A source of electrons for studies of inelastic collisions with excited atoms.

Lucy G. Michail
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A SOURCE OF ELECTRONS FOR
STUDIES OF INELASTIC COLLISIONS
WITH EXCITED ATOMS

by
Lucy G. Michail

A Thesis
Submitted to the Faculty of Graduate Studies Through the
Department of Physics in Partial Fulfillment of
the Requirements for the Degree of Master
of Science at the University
of Windsor

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ABSTRACT

A source of low-energy electrons, based on the principle of the 'Retarding Potential Difference', was designed and constructed in order to use it in the investigation of excitation transfer between the fine structure resonance states of potassium atoms, induced in collisions with the electrons. The 'electron gun' which is simple and inexpensive to build and whose small size permits its incorporation in a fluorescence cell, produced a beam of low energy electrons of satisfactory intensity and energy resolution. It was possible to produce beams of electrons with intensities equivalent to a current of 1μA, with average energies less than 1 eV, and with full energy width at half maximum current of about 0.1 eV. These properties satisfy the requirements of the experiment for which the electron gun was designed. A study of the performance characteristics of the electron gun has led to optimal values of the operating parameters.
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I - INTRODUCTION

The investigation of excitation transfer in electron - atom collisions by methods involving sensitized fluorescence requires a special source of electrons. An ideal source should emit electrons with a mean energy in the range of the energy gap between the energy levels of the atoms under study, that are involved in the excitation transfer process. The design of the electron gun investigated and tested in the present study is based on the retarding potential difference method.

The cell containing potassium atoms in the ground state and the electron gun is irradiated continuously with one of the two components of the potassium resonance doublet. The passage of an electron beam of sufficient energy through a gas of excited potassium atoms in one of the doublet states produces transfer of excitation between the resonance states. The collisions between electrons and excited atoms would be expected to cause the emission of sensitized fluorescence. The total observed fluorescence consists of both the fine structure components. The component of the same wavelength as that used for optical excitation is known as 'resonance' fluorescence.' The component which is not presented in the exciting light and which arises as a result of collisional excitation transfer is called 'sensitized fluorescence'.
R. W. Wood (1912, 1914) first observed sensitized fluorescence in pure sodium vapor. The effect of an inert gas mixed with sodium vapor on the ratio of intensities of sodium D-lines was observed by Wood and Mohler (1918). Ten years later Wood's observations were confirmed by Lochte-Holtgreven (1928), who studied sodium-inert gas mixtures. Later sensitized fluorescence in potassium, rubidium and their mixtures was studied by Thangaraj (1948) while Seiwert (1956), Hoffmann and Seiwert (1961), and Bunke and Seiwert (1962) investigated sodium, potassium and cesium, respectively. All the above studies were carried out at high alkali vapor densities, where the resonance fluorescence is subject to multiple absorptions and reemissions which, in effect, increase the lifetime of the excited state. This effect is known as imprisonment of radiations.

The first studies of sensitized fluorescence in alkali-inert gas mixtures at extremely low alkali vapor densities were carried out in this laboratory and were summarized by Krause (1966). Sensitized fluorescence in rubidium vapor, induced by collisions with excited potassium atoms, was investigated by Hrycyshyn and Krause (1969a), as was excitation transfer between the resonance sublevels of potassium atoms caused by inelastic collisions with rubidium atoms (Hrycyshyn and Krause, 1969b). The lifetime of the resonance states in potassium and the trapping of potassium resonance radiation was studied by Copley and Krause (1969).

The cross-sections for excitation of atoms from the ground state by electron impact were first measured by Haule (1929) and Lees (1932).
who investigated the excitation of ground-state helium atoms to the first excited state. Hanle and Schaffernicht (1930) similarly investigated the excitation cross-sections for mercury. The measurements of optical excitation cross sections by electron impact for sodium was first carried out by Brode (1933) and Michels (1931). These early attempts were hampered by a variety of technical problems and the results were never clear cut. As an example, Brode obtained $q_{\text{max}} = 4.4 \times 10^{-16}$ cm$^2$ as the excitation cross-sections for the resonance lines of potassium, while Fabrikant (1939) obtained $q_{\text{max}} = 2 \times 10^{-14}$ cm$^2$. Recently Volkova and Devyatov (1963) obtained $q_{\text{max}} = 0.42 \times 10^{-14}$ cm$^2$ for the $4^2\text{S}_{1/2} \rightarrow 4^2\text{P}_{1/2}$ excitations and $q_{\text{max}} = 0.90 \times 10^{-14}$ cm$^2$ for the $4^2\text{S}_{1/2} \rightarrow 4^2\text{P}_{3/2}$ excitation. Zapesochnyi and Shimon (1964) studied excitation cross sections for sodium and potassium bombarded with slow electrons (up to 10eV). All the above authors studied excitation of ground state atoms to various excited states, induced by collisions with electrons of energies up to 10eV.

Because of the close spacing of the resonance substates, the determination of the excitation cross sections for particular fine-structure states of atoms in general and of alkali metals in particular, was difficult, while the measurement of cross-sections for transition between the resonance sublevels of an alkali atom, caused by collisions with electrons was an even more difficult task and has not been attempted previously.

In principle, the collisional processes involved in the mixing between the potassium fine-structure states may be represented by the following equation:
\[ K(4^2P_{1/2}) + e^- + \Delta E \rightarrow K(4^2P_{3/2}) + e^- \quad (1) \]

where \( \Delta E \), the energy defect between the resonance sublevels (57 cm\(^{-1}\) or 0.007 eV) is taken from or given up to the kinetic energy of the relative motion of the colliding partners. Such collisions are termed inelastic collisions of the first kind and of the second kind.

A collision between an atom and an electron may be elastic, inelastic of the first kind or inelastic of the second kind; according to the energy exchange between the collision partners. In an elastic collision no energy exchange takes place between the internal energy of the atom and the electron. If the energy exchanged is gained by the internal structure of the atom at the expense of the kinetic energy of the electron, the collision is termed inelastic of the first kind. The reverse process is called inelastic collision of the second kind or superelastic collision, and in it the electron gains energy at the expense of the internal energy of the atom.

