier signal was applied to the X-axis of an X-Y plotter to whose Y-axis was connected the output from a Hall-effect gaussmeter probe mounted close to the fluorescence cell. In this way it was possible to carry out direct Zeeman scanning of the fluorescence as the magnetic field surrounding the fluorescing vapor was varied.

(b) **Zeeman spectroscopy**

In this series of experiments I investigated the collisional relaxation of the dipole, quadrupole and octupole moments in $4^2P$ potassium atoms by resolving and measuring the relative intensities of the Zeeman components constituting the fluorescent spectrum. The arrangement of the apparatus is shown in Fig. 4. The fluorescence emitted in the decay of either the $4^2P_3$ or $4^2P_{3/2}$ state was observed along the direction of the magnetic field. It was collimated and made incident on a piezoelectrically driven Fabry-Perot interferometer (Burleigh Model RC-140), fitted with mirrors of flatness $\lambda/200$ and 96% reflectance in the range 740-920 nm, spaced 0.34 cm apart, providing a free spectral range of 1.47 cm$^{-1}$ and an experimental finesse of 45. The light leaving the interferometer was focused at a 0.05 cm pinhole whose size was determined so as not to detract from the overall finesse (Chabba1, 1953). The fluorescent spectrum produced by scans of the interferometer was focused on the photocathode of the
photomultiplier, whose output signal amplified with the Keithley Model 427 amplifier was applied to the Y-axis input of an X-Y plotter, to whose X-axis was applied a fraction of the ramp voltage used to activate the piezoelectric element of the interferometer.

(c) **Radiation trapping**

In order to calculate the cross sections from the experimental data, account must be taken of radiation trapping which causes the effective lifetime of the resonance $^4\text{P}_\text{3}$ state to exceed its "natural" lifetime. Among the various methods that could be used to make corrections for imprisonment of radiation, Milne's radiation diffusion theory (Mitchell and Zemansky, 1961) appeared most suitable at potassium densities and optical depths that were used in the experiments. The theory permits the calculation of the effective lifetime $\tau$ in terms of the "natural" lifetime $\tau_0$.

$$\frac{\tau}{\tau_0} = 1 + \left(\frac{k_0 \lambda}{\beta}\right)^2$$

(65)

where $\beta$ is the first root of the equation

$$\tan\beta = \frac{k_0 \lambda}{\beta}$$

(66)

$$(0 < \beta < \frac{\pi}{2})$$

$k_0$ is the absorption coefficient at the centre of the line, $\lambda$ is the characteristic length indicating the dimension of the fluorescing vapor and $k_0 \lambda$ is the opacity or optical depth of the vapor. $k_0$ depends on the resonance line shape and $\lambda$ on the
geometry of the fluorescing vapor in the cell. Because of the very low pressures the opacity $k_0 \ell$ was calculated assuming a Doppler shape of the spectral lines for which

$$k_0 = \frac{2}{\Delta \nu_D} \left( \frac{\lambda n_2}{\pi} \right)^\frac{3}{2} \frac{\lambda_0^2}{8\pi} \frac{\nu_0}{\nu_1} \frac{N}{\tau_0}$$  \hspace{1cm} (67)

$$\Delta \nu_D = \frac{2(2\ln 2)}{c} v_0 \left( \frac{T}{M} \right)^\frac{3}{2}$$  \hspace{1cm} (68)

where $\nu_0$ and $\nu_1$ are the statistical weights of the excited and ground states, respectively, $N$ is the vapor density, $M$ the atomic weight of potassium, $c$ the speed of light, $R$ the ideal gas constant and $T$ the temperature. To calculate the effective lifetime $\tau$ of each fine structure $4^2P$ state and at each density, the opacity $k_0 \ell$ was calculated first; next the corresponding value of $\beta$ was found from a graphical solution of Eq. (66) in which the function $\beta \tan \beta = k_0 \ell$ was plotted in the $(k_0 \ell, \beta)$ coordinate system. The thus determined $\beta$ was substituted into Eq. (65) to obtain $\tau$.

Because of the Zeeman splitting, all the optical depths must be multiplied by a factor appropriate to each polarized component (Baylis, 1982). When the magnetic field defines the quantization axis $\hat{z}$, the probability that an emitted photon detected in an arbitrary direction $\hat{k}$ will appear to have polarization vector $\hat{\epsilon}$, is:

$$P_{\hat{k}} = \frac{3}{2} |(\hat{k} \times \hat{\epsilon} \cdot (\hat{k} \times \hat{\epsilon}^\prime)|^2$$  \hspace{1cm} (69)
where $\hat{e}' = \hat{z}$ if the magnetic quantum number has changed during the transition with $\Delta m = 0$, and $\hat{e}' = \pm(\hat{x} \mp i\hat{y})/\sqrt{2}$ if $\Delta m = \pm 1$. The value $P_k(\hat{e}, \hat{e}')$ averaged over directions $\hat{k}$ is given by

$$P(\hat{e}, \hat{e}') = \frac{1}{4\pi} \int \frac{dk}{4\pi} P_k(\hat{e}, \hat{e}')$$

(70)

The relative reabsorption rate $r(m)$ is given by

$$r(m) = \sum \nu A_{n+\nu}(\hat{e}) P(\hat{e}, \hat{e}') A_{\mu+\nu}(\hat{e}')$$

