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MOLECULAR BEAM STUDIES OF ELECTRONIC ENERGY TRANSFER PROCESSES WITH METASTABLE MERCURY ATOMS

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MOLECULAR BEAM STUDIES OF ELECTRONIC ENERGY TRANSFER
PROCESSES WITH METASTABLE MERCURY ATOMS

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ABSTRACT

An apparatus has been constructed to study electronic energy transfer processes with metastable mercury atoms using the molecular beam technique. The present study involves crossing a beam of metastable 6^3P_0 and 6^3P_2 mercury atoms with a velocity selected beam of thallium atoms or alkali halide molecules. The photon emission from the excited thallium atoms produced in the former and the excited alkali atoms in the latter is detected at the collision zone by a photomultiplier. A method is developed to extract the velocity dependence of the relative cross section from the experimental data.

For the $Hg^* + Tl$ system, quantitative information was obtained for the excitation of thallium 5350Å line fluorescence. The relative cross section was found to be a monotonically decreasing function of velocity g with a g^{-2} dependence. An ionic curve crossing model was suggested as one possible way of explaining this dependence.

Lithium iodide, sodium iodide and sodium bromide were selected for study in the experiments with alkali halides. Quantitative results were reported for the last two. The relative cross sections have g^{-3} and $g^{-3.5}$ dependences for NaI and NaBr respectively. The results could possibly be explained by a statistical model.

I. INTRODUCTION

Electronic excitation energy transfer processes between neutral atoms and molecules have always been of interest to chemists. Such processes can be represented schematically as

where A and B can be either atoms or molecules. In certain cases, chemical reactions may occur with the transfer of excitation energy as in

and analogous cases where A is ionized. There are also chemiluminescent reactions such as

We are mainly interested in investigating the energy dependence of processes (1), (7) and (8), although attempts have also been made to study processes (4) and (6).

Process (1), generally labelled as sensitized fluorescence, had been studied as far back as 1923.¹ A few examples of more recent experiments, with improved apparatus, can be found in References 2 to 5.

However, all these experiments are done with the reactants placed in one way or another in sealed glass or quartz tubes. There are several inherent disadvantages when this technique is employed. First, it can hardly be said that the translational energies of the reactants are well defined in such experiments, for there is a Maxwell-Boltzmann distribution of velocities for both reactants. Secondly, since optical excitation is the principal means of producing the excited species, not all the excited states are available for study. Furthermore, quenching of the excited atoms or molecules in the fluorescence tube to their metastable states does occur to an appreciable extent, leading to confusion as to the exact identity of the excited species when energy transfer to its expected collision partner occurs. Thirdly, there is always a high probability that impurities due to outgassing from the walls of the vessel may affect the reaction rate. One possibility is that they may act as third bodies in collisions and enhance the formation of excited dimers or quasi molecules such as $\text{Hg}_2(^3\text{O}_u^+)$ which can alter the rate of the process appreciably. Both McFarland² and Kraulinya⁶ have suspected that such dimers, because of their smaller energy difference with the thallium $7^2\text{S}_{1/2}$ level, would contribute to the excitation of that thallium level although the extent to which they contribute is unknown. In fact, if they do play an important part, the bulb experiments may be studying the energy transfer between entirely different species from what the experimenters had originally claimed. In addition, self-absorption of the emission does take place where the density of ground state atoms is high, thus reducing the intensities of certain resonance levels, and rendering quantitative studies of such lines difficult. Moreover, any

attempt at studying the temperature dependence of the process would have to face the fact that a pressure change would accompany a temperature change and one or more of the above factors may play a part in masking the actual effect of a temperature change, thus rendering the reported results subject to doubt. In view of such limitations, it would seem that the molecular beam technique, as has been employed in our experiments, is uniquely suitable for such investigations. First, the velocities of one or both of the incident beams can be selected by a velocity selector. Even without such a device, the beam temperatures, and thus the velocity distribution of the incident beams, can be varied independently of any other parameter. This enables the experimenter to define the translational energies of the reactants more precisely and observe their true effects on the rate of the process. Secondly, at least in theory, any excited state of the incident beam can be used in our investigation. Metastable states with long enough life times such that attenuation between the region of formation and the collision zone by decay processes is negligible can be produced by electron bombardment prior to entering the collision zone. Resonance levels with short life times (e.g., 10^{-6} or shorter) can be produced at the collision zone by optical excitation although in actual practice this method has not been used because of experimental difficulties. Thirdly, by varying the beam temperatures, it is easy to prevent the formation of dimers or other molecules to any measurable extent as to have an effect on the final outcome of the process. Simple calculations has shown that in our experiments, the amount of dimers in equilibrium with monomers is negligible, and since collision and hence reaction takes place only at the collision zone under single collision

conditions, complications due to third bodies in collision are totally avoided. Moreover, self absorption is totally absent because of the low density of reactants at the collision zone. However, there are limitations, the most serious of which is the low signal to noise ratio usually encountered in such techniques. At least in our case, the velocity selected beam is limited to species with low work function because we have employed an ionization detector instead of an "Universal" detector. In addition, if excited states of low excitation energy, as in our case, ($\text{Hg } ^3\text{P}_{2,0}$ with excitation energies of 5.46 eV and 4.67 eV respectively) is used, the efficiency of detection is much lower than in cases where excited inert gas atoms are used. Moreover, it is quite difficult to obtain absolute cross sections from such experiments.

It is worth while noting that our experiments are done in the thermal energy range. Although there are experiments investigating the velocity dependence of Penning and associative ionization with inert gas atoms⁷ as well as excitation of Hg ground state atoms by collision with a metastable molecule,⁸ our experiments are among the first ones using excited mercury atoms in sensitized fluorescence studies. Some of the other molecular beam experiments involving excited mercury atoms were concerned with intramultiplet conversion. Martin, et al.¹¹ has obtained relative cross sections for the intramultiplet quenching of $\text{Hg}(6^3\text{P}_2)$ to $\text{Hg}(6^3\text{P}_1)$ by D_2 , CO, NO and a variety of other gases, and has attributed the differences in cross sections to competitive processes in which highly reactive molecules tend to have small intramultiplet quenching cross sections. Krause, et al.¹⁰ has measured the velocity dependence of the de-excitation of metastable mercury atoms ($6^3\text{P}_2 \rightarrow 6^3\text{P}_1$) in

collisions with H_2 , D_2 , N_2 , NO and CH_4 by monitoring the 2537Å line of mercury. His results suggested that quenching occurred when electronic-vibrational terms of the quasimolecule intersect. In addition, Fluendy⁹ has studied the elastic scattering of $Hg(6^3P_2)$ atoms of potassium and mercury atoms. It is hoped that the results presented here will serve to further our understanding of the process of electronic energy transfer.

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II. APPARATUS

A. Introduction

The basic plan of the experimental set up consisted of two beam sources with their respective beam paths aligned at right angles to each other, a photomultiplier housing located at the collision zone, an electron gun for producing excited atoms, a velocity selector, the two beam monitors, and the associated electronics for the whole system. A diagram of the apparatus is shown in Fig. II-1.

The apparatus described here is actually an improved version of an existing one jointly set up by the author and David D. Parrish in our initial attempts at sensitized fluorescence experiments on the system $\text{Hg}^* + \text{Tl}$. Thus parts that have been previously described in detail¹ will merely be outlined here.

The experimental set up was designed for experiments with metallic beams. The lack of a universal detector limited the velocity selected beam to that of metal atoms detectable by an ionization detector. Without a differentially pumped source chamber, the metastable beam was limited to some easily condensable atoms like mercury, and excluded the use of metastable inert gas atoms.

Several problems had arisen in the course of our first experiments, limiting the original design to the study of the $\text{Tl } 5350\text{\AA}$ line fluorescence, and the author has endeavored to solve them with moderate success. Firstly, the photon emission from both the electron gun cathode and the ionization filament constituted such an enormous background that detection of a small fluorescence signal was almost impossible except in the more favorable cases. Secondly, the construction

of the oven for the velocity selected beam caused alignment and calibration problems because of its sideways thermal expansion away from the longitudinal axis of the slotted disk velocity selector. Although such alignment errors can be estimated quite accurately,^{1,2} an oven that expands along the axis would certainly be a more appropriate design. Thirdly, the necessity of alignment of the electron gun prior to each experiment was time consuming and increased the chance of poisoning the cathode in air. A design that would position the electron gun precisely in the beam path could save both time and effort.

In addition to these, several minor modifications were made and will be described in the following sections.

B. Vacuum System

The vacuum system consists of a single chamber with four removable flanges, all fabricated from heavy aluminum alloy (Alcoa 6061). Normally two of the flanges are bolted in place permanently to provide support for the velocity selector and the ionization detector assembly. The other two flanges may be removed to provide access to the inside of the chamber. A 12 in. diameter rotating lid is mounted in the top of the vacuum chamber. For the present experiments, the lid is fixed in place, providing support for the mercury oven assembly, photomultiplier housing and the metastable beam detector.

The main pumping for noncondensable gases is obtained from two Consolidated Vacuum Corporations PMC-6B 6 in. oil diffusion pumps

(nominal pumping speed of each is 1400 liters/sec) backed up by a single Welch 1397B two stage mechanical pump with a speed of approximately 15 cubic feet per minute at 10 microns. Since both beams used in the present experiments are condensable at liquid nitrogen temperature, the copper cold shields and liquid nitrogen reservoir lining the inside of the entire chamber provides very high pumping speeds during experiments.

A Hasting thermocouple gauge monitors the fore pump pressure while a Veeco RG-75P ionization gauge measures the main chamber pressure. Diffusion pump power is interlocked to the flow of cooling water, the pump temperature and the fore pump pressure. Vacuum seals and electrical feed throughs are done in the usual manner as described in Parrish's thesis.¹

Typical background pressure during experimental runs was 1.6×10^{-6} Torr and was never allowed to rise above 3×10^{-6} Torr. A low background pressure is essential to the success of the experiment for several reasons. First, a high background pressure would attenuate the velocity selected beam. The fact that Maxwell-Boltzmann velocity distributions for the velocity selected beams at low source pressures had been measured at background pressures mentioned before was a good indication that the background pressure was low enough because the thallium beam path was much longer than the metastable beam path and no pressure attenuation of the low velocity side of the distribution was observed. Thus pressure attenuation of both beams and distortion of their velocity distributions must be negligible during the experimental run. Secondly, due to collisions between excited atoms and background gas molecules

and atoms within the photomultiplier housing, a high background pressure generally led to a high photon background, especially in UV near 2537Å. The high photon background in our experiments was probably caused by this pressure effect. Therefore, should further experiments on such a system be performed, the fluorescence detection chamber should be housed in a differentially pumped ultra-high vacuum chamber in order to enhance the signal to noise ratio.

C. Beam Sources

1. Ovens

The molecular beam ovens used in this apparatus are of the typical design as described by Ramsey.³ Both are double-chambered ovens of stainless steel with adjustable slits on the front faces of the upper ovens. Each chamber is heated by 0.030 in. tantalum wire insulated by ceramic beads. Power is supplied by 140V variable ac powerstats. The upper chamber temperature, which can be varied independently of the lower, defines the beam temperature, while the lower chamber temperature determines the source pressure. Slit widths are adjusted to suit effusive flow conditions during velocity selector calibration runs at low source pressures although the effusive flow condition is no longer valid during experimental runs when the source pressures are much higher. In order to achieve the very high temperatures of the velocity selected beam, three to four layers of 0.001 in. of stainless steel foil are wrapped around both chambers to minimize radiative heat loss.

The mercury oven has a thimble containing mercury which fits into the bottom of the lower chamber. Sealing is achieved by a copper gasket. The velocity selector oven is filled from an opening on the

top of the lower oven and sealed with a stainless steel cap and copper gasket.

One fact worth mentioning is that the upper chamber is mounted on top of the lower oven in such a way that thermal expansion during experimental runs will not cause the center of the slit to deviate from the axis of the velocity selector, thus eliminating the problem outlined previously. Moreover, the lower chamber is purposely made much larger so that even when low density beam materials, such as lithium iodide are used, one filling will last at least eight hours at a source pressure of ~1 Torr.

Both ovens are supported by thin-walled stainless steel tubes welded to the upper chamber in the case of the mercury oven and to the lower chamber in the velocity selector oven.

Both ovens can be repositioned correctly in their mounts by means of pins welded into the supporting tube and the clamp as well as a groove cut in the clamp after initial alignment. The groove fixes the correct height and the pins determine how far the oven can turn in the supporting clamp.

2. Cold Shields, Beam Flag and Collimating Slits

The mercury oven is mounted under the liquid nitrogen trap attached to the rotating lid. The entire assembly of oven, electron gun and electromagnet is enclosed within the same copper cold shields 1/16 in. thick. The copper shields are plated with nickel to prevent corrosion by mercury vapor. It is found that such a configuration effectively eliminates the heated electron gun cathode as a major source of photon background. There is no mechanical beam flag for the metastable

mercury beam. However, the metastable atom beam can be chopped by cutting off the bombarding electron beam as will be described later.

The velocity selector oven is enclosed by double copper cold shields, one immediately surrounding the oven and the other enclosing the entire velocity selector. The oven itself is mounted above the base plate of the velocity selector which is in turn located on top of a small liquid nitrogen tank fed by stainless steel tubing from the outside. Cajon ultra high vacuum fittings with aluminum gaskets have been used successfully to give a leak proof seal both at room and liquid nitrogen temperatures. Repeated resealing entails only a change of gasket and is much more reliable than the swagelok fittings used previously. The velocity selected beam can be cut off by a magnetic beam flag mounted on the front surface of the cold shield.

The metastable beam is defined by the oven slit width and a collimating slit mounted on the photomultiplier housing. The velocity selected beam is defined by the oven slit width and a collimating slit mounted on the front of the velocity selector.

Oven temperatures are measured by chromel-alumel thermocouples inserted in wells in the oven blocks.

3. Velocity Selector

The velocity selector is of the slotted disk type developed by Bernstein⁴ and Rothe.⁵ The actual design is based on that of J. L. Kinsey¹⁰ and modified by D. D. Parrish.¹ It is driven by an IMC Magnetics Corp. BT 2910 H-1 synchronous motor. The velocity selector motor is driven by a synchronous motor driven (designed at the Lawrence Berkeley Laboratory) incorporating a Hewlett Packard 6268B DC power supply to drive the oscillator system.

Details of velocity selector design, alignment and calibration has been described elsewhere¹ and will not be repeated here. The author is indebted to David Parrish for designing the velocity selector used here. The specifications of the velocity selector are given in Table II-1

4. Electron Gun

The metastable atoms in the experiments are produced by electron bombardment utilizing an electron gun of a basic design similar to that of Lichten.⁶ It consists of a cathode, a grid, two parallel plates, a collector and a focusing electromagnet. A schematic of the electron gun is shown in Fig. II-2.

Electrons are emitted from an indirectly heated, impregnated cathode purchased from Philips Metalonics (Mount Vernon, New York) supplied with Type A impregnant which is more resistant to poisoning. The cathode itself is fabricated from porous tungsten, the pores of which have been filled with barium calcium aluminates. In order to achieve a low work function surface, the cathode surface, in its activated state, is covered by a monoatomic layer of barium which can be damaged by positive ion bombardment, oxygen, water vapor, carbon or any organic material which may break down to carbon and vapors of metals which alloy with tungsten, thus reducing the emission from the cathode gradually to zero. Type A impregnant, by evolving more barium to the surface, is therefore less susceptible to poisoning at the expense of a lower emission current. In spite of careful handling and isolation from the atmosphere when not in use the cathode performance deteriorates, requiring replacement after several experimental runs. Therefore, the most important contaminants in our case may be pump

Table II-1. Summary of characteristics of velocity selector rotor.