Inelastic collisions of the first kind were described by Franck and Hertz (1913). This interaction can be described as

\[ (e^- + KE) + A \rightarrow A^* + e^- \quad (2) \]

where \( A \) and \( A^* \) denote a ground state and an excited atom, respectively. Later Klein and Rossland (1921) presented an argument based on very general...
thermodynamic principles to show the existence of inelastic collisions of second kind. They reasoned that such interactions were necessary to preserve equilibrium in a gas containing a swarm of electrons. Such 'superelastic' collisions can be represented by the relation

\[ A + e^- + KE \leftrightarrow e^- + A^* \]  

(3)

Many attempts have been made since 1921 to investigate this phenomenon. Recently accurate cross-sections have been obtained by Burrow (1966) for superelastic collisions between electrons and excited mercury atoms.

The present work presents a modified design of an electron gun based on the method developed by Fox and co-workers (1955) for the study of the ionization of Xe and Cd by electron impact. The modifications were made to make the electron gun adequate for the investigation of the excitation transfer cross sections for mixing between the \( n^2P \) states of an alkali metal. It is possible to obtain, with this design, electron beams with very low average energies amounting to a fraction of an eV. and with \( \Delta E \), the full energy width at half maximum current, of about 0.1eV.

The first section of this thesis deals with the macroscopic theory of collisions between excited potassium atoms and electrons. The subsequent sections describe the apparatus, and the design, construction and performance of the R.P.D. electron gun designed for this particular purpose.
II. RATE EQUATIONS FOR SENSITIZED FLUORESCENCE AND QUENCHING PROCESSES

The processes that take place when low-energy electrons collide with excited potassium atoms in the $4^2P$ states, are shown diagrammatically in Fig. 1. The solid arrows indicate transitions giving rise to sensitized fluorescence and collisional deactivation of the $4^2P$ potassium atoms to the ground state, which manifests itself by the quenching of the resonance radiation. The broken arrows indicate cascade transitions.

The various processes involving single potassium atoms and arising from potassium-electrons collisions may be represented by the following equations

\[
K(4^2S_{1/2}) + h\nu_1 \xrightarrow{S_1} K(4^2P_{1/2}) \quad (4)
\]

\[
K(4^2S_{1/2}) + h\nu_2 \xrightarrow{S_2} K(4^2P_{3/2}) \quad (5)
\]

\[
K(4^2P_{3/2}) + e^- \xrightarrow{Z_{21}} K(4^2P_{1/2}) + e^- + \Delta E \quad (6)
\]

\[
K(4^2P_{1/2}) + e^- \xrightarrow{Z_{12}} K(4^2P_{3/2}) + e^- - \Delta E \quad (7)
\]

\[
K(4^2P_{1/2}) + e^- \xrightarrow{Z_{10}} K(4^2S_{1/2}) + e^- + \Delta E' \quad (8)
\]

\[
K(4^2P_{3/2}) + e^- \xrightarrow{Z_{20}} K(4^2S_{1/2}) + e^- + \Delta E'' \quad (9)
\]
Fig. 1, Energy levels in potassium involved in sensitized fluorescence and in the quenching of resonance radiation. Broken arrows indicate cascade transitions from higher states.
Eqs. (4) and (5) represent the optical excitation of the ground state potassium atoms to the resonance states. $S_1$ and $S_2$ are the densities of atoms excited per second from the ground state to the resonance states $4^2P_{1/2}$ and $4^2P_{3/2}$, respectively, as the optical excitation takes place by the 7699Å or the 7665Å component, respectively. Eqs. (6 - 9) describe the excitation transfer processes. Coefficients $Z_{12}$, $Z_{21}$, $Z_{10}$ and $Z_{20}$ are the numbers of collisions per excited atoms per second, leading to the appropriate processes of excitation transfer. $\Delta E$, $\Delta E'$ and $\Delta E''$ are the energy defects between, the two resonance states ($4^2P_{1/2}$ and $4^2P_{3/2}$), and between the $4^2P_{1/2}$ and the $4^2P_{3/2}$ states and the $4^2S_{1/2}$ ground state, respectively. Eqs. (8) and (9) represent the quenching of the potassium resonance radiation due to superelastic collisions with electrons. Eqs. (10) and (11) correspond to the spontaneous decay of the excited atoms to the ground state. $\tau_1$ and $\tau_2$ are the mean lifetimes of the $4^2P_{1/2}$ and $4^2P_{3/2}$ states, respectively. $\tau_1 = 2.78 \times 10^{-8}$ sec and $\tau_2 = 2.76 \times 10^{-8}$ sec. (Copley and Krause (1969).

The energy of the electron should be selected so as to prevent the further excitation by electron impact of a $4^2P$ potassium atom to the higher states ($5^2S_{1/2}$, $3^2D$ or $4^2D_{3/2}$ states). If, for example an
atom in the $4^2P_{3/2}$ state were to collide with a sufficiently energetic electron, it could either make the desired collisional transitions to the $4^2P_{1/2}$ state or be excited to the $5^2S_{1/2}$, $3^2D$ or $4^2D$ states as a result of energy gained from the electron. Subsequently the atom could decay to one of the $4^2P$ states. Such cascade transitions would obscure the wanted radiation, since there is no way of telling by which route the atom arrived at the $4^2P$ states.