(71)

where $A_{n+\nu}$ is the branching ratio for transitions from ground-state sublevels $\nu$ to excited state sublevels $n$ in a field of unpolarized white radiation, and $A_{\mu+\nu}$ is the branching ratio for decay from excited sublevels $n$ to ground-state sublevels $\mu$. $n_\nu$ is the fraction of ground-state atoms in sublevel $\nu$. The summation is carried out over all $\nu$ and over all excitations that conserve energy and angular momentum. To calculate $r(m)$ the integral (70) has been calculated first, with the following designations:

"+" = $(\hat{x} - i\hat{y})/\sqrt{2}$ and "-" = $-(\hat{x} + i\hat{y})/\sqrt{2}$

Then $P(\hat{x}, \hat{z}) = 4/5$ and $P(+, +) = P(-, -) = 7/10$. For the case of a large magnetic field, in which full isolation of transitions is achieved, the following values of the above factors are obtained.

For the $2p_{3/2}$ state, in which the branching ratios for the various decays are equivalent to the ratios of the transition
probabilities as stated in Chapter II \( A_π : A'_π : A_o = 1 : \frac{2}{3} : \frac{1}{3} \),
the relative reabsorption rates are:

\[
\begin{align*}
    r(m = \frac{3}{2}) &= \frac{21}{40} \\
    r(m = \frac{1}{2}) &= \frac{13}{40}
\end{align*}
\]  
(72)

The two rates are combined to produce the average factor \( \frac{17}{40} \)
which was used in the calculation of \( \tau \); this is justified because of quite good mixing between the Zeeman substates.

For the \( ^2P_\frac{3}{2} \) state, for which the branching ratio is
\( A_π : A_o = \frac{1}{3} : \frac{2}{3} \), the relative reabsorption rate is

\[
    r(m = \frac{1}{2}) = \frac{3}{5}
\]  
(73)

The plot of the ratio \( \tau / \tau_0 \) of the potassium \( ^2P_{3/2} \) state in relation to the potassium vapor density is shown in Fig. 5.
Fig. 5 Ratio of the effective lifetime $\tau$ to the natural lifetime $\tau_0$ of the potassium $4^2P_{3/2}$ state in relation to the potassium vapor density. The opacity $k_0 \lambda$ used to calculate $\tau$ was evaluated as described in section III (c). $\lambda = 3$ mm.
FIG. 5

ATOMIC DENSITY (10^9 cm^-3)

L/L_0
12 10 8 6 4 2
IV. RESULTS AND DISCUSSION

1. Polarization Spectroscopy of the Potassium Resonance Fluorescence

As the magnetic field surrounding the cell is scanned, various coincidences occur between the Zeeman components of the exciting radiation and of the absorption in the vapor. At each particular value of the magnetic field at which there is such overlap, the potassium atoms are excited according to the selection rule $\Delta m_J = \pm 1$ since the exciting light collected from the lamp in the direction parallel to the magnetic field is circularly polarized. In this way the Zeeman sublevels of the $4^2P$ states can be selectively populated, using the appropriate arrangement of interference filter, quarter-wave plate and linear polarizer, as well as suitable "tuning" of the magnetic fields.

(a) Disorientation of the $4^2P_{3/2}$ state

$\sigma^+$ light was used to populate the $4^2P_{3/2}$, $^+$ Zeeman sublevel and the polarization of the fluorescence was monitored in relation to potassium density. A typical polarization spectrum is shown in Fig. 6. Numerous such spectra taken over a range of potassium vapor pressures, yielded data such as are presented in Fig. 7 which shows a plot of the degree of circular polarization of the resonance fluorescence in relation to potassium vapor density, calculated from the temperature-vapor pressure relations (Nesmeyanov, 1963). Although $\sigma^+$ light was mostly used for excitation, identical results were produced using $\sigma^-$ light. Each point shown in the plot represents the average of up to 36
Fig. 6(a) Resonance fluorescence of wavelength 769.9 
emitted from potassium vapor excited with $\sigma^+$ 
radiation; the peak at 2.7 kG arises from a 
$\pi$ impurity in the exciting light.

(b) The $\sigma^-$ component arises mainly from collisional 
depolarization; the $\pi$ impurity is also shown.

(c) Part (b) magnified three times.
Fig. 6
Fig. 7 A plot of the degree of circular polarization of the 769.9 nm resonance fluorescence against potassium vapor density. $P_0$ is obtained by extrapolation to zero density.
measurements. The extrapolation to zero density produces $P_0$ which departs from the theoretical value of unity because of scattered stray light from the lamp and because of imperfections in the circular polarizer and analyser.

The measured values of $P$, obtained in four separate experimental runs, were substituted together with the corresponding $P_0$ in Eq. (33) to obtain the collision numbers $Z$; these are plotted against vapor density in Fig. 8. Each value of $Z$ corresponding to a particular potassium vapor density was calculated using the corresponding lifetime corrected for radiation trapping as described in Chapter III. At the highest densities employed in this experiment ($57 \times 10^{10}$ cm$^{-3}$) $k_0 \tau = 1.8$ (the average distance travelled by resonance fluorescence was about 0.3 cm) and the corresponding $\tau$ was $11.1 \times 10^{-8}$ (as compared to $\tau_0 = 2.77 \times 10^{-8}$ s for the $4^2P_{3/2}$ state). Although this calculation of the effective lifetime is considered satisfactory, especially at $k_0 \tau < 6$, most of the experimental runs (75%) were taken at densities below $25 \times 10^{10}$ cm$^{-3}$ corresponding to opacities $k_0 \tau < 0.7$. The disorientation cross section $\Lambda^{(1)}_3$ was calculated by a least-squares fit from the slope of the plot shown in Fig. 8, which yielded the value $\Lambda^{(1)}_3 = 10 \times 10^{-12}$ cm$^2$, estimated to be accurate within $\pm 15\%$.