	Low Resolution Mode	High Resolution Mode
Number of disks	6	7
Diameter of disks		15.24 cm
Number of slits per disk		240
Radial length of slits		0.635 cm
Slit width, l_1		0.084 cm
Wall thickness between slits, l_2		
at base of slits		0.099 cm
at top of slits		0.116 cm
average value		0.107 cm
Average radius		7.302 cm
Disk thickness, d		0.160 cm
Over-all length of rotor, $L+d$	11.42 cm	22.63 cm
L	11.26 cm	22.47 cm
ϕ	0.0786 rad	0.1568 rad
γ (average)	0.146	0.073
β	0.0142	0.0071
η (average)		0.44
G	0.0524	0.0262
Velocity spread, R	0.132	0.066
η' (average)		0.38
Conversion from rotor frequency		
ν (cps) to velocity v_0 (cm/sec)		$v_0 = 897 \times \nu$

oil and mercury atoms. The cathode, spot welded onto two small pieces of tantalum, is mounted on and electrically isolated from the lower magnetic pole face by a pair of ceramic pieces.

The accelerating grid is constructed from nonmagnetic stainless steel with tungsten wires spot welded across the opening. It serves to accelerate electrons coming off the cathode and controls the magnitude of the electron current reaching the plates and collector.

Both the plates and collector are fashioned from nonmagnetic stainless steel. The almost equipotential region bound by the parallel plates marks the site where electron bombardment and excitation of the mercury beam take place. The collector serves to collect the electrons and gives a measurement of the magnitude of the electron beam crossing the mercury beam path. Various ceramic spacers keep the different components together in a predetermined configuration as well as electrically insulate each component from the others. The grid, plates, collector and ceramic spacers are suspended from two nonmagnetic stainless steel plates fixed on the sides of the lower magnetic pole via four ceramic rods, thus isolating the whole assembly from ground electrically. The physical dimensions of the electron gun are given in Table II-2.

Normally the cathode is operating such that the magnitude of the electron current emitted is space charged limited and the electromagnet, energized by a Kepco Model KQ 12-100M regulated DC power supply, produces the magnetic field that serves to confine the beam in a narrow region between the plates. Thus the electron beam approximates one flowing

Table II-2. Electron Gun Characteristics

Cathode Emitting Surface

Width	0.406 cm
Length	2.38 cm
Distance from accelerating grid	0.318 cm

Accelerating Grid

Width	0.476 cm
Length	1.59 cm
Distance from plates	0.159 cm

Plates

Distance between plates	0.476 cm
Thickness of plate	0.159 cm
Height	2.54 cm
Length	3.175 cm
Distance from collector	0.159 cm

Collector

Length	1.59 cm
Width	0.238 cm
Thickness	0.08 cm

Electron Beam

Width	2.38 cm
Thickness	0.238 cm

Table II-2. Continued

Atomic Beam	
Height	0.79 cm
Thickness	0.159 cm
Magnet	
Pole face width	3.6 cm
Pole face length	3.6 cm
Pole gap	4.4 cm
Measured field intensity	>700 gauss

between two infinite parallel plates. Calculations of potentials etc can then be made using Haeff's⁷ mathematical treatment.

The electromagnet is a C shaped piece of soft iron with enlarged pole faces above and below the electron gun giving a more homogeneous field in the region of the electron beam. The lower pole piece with its smoothly machined L shaped base is removable with the electron gun and replaced precisely in the beam path without going through the trouble of realignment. The magnetic field is estimated to be in excess of 700 gauss, a value that had been measured before the pole faces are eventually enlarged.

That the collimation of the Hg beam is not affected by having the electron gun between the oven and the collimating slit can be easily shown from the mechanics of an inelastic collision between a 14 eV. electron with a Hg atom. Since the electron gun is placed very close to the source slit, the loss of intensity by scattering out of the beam is minimal because the effect is partially compensated by scattering into the beam. Moreover, in comparison with the previous design¹ the present configuration places the mercury oven closer to the scattering center by about 50%, and should approximately double the intensity of the metastable beam at the collision zone.

Figure II-3 shows the form of the excitation function for mercury using a previously designed electron gun. However, the excitation function measured using the present electron gun is very similar in shape. The experimental curve derived from potassium surface measurements has two peaks. The one of higher intensity corresponds to the 3P_0 , 3P_2 states of mercury while the broader peak at a higher voltage is probably

due to some higher metastable state, possibly the 3D_3 state. Borst's¹² experimental data (dotted curve) for the 3P_2 state and a theoretical curve calculated from Moiseiwitsch's results¹³ (dashed curve) are also shown for comparison. We can attribute the lower energy peak to a statistical mixture of 3P_0 and 3P_2 states produced by electron bombardment because this peak disappears when a mercury surface is used in place of the potassium one by letting the mercury beam hit the detector surface for a period of time. This is to be expected because mercury has a work function of 4.53 V, thus rendering the detection efficiency for the 3P_0 and 3P_2 states negligible compared with the 3D_3 state.

In theory, the present electron gun allows separation of the 3P_0 and 3P_2 states of mercury when operated at 0.3 ma emission current. However, in order to improve the signal to noise ratio in our experiment, we were operating the electron gun at a higher current, making it impossible to separate the 3P_0 and 3P_2 states of mercury although separation from the higher metastable states was still achieved. Table II-3 shows the calculated resolution of the electron gun at different electron currents using Haeff's mathematical treatment.⁷ The calculation assumes that the magnetically focused electron beam is flowing between two parallel plates at voltage V_b under space charge conditions. Due to the space charge effect, the potential between the plates drops to a minimum at the center of the electron beam and varies linearly between the plate and the edge of the electron beam where no electrons should be present. Thus $(V_a - V_o)$ represents the energy spread of the electron beam, for the electric potential gradients in

Table II-3. Calculated electron gun resolution.

I = emission current

V_b = voltage on plate in volts

V_a = voltage on edge of electron beam in volts

V_o = voltage at center of electron beam in volts

For $I = 0.3$ ma

V_b	4	5	6	7	8	9	10	11	12
V_o	1.50	3.30	4.53	5.74	6.84	7.87	8.95	9.95	11.10
V_a	2.32	3.88	5.07	6.09	7.20	8.27	9.35	10.33	11.40

For current $I = 0.5$ ma

V_b	6	7	8	9	10	11	12	13	14	15
V_o	3.48	4.62	5.92	7.02	8.25	9.35	10.32	11.43	12.52	13.57
V_a	4.08	5.42	6.64	7.69	8.80	9.84	10.91	12.01	13.09	14.10

For $I = 1$ ma

V_b	9	10	11	12	13	14	15	16
V_o	3.83	5.75	7.26	8.40	9.75	10.91	12.0	13.20
V_a	6.08	7.25	8.52	9.60	10.70	11.9	13.02	14.08

the direction of both the atom beam flow and the electron beam flow are much smaller when we consider only the portion where the two beams intersect, i.e., the region where excitation of the mercury atoms takes place.

Voltages to the grid, collector and plates are supplied by a Lambda regulated power supply Model 28 via a voltage divider. The electron current arriving at each component can be monitored on the oscilloscope or an electrometer. Typically, the collector and plates are held at the same voltage while the grid voltage is adjusted to give the desired magnitude of current, usually between 0.4 and 1 ma. The energizing current to the electromagnetic is raised until the current flowing to the collector is at a maximum.

The electron beam is modulated to allow signal detection by frequency sensitive techniques by applying a square wave to the cathode; the negative half cycle is at ground potential while the positive half is at a potential higher than the plate voltage, typically 40 V. The frequency at which the electrons are chopped has been chosen with the following consideration. At too low a frequency, it would almost be identical to an unchopped beam and the advantages of frequency sensitive detection are largely lost. At too high a frequency, the fast excited atoms of one cycle would "catch up" with the slow excited atoms of the previous cycle at the collision zone, thus invalidating our counting technique. In our experiments, it is found that 40 cps is a reasonable choice. In addition, the frequency is low enough that there is negligible phase shift due to the time of flight of the metastable mercury atoms of approximately 10^{-5} sec. Moreover, with

the time-dependent metastable mercury signal at the detector being a square wave, the Hg^* speed distribution could be measured by time of flight technique.

D. Beam Monitors

1. Ionization Detector

A surface ionization detector is used for the detection of the velocity selected beam, which is limited to a small class of substances with low ionization potentials. In our present system, these include thallium, alkali metals and alkali halides.

In most of the experiments, a directly heated tungsten ribbon 0.002 in. thick and 0.025 in. wide is used to ionize the incident beam molecules. A Universal Electronics transistorized dc power supply provides the heating current. The ribbon is spot welded to a thin nickel plate at one end and another thin nickel plate held at an angle to the ribbon at the other end. This provides a springy support to compensate for the thermal expansion of the ribbon during operation. The author is indebted to Charlotte Sholeen for this useful design.

The ribbon is mounted within a focusing element and an accelerating grid. The focusing element is just a curved piece of wire gauze held by ceramic rods. The curved accelerating grid has an opening slit 1/16 in. wide. This helps to cut off most of the thermally emitted photons from the heated ribbon while providing an adequate entrance and exit opening for the beam molecules.

Ions coming off the hot tungsten ribbon are mass analyzed in an electromagnet where the ions of the right mass would have their trajectory bent by 90° and impinge on the dynode surface of a magnetic

electron multiplier (Model M-306, Bendix Corporation, Cincinnati, Ohio). A John Fluke Mfg Co. Inc., Model 408B high voltage DC power supply (0-6 kV, 0-20 ma) in conjunction with a voltage divider system provide the potentials for the electron multiplier, and two Lambda regulated power supplies provide the potentials for the ionization detector components.

The ion signal, amplified by the electron multiplier is fed into a Keithley electrometer Model 610BR and recorded on a chart recorder which can simultaneously record the metastable beam signal.

2. Metastable Beam Detector

The underlying principle for the metastable beam detector is the process of Auger de-excitation of excited atoms at a metal surface. Theoretically, the process can occur whenever the work function of the metal surface exceeds the excitation energy of the excited atom with the subsequent ejection of an electron from the metal surface. Hagstrum⁸ has presented a theory on Auger ejection of electrons from metal for a smooth and structureless surface.

In our experiments, the excitation energy of the lowest lying excited state of mercury involved is 4.66 eV (3P_0 state); therefore, a potassium surface with a work function of 2.24 V is used in the detector.

The detector includes a crude potassium oven which deposits potassium on a rotating stainless steel cylinder continuously. The oven is fabricated from a piece of stainless steel tubing with a 1/16 in. slit cut in the front. The tube is sealed off at both ends by swagelok-fitting caps. The source temperature is monitored by a chromel-alumel thermocouple inserted in a well in the bottom cap. During operation, it is

found that a source pressure of approximately 0.05 Torr is most suitable.

The rotating steel cylinder where the potassium surface is being formed is driven a small electric motor on top of the detector at a rate of one turn per minute. This continuous deposit of potassium is necessary to maintain an unoxidized potassium surface which is essential for metastable detection. The cylinder is electrically isolated from the motor shaft by a plexiglass sleeve which couples the two components. A nickel plated copper collector surrounds the cylinder with two openings at right angle to each other. One admits the metastable beam while the other allows the potassium beam to enter. Each opening is covered with a piece of wire gauze. During operation, the collector is biased at 45 V above ground potential both to extract the ejected electrons from the potassium surface and to prevent positive ions from entering and hitting the rotating cylinder inside. Two thin stainless steel wires are brought into contact with the stem of the rotating cylinder at one end and spot welded onto the signal lead on the other end. As the electrons are being ejected from the potassium surface a positive potential with respect to ground is built up on the rotating cylinder. This positive signal is measured by an Applied Physics Corporation Cary 31 electrometer and subsequently recorded on the second pen of the two pen chart recorder mentioned earlier.

The upper limit of the theoretical detection efficiency of this detector can be evaluated using Hagstrum's theory⁸ of Auger ejection of electron from metal surfaces. This gives a value of 0.05 for the 3P_0 state and 0.08 for the 3P_2 state of mercury. The experimental efficiency can be estimated from the number of metastable mercury atoms

arriving at the detector and the measured current output from the detector. In this calculation, a rough estimate of the excitation efficiency of the electron gun is needed. Lichten⁶ has suggested a value of 0.1% while Parrish¹ has estimated a value of 0.01%.

In any case, the detection efficiency of the present detector is much lower than the expected theoretical efficiency, possibly due to surface contamination, and the efficiency varies quite a bit from experiment to experiment, probably because of the same reason. Nevertheless, the absolute value of the signal is not too important as the time variation of the signal is what we are after.

The attenuation of the metastable beam intensity due to decay processes is considered to be negligible because the lifetimes of the two metastable states produced are assumed to be long compared to the time of flight from the electron gun to the detector. The $^3P_0 \rightarrow ^1S_0$ transition is forbidden for all types of one photon emission by the selection rule $J = 0 \nrightarrow J = 0$. Hence the 3P_0 state is estimated to have a lifetime of ~ 2.4 sec.¹¹ For the 3P_2 state, transition to the 1S_0 state is forbidden for electric dipole, electric quadrupole and magnetic dipole radiation; however, transition to the 3P_1 state is forbidden for electric dipole, but allowed for magnetic dipole and electric quadrupole. Thus the lifetime of 3P_2 state is ~ 0.1 sec if the principal mode of decay is assumed to be a magnetic dipole transition to the 3P_1 state.⁶ The velocity of the excited mercury atom at our operating oven temperatures is of the order of 2×10^4 cm/sec. Therefore, the time of flight from the electron gun to the detector would be of the order of 10^{-3} sec. Using the above argument, we can safely assume that

attenuation by decay processes is indeed quite negligible.

E. Photon Detection System

The present system is basically the same as the one presented previously.¹ The only changes made being the pulse amplifiers and discriminators. Thus only an outline would be given here.

The EML-9558 QB photomultiplier tube is placed beneath a tubular housing which contains three focusing quartz lenses, a mirror, a diaphragm and the mount for an interference filter immediately above the photomultiplier window. The tubular photomultiplier housing is mounted directly beneath the rotating lid. The filter has to be kept around room temperature to prevent an undesirable shift of the wavelength transmitted during the experiment. The photomultiplier itself is shielded from external magnetic fields by both mu metal and soft iron shields. During an experiment, the two metallic beams crossed at the center of the photomultiplier housing which also formed the focal point of the first set of quartz lenses below it and the center of curvature of the mirror above it. The mirror served to increase the collection efficiency by reflecting the emitted light towards the lens system. The first set of quartz lenses focused the light onto the plane of a diaphragm $3/8$ in. in diameter. A second quartz lens, with its focal point in the plane of the diaphragm, then rendered the light rays parallel before they went through the interference filter. The optics of the first set of lens gave a 1:1 object to image size ratio; therefore, the light collection area would be a $3/8$ in. diameter circle at the center of the photomultiplier housing.

The electronics of the photon counting system is summarized in Fig. II-4. The pulses from the photomultiplier are amplified by two pulse amplifiers (Model 4×906Z, 10-03NS) in series. The pulses are then fed into a 100 Mc interface discriminator (18×120 1P2) which eliminates pulses below a certain height and renders the larger pulses a uniform shape and height for the counter.

The fact that the electron beam can be chopped by a square wave described previously presents a means for frequency sensitive detection. The transistor Specialties Inc., Model 1535 Dual Channel 100 Megacycle pulse counter can have each of its channels separately gated by a Berkeley Nucleonics Co., Model CT-1, Del-A-Gate delay and gate generator.

During an experiment, the square wave frequency is fixed at 40 Hz. The negative going leg of the square wave triggers one Del-A-Gate while the positive going leg triggers the other. The corresponding channels on the counter are then triggered to count for 10 milliseconds after a 2 millisecond delay to allow the excited mercury atom to reach the scattering center. Thus one channel would be counting the background plus fluorescence signal while the other would be counting just the background. The gate periods on both channels are set to within 0.1% between them. The counting period is set by a stop watch and the counts recorded by hand.