It is thus important, that the energy of the electrons should not exceed the energy difference between the $4^2P$ and $5^2S_{1/2}$ states, and it follows that the mean energy of the beam should be about 1 eV. The probability of direct excitation by collisions between electrons and ground state atom would also be very much reduced. If it is assumed that the potassium atoms and the electrons exist in a state of dynamic equilibrium which involves continuous optical excitation of one fine-structure resonance state by means of the appropriate wavelength, spontaneous decay and collisional excitation transfer as represented by Eqs. (4 - 11), the equilibrium may be represented by the following rate equations. When the optical excitation is carried out by the 7665Å component,

$$\frac{dN_2}{dt} = S_2 + n_1 Z_{12} - N_2 \left[ (\tau_2)^{-1} + Z_{21} + Z_{20}^e \right] = 0$$

(12)
\[
\frac{dn_1}{dt} = Z_{21}N_2 - n_1 \left[ (\tau_1)^{-1} + Z_{12} + Z_{10}^e \right] = 0 \quad (13)
\]

If, on the other hand, the optical excitation takes place by the 7699 A component,

\[
\frac{dn_1}{dt} = S_1 + n_2Z_{21} - N_1 \left[ (\tau_1)^{-1} + Z_{12} + Z_{10}^e \right] = 0 \quad (14)
\]

\[
\frac{dn_2}{dt} = Z_{12}N_1 - n_2 \left[ (\tau_2)^{-1} + Z_{21} + Z_{20}^e \right] = 0 \quad (15)
\]

\(N\) refers to the density of atoms in the state being optically excited, \(n\) indicates the density of atoms in the other \(2P\) state which is excited collisionally, \(\tau_1\) and \(\tau_2\) are the lifetimes of the \(4P_{1/2}\) and \(4P_{3/2}\) states, respectively. \(Z_{12} = Z_{12}^e + Z_{12}^k\), where the suffix \(k\) refers to potassium - potassium collisions and the suffix \(e\) refers to potassium - electron collisions.

Solving Eqs. (13) and (15) for \(Z_{12}\) and \(Z_{21}\) gives

\[
Z_{12}^e + Z_{12}^k = \left[ (Z_{21}^k + Z_{21}^e) + (\tau_2)^{-1} + Z_{20}^e \right] \eta_2 \quad (16)
\]

\[
Z_{21}^e + Z_{21}^k = \left[ (Z_{12}^k + Z_{12}^e) + (\tau_1)^{-1} + Z_{10}^e \right] \eta_1 \quad (17)
\]

where:
The fluorescent intensity, $I$, of the component appearing in the denominator refers, in each case, to the same wavelength as that used for the optical excitation.

Assuming $\tau_2 = \tau_1$, the equations for $Z_{12}$ and $Z_{21}$ can be written as follows:

$$Z_{12} = [\tau^{-1} \eta_2 + \eta_1 \eta_2 + z_{10} \eta_1 \eta_2 + z_{20} \eta_1 \eta_2] / (1 - \eta_1 \eta_2)$$

and

$$Z_{21} = \tau^{-1} (\eta_1 + \eta_1 \eta_2) + z_{20} \eta_1 \eta_2 + z_{10} \eta_1 \eta_2] / (1 - \eta_1 \eta_2)$$

Eqs. (20) and (21) indicate the frequencies of 'mixing' collisions that an excited atom in each of the $4^2P$ states undergoes with another excited potassium atom and with an electron. In the absence of the electron beam $Z_{10}^e = 0$ and $Z_{20}^e = 0$, and Eqs. (20) and (21) reduce to the following equations:

$$\eta_1 = \frac{I_1(7699\AA)}{I_2(7665\AA)} = \frac{n_1}{N_2}$$

$$\eta_2 = \frac{I_2(7665\AA)}{I_1(7699\AA)} = \frac{n_2}{N_1}$$
where, \( \eta_1 \) and \( \eta_2 \) represent the ratios of the fluorescent intensities in pure potassium vapor, where only potassium - potassium collisions give rise to sensitized fluorescences.

\[
\eta_1 = \frac{I_1}{I_2} = \frac{n_1}{N_2} \\
\eta_2 = \frac{I_2}{I_1} = \frac{n_2}{N_1}
\]

Substituting Eqs. (22) and (23) in Eqs. (20) and (21)

\[
z_{12}^k = \left[ \eta_2 + \eta_1 \eta_2 / \tau (1 - \eta_1 \eta_2) \right] \\
z_{21}^k = \left[ \eta_1 + \eta_1 \eta_2 / \tau (1 - \eta_1 \eta_2) \right]
\]

\[
z_{12}^e = \left( \left( 1 + \eta_1 \right) \tau^{-1} + z_{10} \eta_1 + z_{20} \eta_2 / \left( 1 - \eta_1 \eta_2 \right) \right) - \\
\left\{ \eta_2 \left( 1 + \eta_1 \right) \tau^{-1} / \left( 1 - \eta_1 \eta_2 \right) \right\}
\]

\[
z_{21}^e = \left( \left( 1 + \eta_2 \right) \tau^{-1} + z_{20} \eta_2 + z_{10} \eta_1 / \left( 1 - \eta_1 \eta_2 \right) \right) - \\
\left\{ \eta_1 \left( 1 + \eta_2 \right) \tau^{-1} / \left( 1 - \eta_1 \eta_2 \right) \right\}
\]
Eqs. (26) and (27) provide the link between the experimental observations \((\eta_1 \text{ and } \eta_2)\) and the collision numbers \(Z_{12}^e\) and \(Z_{21}^e\). By analogy with the gas kinetic cross sections, the total effective cross section \(Q_{ab}^e\) for an inelastic collision leading to excitation transfer \(a \rightarrow b\) is given by:

\[
Z_{ab}^e = N_e Q_{ab}^e \nu_r
\]

where \(a\) and \(b\) refer either to state \((1)\) and \((2)\), respectively or vice versa. \(\nu_r\) is the average relative velocity of the colliding partners involved in a thermal collision

\[
\nu_r = \left(\frac{8kt}{\pi \mu}\right)^{1/2}
\]

where \(\mu\) is the reduced mass of the colliding partners, \(k\) is the Boltzmann constant and \(T\) is the absolute temperature. \(N_e\) is the density of the electrons which can be obtained as follows:

\[
J = \frac{i}{A} = N_e e \nu
\]

where \(J\) is the current density, \(i\) is the total current in the beam and
A is the cross sectional area of the beam which is considered to be equivalent to the area of the hole in the main retarding plate, \( e \) is the electronic charge, and \( v \) is the average velocity of the electrons.