(b) Disorientation and disalignment of the $4^2P_{3/2}$ state

The selective excitation of the $4^2P_{3/2}$ Zeeman sublevels is shown in Fig. 9. At each particular value of the magnetic field at which there is overlap between the Zeeman components in
Fig. 8 A plot of collision numbers $Z(-\frac{1}{2} \leftrightarrow \frac{1}{2})$ against the density of potassium atoms. The four symbols used to represent experimental points correspond to four experimental runs.
Fig. 9  Selective excitation of Zeeman sublevels $\frac{3}{2}$ of the $4^2\text{p}_{3/2}$ state in potassium by $\sigma^+$ light.

(a) Zeeman splitting of the 7665 Å line in the lamp (constant at 5.4 kG) and in the cell (variable). The $\pi$ components are not shown. Intersections corresponding to excitation by $\sigma^+$ light are marked.

(b) Experimental profile of the resonance fluorescence observed parallel to the field $B_2$ in Fig. 3 (solid line, $\sigma^+$ component; dashed line, $\sigma^-$ component).

(b) Experimental profile of the resonance fluorescence observed perpendicular to $B_2$ (solid line, $\sigma$ component; dashed line, $\pi$ component). The inset shows the $\pi$ fluorescence in the third peak magnified ten times.
the exciting light and in absorption, the potassium atoms are excited according to the selection rule $\Delta m_j = +1$ since the exciting light was $\sigma^+$ circularly polarized. When there are no depolarizing collisions which would cause transfers among the Zeeman sublevels, the fluorescent light results from the decay of only those Zeeman sublevels which are excited optically. Under these circumstances, as may also be seen in Fig. 2, the Zeeman scan produces three $\sigma$-polarized fluorescent intensity peaks and two $\pi$-polarized peaks. The corresponding degrees of linear polarization $P_0^\sigma$ and of circular polarization $P_0^\pi$ may be determined experimentally in each peak using Eq. (37). As the potassium vapor density is increased, so is the probability of collisions between the excited atoms in their Zeeman substates and the ground state atoms, which tend to equalize the populations of the Zeeman states and depolarize the fluorescence. As shown in Fig. 9, the depolarization manifests itself by the appearance of the $\pi$ circularly polarized component in the fluorescence observed along the magnetic field, and in an increase in the intensity of the $\pi$ component (compared with the $\sigma$ component) when the fluorescence is observed in the perpendicular direction; the actual experimental traces are shown in Figs. 10A and 10B. In pure potassium vapor this depolarization effect could only be observed at potassium vapor densities above $10^{10}$ cm$^{-3}$. Each intensity peak in Fig. 9 corresponds to a particular pattern of selective excitation; the first peak is due to the excitation of the $m_j = +1$ Zeeman substate and a third arises from the excitation of $m_j = 3/2$. The second (central) peak is caused by simultaneous
Fig. 10A An experimental trace of the 766.5 nm resonance fluorescence observed parallel to the field (corresponding to Fig. 9(b)). The inset shows $\sigma_{3/2}^-$ fluorescence in peak no. 3 magnified three times.
Fig. 10A
Fig. 10B An experimental trace of the 766.5 nm resonance fluorescence observed perpendicular to the field (corresponding to Fig. 9(c)). The inset shows π fluorescence in peak no. 3 magnified three times.
population of both $m_J = \pm \frac{1}{2}$ and $m_J = \pm 3/2$ substates and, consequently, is very much less useful than the other two, which, in principle, can yield unique values of $\gamma_{3/2}^{(1)}$ and $\gamma_{3/2}^{(2)}$, if the degree of polarization is determined in relation to the potassium vapor density. Although the data obtained from the first and third peaks should yield identical values of $\gamma_{3/2}^{(1)}$ and $\gamma_{3/2}^{(2)}$, discrepancies in the results were found which exceeded reasonable limits of experimental error. Upon further consideration, it became apparent that at the magnetic field corresponding to the first peak (3 kG), the Zeeman splitting in the $4^2P_{3/2}$ state is of the order of the Doppler width, making possible a contribution to the observed depolarization, arising from multiple scattering of the resonance radiation. At 8 kG, which corresponds to the third peak, the Zeeman splitting is more than double the Doppler width and any multiple scattering that may be present does not contribute to the depolarization of the fluorescence. Accordingly, all the results that follow are based on the data obtained from the third peak in Fig. 9. The small additional intensity maximum in the vicinity of 1 kG is ascribed to a slight $\pi$' admixture in the $\sigma^+$ exciting light.