The photon background depends on both the metastable beam intensity and the thermal background inside the chamber. Dependence on the metastable beam intensity is due to the mercury fluorescence produced on collisions of excited mercury and background gas molecules. It dominates the photon background when a short wavelength interference

filter (near UV to UV) is used. On the other hand, the thermal background predominates when a longer wavelength filter (e.g., $>6000\text{\AA}$) is used. Therefore, depending on the filter in use, the photon background varies from 40 photons/sec to 3000 photons/sec in our experiments. Judging from the fluctuations in the photon background, the present system is capable of detecting signals as low as 3 to 11 photons per sec for a 50 sec counting period.

F. Ion Detector

Attempts has been made to detect ions resulting from Penning and associative ionization of an alkali metal by excited mercury atoms. The alkali metals used were sodium, potassium and cesium. In these experiments, an ion collector replaced the photomultiplier housing. Unfortunately, though such processes has been reported⁹ with thermal beams, we have not been able to extract a signal from the background noise. Despite the simple design of the ion collector, it should be able to collect over 90% of the ions formed in the collision zone. Therefore, the most probable reasons for our failure lie in the small cross section for ion production and the reduction of beam intensities by the use of a velocity selector. Nevertheless, a brief description of the ion detector will be given below.

The detector consists of a steel tube with entrance and exit ports for both the metastable and velocity-selected beams. Wire gauzes are spot-welded onto each of the openings. The tube itself is isolated electrically from its mounting clamp and hence, from ground potential by a plexiglass cap. This allows the tube to be biased at a positive potential to exclude positive ions from the outside. Inside

the tube and immediately below the scattering center is a platinum grid biased at a high negative potential (typically 700 to 1000 V) to accelerate ions produced in the collision zone to a Bendix Spiraltron electron multiplier mounted at the bottom of the steel tube. The typical acceleration field for ion collection varies from 150 volts/cm to 200 volts/cm. Potential to the accelerating grid is provided by a John Fluke Co. 412B high voltage power supply (0-2000 V), while potential to the spiraltron is provided by a John Fluke Co. Model 408B high voltage power supply (0-6000 V) via a voltage divider placed inside the chamber. Output pulses from the electron multiplier are fed into the counting system described in the previous system.

Initial attempts at detection were plagued by a large number of counts dependent on the electron gun current but not on the alkali beam. The speculation that electrons are accelerated into the ion collector region with subsequent ionization of molecules and atoms inside the tube led to our biasing the electron gun assembly at a more positive potential than that of the ion collector tube. This led to another problem resulting probably from the acceleration of positive ions evaporated from the electron gun cathode into the ion collector tube. Eventually, the voltage bias on both assemblies are adjusted until a compromise situation is reached and the background counts corresponding to the electron gun is at a minimum. Typically, this seems to occur when the electron gun assembly is biased approximately 10 V above the ion collector tube which in turn is biased at 90V above ground potential.

The typical ion background is from 30 to 60 ions/sec. Using a 100 sec counting period and assuming a Poisson distribution, we should be able to detect ion signals larger than one or two counts per sec. Hence, we may conclude that in our present experiments, the rate of ion production at the collision zone is less than that. Knowing the rate of photon production for sensitized fluorescence of $\text{Hg}^* + \text{Tl}$, we have estimated that the ratio of the cross sections for ion production to that of photon production must be less than 0.1. Since sodium can only be ionized by the $^3\text{P}_2$ state of mercury while potassium and cesium can be ionized by both the $^3\text{P}_0$ and $^3\text{P}_2$ states at zero translational energy the cross section for ion production in the latter cases may include contributions from both mercury states.

In summary, the ion detector probably needs a better electrostatic focussing system that can exclude ions produced outside the collision zone and possibly a simple mass spectrometer that can select the product ions with the right masses.

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FIGURE CAPTIONS

- Fig. II-1. Diagram of the apparatus as viewed from above. The beams effuse from double chamber ovens and cross at 90° at the scattering center. The entire surface ionization detector assembly (ionizing filament, ion optics, analyzing magnet, electron multiplier, and electrical shield) may be scanned in the horizontal direction in order to center the filament in the velocity selected beam profile.
- Fig. II-2. Schematic of the electron gun. The electron beam is emitted from the cathode, passes through the accelerating grid, and enters the region between the two plates where it interacts with the atomic beam. Finally, it is collected at the collector above the plates. Ceramic pieces (not shown here) electrically insulate the electron gun components from each other and from ground. A magnetic field, indicated by H , is parallel to the electron flow and serves to confine the beam between the plates.
- Fig. II-3. Excitation functions of mercury. The solid curves are the experimental curves measured in our laboratory. The abscissa is the voltage of the electron gun plate with respect to the cathode; it was calibrated by requiring the peak in the potassium surface curve to coincide with the peak in the curve calculated from Borst's experimental data. The two broken curves were derived by integrating the data from the two indicated references over the calculated space charge potential in the electron gun used in most of the T1 experiments. The mathematical treatment to derive the space charge potential is given in Ref. 7.

Fig. II-4. Schematic diagram of the electronic components of the counting system.

XBL 7311-6632

Fig. II-1.

XBL 706-1277

Fig. II-2.

XBL 709-6555

Fig. II-3.

XBL 706-1278

Fig. II-4.

III. VELOCITY DEPENDENCE OF SENSITIZED FLUORESCENCE OF THE SYSTEM $\text{Hg}^* + \text{Tl}$

A. Introduction

The phenomenon of "sensitized fluorescence" was first predicted by Franck in 1922,¹ and Cario and Franck were the first ones to study the $\text{Hg}^* + \text{Tl}$ system experimentally.² In their experiments, a mixture of mercury and thallium vapors was irradiated with light from a mercury lamp. It was found that the fluorescent light contained not only the mercury resonance line $2537\text{\AA}$, but also several thallium lines. Subsequently, the $\text{Hg}^* + \text{Tl}$ system and sensitized fluorescence in general has been studied by many groups. Other studies involving the $\text{Hg}^* + \text{Tl}$ system are given in Refs. 3 to 17.

Several selection rules have been quoted to predict the relative intensities of the different lines excited in sensitized fluorescence by Winans.¹⁸ These stated that (1) in a mixture of two monatomic gases, A and B, if the excited state of B is lower than that of A, the donor atom, then the intensity of the fluorescence from B would be much greater than when the reverse is true; (2) the intensity of fluorescence of B depended on the energy discrepancy between the excited atoms A and B, the intensity being greater for a smaller energy discrepancy; (3) the intensities of lines in sensitized fluorescence followed the Wigner spin rule which stated that the states with the greatest probability of excitation are those for which $\vec{L}\vec{S}$ is invariant for the collision, in the case of weak spin orbit coupling (in mercury, the spin-orbit coupling is strong, and the cross section for sensitized fluorescence in which the change in $\vec{L}\vec{S}$ is nonzero is not small); (4) the states with

the greatest probability of excitation are those for which ΣJ is invariant for the collision. These rules were being confirmed by early experimenters. For example, experiments with apparatus similar to that of Franck were carried out for mixtures of mercury vapor with vapors of Cd, Pb, Ni, Ag, Na, Zn and Bi²⁷ and provided valuable information for the formulation of the rules. Beutler and Josephy's²⁶ experiments with sodium and mercury served to confirm the second rule. Winans¹⁸ also performed experiments with mercury vapor and vapors of Pb, Cu, Tl and Cr which led to his statement of the fourth rule.

Among the later experimenters working on the $Hg^* + Tl$ system were R. H. McFarland, B. Curnutte, Jr. and E. K. Kraulinya. All these experiments were done with basically the same experimental setup with different refinements and variations. The heart of the system consisted of a fluorescence cell with side arms for the metal vapor sources, i.e., mercury and thallium for the $Hg^* + Tl$ system. The temperatures of the fluorescence cell and both side arms were maintained independent of each other, with the fluorescence cell being kept at the highest temperature. Theoretically, the temperatures of the side arms controlled the vapor pressures of the metal vapors and the fluorescence cell temperature determined the kinetic energy of the collision species. However, in practice, Kraulinya found that variation of the fluorescence cell temperature did have an effect on the number density of thallium atoms in the cell. The mercury atoms were excited to the 6^3P_1 state by a 2537Å line light source and the resulting thallium fluorescence was detected by a photomultiplier at right angles to the exciting light beam. McFarland^{8,9} obtained relative collision cross sections for

excitation of different thallium lines with and without the addition of foreign gases like argon and helium. He explained his results by citing the role of the foreign gases in regulating the number densities of $\text{Hg}(6^3\text{P}_1)$, $\text{Hg}(6^3\text{P}_0)$ and excited mercury molecules $\text{Hg}_2(^3\text{O}_u^-)$ in the collision zone which he believed were the mercury states responsible for the excitation of thallium levels. B. C. Hudson and B. Curnutte, Jr. experimentally determined the de-excitation cross section of the mercury 6^3P_1 state by thallium and the excitation transfer cross section from the mercury 6^3P_1 and 6^3P_0 states to different thallium states. In particular, they found that for the thallium $7^2\text{P}_{3/2,1/2}$ states, which radiate to the lower states through the $7^2\text{S}_{1/2}$ state (5350Å for $7^2\text{S}_{1/2}$ to $6^2\text{P}_{3/2}$ and 3776Å for $7^2\text{S}_{1/2}$ to $6^2\text{P}_{1/2}$, the ground state of thallium), the excitation transfer cross section increased from $17.6 \pm 6.0 \text{Å}^2$ to $23.3 \pm 7.2 \text{Å}^2$ when the temperature of the thallium side arm was raised from 800°C to 900°C. This was explained in terms of the increased number density of thallium atoms which also served to reduce the rate of loss of metastable (6^3P_0) mercury atoms to the walls by reducing the mean free path of the mercury atoms. The research group of E. K. Kraulinia (Refs. 14-17 and 28) has done the most extensive study on the $\text{Hg}^* + \text{Tl}$ system. They measured the absolute cross sections for excitation of 11 thallium lines at thallium side arm temperatures from 437°C to 800°C. Their values for the thallium 5350Å line, after accounting for hyperfine structures, indicated an increase from 25Å^2 to 150Å^2 within the temperature range mentioned above. This was by far the most intense line observed, with an excitation cross section from 5 to over 100 times

larger than those of the other lines. The next in line were those lines coming from the thallium $6^2D_{5/2,3/2}$ levels which should not contribute very much to the population of the $7^2S_{1/2}$ level from which the 5350Å line originated. Since the $7^2S_{1/2}$ level is 1.6 eV below the mercury 6^3P_1 level, the cross section for direct excitation of this level should not be very large according to the selection rules listed before. Thus it is quite likely that the $7^2S_{1/2}$ level is populated to a large extent by cascade transitions from upper levels populated by direct excitation. However, the very small excitation cross sections for the lines originating from those levels which should be mostly responsible for populating the $7^2S_{1/2}$ level did not seem to support that idea. Kraulinya had suggested that the mercury $6^3P_{0,1}$ states as well as some molecular states were taking part in the excitation process, and that not only ground state thallium atoms, but also some thallium atoms in the metastable $6^2P_{3/2}$ state were excited by the mercury atoms. Thus the results from all these bulb experiments, being plagued by all the uncertainties pertaining to that technique as mentioned in Chapter I, did not present a very clear picture of the process of sensitized fluorescence. The present experiments, employing crossed molecular beams of excited mercury atoms and velocity selected thallium atoms and a sophisticated photon detection system, is designed to complement the results of the bulb experiments. Moreover, in the previous experiments, the excited mercury state was either the 6^3P_1 state or the 6^3P_0 state produced by collision with foreign gases or thallium atoms in an intramultiplet conversion. The exact role in the excitation of thallium fluorescence played by the mercury 6^3P_0 state is not clear

and nothing is known as to whether the 6^3P_2 state will also excite thallium fluorescence if present in the collision zone. The present experiments, in working with the 6^3P_0 and 6^3P_2 states of mercury which are produced in a 1:5 statistical ratio, will help to answer that question in part. The advantages as well as shortcomings of this technique were already discussed in the opening chapter and will not be repeated here.

Figure III-1 represents an energy level diagram for thallium. All of the thallium levels involving excitation of the othermost p electron are shown together with the emission lines that have been detected in previous studies of the $Hg^* + Tl$ sensitized fluorescence system. The two metastable states of mercury taking part in the energy transfer in our experiments are also indicated. The mercury 6^3P_1 state, with an excitation energy of 4.86 eV, has not been shown. Because of its short life time, any 6^3P_1 mercury atom produced by electron bombardment would have radiated to the ground state before reaching the collision zone; therefore, the mercury 6^3P_1 state did not take part in exciting thallium atoms in the collision zone. Although 6^3P_1 mercury atoms may be produced by collisions of 6^3P_2 mercury atoms with thallium atoms in the collision zone, they would have passed out of the collision zone before a second collision can take place under our experimental conditions.

B. Experimental Conditions

The apparatus for this study has already been described in detail in the previous chapter, so it is sufficient just to describe the general procedure followed in the course of an experiment.

After the vacuum chamber was cooled and pumped down to a low enough pressure generally in the range of 7×10^{-7} Torr, the two metallic beams were prepared in their respective double-chambered ovens by indirect heating with tantalum wires, care being taken that the upper ovens were always maintained at a higher temperature than the lower ovens. This was done to prevent condensation of beam material in the upper chambers. The temperatures of all four chambers were checked and recorded periodically throughout the experiment. The velocity selector was kept in motion before the thallium ovens heater elements were turned on to ensure that no local clogging of the slots of the disks of the selector would occur. At the same time, the electron gun cathode would be activated by maintaining it at approximately 1100°C for several hours until the emission current had reached a maximum value. After the activation procedure, the cathode temperature was maintained at a value that would give the required emission current which in these experiments was set at 0.3 mamps.* It is not necessary to measure the cathode temperature every time because a calibration chart of cathode temperature against heater current was experimentally determined when the cathodes were first purchased. Since we have been using the same type of cathode

* The electron gun used in the $\text{Hg}^* + \text{Tl}$ experiments was that described in Ref. 22. The electron gun described in Chapter II was used in $\text{Hg}^* + \text{alkali halide}$ experiments described in a later chapter.

throughout these experiments, we could set the heater current corresponding to the correct temperature by referring to the calibration chart. During the electron gun operation, the focusing magnet current was kept at 100 amps, corresponding to a field in excess of 700 gauss. The electron gun current could be adjusted by changing the accelerating grid voltage. In our experience, the life of the cathode could be lengthened if we cooled the vacuum chamber before the diffusion pumps were switched on. This would help to prevent most of the pump oil from attacking the cathode by trapping it on the cooled copper cold shields.

Before the thallium ovens were warmed up to their normal operating temperature during an experimental run, the ionization detector would be cleaned by heating and then positioned at the center of the beam profile. Then a velocity distribution of the thallium beam at very low source pressures was measured. The data was later used for the calibration of the velocity selector. Meanwhile, the metastable detector was readied by allowing the surface of the rotating cylinder to be evenly covered with potassium from the potassium oven. As the sensitivity of the metastable detector became stabilized, the plate and collector voltages of the electron gun were adjusted to the peak of the excitation function corresponding to the mercury 6^3P_0 and 6^3P_2 states. The two channels on the scalar were then set for equal periods with the proper delays as described in the previous chapter. The slight drift in the delay periods during the course of an experiment were not too serious, but the counting periods on the two channels must be kept equal (to within 0.1%) so that we could assert that the small differences in counting rates between the two channels were due to positive photon signals rather

than an inequality of the counting periods. Therefore, the counting periods were checked and corrected periodically throughout the experimental run.

