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CROSSED MOLECULAR BEAMS:
APPARATUS AND DATA ANALYSIS

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Date Transmitted: January 1977

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TABLE OF CONTENTS

	Page
ABSTRACT	v
I INTRODUCTION	1
II APPARATUS	2
A. INTRODUCTION	2
B. VACUUM CHAMBER CONFIGURATION	4
1. MAIN CHAMBER	4
2. SOURCE AND COLLIMATION CHAMBER	11
a. SOURCE CHAMBER MODIFICATIONS	12
3. DETECTOR CHAMBER	13
C. DATA ACQUISITION	18
D. SOURCES	20
1. HIGH TEMPERATURE OVEN	21
2. SUPERSONIC NOZZLE	26
3. HYDROXYL RADICAL SOURCE	32
E. REFERENCES	35-36
III. DATA ANALYSIS	37
A. GENERAL FORMULATION	37
B. EXPERIMENTAL PROCEDURE	41
C. DETERMINATION OF A DIFFERENTIAL CROSS SECTION	44
1. PROGRAM <u>DECON</u>	44
2. VELOCITY RESOLUTION	48
APPENDIX: TOF MEASUREMENT	51
A. INTRODUCTION	51

B. RESPONSE FUNCTION	54
1. PHYSICAL DESCRIPTION	55
2. MATHEMATICAL DESCRIPTION	55
a. SHUTTER FUNCTION	55
b. FINITE IONIZER LENGTH	60
3. DELAY TIME DETERMINATION	61
C. NORMALIZATION	66
D. CALIBRATION	67
E. <u>TOF</u> DECONVOLUTION	68
F. REFERENCES	72-73

ABSTRACT

This report describes a crossed molecular beams apparatus designed to perform experiments involving elastic, inelastic, and reactive scattering of particles under single collision conditions. Included is a description of a high temperature oven capable of heating samples to 2000 K under vacuum conditions. Analysis of data obtained in these experiments is discussed in detail; special emphasis is placed on evaluating data involving particle velocities measured with a time-of-flight technique. Appropriate detector response functions concerning this technique are derived and their effect on velocity resolution discussed.

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INTRODUCTION

This report is intended as a supplementary publication to the doctoral thesis of Richard Behrens, Jr. (University of California, Berkeley - 1975). These publications, in conjunction with an IS report by T. Parr, are intended to provide a reasonably complete description of the crossed molecular beams apparatus extant at Iowa State University and Ames Laboratory. The first part of this report contains a summary of the experimental configuration of the apparatus and a detailed description of a versatile high temperature oven capable of reaching 2000 K under vacuum conditions. Also described is a technique of seeding a relatively heavy gas with helium so as to produce a high energy molecular beam. The second part comprises a description of how data obtained in a crossed molecular beams experiment is analyzed (specifically for reactive scattering). A time-of-flight (TOF) technique for measuring particle velocities is explained and the derivation of appropriate detector response functions given.

II Apparatus

A. Introduction

The purpose of a crossed molecular beams apparatus is to study the dynamics of elastic, inelastic, or reactive scattering events under "single collision" conditions - i. e. when two particles collide, they are either detected or removed from the scattering chamber before they can interact with other particles. This requires high speed pumping and extensive use of cryogenic and differential pumping techniques. Pursuant to this requirement, beam sources must be as intense as possible to allow the study of low probability events consistent with a beam attenuation of 10% or less. These sources must be interchangeable so many different systems can be investigated. The detector of the collision events must be capable of angular, velocity, and internal state resolution of the scattered particles and be universal in its ability to differentiate among chemical species. And the electronic data collecting system must be able to enhance scattered signal with respect to the ambient and experimental background noise. No system yet devised has been able to meet all these criteria although laser induced fluorescence techniques may eventually meet all requirements but the ability to detect any product particle.¹ It is limited by the experimental ability to excite any product to a known stable electronic state and measure and interpret its fluorescence spectrum. This will probably limit this detection technique to atomic, diatomic, and simple triatomic systems.