Assuming \( v_r \approx v_e \), the mean velocity of the electrons is given by

\[
v_e = \left( \frac{2E}{m_e} \right)^{1/2}
\]

where \( m_e \) is the mass of the electron and \( E \) is the mean energy of the electron beam. From Eqs. (28) and (30)

\[
Z^e = Q^e J/e
\]

A plot of \( Z^e \) versus \( J \) would yield a straight line with slope \( Q/e \).

It should be expected by analogy with the case of potassium–potassium collision, that when \( Z^e_{10} \) and \( Z^e_{20} \) (the quenching terms) in Eqs. (26) and (27) are ignored, the plot of \( Z^e \) versus \( J \) will be non-linear specially at high electron currents, where the variation of \( Z_{ab} \) would tend slowly to zero. The departure from the expected linear behavior is attributed to the quenching terms. Therefore the terms containing \( Z^e_{10} \) and \( Z^e_{20} \) can be extracted from the non-linearity of the plots of \( Z \) versus \( J \). Once these quenching terms are obtained for a certain electron current their substitution into Eqs. (26) and (27)
will lead to the values $Z_{12}^e$ and $Z_{21}^e$ which, in conjunction with Eq. (28), will yield the cross-sections $Q_{12}^e$ and $Q_{21}^e$.

It has been assumed in the above treatment that there is no imprisonment of radiation. If resonance radiation were trapped, the effective lifetimes of the $^2P$ levels would no longer be equal to their mean lifetime and this would result in spurious values of the cross-sections.
III. GENERAL DESCRIPTION
OF THE APPARATUS

The arrangement of the apparatus to be used in the investigation of the potassium - potassium and potassium - electrons collisions is shown in Fig. 2. Potassium resonance radiation was emitted from a radiofrequency potassium vapor lamp, passed through a rectangular slit 1.5 mm wide, collimated and then separated into the two fine structure components by a series of three interference filters. Each of these filters transmitted about 60% of the wanted resonance line and about 0.1% of the unwanted component, resulting in a total transmission of 20% of the wanted component and about two parts per million of the unwanted component. The monochromatic beam was then focussed in the collision chamber of the electron gun which was mounted in the fluorescence cell. The latter contained potassium vapor at a controlled pressure and was situated in an oven whose temperature was kept constant within 0.1°C during the experiment. It was intended that the exciting light beam focussed in the collision chamber should be crossed by a collimated electron beam. The resulting fluorescence emitted from the cell, should be collimated normally to the exciting light beam, passed again through a set of neutral density and interference filters to resolve it into its fine structure components, and focussed on the photocathode.
Fig. 2 Schematic Diagram of the Apparatus

A Potassium Lamp, B Fluorescence Cell, Electron Gun and Oven, C Photomultiplier and Cryostat, D Amplifier Discriminator
E Printer, P Pin Hole, L Lenses,
$F_1$ Interference Filters (7665Å), $F'_1$ Interference Filters (7699Å), $F_2$ Neutral Density Filter,
V To Vacuum.
of a liquid air-cooled photomultiplier whose output pulses were to be discriminated, amplified and registered with a scaler.

The complete apparatus was enclosed in light-tight boxes to keep out stray light.

The Light Source

The R. F. lamp consisted of a cylindrical pyrex tube containing a mixture of 0.5 gm potassium and 1.5 torrof argon as a carrier gas. The properties of this type of lamp were described in details by Atkinson, Chapman and Krause (1965). The tube was situated within a coil which formed part of the tank circuit in a push-pull power oscillator, and its lower tip rested in a small electrically heated oven energised by a Variac and a Hammond 210 H transformer. This oven consisted of chromel wire of total resistance about 8 ohms wound around a copper socket. Suitable adjustments in the temperature of the lamp base resulted in narrow, intense and non-self reversed resonance lines.

The push-pull oscillator, whose circuit is shown in Fig. 3, operated at 160 Mc/sec and employed two 4-65 A Philips tetrodes. The coil $L_1$ which surrounded the lamp, consisted of six turns of No. 10 gauge tinned copper wire, 5 cm long and 2 cm in diameter. The control grid coil $L_2$ consisted of 5 turns of similar wire, and was 4 cm long and 2 cm in diameter. The two coils, wound in opposite directions, provided inductive coupling to the r.f. discharge. The oscillator operated at a power of 100 watts.
Fig. 3, Lamp Oscillator Circuit.

R₁ Resistors 16K ohms, 2 watts; R₂ = 1 K ohm, 2 watts; L₁ Lamp Coil 6 turns; L₂ Grid Coil 5 turns; C, Capacitors of 0.075 μF. F, Radiofrequency Chokes. T, 4-65 Philips Tetrodes.
The Interference Filters

Spectrolab type 'U' interference filters were used for the separation of the fine-structure components. A series of stops and slits was used in both the exciting and fluorescent beams, so that the light passing through the interference filters was parallel as it should be for optimal resolution. The filters were mounted in holders which allowed them to be precisely oriented with respect to each other and to the light beam, and to be rotated about the axis of the light beam. The holders were fastened to servomotor-driven slides operated by an electromechanical sequencing system similar to that described by Piter (1965).

The filters used in the experiment are tabulated below, with transmission of the two resonance lines as specified by the manufacturer.

<table>
<thead>
<tr>
<th>Serial No.</th>
<th>Transmission of 7665Å</th>
<th>Transmission of 7699Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>11408</td>
<td>0.700</td>
<td>0.001</td>
</tr>
<tr>
<td>11409</td>
<td>0.710</td>
<td>0.001</td>
</tr>
<tr>
<td>10885</td>
<td>0.625</td>
<td>0.0015</td>
</tr>
<tr>
<td>10975</td>
<td>0.650</td>
<td>0.001</td>
</tr>
<tr>
<td>11412</td>
<td>0.001</td>
<td>0.678</td>
</tr>
<tr>
<td>11411</td>
<td>0.001</td>
<td>0.705</td>
</tr>
<tr>
<td>10897</td>
<td>0.0015</td>
<td>0.590</td>
</tr>
<tr>
<td>10972</td>
<td>0.001</td>
<td>0.710</td>
</tr>
</tbody>
</table>
The transmission of three filters in series was found experimentally, in the case of the $7665\AA$ component, to be $18.8\%$ for the wanted fluorescence component and five parts per million for the unwanted one, while the three $7699\AA$ filters transmitted about $21.9\%$ of the appropriate component and about six parts per million of the other resonance line.