When an experiment was in progress, the photon counts were recorded by hand while the 2-pen chart recorder simultaneously recorded both the metastable beam flux and the velocity selected beam flux. For a typical background counting rate of 400 to 500 counts/sec and a photon counting rate of 30 counts/sec or less in these experiments, we have adopted a counting period of 100 sec. At the start of the experiment, a set of ten to fifteen evenly spaced thallium velocity settings were chosen. At each velocity setting, the rotational frequency of the rotor, the beam fluxes and the photon counts were recorded. The series of velocity settings were then gone through several times at random, the same data being recorded at each setting. Periodically during a scan of the velocities, a counting period was completed with the thallium beam blocked by the magnetic beam flag. These beam flag runs were later used to estimate the time variation of the background counting rate in the data analysis.

Throughout the different velocity scans, the interference filter was kept around room temperature by insulated heating wires around the photomultiplier housing. However, if the filter was allowed to cool down slowly, the photon signal gradually dropped to zero although the beam fluxes were maintained constant. Since the central wavelength of the filter is a function of temperature, (in the case of a $5350\text{\AA}$ filter, there is a shift of $0.2\text{\AA}$ for each 1°C change in temperature) we have effectively proved that the photon emission observed in our experiment

is due to line emission (this has been done for the 5350Å line only) and not a continuous emission.

A separate experiment was performed in which the thallium velocity setting was fixed, but the plate and collector voltages of the electron gun were varied. The purpose of this experiment was to determine whether the metastable mercury states higher than the 6^3P_2 state were responsible for exciting the thallium levels. (These higher states are responsible for the 10 V peak in the excitation function of mercury shown in Chapter II. However, the threshold for their production is lower and may be produced along with the 6^3P_2 state.) If they were, then, the cross section for excitation should continue to rise after the electron gun voltages were raised above the peak of the mercury excitation function corresponding to 6^3P_0 and 6^3P_2 production as more and more of the higher metastable states were produced by electron bombardment. The result of the experiment for excitation of the thallium 5350Å line fluorescence was tabulated in Table III-1. It was found that, within experimental error, at voltages lower or higher than the peak of the excitation function for $6^3P_{0,2}$ production, the calculated relative cross sections were lower. This certainly served to show that only the 6^2P_0 and 6^3P_2 states of mercury were responsible for the excitation of the thallium 5350Å line fluorescence observed in our experiments. Although the 6^3P_1 state would also be produced by electron bombardment at the same time, its short life time of 10^{-7} sec precluded that produced by electron bombardment from taking any part in the energy transfer process at the collision zone for it would have radiated to the ground state long before reaching there. However, there existed the possibility of

Table III-1. Effects of electron gun voltage variation on the relative cross sections.

Electron Gun Voltage	Relative Cross Section (arbitrary units)	Relative Velocity
4 volts	0.332 ± 0.057	4.5×10^4 cm/sec
6 volts	0.419 ± 0.051	4.5×10^4 cm/sec
8 volts	0.056 ± 0.093	4.5×10^4 cm/sec

mercury atoms in the collision zone being excited by photons emitted by 6^3P_1 mercury atoms in the electron bombardment region; therefore, an experiment was performed to measure mercury 2537Å fluorescence in the collision zone as a function of the time of flight from the electron bombardment region to the collision zone. If the emission of 2537Å line fluorescence was due to 6^3P_1 mercury atoms produced in the manner referred to above, the emission would be almost instantaneous. Our measurements did not support this. Instead the results indicated that the fluorescence was mainly due to 6^3P_1 atoms produced by collisions of 6^3P_2 mercury atoms and background gas molecules. A plot of fluorescence intensity against time was reminiscent of the velocity distribution of excited mercury atoms. Thus we may conclude that the mercury 6^3P_1 state does not play a role in the excitation of thallium line fluorescence in our experiments.

Perhaps here is the place to discuss the possibility of species other than thallium atoms and mercury atoms taking part in the collisions. The excited Hg_2 dimer has often been mentioned^{8,16} as a possible contributor to the excitation of thallium fluorescence in bulb experiments. The dimer itself has a dissociation energy of 0.06 eV.¹⁹ Its other molecular constants are listed in the same reference. The bonding is so weak that its percentage composition in a molecular beam of mercury atoms has not been measured. Thus we can only estimate its percentage composition at our operating beam temperature using statistical mechanics. It turned out that the Hg_2 dimer would constitute only about $10^{-6}\%$ of the mercury beam, a totally negligible factor in the process studied. The thallium dimer Tl_2 , with a dissociation energy of 0.6 eV,²⁰

is better known. Miller and Kusch²¹ has claimed that at a source pressure of 4×10^{-2} Torr, the dimer Tl_2 constituted less than 0.05% of their thallium beam composition. Using these values and correcting for the temperature variation of the equilibrium beam composition, we have found that the dimer constitutes less than 0.2% of the beam composition at our operating beam temperature. Even at the lowest thallium velocity setting where the dimer composition should be most significant, the dimer constitutes less than 0.35% of the beam composition. Moreover, if the thallium dimer were contributing significantly to the line emission, it would be quite hard to explain the much higher counting rates at the higher velocities where the dimer concentration is negligible and the monomer concentration is at a maximum. Therefore, we can conclude that the most important process giving rise to the thallium fluorescence is the electronic energy transfer between mercury $6^3P_{0,2}$ atoms and ground state thallium atoms.

C. Data Analysis

The number of photons N emitted per unit time in the collision zone can be represented by the following expression.

$$N = V \iint n_{Tl} n_{Hg} Q_{eff}(g) g P(v_{Tl}) P(v_{Hg}) dv_{Tl} dv_{Hg} \quad (1)$$

where

n_{Tl} , n_{Hg} = number density of Tl , Hg^* atoms in the collision zone of volume V .

v_{Tl} , v_{Hg} = velocity of Tl , Hg^* atoms.

$$g = \text{initial relative velocity} = (v_{Tl}^2 + v_{Hg}^2)^{1/2}$$

$P(v_{Tl}), P(v_{Hg})$ = normalized number density probability density speed distributions of the Tl, Hg* atoms in the collision zone.

$Q_{eff}(g)$ = effective total cross section for excitation of fluorescence from the observed level either by direct excitation or by exciting higher levels that can populate the observed level by cascade transitions.

In our data analysis, we have not attempted to deconvolute $Q_{eff}(g)$ from the thallium and Hg* velocity distributions directly. Instead, a two-step indirect procedure was employed. First, the most probable beam velocities (the most probable Hg* velocity is calculated by $\sqrt{kT_{Hg}/M_{Hg}}$ i.e., the most probable Hg source velocity divided by $\sqrt{2}$. The most probable thallium velocity is that transmitted by the velocity selector) were assigned to both beams in order to extract an approximate effective cross section $Q'_{eff}(g)$ as a function of relative velocity. Secondly, different curves representing the possible velocity dependence of $Q_{eff}(g)$ were averaged over the thallium and Hg* velocity distributions $P(v_{Tl})$ and $P(v_{Hg})$ to reproduce the approximate experimental curve of $Q'_{eff}(g)$ vs g obtained in the first step. The first step has already been discussed in detail in Ref. 22, but will be summarized here for the sake of clarity. The second step and the calculation involving the experimental velocity distributions will be discussed in much greater detail in the following sections.

1. Extraction of an Approximate Curve of
 $Q'_{eff}(g)$ vs g

No attempts have been made in the present study to estimate the absolute cross section for the process, hence we have not tried to determine the detection efficiencies of the beam monitors and the photon detection system experimentally. As a result, only relative cross sections will be reported.

The raw data collected in the experiments were the photon counting rate $S_{h\nu}$, the metastable beam flux S_{Hg} and the thallium beam flux S_{Tl} . If we assigned the most probable Hg^* velocity to the metastable beam and assumed a delta transmission function for the velocity selector, we could evaluate the number densities of thallium and Hg^* atoms at the collision zone to within a constant. (The constant involves detector efficiencies and correction for distances from beam sources to the collision zone instead of to the detectors.) The relationship between beam flux and number density is characterized by:

$$n_{Hg} \propto \frac{S_{Hg}}{\alpha_{Hg}} (\sqrt{2})$$

$$n_{Tl} \propto \frac{S_{Tl}}{v_o}$$

where α_{Hg} = most probable Hg source velocity = $\sqrt{\frac{2kT_{Hg}}{M_{Hg}}}$

T_{Hg} = temperature of mercury upper oven

M_{Hg} = weight of mercury atom

v_o = most probable Tl velocity transmitted by the velocity selector.

The determination of v_o from the rotor frequency will be discussed later. Again assuming monoenergetic beams, the integration through velocities in Eq. (1) will give:

$$N = v n_{Tl} n_{Hg} Q'_{eff}(g) g \quad (2)$$

The photon counting rate $S_{h\nu}$ is proportional to N , therefore, by substitution of S_{Tl} and S_{Hg} for the number densities, we will arrive at the relationship:

$$Q'_{eff}(g) = \frac{S_{h\nu} C}{\left(\frac{S_{Hg}}{\alpha_{Hg}}\right) \left(\frac{S_{Tl}}{v_o}\right) g (\sqrt{2})} \quad (3)$$

where C = proportionality constant representing V , the detection efficiencies and other factors independent of g

$$g = \left(\frac{\alpha_{Hg}^2}{2} + v_o^2 \right)^{1/2}$$

The next problem involves converting the counts recorded from the two scalar channels A and B into the photon counting rate $S_{h\nu}$ (in units of counts/100 sec). Counts on channel A were recorded when the metastable beam was in the "on" cycle of the square wave and thus represented the thallium fluorescence signal, background due to mercury fluorescence and the background due to thermal noise inside the chamber. Counts of channel B were recorded during the "off" cycle of the metastable beam and therefore represented only the background due to thermal noise. For the thallium 5350Å line, the background counts due to mercury fluorescence getting through the interference filter was negligible and during "beam flag" runs in which the thallium beam was blocked, the counts on both channels were almost equal within statistical fluctuations.

However, when a shorter wavelength filter was used (e.g., 2918Å or 2826Å), the mercury fluorescence background became large enough to make the counts on channel A significantly larger than those on channel B during a "beam flag" run. Thus it became necessary to estimate the time variation of this Hg^* dependent background by subtracting the counts on channel B from the counts on channel A when the thallium beam was blocked and dividing the difference by the metastable signal. Since these beam flag runs were taken periodically throughout the experiment, we would have a series of such data points spread out in time. The data points were then fitted to a straight line or a Legendre Polynomial function as a function of time. Then $Bkgd(t)$, the Hg^* dependent background could be estimated by multiplying the Hg^* signal at time t by the value of the fitting function at time t . The photon counting rate was then calculated by subtracting $Bkgd(t)$ from the difference between the counts on channels A and B at time t , the time when that particular photon counting rate was recorded. This can be represented by the equation:

$$S_{hv} = [(NA - NB) 100/TN - Bkgd(t)] \quad (4)$$

where NA, NB = counts recorded on channels A and B

TN = counting period in sec

By substituting for S_{hv} in Eq. (3), rearranging terms and setting the relative cross section $Q'_{rel}(g)$ equal to $Q'_{eff}(g)/C$, we have arrived at an equation for calculating the initial values of $Q'_{rel}(g)$.

$$Q'_{rel}(g) = [(NA - NB) 100/TN - Bkgd(t)] \quad (5)$$

$$\left(\frac{1}{v_o} + \frac{2}{\alpha_{Hg}}\right)^{-1/2} (S_{Hg} S_{Tl})^{-1}$$

The next step is to time normalize the relative cross sections obtained above. The need for time normalization arises because during the course of the experiment, the detection efficiency of the beam monitors and photon detection system could change, and the relative cross section for a given velocity setting might change by a factor of 3 or 4 during the experiment even though the beam fluxes were monitored. One of the ways to correct for this is described below. The procedure used here utilizes all the data points by fitting "reduced" relative cross sections to a Legendre polynomial expansion in time. The "reduced" relative cross section for a given velocity setting is calculated by dividing the relative cross section calculated for that velocity by the average relative cross section of the same velocity for that particular experiment. After normalization, a new set of relative cross sections can be calculated from the time-normalized "reduced" cross sections. This procedure is repeated until a satisfactory fit which will not blot out the natural scatter of the data points is obtained. The final form of the curve of $Q'_{rel}(g)$ vs g is the approximate curve mentioned in the beginning of this section. The theoretical standard deviations are calculated by error propagation and the experimental standard deviations are calculated from the actual scatter of the final data points from the mean value. The standard deviations calculated in

both ways agree with each other, indicating that we have not over-corrected our results in the time normalization procedure. All the above calculations were being incorporated into a computer program for analysing the thallium data. Some of the limitations of this program will be discussed in the next chapter.

2. Velocity Selector Calibration and Beam Velocity Distributions

There is a definite relationship relating the rotational frequency of the rotor to the actual velocity of beam particles transmitted through the rotor. The derivation of that relationship for a perfectly aligned beam has already been dealt with in Ref. 23. However, in real life, this is not always possible. When an optical alignment procedure is relied upon, we can only align the beam axis with the rotor axis to within the thickness of the cross hairs of the cathotometer, i.e., to within 0.001 in. or so. If account is taken of the error that can be introduced when the thallium oven is repositioned in its mount without realignment, the accuracy of the alignment is probably only within a few thousandth of an inch. Misalignment will shift the peak of the transmitted velocity and affect the transmission function of the rotor. The effect on the latter will be discussed in the next section. For a beam misaligned by an angle α , i.e., when the beam axis deviates from the rotor axis by an angle α , the most probable velocity v_0 transmitted is:

is:²²

$$v_0 = \left[\frac{2\pi L}{\phi} \left(1 + \frac{L\alpha}{\phi r} \right)^{-1} \right] v \quad (6)$$

where ν = rotational frequency of the rotor

L = length of the rotor

r = disk radius

ϕ = angle through which the rotor disk turns while a molecule with velocity v_0 travels the length L .

In this equation, the small angle approximation is used. The quantities inside the square brackets represent the conversion factor R_0 . The purpose of the calibration procedure is to evaluate R_0 . The method hinges on obtaining a Maxwell-Boltzmann flux distribution at very low source pressures for the thallium beam at the beginning of the experiment. One can then match the peak of the experimental flux distribution curve with that of a theoretical one. Reference 22 has presented a procedure by which this can be done. The procedure resorted to here utilizes all the data points collected in the velocity measurements and is described below. Both procedures give almost identical values of R_0 within experimental errors.

For a molecular beam at very low source pressures, the flux distribution $I(\nu)$ is Maxwell-Boltzmann, i.e.,

$$I(\nu) \propto \nu^3 \exp[-(\nu/\alpha_{Tl})^2]$$

where α_{Tl} = most probable source velocity of thallium. However, when a slotted disk velocity selector is used, the transmission of the rotor $T(\nu_0)$ is determined by both the flux distribution of the beam $I(\nu)$ and the effective slitwidth or admittance of the selector $B(\nu, \nu)$ for different velocities. If one assumes a homogeneous distribution within the small velocity range admitted for a given rotor frequency ν ,

then $I(v)$ can be replaced by $I(v_0)$. It can be shown²³ that the following equation for the transmission of the rotor can be obtained.

$$T(v_0) = G v_0^4 \exp[-(v_0/\alpha_{T1})^2] \quad (7)$$

where G = a proportionality factor involving the geometry of the rotor and integration constants independent of velocity. The extra velocity factor v_0 arises from the fact that the transmission of the rotor is itself proportional to the velocity of the transmitted particle. Thus the percentage resolution of the velocity selector is not a function of v_0 . In terms of the rotor frequency ν Eq. (7) becomes:

$$T(v_0) = G(R_0 \nu)^4 \exp[-(R_0 \nu/\alpha_{T1})^2] \quad (8)$$

By rearranging terms and taking the natural logarithms on both sides, Eq. (8) becomes:

$$\ln\left(\frac{T(v_0)}{\nu^4}\right) = \ln(GR_0^4) - R_0^2\left(\frac{\nu}{\alpha_{T1}}\right)^2 \quad (9)$$

This is the equation for a straight line characterized by the form $y = a + bx$; therefore, if $\ln\left(\frac{T(v_0)}{\nu^4}\right)$ is plotted against $(\nu/\alpha_{T1})^2$, a straight line should result with the slope equal to $(-R_0^2)$. Thus, whenever a Maxwell-Boltzmann flux distribution is applicable, this procedure can provide a simple way of obtaining R_0 . The value of R_0 obtained deviates from the theoretical value for perfect alignment by less than 5% in most cases. In the event that a Maxwell-Boltzmann flux distribution is not obtained in the calibration run, an approximate procedure²² using a flux distribution predicted by the Laval nozzle theory is employed, or

the misalignment angle α can be estimated from the deviation of the center of the beam profile from the position for perfect alignment, and R_0 is then calculated using Eq. (6).