The first crossed beams experiments met the above criteria with limited success.² These studies were of the alkali metal systems involving the use of two essentially effusive flow sources. The lack

of intense sources was compensated for by short beam paths and use of a flux detector with effectively 100% detection efficiency. The flux detector utilized surface ionization of a tungsten or platinum-tungsten alloy plate by the alkali metals, whose ionization potentials are lower than the work function of the tungsten plates. Unfortunately this technique is limited to alkali systems and is not universal; it is also hampered by a difficulty in distinguishing the alkali metal from an alkali salt. But the detection efficiency coupled with the large probability of a scattering event in these systems and the ease of producing an alkali beam have made this group of the periodic table the most extensively studied and well characterized. Two experimental breakthroughs led to the construction of so-called "supermachines": the development of supersonic nozzle sources³ and a universal detector involving an electron bombardment ionizer and quadrupole mass filter. These machines utilize differentially pumped source chambers as well as detector chambers with ion pumps, titanium sublimators and liquid nitrogen and helium cooling.^{4, 5}

The design of our machine followed that of Lee, et. al.⁵ which has also been utilized by Grice.⁶ Stationary sources are housed in their own differentially pumped chambers which are bolted to a main scattering chamber which also contains large cryogenically pumped surfaces. Three differentially pumped chambers housing various parts of the detector are suspended from a large rotating ring in the top of the main chamber. The detector chambers utilize ion and sublimation pumps as well as extensive cryogenically cooled surfaces to reach ultra-high vacuum, which can be maintained while the rest of the apparatus is vented. Our number density detection system involves electron bombardment ionization coupled with an ion scintillation counter; mass selection is provided by a quadrupole mass filter. Data acquisition is handled by a DEC PDP-8e

computer. This system is capable of angular and velocity resolution; the latter information is provided by measurement of time of flight (TOF) spectra. The following sections will contain a summary of our apparatus; complete details on design considerations alignment procedures, and schematic details have been delineated by R. Beherens, Jr.⁷ Where mentioned, more discussion will be contained in the thesis of T. Parr.⁸

B. Vacuum Chamber Configuration

The apparatus is physically constructed of four main compartments: the main chamber with rotating ring, a lid containing the detector chambers which fits in the ring, and two side chambers which bolt onto the main chamber. The main chamber is further partitioned so that a collimation chamber is created as a buffer between the sources in the side chamber and the scattering chamber which occupies the rest of the main chamber. The source chambers are defined by the side chambers and the inside source chambers. The collimation chambers are defined by the inside source chambers and the partition in the main chamber. The source chambers are perpendicular to one another so that the beams intersect at 90°. The detector rotates around the collision zone in the plane defined by the beams. Both the source and detector chambers were designed so that they could be as close to the collision zone as possible without sacrificing angular or velocity resolution or pumping speed. The detector "lid" contains a mount for a motor driven chopping wheel which is used for TOF resolution. The reader is referred to Figures II-1 and II-2 which show cross sectional views of the apparatus; they will aid in understanding the following discussion.

1. Main Chamber

The main chamber is constructed of 1.5 inch thick 304 stainless

-5-

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Fig II-1. Cross sectional view of the apparatus

Figure II-1. Cross Sectional View of the Apparatus

1. Main chamber.
2. Collimation chamber #2.
3. Source chamber #2.
4. Detector chamber #1.
5. Detector chamber #2.
6. Ionization chamber.
7. Nozzle source #2.
8. Beam source #1.
9. Rotating detector lid.
10. Gate valve drive rod.
11. Detector gate valve.
12. Liquid nitrogen cooling reservoirs.
13. Rotating ring.
14. Rotating lid O-ring seal.
15. Kaydon KG350XPO 35 inch bearing.
16. Bearing retainer ring.
17. Tec-Ring seals #A-01926.
18. Ionizer
19. EAI Quad 250 quadrupole mass filter.
20. Quadrupole exit lenses.
21. EMI 9524S photomultiplier tube.
22. Pilot B plastic scintillator.
23. High voltage cathode.
24. Time of flight chopping wheel.
25. IMC time of flight motor.

Figure II-1 ((cont'd).

- 26. Access port.**
- 27. Detector chamber 1 entrance slit.**
- 28. Detector chamber 2 entrance slit.**
- 29. Ionization chamber entrance slit.**
- 30. Cold shield.**

Figure II-2. Top Cross Sectional View of the Apparatus.