Figures 11A and 11B show the dependence of the degrees of circular and linear polarization on potassium density. Results of two experimental sequences are presented, each corresponding to a slightly different value of $P_0$, the (extrapolated) degree of polarization at zero potassium density. The theoretically calculated values for $P_0$ and $P_0'$ are 1 and -1, respectively, (Berdowski
Fig. 11A Variation of the degree of circular polarization $P_3$ with potassium density. The error bars indicate limits of statistical error.
Degree of Polarization ($p_3$) vs. Atomic Density ($10^{10}$ Atoms/cm$^3$)

Fig. 11A
Fig. 11B  Variation of the degree of linear polarization $P'_3$ with potassium density. The error bars indicate limits of statistical error.
and the experimental values are slightly smaller, because of the $\pi$ and $\sigma^{-}$ admixtures in the $\sigma^{+}$ exciting light, due to the finite solid angle over which the light was emitted from the lamp and imperfections of circular polarizers. There are also slight variations in $P_{0}$ and $P_{0}^{1}$ values from one run to another because a new discharge lamp was used in each, causing some small changes in the geometry of the exciting light beam. Even though the stray-light can be reduced by coating portions of the lamp with Aquadag, its total elimination is well-nigh impossible. The experimentally determined degrees of polarization were substituted in Eqs. (48) and (49) which yielded the decay rates $\gamma_{3/2}^{(1)}$ and $\gamma_{3/2}^{(2)}$ corrected for radiation trapping. Plots of $\gamma_{3/2}^{(1)}$ and $\gamma_{3/2}^{(2)}$ in relation to the potassium density are shown in Fig. 12; the plot includes data from three experimental runs. To obtain disorientation and disalignment cross sections for resonant collisions, the slopes of the above plots were calculated by least-squares fitting. The resulting disorientation and disalignment cross sections are:

$$\Lambda_{3/2}^{(1)} = 9 \times 10^{-12} \text{ cm}^2 \quad \Lambda_{3/2}^{(2)} = 11 \times 10^{-12} \text{ cm}^2$$

2. Zeeman Spectroscopy of the Potassium Resonance Fluorescence

The results described in this section were obtained by the analysis of the Zeeman spectrum of the potassium resonance fluorescence. With the correct adjustment of the two magnetic fields to produce coincidence between Zeeman components in the exciting light and in the absorbing vapor (as shown in Fig. 9), excitation with $\sigma^{-}$ polarized 769.9 nm or 766.5 nm radiation resulted in the
Fig. 12 Variation of decay rates $\tau_{\gamma_1}$ and $\tau_{\gamma_2}$ with potassium density. The plot includes data from 3 experimental runs.
selective population of the $^4P_{3/2, -3/2}$ state (Berdowski and Krause, 1968) or the $^4P_{3/2, -3/2}$ state (Berdowski et al. 1971), respectively. At low vapor densities and in the absence of a buffer gas, the observed fluorescence would be expected to consist of just one component arising from the decay of the optically populated Zeeman substate. However, because of imperfection of the circular polarizer, the exciting light contained a small $\sigma^+$ admixture, which caused the excitation of the $^2P_{3/2, 3/2}$ (or $^2P_{3/2, 3/2}$) state. This "$\sigma^+$ leak" was directly determined from an interferogram of the 769.9 nm exciting radiation, which is shown in Fig. 13A and which, in addition to the $\sigma^-$ component, also includes traces of $\sigma^+$ and $\pi$ components. A similar interferogram of the 766.5 nm resonance component emitted by the lamp is shown in Fig. 13B. It shows, in addition to the two desired $\sigma^-$ components, also traces of $\sigma^+$ and $\pi$ components. The latter are unimportant because they occur at frequencies which are not absorbed in the vapor at the particular value of the magnetic field; neither is the $\sigma^+$ component corresponding to the $^4S_{1/2, -1/2} + ^4P_{3/2, 1/2}$ transition. The relative proportion of the $\sigma^+$ impurity affecting the $^4S_{1/2, -1/2} + ^4P_{3/2, 3/2}$ transition was found to be 2.6% of the $\sigma^-$ ($^4S_{1/2, -1/2} + ^4P_{3/2, -3/2}$) component (21 interferograms of the lamp spectrum were examined). The corresponding "$\sigma^+$ leak" for the $^4P_{3/2}$ state was similarly found to be about 3.2%. Subsequently, all the measured $I_4/I_{-1/2}$ and $I_{3/2}/I_{-3/2}$ intensity ratios were corrected by subtracting from them the appropriate correction for the "$\sigma^+$ leak".