During the actual experimental run, the source pressure is usually so high that the velocity distribution differs appreciably from that predicted by the Maxwell-Boltzmann distribution. In order to obtain an algebraic expression that can adequately describe the shape of the distribution for calculations in the deconvolution procedure, we have adopted an empirical formula²⁴ which probably has no theoretical basis and is only useful when we already know the value of R_0 . Moreover, it should be emphasized here that the actual form of the distribution function has little effect on the deconvolution as will be evident from the results later. In this empirical formula, Eq. (7) becomes:

$$T(v_0) = G(v_0 - aR_0)^2 v_0^2 \exp[-(v_0 - aR_0)^2 / (b\alpha_{T1})^2] \quad (10)$$

Hence, Eq. (9) becomes

$$\ln\left(\frac{T(v_0)}{(v-a)^2 v^2}\right) = \ln(GR_0^4) - R_0^2 \left(\frac{v-a}{b\alpha_{T1}}\right)^2 \quad (11)$$

where a and b are the parameters that can be varied such that for a known value of R_0 , the best straight line fit is obtained. The resulting empirical expression for the transmission function is then used in the deconvolution computer program.

The flux distribution of unexcited mercury atoms emerging from the upper oven may be close to that predicted by a Maxwell-Boltzmann distribution, but flux distribution of the excited mercury atoms arriving

at the collision zone is very different. The number of metastable mercury atoms constitutes only 0.01% to 0.1% of the beam composition (see Chapter II) after excitation by electron bombardment. Since the efficiency of excitation is far below the saturation level where very mercury atom is excited, the longer an atom stays in the electron bombardment region, the greater the probability that it will be excited i.e., the probability of excitation is inversely proportional to the velocity of the atom. Thus, the metastable mercury velocity distribution should show an enhanced intensity on the low velocity side. Therefore, for the reason stated before, it was decided to adopt the following flux distribution for the metastable mercury atoms in the deconvolution program.

$$I(v_{\text{Hg}}) \propto v_{\text{Hg}}^2 \exp[-(v_{\text{Hg}}/\alpha_{\text{Hg}})^2]$$

3. Transmission Function of the Velocity Selector For a Misaligned, Divergent Beam

The flux of particles with velocity v that passes through a velocity selector is the product of the flux distribution of the parent beam and the admittance of the selector to that velocity. The first term has been dealt with in the previous section. The admittance of the selector will be described here.

The admittance of the selector $B(v, \nu, \alpha)$ is a function of the velocity, the rotor frequency ν as well as the angle of misalignment α . Bernstein²³ has derived equations for the admittance of a slotted disk selector from the geometry of the rotor for a perfectly aligned, non-divergent beam. Gillen²⁵ has further generalized the equations to describe the

$B(v, \nu, \alpha)$ function for a misaligned, non-divergent beam. In the case of a misaligned, divergent beam, the situation is further complicated by the resulting distribution of misalignment angles. Perhaps Fig. III-2 can help to describe the parameters used in the ensuing discussion. As is evident from the figure, α'_0 is the angle between the main beam axis and the rotor axis. α' and δ are always positive quantities. The distribution of angles ranges from $(\alpha'_0 - \alpha')$ to $(\alpha'_0 + \alpha')$ designated by $\alpha_{\min}$ and $\alpha_{\max}$ respectively from now on. The parameters α' and δ are defined by the geometry of the beam defining elements, the first of which is the width of the upper oven slit. The second element is determined either by the width of the collimating slits or the width of the area across the beam path from which the beam is viewed. The more constricting of the two applies. Thus at the collision zone where the reaction takes place, the collimating slit width will serve to define α' and δ whereas in a velocity distribution measurement, the width of the ionization ribbon will determine α' and δ because the detector is not wide enough to "see" the entire width of the beam. Since at each misalignment angle α the range of velocities transmitted is different, a distribution of α will widen the spread of velocities transmitted through the rotor. In the case of a velocity distribution measurement, the effect is not too important, but at the collision zone, the distribution of α is greater and the effect on the range of velocities transmitted is no longer negligible when compared with a parallel beam. In addition, the angle α'_0 affects directly the most probable velocity transmitted through the rotor. This is obvious when α'_0 in radians is substituted in Eq. (6). Therefore, it is deemed necessary

to derive analytic expressions for the transmission function for a misaligned, divergent beam to be used in the deconvolution step of the data analysis.

Before going further, it should be mentioned that another factor could affect the transmission of the rotor. This is the effect caused by the deposit of beam material between the slits of the selector disks. From our experience, the beam material was only deposited on the side of the slit rotating towards the rotor and, therefore, only attenuated the high velocity side of the admittance function $B(v, \nu, \alpha)$. Moreover, calculations have shown that this is only a minor effect and we are justified in neglecting this effect in our derivation. We also assume that the disk thickness d is equal to zero, for in actual calculations, the value of (d/L) and not the value of d is the important one. (The value of d occurs in the equations for the velocity selector as a correction term for the actual path length through the rotor i.e., $(L + d)$ instead of L ; hence, the term (d/L) is a measure of the error in an infinitely thin disk assumption.) In our rotor design, d/L is equal to 0.0142. The slit widths of the disks are assumed to be equal and they are machined within very narrow tolerances (0.001 in.). In addition, the derivation is made for the beam geometry in our experiment in which the thallium oven slit width is equal to the collimating slit width, i.e., $\delta = 0$. Before proceeding further, it should be emphasized that the expressions derived here are only valid for $(\alpha'_0 \pm \alpha')$ smaller than θ , where θ represents the ratio ℓ_1/L with ℓ_1 being the average width of the slot of the selector. If this is not so, the beam may be blocked by the wall between the of the intervening rotor disks. In such a

case, all the expressions for the transmission and resolution of the rotor will no longer be applicable. Figure III-3 is a rolled-out diagram of part of the selector. It may make the above section clearer and also serves to define some of the symbols used in our derivations.

It has already been stated at the beginning of this section that the probability of a particle traveling with velocity v getting through the selector rotating at a frequency ν is a product of two terms. It will be derived below.

$$P_{\bar{f}}(v, \nu) = \int_{-\infty}^{\infty} B(v, \nu, \alpha) D(\alpha) I(v) d\alpha \quad (12)$$

where $P_{\bar{f}}(v, \nu)$ = the probability function stated above

$D(\alpha)$ = angular weighing function dependent on the beam geometry.

(It will be described later.)

$I(v)$ = probability density flux distribution of the parent beam.

$I(v)$ is not dependent on α and $D(\alpha)$ is a function that has been normalized to 1, i.e.,

$$\int_{-\infty}^{\infty} D(\alpha) d\alpha = 1 \quad (13)$$

If we define the α independent admittance function $B(v, \nu)$ as:

$$B(v, \nu) = \int_{-\infty}^{\infty} B(v, \nu, \alpha) D(\alpha) d\alpha \quad (14)$$

then we shall have

$$P_{\bar{f}}(v, \nu) = B(v, \nu) I(v) \quad (15)$$

By integration of $P_f(v, v)$ through velocity we can calculate the transmission of the selector $T(v_0)$, a function that has been dealt with in the previous section. We shall now concentrate on deriving analytic expressions for $B(v, v)$.

Expressions for $B(v, v, \alpha)$ have already been derived by Gillen²⁵ and summarized in Ref. 22. They are again listed below. For a fixed rotational frequency v ,

$$B(v, v, \alpha) = 0 \quad \alpha < \beta_L(v) \quad (16)$$

$$B(v, v, \alpha) = B_1(v, v, \alpha) = \eta \left[1 - \left(\frac{2\pi v L}{v} - \phi - \frac{\alpha L}{r} \right) \frac{r}{\ell_1} \right] \quad (17)$$

$$\beta_L(v) \leq \alpha \leq \beta_x(v)$$

$$B(v, v, \alpha) = B_2(v, v, \alpha) = \eta \left[1 + \left(\frac{2\pi v L}{v} - \phi - \frac{\alpha L}{r} \right) \frac{r}{\ell_1} \right] \quad (18)$$

$$\beta_x(v) \leq \alpha \leq \beta_u(v)$$

$$B(v, v, \alpha) = 0 \quad \alpha > \beta_u(v) \quad (19)$$

where η = fractional opening time of the rotor = $\ell_1 / (\ell_1 + \ell_2)$

ℓ_2 = thickness of the wall between slots in a selector disk

The angles $\beta_u(v)$, $\beta_x(v)$ and $\beta_L(v)$ are best defined by referring to Fig. III-3. In the figure, the main beam axis coincides with the rotor axis when there is perfect alignment. It can be seen that if a particle with velocity v travels along a path at an angle $\beta_x(v)$ to the rotor axis, it is most likely to pass through the slots. However, if the same particle travels along a path at an angle greater than $\beta_u(v)$ or less

than $\beta_L(v)$ to the rotor axis, it will hit the wall between the slots. For infinitely thin disks, $\beta_x(v)$ is midway between $\beta_u(v)$ and $\beta_L(v)$, the angle between $\beta_x(v)$ and $\beta_u(v)$ or $\beta_L(v)$ being θ . θ , the angle subtended by a slot on the last disk of the selector to the corresponding slot on the entrance disk of the selector, is defined by the ratio l_1/L . $\beta_x(v)$ can be derived from the geometry and rotational frequency of the rotor.

$$\beta_x(v) = \frac{2\pi vr}{v} - \frac{\phi r}{L} \quad (20)$$

Now we have to obtain an algebraic expression for $D(\alpha)$. Physically, $D(\alpha)$ can be interpreted as the probability that a particle traveling along a path making an angle with the rotor axis will get through the two beam defining elements irrespective of its velocity. If we are "viewing" the particle from the collision zone, the beam defining elements will be the even slit width and the collimating slit width. In the particular geometry of our apparatus, $D(\alpha)$ will be triangular in shape when plotted against α . Any particle traveling along a path making an angle larger than $\alpha_{\max}$ or less than $\alpha_{\min}$ with the rotor will not get through at all. This should be evident if we look at Fig. III-2 again. The angular spread is from $\alpha'_o - \alpha' (= \alpha_{\min})$ to $\alpha'_o + \alpha' (= \alpha_{\max})$, the value of α' being the important parameter. Thus we shall now list the normalized $D(\alpha)$ functions.

$$D(\alpha) = 0 \quad \alpha < \alpha_{\min} \quad (21)$$

$$D(\alpha) = D_1(\alpha) = \frac{\alpha - \alpha_{\min}}{2\alpha} \quad \alpha_{\min} \leq \alpha \leq \alpha_o' \quad (22)$$

$$D(\alpha) = D_2(\alpha) = \frac{\alpha_{\max} - \alpha}{\alpha'} \quad \alpha'_0 \leq \alpha \leq \alpha_{\max} \quad (23)$$

$$D(\alpha) = 0 \quad \alpha > \alpha_{\max} \quad (24)$$

Now we are ready to evaluate $B(v, \nu)$. Since $D(\alpha)$ and $B(v, \nu, \alpha)$ each has three transition points, the resulting admittance function $B(v, \nu)$ will have nine points of transition dividing the function into ten analytic regions. Depending on the values of θ and α' , four different cases exist. In each case, the ten analytic regions are divided in a different way. The four cases are:

- Case 1 $0 \leq \theta \leq \alpha' / 2$
- Case 2 $\alpha' / 2 \leq \theta \leq \alpha'$
- Case 3 $\alpha' \leq \theta \leq 2\alpha'$
- Case 4 $2\alpha' \leq \theta$

The rotor design and beam geometry fits Case 3 (in our case, $\theta = 0.00746$ rad and $\alpha' = 0.007306$ rad); therefore, Case 3 will be described first. The ten regions and the shape of the $D(\alpha)$, $B(v, \nu, \alpha)$ functions are illustrated in Figs. III-4 and III-5. $B(v, \nu, \alpha)$ is not actually triangular in shape, but is approximated as such in the drawings to simplify matters a bit. The sides of that triangle is actually slightly curved. The following functions are defined in order to simplify the mathematical description of the function $B(v, \nu)$. For a fixed rotor frequency ν ,

$$I_{11}(\alpha_1, \alpha_2) = \int_{\alpha_1}^{\alpha_2} B_1(v, \nu, \alpha) D_1(\alpha) d\alpha \quad (25)$$

$$I_{12}(\alpha_1, \alpha_2) = \int_{\alpha_1}^{\alpha_2} B_1(v, v, \alpha) D_2(\alpha) d\alpha \quad (26)$$

$$I_{21}(\alpha_1, \alpha_2) = \int_{\alpha_1}^{\alpha_2} B_2(v, v, \alpha) D_1(\alpha) d\alpha \quad (27)$$

$$I_{22}(\alpha_1, \alpha_2) = \int_{\alpha_1}^{\alpha_2} B_2(v, v, \alpha) D_2(\alpha) d\alpha \quad (28)$$

The next three equations have been listed in Ref. 22 and will not be derived here.

$$v_{\max}(\alpha) = \frac{2\pi v L r}{\phi r - \ell_1 + L\alpha} \quad (29)$$

$$v_o(\alpha) = \frac{2\pi v L r}{\phi r + L\alpha} \quad (30)$$

$$v_{\min}(\alpha) = \frac{2\pi v L r}{\phi r + \ell_1 + L\alpha} \quad (31)$$

The sign of angle α is defined as positive when the motor has to rotate through an angle larger than ϕ to transmit the nominal velocity v_o . For Case 3, where $\alpha' \leq \theta \leq 2\alpha'$, the ten analytic expressions can be represented in matrix form as follows.

$$\text{Region 1} \quad B(v, v) = B_1(v, v) \quad v > v_{\max}(\alpha_{\min}) \quad (32)$$

$$\text{Region 2} \quad B(v, v) = B_2(v, v) \quad v_{\max}(\alpha_o) \leq v \leq v_{\max}(\alpha_{\min}) \quad (33)$$

$$\text{Region 3} \quad B(v, v) = B_3(v, v) \quad v_o(\alpha_{\min}) \leq v \leq v_{\max}(\alpha_o) \quad (34)$$

$$\text{Region 4} \quad B(v, v) = B_4(v, v) \quad v_{\max}(\alpha_{\max}) \leq v \leq v_o(\alpha_{\min}) \quad (35)$$

$$\text{Region 5} \quad B(v, v) = B_5(v, v) \quad v_o(\alpha_o) \leq v \leq v_{\max}(\alpha_{\max}) \quad (36)$$

$$\text{Region 6} \quad B(v, v) = B_6(v, v) \quad v_{\min}(\alpha_{\min}) \leq v \leq v_o(\alpha_o) \quad (37)$$

$$\text{Region 7} \quad B(v, v) = B_7(v, v) \quad v_o(\alpha_{\max}) \leq v \leq v_{\min}(\alpha_{\min}) \quad (38)$$

$$\text{Region 8} \quad B(v, v) = B_8(v, v) \quad v_{\min}(\alpha_o) \leq v \leq v_o(\alpha_{\max}) \quad (39)$$

$$\text{Region 9} \quad B(v, v) = B_9(v, v) \quad v_{\min}(\alpha_{\max}) \leq v \leq v_{\max}(\alpha_o) \quad (40)$$

$$\text{Region 10} \quad B(v, v) = B_{10}(v, v) \quad v < v_{\min}(\alpha_{\max}) \quad (41)$$

$$\begin{pmatrix} B_1(v, v) \\ B_2(v, v) \\ B_3(v, v) \\ B_4(v, v) \\ B_5(v, v) \\ B_6(v, v) \\ B_7(v, v) \\ B_8(v, v) \\ B_9(v, v) \\ B_{10}(v, v) \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 \\ 0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} I_{11}(\alpha_{\min}, \alpha_x(v)) \\ I_{11}(\alpha_{\min}, \alpha_o) \\ I_{11}(\beta_x(v) - \theta, \alpha_o) \\ I_{12}(\alpha_o, \beta_x(v)) \\ I_{12}(\alpha_o, \alpha_{\max}) \\ I_{12}(\beta_x(v) - \theta, \alpha_{\max}) \\ I_{21}(\alpha_{\min}, \beta_x(v) + \theta) \\ I_{21}(\alpha_{\min}, \alpha_o) \\ I_{21}(\beta_x(v), \alpha_o) \\ I_{22}(\alpha_o, \beta_x(v) + \theta) \\ I_{22}(\alpha_o, \alpha_{\max}) \\ I_{22}(\beta_x(v), \alpha_{\max}) \end{pmatrix} \quad (42)$$

Figure III-6 shows a plot of $B(v, v)$ vs v for both a divergent beam and a parallel beam for our beam and velocity selector geometry. Note the much wider spread of the transmitted velocities in the case of a divergent beam. Also, the $B(v, v)$ function is asymmetric about its peak. This arises from the way $B(v, v, \alpha)$ depends on v . (i.e., v appears in the denominator.)