The Fluorescence Cell and Oven

The fluorescence cell shown in Fig. 4, was designed in such a way as to minimize reabsorption, scattering and trapping of the resonance radiation. This was accomplished by placing the entrance and exit windows perpendicularly to each other. The incident beam was focussed in the region between the two windows. To prevent reflections, the body of the cell was coated with 'aquadag' a colloidal dispersion of graphite.

The side-arm, containing the liquid potassium, was almost 4 1/2" long and 3/4" in diameter. Its temperature was controlled by water circulating from a Calora type K-4439 thermostat through a closely fitting copper coil 3/16" in diameter, surrounding the side-arm. Copper foil was wrapped around the side-arm to ensure uniformity of temperature which controlled the potassium vapor pressure in the cell and which was left constant within $\pm 0.05^\circ\text{C}$.

The fluorescence cell was located in an oven which was essentially a rectangular double-walled box. The inner box 7.2" long, 4" wide and 5.2" high was made of aluminum, 5/16" thick, and to its
Fig. 4, Schematic Diagram of the Fluorescence Cell. A, Entrance Window; B, Exit Window; O, Observation Window; F, Flange Cover; S, Side Arm; V, Connection to the Vacuum System; G, Electron Gun;
outer surface was fastened chromel wire of total resistance 10 ohms. The wire was cemented to the aluminum by Sauereisen No. 1, covered by asbestos paper for insulation and connected to a Variac so as to provide heat for the main oven whose temperature could be maintained constant within $\pm 0.1^\circ$C over a long time. The outer box, 8.5" long 5.7" wide and 6.5" high, was made of phenolite 3/16" thick. The space between the two boxes was filled by fiber glass which acted as an insulator.

The side-arm and the tube connecting the cell to the vacuum system protruded through holes 3/4" in diameter in the main oven walls. The cell was connected to a vacuum system through a capillary 2 mm in diameter, which allowed to maintain vacuum in the cell and, at the same time, prevented migration of potassium vapor out of the cell.

The Vacuum System

The vacuum in the pyrex system was produced by an Edwards E04 water-cooled diffusion pump, equipped with an Edwards H7L4A baffle value and a low resistance liquid air trap, and backed by an ES 150 rotary pump. The diffusion pump was protected from cooling water failure by an FSM-1 Flowtrol unit. The lowest reproducible pressure obtained, using Dow Corning 704 silicone fluid in the diffusion pump, was about $5 \times 10^{-9}$ mm Hg, but during the experiment $5 \times 10^{-7}$ mm. Hg was usual. The vacuum gauges used in measuring the pressure were as listed below. A GI C-015 CVC ion tube was used for the high vacuum measurements.
Table 2

Vacuum Gauges

<table>
<thead>
<tr>
<th>Vacuum Gauge</th>
<th>Low Pressure (torr)</th>
<th>Upper Limit Pressure (torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. L.K.B. Autovac gauge type 3294</td>
<td>$10^{-3}$</td>
<td>2</td>
</tr>
<tr>
<td>2. CVC Ionization gauge type GIC 110-B</td>
<td>$10^{-8}$</td>
<td>$10^{-4}$</td>
</tr>
</tbody>
</table>

The Detection and Recording System

An I.T.T. type FW 118,16 stage multiplier phototube, housed in a liquid air-cooled cryostat, was used to detect the fluorescent light. The tube was operated at 1.5 kV supplied by a 412-B Fluke regulated power supply. The Ag-O-Cs photocathode which had an S-1 spectral response and a maximum sensitivity centered around 8000Å, was 1/8" in diameter. Pulses from the anode load resistor of the photomultiplier, were directed into a Philips PW 4270 amplifier - discriminator and were recorded on a PW 4236 scaler connected to a PW 4263 timer. The results were registered by means of a Premier printer used in conjunction with a PW 4255 printer control. The dark noise of the photomultiplier amounted to 30 counts per minute which is equivalent to $10^{-12}$ amps. The efficiency of the S-1 cathode was about the same for the two potassium resonance wavelengths and was equal to about 0.6 per cent.
IV. THE ELECTRON GUN

A. The Design and Construction

The method of producing a beam of low-energy electrons to be used in this experiment, was the Retarding Potential Difference method of Fox and Hickam (1955), to which I shall hereafter refer as R. P. D.

The R. P. D. gun was chosen because it is capable of producing pseudo - monoenergetic electron beams with energies of 1 eV or lower. It also provides a large electron current and it is easy to build, including no curved plates that form part of other types of electron energy selectors.

The basic layout of the Fox gun is shown in Fig. 5. Electrons from the heated cathode are accelerated through a series of circular apertures into the collision chamber and then to an electron collector. The most common source of electrons is a thermionic cathode which emits electrons with a maxwellian energy distribution as shown in Fig. 6a. Electrons accelerated toward the first plate arrive with a certain spread in energy and with $V_1$ electron volts of energy plus the contact potential difference $S_1$ and the filament as shown in Fig. 6b. Plate $S_1$ (the accelerating plate) is kept at a positive potential (+13.5 volts) greater than the potential of the cathode (-6.5 volts). The electrons passing through the aperture in $S_1$ are then retarded by the plate $S_3$. The
Fig. 5, Schematic Diagram of the Fox-Hickam Gun

F, Filament; $S_1$, Accelerating Plate; $S_3$, Retarding Plate, C, Collision Chamber E.C. Electron Collector.
Fig. 6a, on the Cathode  