Another indirect way to measure the "$\sigma^+$ leak" was to
Fig. 13A A trace of the Zeeman spectrum of the 769.9 nm resonance radiation emitted by the lamp. The \( \sigma^- \) component was used for excitation of the fluorescence. The \( \sigma^- \) component is due to the "\( \sigma^- \) leak"; the \( \pi \) components arise from the light scattered inside the lamp.
Fig. 13B  A trace of the Zeeman spectrum of the 766.5 nm radiation emitted by the lamp.
The $\sigma_{-3/2}$ ($4^2S_{1/2}, -1/2 \rightarrow 4^2P_{3/2}, -3/2$) component.
was used for excitation of the fluorescence.
Both $\pi$ components arise from the light scattered inside the lamp. The $\sigma_{+3/2}$ ($4^2S_{1/2}, 1/2 \rightarrow 4^2P_{3/2}, 3/2$)
component is due to the "$\sigma^+$ leak".
Fig. 13B
measure the intensities of the Zeeman components in fluorescence at very low potassium vapor densities at which collisional transfer between $m_j$ sublevels could be assumed to be effectively absent, so that only fluorescence from optically populated sublevels would be expected, with intensities in the same ratio as the corresponding components in exciting light. The "$\sigma^+$ leak" determined in this way was in very good agreement with the results of the direct determinations. An increase in the potassium vapor density or the addition of argon caused the appearance of collisionally induced Zeeman components in the fluorescent spectrum, whose intensities depended on the density of the ground-state atoms acting as collision partners. A typical $^2P_{3/2}$ Zeeman spectrum produced by K-Ar collisions is shown in Fig. 14A; the corresponding Zeeman spectrum arising from the decay of the $^2P_{3/2}$ state is shown in Fig. 14B. The peak separations were measured by calibrating the system using the known hyperfine structure of the 894.346 nm Cs line (Millman and Kusch, 1940), whose hfs spectrum is shown in Fig. 15. For the $^4P_{3/2}$ state, the fluorescent intensity measurements were carried out in three experimental runs with pure potassium vapor and two runs with argon (at constant K densities). For the $^4P_{3/2}$ state, two separate runs were taken with pure potassium vapor and one with argon. At each Ar or K density ten scans of the spectrum were recorded, each consisting of two interference orders. The scatter between intensities measured at identical temperatures and pressures did not exceed 10%. The experiments with Ar were carried out at
Fig. 14A  A trace of the Zeeman spectrum of the 769.9 nm resonance fluorescence emitted from a mixture of K vapor with 0.19 Torr Ar.
Fig. 14B A trace of the Zeeman spectrum of the 766.5 nm resonance fluorescence emitted from a mixture of K vapor with 0.28 Torr Ar. The $4^2p_{3/2,-3/2}$ sublevel is optically excited, the other Zeeman substates are populated by collisional transfer.
Fig. 15 The hyperfine structure spectrum of Cs 894.346 nm resonance radiation ($5^2P_{3/2} - 6^2S_{1/2}$) produced by the scanning Fabry-Perot interferometer. The first double peak arises from the $6^2P_{3/2}, F = 3, 4 + 6^2S_{1/2}, F = 3$ transitions; the second double peak corresponds to the $6^2P_{3/2}, F = 3, 4 + 6^2S_{1/2}, F = 4$ transitions. The intensities of the four components should be in the ratio 21:15:7:21 (in good agreement with the recording), and the hfs separation in the ground state is 0.3066 cm$^{-1}$ (Millman, Kusch 1940).
side-arm temperatures of 348 K (corresponding to $6.3 \times 10^{10}$ K atoms/cm$^3$) and 356 K ($1.3 \times 10^{11}$ K atoms/cm$^3$) for the $^2P_{1/2}$ state, and at 344 K ($4.8 \times 10^{10}$ K atoms/cm$^3$) for the $^2P_{3/2}$ state. In the experiments with pure potassium the side-arm temperatures ranged from 368 to 387 K, corresponding to a density range $3-12 \times 10^{11}$ atoms/cm$^3$. The potassium densities were calculated from temperature-vapor pressure relations (Nesmeyanov, 1963). In the calculation of the cross-sections from the experimental data, account was taken of radiation trapping as described in Chapter II.

In the K-Ar mixtures, the effective lifetime $\tau$ exceeded the "natural" lifetime $\tau_0$ by 27-50%. The excellent agreement between results obtained from two separate runs performed at different potassium vapor densities indicates the success of the method used to calculate the effective lifetimes.

In pure potassium vapor where higher densities were employed to obtain acceptable signal-to-noise ratio, the effective lifetime varied with the density and, at the highest density $12 \times 10^{11}$ cm$^{-3}$, $\tau = 12\tau_0$. The measured (and corrected for "o" leak") intensities of the Zeeman components in the fluorescent spectra are plotted in Figs. 16, 17 and 18, relative to the intensities of the components emitted in the decay of the optically populated $^2P_{1/2, -1}$ or $^2P_{3/2, -3/2}$ Zeeman substates, against the densities of the ground-state K or Ar atoms.

To eliminate effects due to radiation trapping which are density dependent, the intensity ratios plotted for pure K vapor in Figs. 16 and 18 were divided by $\tau$, the effective lifetime which was calculated at each potassium density. The linearity of these
Fig. 16 Plots of Zeeman fluorescence intensity ratios for the $4^2P_g$ state. ○, results from pure K vapor (in units of $10^4$ s$^{-1}$); □, effects of K-Ar collisions (in units of $10^{-2}$). The error bars show statistical scatter of the measurements and are representative of each system.
Fig. 16

DENSITY $K(\alpha) \times 10^{11}$ cm$^{-3}$, $Ar(\alpha) \times 10^{15}$ cm$^{-3}$.
Fig. 17 Plots of Zeeman fluorescent intensity ratios (in units of $10^{-2}$) for the $4^2P_{3/2}$ state showing effects of $m_j$ mixing induced in K-Ar collisions. The error bars represent statistical scatter of the measurements.
$3 \frac{I_{1/2}}{I_{-3/2}}(\circ)$ or $3 \frac{I_{3/2}}{I_{-3/2}}(\square) \times 10^{-2}$