Since the equations for Cases 1, 2 and 4 will not be used in the present deconvolution procedure, they will not be shown under this section, but will be presented in Appendix A to this chapter. Lastly, it should be mentioned that equations for the admittance function of a velocity selector for a divergent beam in which $D(\alpha)$ is set equal to 1 for α between $\alpha_0 + \delta$ and $\alpha_0 - \delta$ and zero everywhere else has been derived previously.²⁹ The present derivation, therefore, represents a further refinement as well as a more realistic case.

4. Deconvolution of the Relative Cross Section from the Velocity Distribution of the Two Beams

In this section, we shall be describing the procedure with which $Q_{eff}(g)$ can be extracted. If we go back to Eq. (2) and substitute Eq. (1) for N on the left-hand side and $Q'_{rel}(g)$ for $Q'_{eff}(g)$ on the right-hand side, $Q_{rel}(g)$ for $Q_{eff}(g)$ on the left-hand side, and rearrange terms, we will have:

$$Q'_{rel}(g) = \frac{C'}{g} \int_0^{\infty} \int_0^{\infty} Q_{rel}(g) g P(v_{T1}) P(P_{Hg}) dv_{T1} dv_{Hg} \quad (43)$$

where $C' =$ the new proportionality constant

$Q_{rel}(g) =$ true velocity dependent relative cross section for the process, differing from $Q_{eff}(g)$ by a constant.

We do not care about the actual value of C' as long as we know it is independent of velocity and does not affect the rest of our calculations. The $P(v_{Tl})$ and $P(v_{Hg})$ are normalized number density velocity distributions that can be obtained from the flux distributions derived earlier by dividing the flux distributions by velocity and the integration constants. Thus,

$$P(v_{Hg}) = \frac{2v_{Hg}}{\alpha_{Hg}^2} \exp[-(v_{Hg}/\alpha_{Hg})^2] \quad (44)$$

and

$$P(v_{Tl}) = \frac{P_f(v_{Tl}, v)}{\int_0^\infty \frac{P_f(v_{Tl}, v)}{v_{Tl}} dv_{Tl}} \quad (45)$$

where $P_f(v_{Tl}, v)$ is that described in Eq. (15). The parameters for the flux distribution of the thallium beam before velocity selection $I(v_{Tl})$ was estimated by the method described in Section 2 of this chapter. By substituting trial curves of $Q_{rel}(g)$ vs g into Eq. (43), we shall attempt to reproduce the $Q'_{rel}(g)$ vs g relationship extracted by the procedure discussed in Section 1 of this chapter. Therefore, in this indirect way, we can extract the coarse velocity dependence of the relative cross section for the sensitized fluorescence process for the $Hg^* + Tl$ process. The fine structures that may be present will be obscured by the limited energy resolution and experimental standard deviations in our experiments.

D. Results and Discussion

Attempts have been made to study the velocity dependence of the cross sections for sensitized fluorescence production of several thallium lines, notably, the 5350Å, 2826Å and 2918Å lines. We have also tried to measure the velocity dependence of mercury $6^3P_2 + 6^3P_0$ intramultiplet conversion in collisions with thallium atoms by monitoring the 2537Å line emission. The 5350 Å ($7^2S_{1/2} + 6^2P_{3/2}$) and 2826Å ($9^2S_{1/2} + 6^2P_{3/2}$) lines involves emission from $2^2S_{1/2}$ levels, but the $9^2S_{1/2}$ level is higher in energy and only 0.108 eV below the mercury 6^3P_2 level in energy. Thus it can provide us with an opportunity to study fluorescence from a level that is primarily caused by direct excitation of the level by collision in contrast to that from the $7^2S_{1/2}$ level which may be heavily populated by cascade transitions, especially from the $2^2P_{1/2,3/2}$ levels. The 2918Å line ($7^2D_{5/2} + 6^2P_{3/2}$) involves fluorescence from a D level excited mostly by direct collision with mercury 6^3P_2 atoms. As will be seen later, the 2^2D levels contribute very little to the population of the $7^2S_{1/2}$ level and hence the 5350Å line fluorescence by cascade transition. Thus study of sensitized fluorescence from this line will provide information for electronic energy transfer to D levels by collision. However, because of the closeness of the 2826Å and 2918Å lines to the 2537Å line due to the mercury fluorescence background, quantitative information cannot be extracted from the data because of the large photon background due to mercury fluorescence transmitted through the interference filter. Nevertheless, results from the 2918Å line indicated that in a $Q_{rel}(g)$ vs g plot, the relative cross section was quite flat throughout

most of the velocity range measured with perhaps a slight rise at the lowest velocities which is much less pronounced than that in the 5350Å line. Quantitative information of the velocity dependence of the relative cross section for sensitized fluorescence is extracted for the 5350Å line of thallium only. Figure III-7 shows the result in a plot of $Q_{rel}'(g)$ vs g .

Since a positive photon signal did appear in our experiments with the 2826Å and 2918Å lines, by comparing the photon counting rates and estimated beam intensities with those in the experiments with the 5350Å line, we can set an approximate upper limit for the cross section of fluorescence production of these lines as compared to the 5350Å line. The upper limit for the 2826Å line is about 1/3 of that for 5350Å fluorescence production while that for the 2918Å line is approximately 1/20 of the cross section for the 5350Å line at relative velocities around 4.5×10^4 cm/sec.

When we look at the $7^2S_{1/2}$ level from which the 5350Å line originate, we realize that a fraction of its population may come from cascade transitions from levels above which are excited by direct collision with the metastable mercury atoms. Now we are confronted by two problems. First, does the levels radiate through the $7^2S_{1/2}$ level before they leave the photon collection area of the photomultiplier housing? Second, which higher levels are expected to contribute to the population of the $7^2S_{1/2}$ level and hence the 5350Å fluorescence intensity?

To answer the first question we must estimate the residence time of the emitting thallium atom in the photon collection area. The

diameter of that area is $3/8$ in., so the distance traveled by a thallium atom before leaving the collection area assuming excitation at the center of the collection area is $3/16$ in. The worst case is that in which the thallium atom is excited by the 6^3P_2 state of mercury to the $7^2S_{1/2}$ level directly and the excess energy going to the thallium atom exclusively as translational energy of the excited atom. In such an instance, the residence time of the thallium atom is approximately $1/3$ of a microsecond. The $(7^2S_{1/2} \rightarrow 6^2P_{3/2})$ transition has a life time of $\sim 3 \times 10^{-8}$ sec,⁸ therefore, it should radiate before leaving the collection area. If a higher level is excited, the residence time is longer. As will be shown later, most of the levels contributing to the $7^2S_{1/2}$ level population have life times of the order of 10^{-7} sec or considerably less, thus we can claim that our collection area is large enough for the purpose.

To answer the second question, we have to calculate the fraction of the population of the higher states produced in the collision that eventually end up in the $7^2S_{1/2}$ level of thallium. Knowing that the mercury $6^3P_{0,2}$ states are the ones that are responsible for the production of 5350Å fluorescence, we shall now consider only the thallium levels that are energetically accessible at zero translation energy. The result of these calculations are shown in Table III-2. The fractions are calculated by dividing the sum of the transition probabilities of the transitions that can lead to the $7^2S_{1/2}$ level by the sum of the transition probabilities of all possible transitions from the level under consideration. The transition probabilities are calculated from oscillator strengths using a method presented in Ref. 30.

Table III-2a. Radiative lifetimes of thallium excited states contributing to the $7^2S_{1/2}$ level population.

Thallium Transitions	A sec ⁻¹	Radiative Lifetimes $\frac{1}{\sum A_i}$ in Sec
$9^2S_{1/2} \rightarrow 6^2P_{1/2}$	7.67×10^6	4.5×10^{-8}
$\quad \quad \quad \rightarrow 6^2P_{3/2}$	9.88×10^6	
$\quad \quad \quad \rightarrow 7^2P_{1/2}$	1.19×10^6	
$\quad \quad \quad \rightarrow 7^2P_{3/2}$	1.40×10^6	
$\quad \quad \quad \rightarrow 8^2P_{1/2}$	0.868×10^6	
$\quad \quad \quad \rightarrow 8^2P_{3/2}$	1.19×10^6	
$8^2S_{1/2} \rightarrow 6^2P_{1/2}$	1.73×10^7	2.1×10^{-8}
$\quad \quad \quad \rightarrow 6^2P_{3/2}$	2.21×10^7	
$\quad \quad \quad \rightarrow 7^2P_{1/2}$	3.62×10^6	
$\quad \quad \quad \rightarrow 7^2P_{3/2}$	5.13×10^6	
$8^2P_{1/2} \rightarrow 6^2D_{3/2}$	1.20×10^6	1.7×10^{-7}
$\quad \quad \quad \rightarrow 7^2S_{1/2}$	2.10×10^6	
$\quad \quad \quad \rightarrow 8^2S_{1/2}$	2.66×10^6	
$8^2P_{3/2} \rightarrow 6^2D_{3/2}$	6.62×10^4	1.2×10^{-7}
$\quad \quad \quad \rightarrow 7^2S_{1/2}$	4.51×10^6	
$\quad \quad \quad \rightarrow 8^2S_{1/2}$	3.38×10^6	
$7^2P_{1/2} \rightarrow 7^2S_{1/2}$	1.10×10^7	9.0×10^{-8}
$7^2P_{3/2} \rightarrow 7^2S_{1/2}$	1.32×10^7	7.6×10^{-8}
$7^2D_{3/2} \rightarrow 6^2P_{1/2}$	7.21×10^7	1.1×10^{-8}
$\quad \quad \quad \rightarrow 6^2P_{3/2}$	1.06×10^7	
$\quad \quad \quad \rightarrow 7^2P_{1/2}$	5.09×10^6	

Table III-2a. Continued

Thallium Transitions	A sec ⁻¹	Radiative Lifetimes $\frac{1}{\sum A_i}$ in sec
$7^2P_{1/2} \rightarrow 7^2P_{3/2}$	1.31×10^6	1.1×10^{-8}
$\rightarrow 8^2P_{1/2}$	6.81×10^4	
$\rightarrow 8^2P_{3/2}$	1.0×10^3	
$7^2D_{5/2} \rightarrow 6^2P_{3/2}$	6.34×10^7	1.4×10^{-8}
$\rightarrow 7^2P_{3/2}$	7.55×10^6	
$\rightarrow 8^2P_{3/2}$	9.21×10^3	
$6^2D_{3/2} \rightarrow 6^2P_{1/2}$	1.74×10^8	5.0×10^{-9}
$\rightarrow 6^2P_{3/2}$	2.78×10^7	
$\rightarrow 7^2P_{1/2}$	4.36×10^5	
$\rightarrow 7^2P_{3/2}$	1.02×10^4	
$6^2D_{5/2} \rightarrow 6^2P_{3/2}$	1.86×10^8	5.4×10^{-9}
$\rightarrow 7^2P_{3/2}$	8.15×10^4	

Table III-2b. Estimated contributions to the $7^2S_{1/2}$ level population by higher excited states of thallium.

Thallium Level	Fraction of Population Going to $7^2S_{1/2}$ Level
$9^2S_{1/2}$	0.166
$8^2S_{1/2}$	0.182
$7^2S_{1/2}$	1.00
$8^2P_{1/2}$	0.433
$8^2P_{3/2}$	0.596
$7^2P_{1/2}$	1.00
$7^2P_{3/2}$	1.00
$7^2D_{3/2}$	$7.22 \cdot 10^{-3}$
$7^2D_{5/2}$	0.106
$6^2D_{3/2}$	$2.21 \cdot 10^{-3}$
$6^2D_{5/2}$	$4.38 \cdot 10^{-4}$
$5^2F_{5/2}$	---
$5^2F_{7/2}$	---

The radiative lifetimes are the reciprocals of the transition probabilities. The formula used in Ref. 30 is:

$$A = 0.6669 \times 10^{14} \frac{1}{\lambda^2} |f| \quad (46)$$

where A = Einstein A coefficients (transition probabilities)

λ = wavelength of the emission in nanometers

f = oscillator strength of the transition

It can be seen that the $^2P_{3/2}$ and $^2P_{1/2}$ states contribute heavily while the $^2S_{1/2}$ levels also contribute noticeably. The $^2D_{3/2}$ levels hardly contribute in most cases. However, the $^2D_{5/2}$ level does contribute quite a bit. If the cross section for direct excitation of this level were greater than that for the $^2S_{1/2}$ level by two orders of magnitude, its contribution to the relative cross section measured would be comparable to that from direct excitation of the $^2S_{1/2}$ level. This in fact is what prompted us to study the excitation of thallium 2918Å line fluorescence which originate from the $^2D_{5/2}$ level. As mentioned before, the cross section for excitation of this line is small compared to that for the 5350Å line, so we can conclude that the $^2D_{5/2}$ level also contribute negligibly to the population of the $^2S_{1/2}$. The 2F levels have to radiate through the 2D levels to reach the $^2S_{1/2}$ level; therefore, their contribution to the population of the $^2S_{1/2}$ level, and hence the 5350Å line fluorescence intensity is negligible. Thus the relative cross section for excitation of 5350Å line fluorescence measured in our experiments correspond to the excitation of 2S and 2P levels of thallium by collisions with excited mercury atoms. (6^3P_0 and 6^3P_2 states.)

Our results as shown in Fig. III-7 show that the relative cross section for 5350Å fluorescence production is a smooth varying function of velocity before averaging over the beam velocity distributions. This results from the averaging over any undulations or fine structures that may be present in the relative cross section vs relative velocity plot but cannot be resolved in our experiments. The curve rises sharply at low velocities and levels off gently at velocities greater than 6×10^4 cm/sec. The velocity averaging procedure adopted in the deconvolution step, as expected, did not change the shape of the curve appreciably.

The most obvious trial functions are those of the form,

$$Q \propto \frac{1}{g^s}$$

where s = power to which g is raised and is not necessarily an integer, or combinations of several $1/g^s$ terms. A plot of $\log Q'_{\text{rel}}(g)$ vs $\log g$ indicates that at low velocities $Q'_{\text{rel}}(g)$ varies as $\sim g^{-3}$, whereas at the high velocity end, $Q'_{\text{rel}}(g)$ varies as $\sim g^{-1}$. This would seem to raise the possibility of two different processes with different velocity dependences contributing to the relative cross section. However, the experimental error is large enough especially at the low velocity end to prevent us from claiming that this is the only way to fit the experimental curve. In fact, a set of trial curves with $Q_{\text{rel}}(g)$ varying as g^{-s} with s ranging from 1.4 to 2.4 fit the experimental curve nicely within the error bars. This would imply an approximate g^{-2} dependence for the relative cross section. Three of these trial curves are shown in Fig. III-7.