Figure II-2. Top Cross Sectional View of the Apparatus

1. Detection Chamber #1.
2. Detection Chamber #2.
3. Ionization Chamber.
4. Collimation Chamber 1.
5. Collimation Chamber 2.
6. Source Chamber 1.
7. Source Chamber 2.
8. Detector Chamber 1 entrance slit.
9. Detector Chamber 2 entrance slit.
10. Ionization Chamber entrance slit.
11. Beam 1 Collimating slit.
12. Beam 2 Collimating slit.
13. Skimmers
14. Nozzles
15. Heating or cooling fluid tubes.
16. Gas inlet.
17. Beam Flag 1.
18. Beam chopper.
19. Beam Flag 2.
20. Time-of-flight wheel.
21. Liquid nitrogen cooling.
22. Main Chamber.

steel and is a box which is 132 cm long, 130 cm wide, and 84 cm high. It maintains the relative alignment between the source chambers and the detector as well as providing the actual scattering chamber. Access to the chamber is provided by a removable flange encompassing the entire side facing side chamber I (which defines the angle of zero degrees). The scattering chamber is pumped by liquid nitrogen baffled diffusion pumps (CVC 6-inch and 10-inch) which are backed by one 15 cfm Kinney KC-15 mechanical pump, Dow-Corning 705 silicon diffusion pump fluid is used in both diffusion pumps.

The most critical part of the main chamber is the rotating seal which allows the rotating ring which supports the detector ("lid") to maintain a vacuum seal at all times. A radial vacuum seal is made between the outer radial wall of the ring and the radial wall of the hole cut in the top of the main chamber using two special Tec-rings. Each of these o-rings is constructed of a carbon-impregnated Teflon sheath with a U-shaped cross section surrounding a coiled stainless steel expander ring which exerts a force against the sheath causing a seal to be made. The detector lid (which holds the detector chambers) can just be lowered into the rotating ring with a vacuum seal made by a Viton o-ring.

In order to provide increased cryogenic pumping in the scattering chamber, a nickel-plated liquid nitrogen cooled copper cold shield is placed in the main chamber. This cold shield rests on three needle point stainless steel screws to minimize heat conduction. It reaches close enough to the walls of the chamber to effectively form a separate chamber. The ten inch diffusion pump has direct access to this "chamber" while the six-inch pump acts only on the volume between the shield and the walls of the main chamber. On the walls of the cold shield opposite

the beams, a hole has been cut. A stainless steel wedge is placed in the hole to act as a beam deflector, molecules of the beam are more likely to deflect behind the cold shield than back into the scattering chamber.

2. Source and Collimation Chambers

The source chambers are formed in front by an "inside source chamber" and in the rear by the side chambers. The inside source chambers slide into a hole cut in the side of the main chamber, are bolted on, and make a vacuum seal with a Viton o-ring. Source chamber I defines zero degrees for the detector (see Figure II-2). A beam chopper assembly and flag bolts on to the front face of the inside source chamber I. These inside chambers are fairly easy to remove for repairs on the beam chopper which were often necessary when using corrosive gases. The nozzle source bolts onto the back of the front face of the inside chambers.

The back portion of the source chamber is formed by the side chamber which bolts onto the main chamber through the inside source chamber flange. The side chambers are bolted on top of a mobile stand so that they can be rolled back and forth from the main chamber. They also have two round 16 inch diameter ports - one contains a flange which provides water, electrical, and gas inlet feed-throughs to the source chamber and one which gives access to the source chamber to make final connections before pumpdown. Each source chamber is pumped by a 10" CVC diffusion pump (Dow-Corning 704 silicon oil) mounted on the bottom of the side chamber. Source chamber I is roughed by a combination of a Kinney KMB-230 Boostivac blower and a single stage K DH-65 mechanical pump. Source chamber II is roughed by a Kinney KDH-80 mechanical pump.