**Figure 17**

**Ar. Density**

$10^{15}$ cm$^{-3}$

$20$

$25$

$3 \frac{I_{1/2}}{I_{-3/2}}(\circ)$

$3 \frac{I_{-1/2}}{I_{-3/2}}(\circ) \times 10^{-2}$
Fig. 18 Plots of Zeeman fluorescent intensity ratios (in units of $10^4$ s$^{-1}$) for the $4^2P_{3/2}$ state showing effects of $m_J$ mixing induced by K-K collisions. The error bars represent statistical scatter of the measurements.
Fig. 18
plots and the fact that they pass through the origin suggest good consistency of the applied corrections for radiation trapping. The plots are expected to be linear at low densities at which the collision frequencies are very low, amounting to less than one collision per lifetime of $4^2P$ state. Under these conditions only one collisional transfer is likely to occur from optically populated to another Zeeman substate. At densities above $5 \times 10^{15} \text{ cm}^{-3}$, subsequent transfers (including back-transfer) manifest themselves by a curvature in K-Ar plots. Under single-collision conditions the cross sections for transfer between the Zeeman sublevels are given by Eqs. (61)-(64) which permit the calculation of the cross sections $Q(m \rightarrow m')$ from the K-K plots and the linear parts of the K-Ar plots in Figs. 16, 17 and 18 (except for $Q_{3/2}(\frac{1}{2} \leftrightarrow -\frac{1}{2})$). It was found that the values thus obtained agreed to within 5% with the cross sections calculated from all the data using Eqs. (30), (56)-(58) and (14)-(18).

The resulting relaxation cross sections $\Lambda_J^{(1)}$, $\Lambda_J^{(2)}$ and $\Lambda_J^{(3)}$, upon substitution in Eqs. (14)-(18) yielded the Zeeman mixing cross sections $Q_J(m \rightarrow m')$. Finally, the relaxation cross sections $\Lambda_J^{(L)}$ were combined, as shown in Eq. (13), with $\sigma_J^{(0)}$, the $^2P_\frac{3}{2} - ^2P_\frac{1}{2}$ fine structure mixing cross sections to produce $\sigma_J^{(L)}$, the cross sections for multipole moment decay. In the case of K-K collisions $\sigma_J^{(0)} \ll \Lambda_J^{(L)}$ and $\sigma_J^{(L)} = \Lambda_J^{(L)}$. For the K-Ar system recently re-measured $\sigma_J^{(0)}$ values (Ciurylo and Krause, 1982) were used. All the cross sections, which are listed in Tables 1 and 2, are estimated to be accurate within $\pm 15\%$, with the uncertainty arising from scatter in intensity measurements and from possible systematic
errors in the K and Ar densities. As expected, (Krause, 1975), the cross sections for resonant K-K collisions exceed the K-Ar cross sections by over two orders of magnitude. The previously published values of K-K cross sections (Skalinski and Krause, 1979, 1980) were found to be inflated because of an error in the calculation of \( \tau \). The values \( \sigma^{(1)}_{1/2} \), \( \sigma^{(1)}_{3/2} \) and \( \sigma^{(2)}_{3/2} \), determined from the polarization measurements, which are shown in Table 1, have been properly recalculated and, except for \( \lambda^{(1)}_{1/2} \), are found to be in very good agreement with those determined from the Zeeman spectra.

There is adequate agreement with the theoretical values calculated using an impact approximation (Berman and Lamb, Jr. 1969, Carrington et al. 1973) which yields the following decay rates:

\[
\begin{align*}
\gamma^{(1)}_{1/2} &= 1.9 \times 10^{-2} \, N\lambda_1^3 \tau \\
\gamma^{(1)}_{3/2} &= 2.47 \times 10^{-2} \, N\lambda_2^3 \tau \\
\gamma^{(2)}_{3/2} &= 2.25 \times 10^{-2} \, N\lambda_2^3 \tau \\
\gamma^{(3)}_{3/2} &= 2.43 \times 10^{-2} \, N\lambda_2^3 \tau
\end{align*}
\]

where \( \lambda_1 = 769.9 \) nm, \( \lambda_2 = 766.5 \) nm and \( \Gamma = 1/\tau \). The corresponding cross sections are listed in Table 1, and are compared with my experimental results. There is also agreement within order of magnitude with Gay and Schneider's (1979) cross section for Na-Na collisions, \( Q(-3/2 \leftrightarrow 3/2) = 0.8 \times 10^{-12} \) cm\(^2\).

As is apparent in Table 2, depolarizing collisions with noble gases have been studied much more extensively than K-K collisions. For the \( ^2P_\frac{3}{2} \) state, the previously reported K-Ar
TABLE 1. Cross sections for K-K collisions (in $10^{-12} \text{ cm}^2$)