Several thallium levels lying above the mercury 6^3P_2 state in energy could be excited theoretically if the excess energy can be provided by the relative translational energy of the collision partners. However, in such cases, there is a threshold energy below which that level is energetically inaccessible. The lowest lying of such levels is the $9^2P_{1/2}$, which, if excited by the 6^3P_2 state of mercury, would contribute substantially to the population of the $7^2S_{1/2}$ level by direct or cascade transitions. The threshold energy in this case is 0.042 eV or 2.83×10^4 cm/sec on the relative velocity scale. In order to determine whether this level contributes significantly to the measured relative cross section, all the trial curves used in the deconvolution step were given a threshold of 2.83×10^4 cm/sec. In every case, the resulting cross section after averaging over the beam velocity distributions starts to fall off at low velocities where the experimental relative cross section is still rising sharply. This is shown as a dotted curve in Fig. III-7 for one of the trial curves. Hence, it is safe to claim that levels lying above the mercury 6^3P_2 state in energy cannot possibly be excited by collision to any appreciable extent at low relative velocities, otherwise, they would contribute to the relative cross section to a noticeable extent.

One of the simplest models that can be proposed to fit the data is one in which a particle has to possess enough energy to penetrate to a distance r_m from the target particle before reaction can take place. The cross section for reaction can be expressed as a function of kinetic energy E . The relationship is shown in Eq. (47) below.

$$Q = \pi r_m^2 \left(1 - \frac{v(r_m)}{E} \right) \quad (47)$$

$$E = \frac{1}{2} \mu g^2 \quad (48)$$

where $v(r_m)$ = potential energy at r_m

μ = reduced mass of the collision partners

Q = cross section for the reaction.

This model is applicable usually only at high energies and a transition to the orbiting model takes place at lower energies, but the orbiting model would give a weaker g dependence³¹ than the g^{-2} dependence observed here at low energies, so we probably have not reached a low enough energy in our measurements in which this transition to the orbiting model takes place.

By submitting this function as a trial curve, we have been able to determine the lower limit of $v(r_m)$ as -0.6 eV. The fitting curve is shown in Fig. III-8. The critical distance of separation r_m cannot be evaluated because we did not measure the absolute cross section for the process. However, an estimate of the order of magnitude of the absolute cross section can be obtained by using estimates of expected beam intensities at the collision zone, the photon counting rate, the geometry and the efficiency of the photon collection system. This places the cross section somewhere between 2 to $6\text{\AA}^2$ at a relative velocity of about 4.5×10^4 cm/sec. Since the estimates of the efficiency of metastable production by electron bombardment and the photon detection efficiency are only approximate, this estimate of the absolute cross section is only accurate to within a factor of ten. The model suggested above usually would indicate a larger cross section than is estimated here. However, we can explain the present situation by

multiplying the right-hand side of Eq. (47) by a ω factor which represents the probability of exiting through the right product channel after penetrating to a distance r_m . If ω is small and essentially energy independent, as may be happening in our case, then the cross section for reaction is also small.

The phenomena of sensitized fluorescence is often explained by a curve crossing or pseudo curving-crossing model because of its relatively large cross section for reaction and high probability of electronic energy transfer when the energy discrepancy between the total electronic energy of the separated atoms in their initial and final states is small. The final picture presented by our study of the $\text{Hg}^* + \text{Tl}$ system seemed to be consistent with such a model. The Landau-Zener theory³² for curve crossing stated that the cross section is small when the transit time of the atoms through the vicinity of the crossing point is long compared to $\hbar/\Delta E$. (ΔE is the energy discrepancy between the two potential curves at the crossing point.) By ignoring long range attractive interaction, their cross section vs velocity plot would show a maximum at some point of the velocity range. Our estimated relative cross section is still rising rapidly at the lowest measured velocity. Thus, if the Landau-Zener theory is applicable, we would be looking at the high velocity end of their plot, where the cross section should be even smaller than what we have estimated. A method to estimate the coupling matrix elements between the crossing curves was presented in Ref. 33. Moreover the Landau-Zener theory predicted a $1/g$ dependence at high velocities which is a bit too weak to apply in our case. Therefore, it would seem that their theory for curve crossing may not

be very appropriate. The curve crossing model we propose is one of the ways of explaining the process studied. It predicts the existence of some electron transfer mechanism leading to the formation of an ionic intermediate Tl^+Hg^- as the two atoms approach. The long range coulombic potential of the ionic intermediate then serves to link together the potential curves of interaction between different thallium levels and the ground state mercury atom as well as that between the mercury $6^3P_{0,2}$ states and a ground state thallium atom, forming a network of potential curves with multiple crossing points. As a thallium atom and a metastable mercury atom approach along a $Hg^* + Tl$ potential curve, it can switch over to the ionic curve and exit along different allowed product channels involving different excited thallium levels. Our estimate of the lower limit of $V(r_m)$ indicates that the transition takes place when the two atoms approach a point on the potential curve where the attractive potential reaches -0.6 eV with respect to the original curve of approach. The acceleration of the incoming particles is so great as they approach that the initial relative kinetic energy of the particles does not really produce any pronounced effect on the outcome of the reaction. Thus we have a relative cross section that varies inversely with the kinetic energy of the collision partners. Moreover, the energy resonance criteria may not be dominant for the $Hg^* + Tl$ system. Energy levels in close resonance with the mercury $6^3P_{0,2}$ levels like the $9^2P_{1/2}$ level mentioned before do not appear to have a bigger cross section for excitation than the $7^2S_{1/2}$ level which lies way below even the mercury 6^3P_0 state.

Further studies of the $\text{Hg}^* + \text{Tl}$ system should be directed towards measuring the relative cross sections for excitation of different thallium lines in order to be able to determine the probabilities of exit through different product channels of the ionic model proposed. In fact, the experimental set up has already been designed and built by the author. Hopefully, the experiment would be performed in the not too distant future. Studies using lighter atoms e.g., lithium as the velocity selected beam material are also suggested, as this should give better energy resolution if any fine structures in the $Q_{\text{rel}}(g)$ vs g curve exist.

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FIGURE CAPTIONS

Fig. III-1. Thallium energy level diagram. All energies are given in electron volts. For Tl levels below 4 eV the energy of the level above the ground state is indicated, but for the higher energies the difference between the Tl level and the nearest metastable Hg level is given. Note the scale change at 4 eV. The two lower dashed lines indicate the energies of the low lying metastable Hg levels, while the upper dashed line gives the Tl ionization potential. The diagonal lines indicate the emission lines observed in the mercury sensitized fluorescence spectrum of thallium; the number labeling each line gives the wavelength in Å.

Fig. III-2. Parameters defining the geometry of a misaligned beam with respect to the rotor axis. The first beam defining element is always the width of the source slit. The second one could be the width of the collimating slit or the width of the ionizing filament of the detector. δ and α' are calculated from the geometry of the beam defining elements while α'_0 is calculated from R_0 , the velocity conversion factor of the velocity selector.

Fig. III-3. A rolled-out diagram of the velocity selector. The beam axis coincides with the rotor axis for perfect alignment. The intervening disks are not shown here as they only serve to eliminate side bands that could be passed by the selector in their absence.

Fig. III-4. The $D(\alpha)$ and $B(v, \alpha)$ functions. The $D(\alpha)$ function shown here is that appropriate to our beam geometry ($\delta = 0$). The sides of the $B(v, \alpha)$ function are in actual fact not straight lines but slightly curved. It is shown as such here for the sake of simplicity.

Fig. III-5. Analytic regions of $B(v, v)$ for $\alpha' < \theta < 2\alpha'$. The sequence of figures do not actually indicate the different regions but rather the transition points between the different regions as the two triangles representing the two functions slide past each other.

Fig. III-6. A plot of the admittance function against velocity. The solid curve represents the admittance function for our beam geometry for perfect alignment. The dashed curve shows the admittance function for a parallel, perfectly aligned beam. The small angle approximation is applicable in both cases.

Fig. III-7. Velocity dependence of the relative cross section for the formation of $Tl\ 7^2S_{1/2}$ in collisions with $Hg\ 6^3P_{0,2}$ metastable atoms. The different symbols indicate separate experimental runs which have been normalized to give the best overall agreement. The error bars to the left indicate the standard deviation evaluated by error propagation and those to the right indicate the standard deviation of the actual data points. The solid, dashed and dotted-dashed curves represent trial curves of $Q_{rel}(g) \propto g^{-s}$ after having been averaged over

the beam velocity distributions. The dotted curve represents a trial curve of $Q_{\text{rel}}(g) \propto g^{-2}$ with a threshold energy of 0.042 eV. The kinetic energy scale is calculated by $1/2 \mu g^2$ where μ is the reduced mass.

Fig. III-8. Velocity dependence of the relative cross section for the formation of Tl $7^2S_{1/2}$ in collisions with Hg $6^3P_{0,2}$ metastable atoms. the different symbols represent different experimental runs and the error bars represent standard deviations evaluated by error propagation. The solid curve is the trial curve evaluated by using Eqs. (47) and (48) with $v(r_m) = -0.6$ eV.

XBL 709-6672

Fig. III-1.

XBL 7312-7176

Fig. III-2.

XBL7311-6731

Fig. III-3.

For a fixed ν

XBL 7312-7119

Fig. III-4.

XBL 7312-7120

Fig. III-5.

Fig. III-6.

XBL73II-6728

Fig. III-7.

XBL 7311-6730

Fig. III-8.

IV. VELOCITY DEPENDENCE OF ELECTRONIC ENERGY TRANSFER BETWEEN MERCURY $6^3P_{0,2}$ ATOMS AND ALKALI HALIDES

A. Introduction

Electronic energy transfer between metastable mercury atoms ($6^3P_{0,2}$ states) and alkali halides is a potentially interesting system that has hardly been studied at all. Recently, Martin and VanItallie¹ have reported the detection of sodium (3^2P) fluorescence when a thermal beam of sodium iodide was crossed with a metastable mercury ($6^3P_{0,2}$) beam. However, they have been unable to measure the potassium (4^2P) fluorescence when metastable mercury and potassium iodide beams were crossed. The energetics of the system indicates that if reaction occurs, there are two possible product channels which can be studied with our apparatus. These are shown below.

and

where M, X represent the alkali metal and the halide respectively. Using the metastable mercury 6^3P_0 and 6^3P_2 states as the excited species, M^* represents an alkali atom in a 2P state because it is the only excited state of lithium, sodium or potassium that is energetically accessible at zero translational energy. If a velocity selected beam of alkali halide molecules is crossed with a metastable mercury atom beam, the light emission from the excited alkali atoms produced in the collision zone can be monitored. In this way, employing the data

analysis method developed in Chapter III, we can extract the velocity dependence of the process.

Table IV-1 presents the energetics for both processes (1) and (2) with different alkali halides. The heats of reaction $\Delta H_o(1)$ and $\Delta H_o(2)$ for process (1) and (2) respectively are calculated by the following formula.

$$\Delta H_o(1) = E_M^* - E_{Hg}^* + D_o(MX)$$

$$\Delta H_o(2) = E_M^* - E_{Hg}^* + D_o(MX) - D_o(HgX)$$

where E_M^*, E_{Hg}^* = excitation energies of the M, mercury atoms

$D_o(MX), D_o(HgX)$ = dissociation energies of MX and HgX.

The values of ΔH_o will be negative if the reaction is exothermic. The values for the dissociation energies have been taken from Ref. 2. The uncertainties of these values are of the order of 2 to 3 kcal/mole. Moreover, if we include the vibrational and rotational energies of the alkali halides at our operating temperatures, another 4 or 5 kcal/mole will be available. These values are important in view of the fact that the exothermicity (or endothermicity) of the reactions is only a few kcal/mole in a number of cases. In addition, a glance at the table will reveal that the 6^3P_0 state of mercury is too low in energy to participate in most cases, so we shall concentrate on the 6^3P_2 state of mercury. In selecting the alkali halides for study, we would prefer to look at one in which only process (2) is energetically accessible at zero translational energy and another in which both processes (1) and (2) are possible. It is seen that NaBr and NaI satisfy our selection requirements. Furthermore, LiI presents an interesting case in which

Table IV-1. Energetics of some $\text{Hg}^* + \text{MX}$ reactions.

Alkali Atom	Emission Line	Energy (kcal/mole)
Li	6707.85Å	42.6
Na	5889.96Å	48.52
	5895.93Å	48.48
K	7644.94Å	37.38
	7699.01Å	37.12

ΔH_o is in kcal/mole

Alkali Halide	$\Delta H_o(1)$ (Hg 6^3P_0)	$\Delta H_o(2)$ (Hg 6^3P_0)	$\Delta H_o(1)$ (Hg 6^3P_2)	$\Delta H_o(2)$ (Hg 6^3P_2)
LiI	17.3	9.1	-1.0	-9.2
LiBr	35.6	19.2	17.3	0.9
LiCl	48.0	25.0	29.7	6.7
NaI	11.2	3.0	-7.1	-15.3
NaBr	28.9	12.5	10.6	-5.8
NaCl	38.9	15.9	20.6	-2.4
KI	8.3	0.1	-10.0	-18.2
KBr	20.7	4.3	2.4	-14.6
KCl	30.3	7.3	12.0	-11.0

process (1) is just barely accessible energetically. The potassium halides do not really present anything new. Besides, the potassium emission is in the longer wavelength region which means that we will have to cope with a high background due to black body radiation inside the chamber (from the beam ovens, ionization filament, etc.). Thus we have decided to work with LiI, NaI and NaBr in our experiments.

However, there is one complication in working with alkali halides which are known to form dimers readily.³⁻⁵ A simple thermodynamics calculation using data from Ref. 6 indicates that the beam composition contains 10 to 20% of dimer. Thus there is the possibility of dimers taking part in reactions like,

We are not concerned with reactions like (7) or (8) because we are monitoring only M^* radiation and not ion production or other emission lines. On the other hand, reactions (3) to (6) do present a problem in our data analysis because we cannot distinguish between the emission due to the dimers and that due to the monomers. We shall deal with this problem in more detail in later sections.

B. Experimental Conditions

Experimentally, the same basic apparatus set up as used in the $\text{Hg}^* + \text{Tl}$ experiments was used with a few changes. Thus this section would be limited to a brief description with emphasis on the changes that were made.

1. Beam Sources

The mercury and alkali halide ovens used were the same ones that were used previously. The mercury oven, operated at the same source pressure and beam temperature as before, gave a mercury beam with negligible amounts of dimers. However, the same cannot be said about the alkali halides. At our beam temperatures, the alkali halide vapor consisted of an equilibrium mixture of both monomers and dimers. To minimize the percentage of dimers present we could operate at lower source pressures and higher upper oven temperatures. Table IV-2 shows the beam compositions at different settings of the velocity selector under our operating conditions for LiI , NaI and NaBr . It is seen that at the higher velocities we would have a beam that consisted almost completely of monomers. These values were calculated from thermodynamic quantities (ΔH_{1000} and ΔS_{1000}) taken from Ref. 6 for the dimerization of alkali halides. Since Maxwell-Boltzmann velocity distributions have to be assumed for both dimers and monomers in calculating the percentage composition of dimers at a given velocity, the values are only approximate, for we know that the actual velocity distributions are different. These values will be used in our data analysis later and further discussion will be continued in later sections.