The collimation chambers are formed by the inside source chamber and the partition on the main chamber. The partition, which is bolted into the main chamber, must be the first thing installed in the apparatus. The collimation chamber is there purely for differential pumping. Only molecules traveling directly in the beam will pass through to the scattering chamber; everything else will be pumped out through the NRC VHS-6 six inch diffusion pumps backed by Kinney KC-15 mechanical pumps. Adjustable collimation slits on the front of the partition along with the beam source define the beam geometry. The efficacy of such an arrangement is demonstrated by the fact that there is no discernible pressure rise in the main chambers when nozzle sources in both source chambers are being used and the source chamber pressure is 2×10^{-4} torr.

a. Source Chamber Modifications. The above arrangement is suitable when doing experiments with two nozzle sources. In all the studies described in this thesis only one nozzle source was used, the other being replaced by a high-temperature source in source chamber II. In this arrangement, the inside source chamber is removed, combining the source and collimation chambers into one. The mount for the high temperature oven is installed directly in the collimation chamber area so as to place the source as close to the collision zone as possible. There is no problem with the reduced effective pumping speed since barium, tin, alkaline earth halide salts, etc. are all pumped by room-temperature surfaces. A steel plate was put over the six-inch diffusion pump to prevent its contamination by "junk" from the oven.

A more radical change was made midway through the barium experiments. After many months of not being able to measure an attenuation under normal operating conditions, it was decided that our nozzle source was too weak.

To gain more intensity, we removed the inside source chamber in chamber I as we had done in chamber II. The nozzle mount was bolted directly to the collimation chamber partition where the collimation slits had been. This increased the intensity tremendously but caused several problems. First, the beam had been chopped by a slotted wheel positioned in the collimation chamber but mounted on the inside source chamber; second, the collimation slits had been removed. And third, the nozzle would create a high background pressure in the main chamber. The first problem was solved by mounting a vane attached to a solenoid mechanism in the main chamber and cycling it at approximately 2.5 hz. Collimation was provided by a strip of metal spot welded to the partition but passing between the chopper and collision zone. A hole was cut in the piece of metal with dimensions calculated to prevent a viewing factor. The edges of the strip were bent in such a way so as to deflect background gas away from the collision zone. The source pressure was regulated so that the pressure in the scattering chamber did not rise above 3×10^{-6} torr so that background gas would not contribute to the scattering. Complete details of this modification and test procedures are described by Tim Parr.⁸ A table providing comparisons of the two configurations is included.

3. Detector Chamber

The stainless steel detector chambers are housed in what is referred to as the "lid" which is inserted in the rotating ring on the top of the main chamber. The lid rotates around the collision zone so that the detector is in the plane defined by the two beams. When an angular distribution is being recorded the detector can be rotated from -8° to 108° and when the TOF wheel is in place from -1° to 91° . There are three chambers: the buffer chamber (No. 1.), detector chamber (No. 2),

Table II-1

Source Chamber I Modification Parameters

<u>Parameter</u>	<u>Old</u>	<u>New</u>
Nozzle		
Distance to COR (center of rotation) ^a	12.21 cm	4.44
Diameter	.02	.02
Skimmer		
Distance to COR	10.53	2.76
Diameter	.10	.10
Collimation Slit		
Distance to COR	.95	.95
Width	.35	.22
Beam Width (FWHM) ^b	1.1°	7°
Attenuation of Metal Atom Beam	<.1 %	.5-4.0
Scattering Chamber Pressure	6×10^{-7} torr	$1-3 \times 10^{-6}$
Detector Chamber No. 1 Pressure	$<1 \times 10^{-7}$	5×10^{-7}

^a at 20 turns back from the skimmer (n=20) nozzle-skimmer distance = .08+.08n cm

^b as calculated

and the ionization chamber. The buffer chamber acts only as one more stage in the differential pumping system. It is pumped by an Ultek 150 liter/sec ion pump and a titanium sublimator with a liquid nitrogen cooled shroud. The front opening of this chamber has a gate valve which can isolate the detector when the apparatus is vented. It also contains two apertures which define what part of the collision zone is seen by the detector. A large hole (.380 cm) is used for measuring scattered signal while a much smaller hole (.008 cm) is used to measure beam intensities. The front of this chamber is double walled to provide liquid nitrogen cryo-pumping.

The second or detector chamber totally encircles the ionization chamber. Molecules which reach the ionization chamber and are not ionized "fly-through" to the back of the detector chamber and are pumped out. This chamber is entirely surrounded with a double-walled liquid nitrogen filled jacket. The ionization chamber is removable and actually fits in a hole in the top of the lid. As the most deeply nested in a series of differentially pumped chambers, it has the lowest pressure. It too is cryo-pumped with liquid nitrogen and also has a liquid helium pump (Janis No. 6CP). The detector chamber has a Veeco 225 l/sec Mag-Ion pump and titanium sublimator while the ionization chamber is pumped by a Veeco 100 l/sec noble gas ion pump. A "tee" is attached to the back of the detector chamber for additional space to house the quadrupole, exit lenses, and scintillator. A slit on the ionization chamber along with the aperture in the gate valve define the angular resolution.