<table>
<thead>
<tr>
<th>Designation</th>
<th>Zeeman Spectroscopy</th>
<th>Polarization Spectroscopy</th>
<th>Theory$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Lambda_{3/2}^{(1)}$ or $\sigma_{3/2}^{(1)}$</td>
<td>$5.7 \pm 0.9$</td>
<td>10</td>
<td>4.9</td>
</tr>
<tr>
<td>$\Lambda_{3/2}^{(1)}$ or $\sigma_{3/2}^{(1)}$</td>
<td>$8.1 \pm 1.4$</td>
<td>9</td>
<td>6.2</td>
</tr>
<tr>
<td>$\Lambda_{3/2}^{(2)}$ or $\sigma_{3/2}^{(2)}$</td>
<td>$11.4 \pm 2.0$</td>
<td>11</td>
<td>5.6</td>
</tr>
<tr>
<td>$\Lambda_{3/2}^{(3)}$ or $\sigma_{3/2}^{(3)}$</td>
<td>$9.8 \pm 1.5$</td>
<td>6.1</td>
<td></td>
</tr>
<tr>
<td>$Q_{3/2}(-\frac{1}{2} \leftrightarrow \frac{1}{2})$</td>
<td>$2.8 \pm 0.5$</td>
<td>2.4</td>
<td></td>
</tr>
<tr>
<td>$Q_{3/2}(-\frac{3}{2} \leftrightarrow \frac{1}{2})$</td>
<td>$2.0 \pm 0.8$</td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td>$Q_{3/2}(-\frac{3}{2} \leftrightarrow -\frac{1}{2})$</td>
<td>$3.1 \pm 0.6$</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>$Q_{3/2}(-\frac{3}{2} \leftrightarrow 3/2)$</td>
<td>$2.6 \pm 0.5$</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>$Q_{3/2}(-\frac{3}{2} \leftrightarrow 3/2)$</td>
<td>$1.3 \pm 0.4$</td>
<td>1.7</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Derived from Carrington et al. (1973) and Eqs. (14)-(18)
TABLE 2. Cross sections for K-Ar collisions (in $10^{-16}$ cm$^2$)

<table>
<thead>
<tr>
<th>Designation</th>
<th>This investigation</th>
<th>Berdowski et al.\textsuperscript{a} corrected for $\tau$</th>
<th>Lewis et al.\textsuperscript{b}(1977)</th>
<th>Boggy &amp; Franz\textsuperscript{c}(1982)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Lambda_{\frac{3}{2}}^{(1)}$</td>
<td>$65 \pm 10$</td>
<td>73</td>
<td></td>
<td>56\textsuperscript{a}</td>
</tr>
<tr>
<td>$Q_{\frac{3}{2}}^{\left(-\frac{3}{2} \leftrightarrow \frac{1}{2}\right)}$</td>
<td>$32 \pm 5$</td>
<td>36</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\sigma_{\frac{3}{2}}^{(0)}$</td>
<td></td>
<td>16\textsuperscript{b}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\sigma_{\frac{3}{2}}^{(1)}$</td>
<td>$81 \pm 12$</td>
<td></td>
<td>278\textsuperscript{c}; 35\textsuperscript{d}</td>
<td></td>
</tr>
<tr>
<td>$\Lambda_{\frac{3}{2}}^{(2)}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Lambda_{\frac{3}{2}}^{(3)}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Q_{\frac{3}{2}}^{\left(-\frac{1}{2} \leftrightarrow \frac{1}{2}\right)}$</td>
<td>$36.8 \pm 16$</td>
<td></td>
<td>18.6\textsuperscript{e}</td>
<td>52.5\textsuperscript{e}</td>
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<tr>
<td>$Q_{\frac{3}{2}}^{\left(-\frac{3}{2} \leftrightarrow -\frac{1}{2}\right)}$</td>
<td>$59.8 \pm 3.0$</td>
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<td>37.7\textsuperscript{e}</td>
<td>86.2\textsuperscript{e}</td>
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<tr>
<td>$Q_{\frac{3}{2}}^{\left(-\frac{3}{2} \leftrightarrow \frac{1}{2}\right)}$</td>
<td>$55.3 \pm 2.0$</td>
<td></td>
<td>35.3\textsuperscript{e}</td>
<td>84.4\textsuperscript{e}</td>
</tr>
<tr>
<td>$Q_{\frac{3}{2}}^{\left(-\frac{3}{2} \leftrightarrow 3/2\right)}$</td>
<td>$30.8 \pm 2.0$</td>
<td></td>
<td>15.4\textsuperscript{e}</td>
<td>50\textsuperscript{e}</td>
</tr>
<tr>
<td>$\sigma_{\frac{3}{2}}^{(0)}$</td>
<td>11.2\textsuperscript{b}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\sigma_{\frac{3}{2}}^{(1)}$</td>
<td>$186 \pm 27$</td>
<td></td>
<td>242\textsuperscript{c}; 187\textsuperscript{c}</td>
<td></td>
</tr>
<tr>
<td>$\sigma_{\frac{3}{2}}^{(2)}$</td>
<td>$241 \pm 37$</td>
<td></td>
<td>346\textsuperscript{c}</td>
<td></td>
</tr>
<tr>
<td>$\sigma_{\frac{3}{2}}^{(3)}$</td>
<td>$201 \pm 32$</td>
<td></td>
<td>225\textsuperscript{c}</td>
<td></td>
</tr>
</tbody>
</table>
TABLE 2 continued


c Approximate theory.

d From Hanlé experiment.