Table IV-2. Alkali halide beam composition at different velocity selector settings.*

Alkali Halide	Source Pressure (Torr)	Beam Temperature (°K)	Velocity (10^4 cm/sec)	% Dimer
LiI	0.4	1013	1.79	24.7
			3.14	16.2
			5.16	4.9
			7.26	0.6
			10.10	$7.6 \cdot 10^{-4}$
NaI	0.5	1093	2.72	15.9
			4.44	6.5
			6.16	1.5
			7.91	0.2
			8.82	0.06
NaBr	1	1153	2.13	34.2
			3.93	22.5
			6.32	7.2
			8.80	1.1
			10.03	0.3

* These are not the only velocity settings used in the experiments, but are enough to demonstrate the importance of dimers within our measured velocity range.

2. Electron Gun

The electron gun used in these experiments was that described in Chapter II. Thus we were able to operate at an emission current level between 0.5 ma and 1 ma without producing mercury metastable states higher in energy than the 6^3P_2 state. This is especially important because we will show later that the higher metastable states will also produce excited alkali atom emission lines.

3. Photon Detection

The system described in Chapter II was employed here. For LiI, a 6067Å interference filter was used, while the 5889Å filter was used for both NaI and NaBr. The lifetimes of these excited states of alkali atoms are short enough so that any excited alkali atoms produced in the collisions would radiate before leaving the photon collection area. The geometry of our focusing optics gives a total solid angle of collection of 1.2π above and below the collection zone. Polarization of the emitted radiation which may be important in direct energy transfer between atoms* is probably not so in these cases where an actual chemical reaction occurs.

4. Electron Gun Voltage Variation Experiments

An experiment was performed in which the plate and collector voltages of the electron gun were varied while the velocity setting for the NaBr beam was kept constant. The results of the experiment is shown in

* In the 5350Å line studied in the Hg* + Tl system the emission is from a $^2S_{1/2}$ level. Hence, the angular distribution of photon emission is isotropic.

Table IV-3. If we refer back to the mercury excitation function in Chapter II, we will notice that a positive photon signal is observed when the electron gun voltage is set at either of the peaks, i.e., at 6 and 10 volts respectively. In between, the relative cross section drops to a negative value. Thus this indicates that both the mercury $6^3P_{2,0}$ and higher metastable states can lead to reaction with the production of excited alkali atoms. However, with the resolution of our electron gun, we are certain that we are only looking at processes involving the mercury $6^3P_{2,0}$ states.

As far as experimental procedure and data collection is concerned, we followed the same procedure as in the $Hg^* + Tl$ experiments. Thus no further description is necessary.

C. Data Analysis

Basically, the same procedure as that discussed in Chapter III is used in all stages of the data analysis. The difference arises from the nature of the background noise. During the alkali halide experiments, we often had sudden pressure rises when the alkali halide ovens cold shields were not cooled fast enough as the liquid nitrogen trap of the velocity selector was being filled. The photon counting has to be interrupted until the background pressure had dropped back to a low enough level. There is often a difference between the background counts before and after the interruption. Thus if the data on the background is submitted to the computer in the usual way, the curve fitting procedure may give a curve that oscillates rapidly near the point of interruption. Therefore, it is decided that the data should be analysed by hand.

Table IV-3. Effect of electron gun voltage on the relative cross section for the reaction $\text{Hg}^* + \text{NaBr}$.

Electron Gun Voltage (volts)	Relative Cross Section (Arbitrary Units)	Relative Velocity (10^4 cm/sec)
6	2.2 ± 0.7	4.19
8	-2.3 ± 0.8	4.19
10	0.92 ± 0.9	4.19
12	-0.19 ± 1.0	4.19

Another problem arose because the velocity selected beam signal contained contributions from both dimers and monomers. The percentage of each could be estimated approximately as described in the previous sections. However, we do not know whether both the dimer and monomer contribute to the relative cross section for reaction or only one does. Consequently, we analyse our data in two different ways, making the assumption that only the dimer can contribute in one case and that only the monomer can contribute in the second case. Results from these analyses will be discussed in the next section.

After the approximate curve of $Q_{rel}^1(g)$ vs g is obtained by hand calculations, the rest of the steps can be done by the computer as described in Chapter III.

D. Results and Discussion

It is appropriate to mention at this point that our analysis of the data can only be meaningful if only the monomer or the dimer is contributing significantly to the relative cross section for reaction. Thus, before proceeding further, we should examine our data and see whether we can claim that the above is true.

First, we can look at the energetics of reactions (1) through (6), and make comparisons between them. When we compare reactions (1) and (3), we can consider reaction (3) as occurring in three steps.

Thus, it comes down to comparing the heats of reactions of (9) and (11). The MX_2 molecule has been predicted as a stable molecule. The heats of

formation of LiF_2 ,⁷ RbF_2 and CsF_2 ⁸ and the heats of reaction of reaction (9) for the last two have been calculated. The heats of dimerization (reaction (9)) for the alkali halides are well known.⁶ In all three cases, the sum of the heats of reaction for (9) and (11) is positive. This is probably also true for other alkali halides. Since reaction (10) is the same as reaction (1), reaction (3) is less exothermic and hence less probable than reaction (1). Similarly, reactions (4), (5) and (6) can be compared with reaction (2). Reaction (4) can be considered as occurring in two steps.

Thus reaction (4) is less exothermic than reaction (2) by the heat of dimerization which is about 40 kcal/mole for the alkali halides under study in this project. Reaction (5) can be thought of as occurring in three steps.

If reaction (5) were to be as exothermic as reaction (2), the heat of reaction of the formation of MXXHg would have to be as exothermic as reaction (14) is endothermic. The M_2X_2 molecule is planar with the M and X atoms at the corners of a rhombic structure.^{9,10} Each M atom is bound to its two neighboring X atoms by strong ionic bonds. On the other hand, the Hg-X bond is much weaker than the ionic bond between M and X. Thus reaction (5) is probably less exothermic and consequently less probable than reaction (2). Lastly, reaction (6) can be viewed

as occurring in four steps.

The exothermicity gained in reaction (20) cannot overcome the huge endothermicity of reactions (17) and (19). For example, the heat of reaction is -19.7 kcal/mole for reaction (20) when X is I. The endothermicities for reactions (17) and (19) are 41.2 kcal/mole and 70.3 kcal/mole respectively. Thus, again we can say that reaction (6) is much less probable than reaction (2). The conclusion from all this is that the production of M^* atoms is much more likely when the excited mercury atoms are colliding with alkali halide monomers from the view point of the energetics of the reactions.

Now we shall consider the results of the two analyses assuming that only the dimer or the monomer can contribute significantly to the relative cross section for reaction. In the case where the monomer is contributing, the relative cross section is a monotonically decreasing function with increasing velocity. For NaI and NaBr. For the LiI, there is a slight rise in the relative cross section at the high velocity end as well. However, in the case where the dimer is contributing, the relative cross section decreases at the lowest velocities and then rises steeply with increasing velocity. The rise is especially steep for LiI where the relative cross section at a relative velocity of 10^5 cm/sec is over 10^4 times the value at a relative velocity of about 3×10^4 cm/sec. Coupled with the fact that the photon

counting rate is still quite high at the highest velocities where the percentage of dimer is 0.3% or considerably less and about 10 times smaller at the lowest velocities where the percentage of dimers is considerable, we may conclude that it is quite probable that only the monomers are contributing significantly in our measured velocity range. Moreover, the energetics of the reactions discussed in a previous paragraph suggest this also.

Figures IV-1 and IV-2 show the results of our experiments with NaI and NaBr. Trial curves assuming a velocity dependence of g^{-s} averaged over the beam velocity distributions are shown together with the data points which represent the arithmetic mean of 5 to 10 measurements at the given velocity. The error bars indicate the experimental standard deviation of the data points. It is seen that for NaI, the best value for s is 3, while that for NaBr is 3.5. The results for the experiment with LiI are shown in Table IV-4. The data indicates a rise in the relative cross section at both the low and high velocity ends of the measured velocity range. For reasons that will be mentioned later, these results are considered to be less reliable than those obtained for NaI and NaBr. Knowing the photon counting rates, photon collection efficiency and estimating the beam intensities at the collision zone as in the previous chapter, we can place the cross section for M^* production at a relative velocity of about 5×10^4 cm/sec at $7\text{\AA}^2$ and $0.3\text{\AA}^2$ for NaI and NaBr monomers respectively.

The rather strong velocity dependence of the relative cross sections for Na fluorescence production in both NaI and NaBr suggest that the reaction may not occur by direct interaction. A statistical

Table IV-4. Velocity dependence of the relative cross section for Li 2^2P (6707Å line) production in the $Hg^* + LiI$ system.

Relative velocity g (10^4 cm/sec)	Relative Cross Section (Arbitrary Units)
2.32	0.61 ± 0.27
2.88	0.10 ± 0.03
3.47	0.046 ± 0.024
4.09	0.036 ± 0.010
4.73	0.042 ± 0.065
5.37	0.051 ± 0.070
6.03	0.081 ± 0.089
6.70	0.052 ± 0.045
7.41	0.053 ± 0.042
8.13	0.033 ± 0.017
8.82	0.058 ± 0.034
9.52	0.20 ± 0.06
10.21	0.13 ± 0.05

model may be more appropriate. In fact, calculation will be performed to determine its suitability. In any case, it seems to be qualitatively correct. We can envision that as the MX molecule and Hg^* atom approach each other, a transition complex MXHg may be formed with a statistical redistribution of the available energy among the M-X and Hg-X bonds. The total available energy will include the excitation energy of the Hg^* atom, the translational energy of relative motion and the vibrational and rotational energy of the MX molecule. Depending on the relative bond strengths of the Hg-X and M-X bonds, the complex may exit along the product channel with the formation of M^* and HgX or reform the reactants. As the relative velocity increases, the probability of forming a stable complex diminishes and the relative cross section decreases until reaction (1) becomes important as the relative velocity increases further and the relative cross section would rise with increasing velocity.

For NaBr, reaction (1) is endothermic and the monotonically decreasing relative cross section gives no indication that reaction (1) may be becoming important. For NaI, both reactions (1) and (2) are exothermic. However, we did not observe a rise in the relative cross section at the high velocity end of the measured velocity range. Thus we believe that we have not reached the energy range where reaction (1) becomes important. There is one disturbing fact as we look at the data for $\text{LiI} + \text{Hg}^*$ which did seem to indicate a rise in the relative cross section at the high velocity end. The energetics for LiI suggests that its behavior should lie between that of NaI and NaBr. This is not true if we have full confidence in our data on LiI. Lithium iodide is by far the most unstable alkali halide we have worked with

in the laboratory. It is easily decomposed on exposure to light and moisture. Therefore, it is suspected that products of decomposition or impurities may be present in the beam during the experiment. Entities like Li_2O or Li which would be present in greater quantities at high velocities may alter the outcome of the reaction. Moreover, the noise in the data for LiI is much more severe than either NaI or NaBr . Thus further experiments should be performed on the $\text{Hg}^* + \text{LiI}$ system to determine whether the rise in the relative cross section at high velocities is real or not. If it is true, we may have to reconsider our current interpretation.

In conclusion, we have to admit that we still know very little about the nature of the reaction $\text{Hg}^* + \text{MX}$. Further experiments could be conducted to determine the identity, angular distribution and the translational energies of the product fragments or even the cross section for production of ionic products of which reaction (8) is an example. Perhaps after all these experiments are performed successfully, we can begin to understand the process better.

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FIGURE CAPTIONS

- Fig. IV-1. Velocity dependence of the relative cross section for the formation of $\text{Na}4^2\text{P}$ atoms in collisions of NaI with $\text{Hg } 6^3\text{P}_{0,2}$ metastable atoms. The error bars represent standard deviations evaluated from the deviation of the experimental data points from the mean value. The solid, dashed and dotted-dashed curves are trial curves with $Q_{\text{rel}}(g) \propto g^{-8}$ and averaged over the beam velocity distributions. The kinetic energy scale is evaluated by setting $E = \frac{1}{2} \mu g^2$.
- Fig. IV-2. Velocity dependence of the relative cross section for the formation of $\text{Na } 4^2\text{P}$ atoms in collisions of NaBr with $\text{Hg } 6^3\text{P}_{0,2}$ metastable atoms. The error bars represent standard deviations evaluated from the deviation of the experimental data points from the mean value. The different curves are trial curves with $Q_{\text{rel}}(g) \propto g^{-8}$ and averaged over the beam velocity distributions. The kinetic energy scale is evaluated by setting $E = \frac{1}{2} \mu g^2$.

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Fig. IV-1.

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Fig. IV-2.

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APPENDIX. Analytic Expressions for the Admittance Function $B(v, v)$ for Cases 1, 2 and 4.

Case 4 $\theta \geq 2\alpha$

Region 1 $B(v, v) = B_1(v, v) \quad v > v_{\max}(\alpha_{\min}) \quad (1)$

Region 2 $B(v, v) = B_2(v, v) \quad v_{\max}(\alpha_o) \leq v \leq v_{\max}(\alpha_{\min}) \quad (2)$

Region 3 $B(v, v) = B_3(v, v) \quad v_{\max}(\alpha_{\max}) \leq v \leq v_{\max}(\alpha_o) \quad (3)$

Region 4 $B(v, v) = B_4(v, v) \quad v_o(\alpha_{\min}) \leq v \leq v_{\max}(\alpha_{\max}) \quad (4)$

Region 5 $B(v, v) = B_5(v, v) \quad v_o(\alpha_o) \leq v \leq v_o(\alpha_{\min}) \quad (5)$

Region 6 $B(v, v) = B_6(v, v) \quad v_o(\alpha_{\max}) \leq v \leq v_o(\alpha_o) \quad (6)$

Region 7 $B(v, v) = B_7(v, v) \quad v_{\min}(\alpha_{\min}) \leq v \leq v_o(\alpha_{\max}) \quad (7)$

Region 8 $B(v, v) = B_8(v, v) \quad v_{\min}(\alpha_o) \leq v \leq v_{\min}(\alpha_{\min}) \quad (8)$

Region 9 $B(v, v) = B_9(v, v) \quad v_{\min}(\alpha_{\max}) \leq v \leq v_{\min}(\alpha_o) \quad (9)$

Region 10 $B(v, v) = B_{10}(v, v) \quad v \leq v_{\min}(\alpha_{\max}) \quad (10)$

$$\begin{pmatrix} B_1(v, v) \\ B_2(v, v) \\ B_3(v, v) \\ B_4(v, v) \\ B_5(v, v) \\ B_6(v, v) \\ B_7(v, v) \\ B_8(v, v) \\ B_9(v, v) \\ B_{10}(v, v) \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 \\ 0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} I_{11}(\alpha_{\min}, \beta_x(v)) \\ I_{11}(\alpha_{\min}, \alpha_o) \\ I_{11}(\beta_x(v) - \theta, \alpha_o) \\ I_{12}(\alpha_o, \beta_x(v)) \\ I_{12}(\alpha_o, \alpha_{\max}) \\ I_{12}(\beta_x(v) - \theta, \alpha_{\max}) \\ I_{21}(\alpha_{\min}, \beta_x(v) + \theta) \\ I_{21}(\alpha_{\min}, \alpha_o) \\ I_{21}(\beta_x(v), \alpha_o) \\ I_{22}(\alpha_o, \beta_x(v) + \theta) \\ I_{22}(\alpha_o, \alpha_{\max}) \\ I_{22}(\beta_x(v), \alpha_{\max}) \end{pmatrix}$$

For Case 1 and 4, since $\alpha' > \theta$ in these cases, part of the triangle representing $B(v, v, \alpha)$ will be truncated and the admittance function $B(v, v)$ becomes quite complicated. If the $B(v, v, \alpha)$ function is known for a specific case, $B(v, v)$ can be evaluated in a similar way (i.e., by sliding a truncated triangle representing $B(v, v, \alpha)$ across a triangle representing $D(\alpha)$). Thus these cases will not be dealt with in detail here.