An electron bombardment ionizer similar in design to that of Brink⁹ is mounted on the inside back wall of the ionization chamber. A series of lenses extract the positive ion from the ionizer and focus them towards

the RF quadrupole mass filter (EAI Quad 250) which is mounted on the back of the rear ionization chamberwall, thus protruding into the detector chamber. The mass selected ions are then extracted from the quadrupole by a set of electrostatic lenses and propelled to a high voltage aluminum cathode. Their impact causes the ejection of several secondary electrons which are accelerated to a Pilot B plastic scintillator. The scintillator produces 1 photon per 2.5 KeV of electron energy (the cathode is set at -30KV). The surface of the scintillator is coated with two 500 Å thick layers of vacuum deposited aluminum which keeps out background light and increases the collection efficiency of photons from the scintillator. An EMI-9524S photomultiplier tube amplifies the light pulse with a Signetics NE 529K discriminator used to block out photon pulses and electrical noise. Optical contact between the photomultiplier and scintillator is made with Dow-Corning 705 silicon oil in order to minimize reflective losses. One should note that ions produced by chemi-ionization processes in the scattering chamber are not detected as the ionizer is biased positive (as determined by the ion energy) with respect to ground thus imposing a barrier to entrance of positive ions.

The detector is designed to discriminate against signal produced by background gas. If one does a simple calculation of the expected flux from reactive scattering in the collision zone, one concludes that it corresponds to an effective pressure orders of magnitude lower than the background pressure. This accounts for the extensive use of cryogenic pumping and large ion pumps. Carefully aligned slits insure that only molecules on axis from the collision zone through the detector can be detected and not pumped out. The most important feature is the separate chamber for the ionizer and the "fly-through" design; this insures that ambient gas in the ionization chamber does not build up and contribute to the non-modulated

signal. The scintillation system avoids background from stray photons and electrons; the photomultiplier, unlike an electron multiplier, is not subject to contamination as it is not physically inside the detector.

The "home-made" (henceforth labeled Behrens') ionizer proved to be less efficient than expected; its ionization efficiency was estimated to be on the order of less than one hundredth of one percent. Another problem was the EAI quadrupole which did not have good resolution at high masses due to its five-inch long poles and low frequency mode of operation. It also seemed to have a propensity towards changing its mass calibration as the resolution was altered. In fact, the entire calibration scale shifted to another curve on two occasions. Before running the tin experiments, an Extranuclear No. 041-1 axial ionizer and No. 4-270-9 quadrupole mass filter were installed. Extranuclear controls and power supplies were also bought. (Ionizer control No. 020-2 and Quadrupole Power Supply No. 011-15). This quadrupole maintained a resolution of 1000 ($M/\Delta M$) at 500 atomic mass units. Interchangeable "High-Q Heads" (11, 13, 15), which act as high voltage transformers, improve resolution at given mass ranges. The first head provided a range of 0-40 amu, the second a range of 0-180 amu, and the last one reached a range of 0-600. The ionizer contained an extraction and focusing lens system which could be regulated carefully (a feature not available on the original Behrens' lens system). An extender for the "tee" had to be provided to house the extra long poles (9 inches). As this ionizer is designed to work in the ion space charge limit, care had to be taken that time-of-flight distributions were not distorted. We therefore used a fairly low electron emission and severe extractor voltages - at least as far as typical settings for maximum sensitivity are concerned.

C. Data Acquisition System

The data acquisition system is centered around a Digital Electronic Corporation PDP-8e mini-computer with 4 K memory. It is used to store data and output the results on hard copy which can be used for further analysis. Two 256 location memory banks are set apart to collect data in the "beam off" and "beam on" mode (refer to Figure II-3). These modes are defined by a chopping wheel or vane which modulates the beam from side chamber I. The "beam off" mode should only contain signal resulting from ambient background; this background signal ranges from ten counts per second for high masses to 10^5 counts per second for mass peak 28 which corresponds to nitrogen and carbon monoxide. The computer controls provide for a variable throw out time which prevents contribution to signal from the transient mode of the beam "turning on or off".