e Derived from Boggy and Franz (1983) and Eqs. (15)-(18).
cross section (Berdowski and Krause, 1969) was determined at K densities at which radiation trapping was significant, though no allowance for it was made. A recalculation using the corrected value of \( \tau \) produces very good agreement with the present cross section \( \Lambda^{(1)}_3 \) which, as expected (Krause 1975), lies between the recently determined values (Boggy and Franz, 1982) for Ne and Kr; a parallel relationship may be seen in the \( ^2P_{3/2} \) state with respect to \( \Lambda^{(1)}_{3/2}, \Lambda^{(2)}_{3/2}, \) and \( \Lambda^{(3)}_{3/2} \) where there is excellent accord with previously measured disorientation and disalignment cross sections (Berdowski et al. 1971), and satisfactory agreement with \( \sigma^{(1)}_{3/2} \) approximately calculated by Lewis, Wheeler and Wilson (1977), who also determined \( \sigma^{(1)}_{3/2} \) using the Hanle effect and correcting their measurements for the effects of nuclear spin. The agreement is not nearly as good for the \( ^2P_{3/2} \) case where the calculated cross section \( \sigma^{(1)}_3 \) greatly exceeds all the experimental values. A worthwhile comparison can be made with the predictions of Okunevich and Perel (1970) who calculated ratios of the \( ^2P_{3/2} \) relaxation cross sections assuming van der Waals interaction between the colliding atoms. Table 3 shows the predicted \( \Lambda^{(L)}_{3/2} \) ratios which are in total harmony with the corresponding ratios found in this investigation, as well as those calculated from the values of Boggy and Franz (1982) for Ne and Kr. The corresponding \( \Lambda^{(L)}_{3/2} \) ratios were also derived from the theoretical \( \sigma^{(L)}_{3/2} \) values of Lewis et al. (1977) by subtracting from them the experimentally determined \( \sigma^{(0)}_{3/2} \) (Ciurylo and Krause, 1982). The resulting agreement is not nearly as good as with the values
TABLE 3. Ratios of $\Lambda^{(L)}_{3/2}$ relaxation cross sections

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Lambda^{(1)}<em>{3/2}/\Lambda^{(2)}</em>{3/2}$</td>
<td>0.76</td>
<td>0.71</td>
<td>0.79</td>
<td>0.81</td>
</tr>
<tr>
<td>$\Lambda^{(2)}<em>{3/2}/\Lambda^{(3)}</em>{3/2}$</td>
<td>1.21</td>
<td>1.32</td>
<td>1.24</td>
<td>1.13</td>
</tr>
<tr>
<td>$\Lambda^{(1)}<em>{3/2}/\Lambda^{(3)}</em>{3/2}$</td>
<td>0.92</td>
<td>0.93</td>
<td>0.98</td>
<td>0.91</td>
</tr>
</tbody>
</table>

\(^a\) $\Lambda^{(L)}_{3/2}$ were obtained by subtraction of $\sigma^{(0)}_{3/2}$ taken from (Krause 1975) from authors' $\sigma^{(L)}_{3/2}$. 
of Okunevich and Perel, perhaps reflecting the approximate nature of the theoretical treatment (Lewis et al. 1970).
V. SUMMARY AND CONCLUSIONS

In this dissertation I describe a series of experiments in which I determined the cross sections for dipole, quadrupole and octupole relaxation in $4^2P$ potassium atoms, induced in K-K and in K-Ar collisions. The experiments also yielded the cross sections for transfers between the Zeeman sublevels within the $2^2P_{\frac{1}{2}}$ and $2^2P_{3/2}$ fine-structure states.

Two separate experimental approaches were employed.

(a) Polarization Spectroscopy: This method involved the excitation of potassium vapor contained in a fluorescence cell, pure or mixed with argon, by circularly polarized monochromatic potassium resonance radiation, and the investigation of circular and linear depolarization of the resulting fluorescence in relation to the density of the ground-state atoms serving as collision partners. The resulting depolarization data yielded the cross sections for disorientation and disalignment of the $4^2P$ potassium atoms induced in K-K and K-Ar collisions.

(b) Zeeman Spectroscopy: Here the excitation was carried out as in (a) above and, by appropriate adjustment of the magnetic fields in which the lamp and fluorescence cell were located, resulted in the optical population of a single Zeeman substate ($2^2P_{\frac{1}{2}}, -\frac{1}{2}$ or $2^2P_{3/2}, -\frac{3}{2}$). The resulting fluorescence was analysed with a piezoelectric scanning Fabry-Perot interferometer which resolved all the components of the Zeeman spectrum; measurements of their intensities in relation to ground-state atomic densities lead to cross sections for disorientation, disalignment and
octupole relaxation as well as for collisional transfers between all the Zeeman sublevels within the $^2P_{3/2}$ and $^2P_{1/2}$ states.

All the results are listed in Tables 1 and 2 where it may be seen that there is very satisfactory agreement between the results produced by the two experimental methods, as well as between my experimental values and theoretical calculations reported elsewhere.

A comparison of the two experimental methods indicates that Zeeman spectroscopy provides a more powerful and comprehensive method for these studies than polarization spectroscopy. Only Zeeman spectroscopy yields the complete set of decay rates for the multipole moments, as well as the cross sections for $m_J$ mixing between the individual Zeeman sublevels. The inherent high precision of the interferometric method ensures reliability of the results. The technique of Zeeman spectroscopy possesses considerable versatility which will be useful in further studies of atomic depolarization induced in collisions with molecules and depolarization of atoms in Rydberg states.
REFERENCES


Mrozowski, S. 1932. Z. Physik, 78, 826.
VITA AUCTORIS

I was born on April 10, 1944 in Warsaw, Poland. I attended primary and secondary schools there and after graduation in 1961 I attended Warsaw University. In 1967 I obtained a Master of Science degree. I worked at Warsaw University as a Teaching Assistant and Senior Teaching Assistant until 1975. In 1975 I enrolled in the University of Windsor Faculty of Graduate Studies to work toward a Ph.D. degree. I held a University of Windsor Postgraduate Scholarship for five years. In 1965 I married Ewa Gasinowska and we have a son, Paul.