Fig. 6b, Plate $S_1$  

Fig. 6c, Plate $S_3$  

Fig. 6d, at Plate $S_5$  

Fig. 6e, Plate $S_3$  

Fig. 6f, at Plate $S_5$

Fig. 6, Electron Energy Distribution on the Plates of the Electron Gun
potential on $S_3$ is selected such that almost a half of the electron beam is rejected and the point $a$ corresponds to zero kinetic energy. In Fig. 6a, two points $a$ and $b$ are marked for reference on the distribution curve. Those electrons which are emitted from the cathode with comparatively low energies would not be allowed to reach $S_3$. Fig. 6c, shows the energy distribution at $S_3$. This truncated distribution is then accelerated by $S_5$ which forms the entrance to the collision chamber. In the latter the electrons will be made to collide with the atoms under study. If the potential of plate $S_3$ is changed next by a small amount $\Delta V$, the distribution at $S_3$ will be shifted slightly as shown in Fig. 6e, with point $b$ corresponding to zero kinetic energy. A typical value of $\Delta V$ used was 0.1 V. The current difference corresponding to this change $\Delta V$ is due to the electrons lying in an energy range between $E$ and $E + \Delta E$ (slice ab in Fig. 6a). The mean energy of these electrons corresponds to the potential difference between $S_3$ and $S_5$ or, in other words, the voltage differences between $S_3$ and $S_5$ give the energy of the pseudo-monoenergetic electron beam, as shown in Figs. (6d and 6f).

The design of the actual electron gun used which is similar to the design of Burrow (1966), is shown in Fig. 7. Plates $S_2$ and $S_4$ were added on each side of the retarding plate $S_3$. The purpose of plates $S_2$ and $S_4$, which were connected, was to act as guard plates and to prevent field distortion at $S_3$, since there was a considerable potential difference between $S_1$ and $S_3$ (+20 volts). $S_3$ was the main retarding plate. The positive potential on $S_5$ with respect to $S_3$
Fig. 7a, Schematic Diagram of the R.F.D. Electron Gun. F, Filament; S₃, Accelerating Plate; S₃, S₄ and S₅, Guard Plates; S₆, Main Retarding Plate, S₇-S₉, The Collision Chamber. S₁₀, The Second Retarding Plate, S₁₀, Shield Plate; E.C., Electron Collector Cup

(b) 7b, Voltage Distribution Along the Electron Gun.
reaccelerated the electrons towards the collision region. The latter was located in the equipotential region between $S_5$ and $S_6$, which were connected to each other. Thus electrons in the collision chamber were moving with energy acquired in being accelerated by the potential difference between $S_3$ and $S_5$. In this region the electrons would collide with the excited alkali atoms.

The electron gun, which was more elaborate than the original Fox - Hickam model followed Burrow's (1966) design and contained an additional retarding plate $S_7$. The main purpose of this plate was to analyse the energy of the main electron beam. Another plate $S_8$ was added which, together with plate $S_6$ guarded plate $S_7$. Plate $S_9$ formed a shield for the electron collector. The apertures in all the plates, except for the electron collector which was a cup, were circular holes. Their diameters were as follows; 0.040" in $S_1$, 0.030" in $S_2$, 0.020" in $S_3$, 0.030" in $S_4$, 0.040" in $S_5$, 0.050" in $S_6$, 0.050" in $S_7$ and 0.0625" in $S_8$ and $S_9$.

The gun was assembled using components supplied by the Nuclide Corporation of Acton Massachusetts. All the electrodes, except for the electron collector which was made of tungsten, were fabricated of a non-magnetic stainless steel No. 304 in order to eliminate stray magnetic fields and to minimize contact potentials. The spacers between the plates were ceramic. The spacing between the successive electrodes was as shown in Fig. 7, the plates were 0.424" square and 0.010" thick.

There were three general design considerations which led to
the choice of the above dimensions. First, the electric field penetration of adjacent holes must be small and therefore the separation between the plates should preferably be larger than the diameter of the holes. Secondly, in order to obtain the maximal current, the spacing between the filament and the accelerating plate $S_1$ should be kept small since, according to the diode law $J \propto \frac{V^{3/2}}{d^2}$, where $J$ is the current density, $V$ the potential on $S_1$, and $d$ the distance between $S_1$ and the filament. Thirdly, the spacing between the adjacent electrodes should be relatively small since the larger the spacing, the larger will be the effect of the space charge. If the spacing between the adjacent electrodes is large, the electron beam will be more divergent increasing the space charge effect which will reduce the intensity of the electron beam.

The electric connections between the electrodes and the connecting wires were spot-welded. The entire system of electrodes was held together by four ceramic rods 0.060" in diameter. The cathode was a thoriated iridium hair-pin filament. This material was chosen because it is inert to hot potassium vapor.

The total current emitted from the cathode is given by Richardson's equation:

$$I = J d A = 120T^2 \exp \left(-\frac{\Phi}{kT}\right) dA \quad (33)$$

where $\Phi$ is the work function and is a property of the cathode material;
$dA$ is the cathode area, $k$ is the Boltzman constant and $T$ is the absolute temperature. From equation (33) it follows that the three factors which govern the choice of the material and the shape of the cathode are the temperature $T$, the work function $\phi$ and the emitting area $dA$.

It should be borne in mind that as the temperature of the filament increases, both the total current and the width of the energy distribution (defined as the full half-width $\Delta E_{1/2}$) increase so that the optimum temperature must be chosen in such a way as to effect a compromise between the total current and $\Delta E_{1/2}$.

It is advantageous to use a cathode material with a work function $\phi$ as low as possible. However, certain materials with low work functions are easily poisoned by the alkali metal (potassium) and by the evaporation of the cathode itself. The advantages of thoriated iridium as a cathode are that it is a good emitter, it is relatively inert to potassium, it suffers almost no evaporation and it is easy to obtain since it is a common material used in ionization gauges. It is also easy to mount as a standard component. But the hair-pin filament was found to be mechanically fragile and could be broken easily. It also had a comparatively small emitting area and its greatest disadvantage was that it emitted light which could mask the fluorescence that was to be investigated.