The scattered signal is chopped by a slotted wheel mounted next to the detector opening in the gate valve. When molecules begin to move through the slot in the wheel, a photodiode signal is sent to the computer setting the first location as the first time bin. An adjustable bin time generator sets the length of each bin (a minimum of 3 microseconds) and the number of bins to be used for each pulse (typically 35 bins of 40 microseconds each are used to collect time-of-flight data). The molecules travel to the ionizer, are ionized and accelerated through the quadrupole to the scintillation unit where they are detected and formed into a pulse by the photomultiplier. This pulse goes through a gate and into one of two counters. The bin time generator then tells the counter to dump its information into a particular time bin (computer location) corresponding to the length of time from the initial photodiode signal. While this is happening, the other counter is available for data collection. This time of flight histogram is

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Figure II-3. Schematic Diagram of the time-of-flight data acquisition system. Blocks inside of dotted line are contained in the computer.

accumulated in beam off and on modes. This information provides the velocity distribution of the scattered particles; analysis of this data is described in the next chapter. When an angular distribution is measured, the slotted wheel is removed thus increasing transmission of scattered signal. The signal from the photodiode is mimicked by a pulse generator and all the data are stored in one time bin. This mode of operation is used to normalize the TOF data as the signal-to-noise ratio in the TOF mode is much worse than in the angular distribution mode since the wheel has such a low transmission factor (4-13%). During data collection, distributions of the beam on mode, beam off mode, and the difference between the two can be displayed on an oscilloscope. When data acquisition is ended, the stored contents of each bin can be outputted on a teletype. Complete details of this system, including schematics, can be found in Tim Parr's thesis.⁸

D. Sources

The major requirements for beam sources are versatility and ability to produce high intensities. The first source discussed, the high temperature oven, was designed to heat several species to temperatures of up to 2000 K in order to reach pressures of several torr. As the list of intended reagents included alkaline earth halide salts, alkaline earth metals, tin, aluminum, and silicon, the design problems were numerous and are described in detail. Several failures are described so as to prevent other research groups from repeating our errors. The second section describes a highly versatile supersonic nozzle source which produces high intensity beams of any species with an appreciable vapor pressure at room temperature (in our experiments, above fifteen torr). Also described is the technique of

"seeding" a heavy gas with a great overabundance of light gas (helium) in order to produce high energy beams. These two sources were used in conjunction in all the experiments described in later chapters. The third section involves an unsuccessful attempt to produce hydroxyl radicals utilizing high temperature dissociation of water; subsequent attempts to remedy this failure were curtailed due to time limitations.

1. High Temperature Oven

The major criteria for designing a high temperature molecular beam source are that the source reach the needed temperature, withstand corrosion caused by the charge, be mechanically stable, be able to undergo limitless thermal cycling, and be large enough to contain enough charge for many hours operation at the desired pressure. Meeting these requirements under vacuum conditions was non-trivial and successfully accomplished with much trial and error. The temperature requirement was set at 2000 K in order to produce a silicon beam; at the same time, stability at 1000 K was needed to produce barium. The range of chemicals to be used or charges included alkaline earth halide salts, aluminum, tin, barium and silicon. A minimum charge equivalent to 20 hours duration at several torr was considered necessary to insure the smooth running of experiments. And perhaps most crucial, the crucible had to be aligned within five thousandths of an inch and maintain that alignment during repeated cycling. This was made more difficult by the fact that the beam sources were mounted in the horizontal plane so that thermal expansion in the vertical direction had to be accounted for.

Our approach was guided by familiarity with resistive heating sources and the possession of a 10-volt, 600 ampere stepdown transformer. We decided to resistively heat a mantle which in turn radiatively heated a crucible containing the desired reagent. This was extremely flexible as a

HIGH TEMPERATURE OVEN

Figure II-4. High Temperature Oven

crucible could be chosen to fit the reagent without interfering in oven operation. Radiofrequency induction heating does not meet this requirement as either the crucible or its contents must be electrically conductive. Electron bombardment heating was rejected as it can produce excited electronic and charged species of the reagent. The high temperatures required the use of refractory metals²⁰ (tungsten, molybdenum, tantalum) with extensive heat shielding to lessen power requirements and protect the rest of the apparatus. A year's operation of the oven caused several fissures in welded seams of the collimation chamber partition (made of stainless steel) which had to be repaired before experiments could be resumed. First the construction and assembly of the oven and then the choice of crucible materials will be discussed.