In the experiment, the gun was placed as close as possible to the entrance and exit windows of the fluorescence cell in such a way, that the gun axis was perpendicular to the exciting and fluorescent.
light beams. The gun was supported from above by four long stainless steel rods about 3.75" long. The rods were screwed into the stainless steel flange which closed the neck of the fluorescence cell and were adjusted to align the collision chamber with the exciting and fluorescent light beams as shown in Fig. 4.
B. The Performance of the Electron Gun

In order to operate the gun correctly, it is necessary to adjust the voltages of the various plates and the collimating magnetic field in such a way, as to collect the maximal number of electrons with the desired energy.

The voltages on the plates were generated by means of Hewlett Packard 6215 regulated and stabilized voltage power supplies, were adjusted manually using helical potentiometers and were measured with a Hewlett Packard 3440-A digital voltmeter. The power supply circuits are shown in Fig. 8. The voltages on the plates were measured with respect to zero at ground and were set as follows: the cathode was set at -6.5 volts, $S_1$ at about +13.5 volts, $S_2$ and $S_4$ connected together were at the filament potential of -6.5 volts. The voltages on $S_3$ and $S_7$ were varied in the course of the experiments from -7.5 volts to -10.5 volts. The plates $S_6$, $S_8$ and $S_9$ were kept at the potential of $S_5$, -6.0 volts. The electron collector was biased to ground. Because $S_9$ was at negative potential with respect to the electron collector, the effect of electrons reflected from the collector cup was reduced. It was found experimentally that the presence of $S_9$ became more important as $S_3$ or $S_7$ became more negative. As $S_7$ was made more negative, any variation in the potential of $S_9$ from -1 volt towards zero (the collector cup potential), was found to give rise to a peak in the total collected current.
Fig. 8, The Electron Gun Power Supply.
as in Fig. 9. The energetic electrons after passing through $S_7$ collided with the collector cup and then were reflected backwards, and as a result the total collected current at low $S_7$ (retarding potential) was smaller than it should be in the absence of this back scattering effect. The ideal voltage on $S_9$ at which no such peak would be observed was found to be -6.0 volts, as then all the electrons were retained by the collector.

The total electron current on the collector was measured by a model 417 Keithley picoammeter of high internal impedance, connected directly to the collector cup. The emission current from the cathode to plate $S_1$ was monitored by a milliammeter. The emission current had a typical value of 4.3 mA.

The best energy resolution in the electron beam is obtained when the cutoffs on $V_3$ are placed symmetrically at about the peak of the distribution shown in Fig. 6a, as in this way for a given energy width $\Delta E$, the cutoff corresponds to a maximum in the difference current. $V_3$ was varied between -1.0 and -4.0 volts with respect to the cathode (-7.5 to -10.5 volts with respect to ground). The energy of the main electron beam was analysed by means of the plate $S_7$. The total energy distribution was obtained by keeping the voltage on $S_3$ (the main retarding plate) constant and measuring the total collector current as a function of $V_7$ as shown in Fig. 10. In this case the R.P.D. technique was not used and the electron gun behaved as a normal source of electrons. The derivative of the curve $V_7$ versus $I$, which was obtained
Fig. 10. A Retarding Curve and its Derivative Showing the Electron Distribution at $S_7$.
graphically, is also shown in Fig. 10, and indicates the energy distribution of the electrons, broadened by the imperfect retarding of $S_7$ and by the effect of space charge. The effects of space charge on the electron beam will be discussed later.

Alternatively, the energy distribution of the electrons within the slice $ab$ in Fig. 6, arising from the application of the R.P.D. technique applied on $S_3$, can be analysed by means of $S_7$. The retarding curve shown in Fig. 11, shows the variation of the retarding voltage $V_7$ and the corresponding electron current difference $\Delta i$. The latter corresponds to the cutoff voltage increment $\Delta V$ placed at about the maximum of the electron energy distribution. The voltages on $S_7$ were measured with respect to ground. The negative slope of this curve was also determined graphically and is plotted against $V_7$, giving the actual energy distribution of the electrons.

If the potential on $S_7$ is sufficiently negative with respect to $S_5$, the main beam will be entirely retarded and will not penetrate beyond $S_7$. In such a case, the only current arriving at the collector, would be due to electrons which, having collided with excited atoms, gained kinetic energy at the expense of the atoms. These superelastic electrons can be collected and their energy can be measured (Burrow 1966).

It was assumed in this discussion, that all electrons emitted from the filament, had their initial thermal velocities parallel to the axis of the gun. Actually, the electrons are emitted in all directions. However, two ways were used to make the number of electrons collected
Fig. 11, A Plot of the Retarding Voltage on S₁, versus the Current Differences Corresponding to the Cutoff on S₁.
as large as possible. The holes in the plates were made very small in order to prevent electrons with an appreciable transverse velocity component from entering the collision chamber, since the retarding potentials affect only their momentum components parallel to the gun axis.

In addition, a collimating magnetic field of 100 - 130 gauss was applied in the direction of the gun axis. It was generated by a pair of Helmholtz coils 13.75" in diameter and consisting of 250 turns of No. 14 gauge copper wire, giving a field of approximately 13 gauss per ampere. The coils were water-cooled. The water was allowed to flow through a copper coil of diameter 3/16" attached to the surfaces of the principal coils. The current in the coils was supplied by a highly regulated Sorensen supply, Nobatron DCR - 150 15.

Effects of the Magnetic Field:

The adjustments of the magnitude and direction of the magnetic field played a very important role in the successful operation of the gun. The effects of the incorrect magnitude and alignment of the magnetic field on the collector current are several and are often complicated and difficult to interpret.

Electrons emitted with their initial thermal velocity components not parallel to the axis of the gun, are forced by the magnetic field to spiral around the axis and to travel in helical paths. The radius of the electron spiral depends in the following manner on the strength of the magnetic field, and on the velocity component perpendicular to the axis.
\[ r_s = \frac{mv}{eB} \] (34)

where \( r_s \) is the radius of the spiral, \( m \) and \( e \) are, respectively, the mass and charge of the electron, \( v \) is the average velocity of the electrons and \( B \) is the magnitude of the magnetic field. For example, in a field of 100 G, an electron with a transverse velocity component corresponding to 0.25 eV would travel in a spiral of radius 0.013". Such electrons cannot quite pass through the apertures of the electron gun since the diameter of the spiral is larger than the smallest aperture in the gun, whose diameter is 0.020" (in the main retarding plate). It was found in practice, that the magnitude of the field should be at least 120 G, to obtain a reasonable number of electrons travelling to the collision chamber with radii of spiral smaller than the aperture of the main retarding plate. In addition, it was found, at times that the total current varied randomly as shown in Fig. 12, and that dropping the magnitude of the magnetic field to below about 70 Gauss did not affect the electron current. This condition of instability of the electron beam was due to faulty alignment of the magnetic field and could be eliminated by small adjustments to make the direction of the field completely parallel to the axis of the gun. It thus appears that if the magnitude of the magnetic field is important, its alignment is equally important. The alignment of the two coils parallel to the plates of the gun was very critical and was carried out by maximising the electron collector current with no retarding potentials on the gun plates. The total collector current was then monitored as a function

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Fig. 12, A Plot Showing the Effect of Uncorrect Alignment of the Magnetic Field.
of the electron energy. With the proper alignment of the magnetic field, the current would become independent of the accelerating potentials and consequently the plot of Fig. 12, would become a horizontal straight line. The electron collector current was also observed at times to behave differently as a function of the retarding potentials, depending on whether the retarding was done at plate $S_3$ or at plate $S_7$. These differences which are apparent in Fig. 13, may be caused by focusing effects on the electron beam, by space charge or by surface charge effects. But these differences were much reduced by careful minute adjustments in the alignments of the magnetic field, as may be seen in Fig. 13. Typical total electron currents produced by the gun ranged from $10^{-7}$ to $10^{-6}$ Amperes.

The space charge is particularly pronounced within the collision chamber and in the vicinity of the apertures in the retarding plates. This effect would be expected to manifest itself in the following ways. First, due to the slow motion of the electrons in the vicinity of the apertures, the electrons tend to pile up in these regions and form a cloud spreading in all directions with the resulting defocussing effect. One of the consequences arising from this phenomenon is, that the electrons travelling through the centre of the aperture will tend to experience a different retardation or acceleration than those passing near the edges. Secondly, even within a supposedly field-free space, the space charge effect creates a field and causes the beam to spread out even in the presence of the magnetic field. Consequently the energy
Fig. 13, Variations of Total Current With Respect to Retarding Voltages at \( S_3 \) and \( S_7 \). In the Presence and Absence of Improper Magnetic Field.
band (ab Fig. 6a) may be broader than expected from the measured value of $\Delta E$. The influence of space charge on the electron energy distribution in an R.P.D. gun has been discussed by Marmet (1964).

The value of $\Delta E$ may also be affected by the formation of surface charge which can accumulate on accelerating and retarding plates and give rise to variations of potential across the surface of a particular plate. Such an effect may be further magnified by contamination of the plate surfaces by deposits of potassium and by other impurities evaporated from the filament or originating from other parts of the system, all of which would cause nonuniformities in the surfaces of the plates.

The building up of surface charge on accelerating and retarding plates gives rise to two types of difficulties. Since the potentials of the plates are measured at their outer edges, their values are not necessarily identical with the potentials at the apertures, that are experienced by the accelerated or retarded electrons, with possible variations amounting to significant fractions of a volt. Secondly, as a result of the surface charge effect a retarding plate would no longer define a plane of nearly constant potential and, consequently the energy cutoff would not be sharp.
VI CONCLUSION

The method of generating electrons which is described in this thesis, is based on the method of retarding potential differences, known as the R. P. D. method. The electrons were produced by a hair-pin thoriated iridium filament. This material is a good emitter, hard to evaporate and very easy to obtain since it is a common material used in ionization gauges; it does, however, emit light. In cases where the R. P. D. gun is used in experiments in which data are analysed optically, this light emission from the filament could be a source of stray light which would obscure the wanted signal. Therefore it would be better to use an indirectly heated cathode in an R. P. D. electron gun designed for the study of optical phenomena. Such a cathode would form a shield for the filament and would prevent the emission of stray light. An indirectly heated cathode can also be regarded as an equipotential surface, thus diminishing the inhomogeneity in the energy of the emitted electrons, arising from the effect of the potential drop along the filament. A matrix cathode with a large surface area would also emit a large electron current than a hair-pin cathode.

The R. P. D. electron gun as described in this thesis is useful for studies of excitation transfer between excited alkali atoms, induced by electron impact and leading to transitions $[n^2P_{1/2} \rightarrow n^2P_{3/2}]$.
and \([n^2P_{1/2} \rightarrow n^2P_{3/2}]\), and also for studies of superelastic collisions. To improve the signal-to-noise ratio it might be useful to employ with the present design a pulse generator accross \(S_2\) and \(S_3\), which would cause stepwise and repetitive changes in the potential of \(S_3\), as required by the R. P. D. technique. Such an arrangement would permit a larger number of readings within the same interval of time.

Alternatively, a cylindrical R. P. D. electron gun (Schulz 1963) could be used in similar investigations. Recently a cylindrical R. P. D. electron gun similar to the Schulz model but with much more refined electron optics, was introduced by Golden and Zecca (1969), who used no axial magnetic field but with the aid of electrostatic lenses, produced a large signal with much better energy resolution than that obtainable from a simple R. P. D. monochromator. As example the Golden electron gun allows a full width at half maximum current of about 0.01 eV and approximately constant \(I/\Delta E\) ratio of about \(10^{-7}\) (A/eV).

Care must be taken to allow for contact potentials, space charge and surface charges existing between and on the various plates of the electron gun. These space and surface charges and contact potentials may give rise to effects of the order of one to two volts and may vary with time. To correct for them, the apparatus should be calibrated in terms of the critical potentials of helium or ionization potential of potassium or by means of any other potentials known accurately from spectroscopic data.
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