The heating mantle consisted of two interwoven helical coils made from molybdenum. Two 3/16" rods were wound individually around a mandril while being heated to red hot by a torch. They were then wound together and nickel brazed into a molybdenum bottom plate and open top ring. Each coil contained nine turns one inch apart and was situated with respect to the other so that they evenly covered the surface of the crucible while allowing the crucible slit adequate space to peak out (Figure II-4). To insure proper alignment of the crucible inside the mantle, two matching hemispherical indentations were drilled in the bottom plate of the mantle. In these indentations resided two ceramic (alumina) balls.¹⁰ The crucible with the same indentations sat on top of the balls thus locating and electrically insulating it from the coils. The top of the crucible was held in place in a similar fashion;

a molybdenum plug tightly inserted into a channel in the top copper block (see Figure II-4) under pressure from a tungsten spring exerted force on the top cap of the crucible through a ceramic ball located by an indentation. The top and bottom of the mantle were bolted to water cooled copper blocks which with the water lines served to bring the electrical current to the oven. The heating mantle was located on the top copper block by 1/8" stainless steel pins.

Heat shielding was provided by Zircar fibrous insulation¹¹ made from zirconium oxide. As this material has a consistency worse than that of asbestos (and probably worse for one's lungs), it was placed in stainless steel foil and rolled around a tube of the same diameter as the mantle. It was tied up with tantalum wire, removed from the tube, and slid over the mantle with an appropriate opening for the crucible slit. Final heat shielding was provided by a copper shield which bolted to the top copper block. Stainless steel plates were bolted to both copper blocks and stainless steel side supports attached to them. The bottom plate was electrically insulated using thin mica sheaths and Bakelite bushings. Thus the oven, once assembled, was totally rigid and not prone to misalignment due to thermal expansion.¹² The molybdenum coils comprising the mantle contracted like a spring when they were heated thus not disturbing the crucible. The thermal expansion of the crucible could be calculated and compensated for when aligning the oven in the side chamber. The spring loading mechanism on the top of the crucible held it in place even while it expanded.

A beam flag was attached to the top steel block (not shown in the figure); it consisted of a flag moving up and down in a channel with a weight attached to the bottom of the flag. The oven was then

bolted to the mount in the side chamber, which was constructed of 1/2" thick stainless steel bars and allowed for independent motion in both vertical and horizontal directions. A braided steel wire attached to the top of the beam flag was wound around a pulley which was situated on top of the mount and connected to a solenoid mounted in the side chamber. When current was sent to the solenoid, the beam flag was pulled into a position blocking the beam. When the solenoid was turned off, the flag fell down; thus if the flag failed, the beam was always on. Water cooling was supplied to the copper blocks by connecting flexible copper bellows tubing using copper swagelocks to a feed through in the side chamber. Typically 10-20% of the total voltage drop occurred in the wire leads to the side chamber from the transformer. Typical operating conditions were six volts at 400 amperes while reaching 1750 K.

The crucibles for the alkaline earth halide salts were made from molybdenum which could withstand the temperatures (1500K) and was impervious to chemical attack. A .75" o. d. rod was bored out using a 39/64" drill; the slit in the crucible was .250" long and .010" wide and was made using an electron discharge machine. The area around the slit was beveled to .010" thickness so that the beam would not emerge from a long channel. The top lid was attached using a press fit with a platinum wire wedged around the edge. This particular procedure was not spectacularly successful as sample did leak out although not impairing the beam. This press fit was extremely susceptible to creep of the sample up the walls of the crucible. When running the barium experiments, the crucible was welded shut with an electron beam welder, thus insuring a leakproof fit; the top cap was cut off when refilling the crucible. The construction

of the crucible was altered too. A 0.75" molybdenum tube with 0.040" wall thickness was cut to the proper length and the bottom end electron beam welded on. The crucible slit was cut with a 0.75" saw blade and then "patched up" with the electron beam so as to make the slit 0.20" long.

Materials problems for tin, aluminum, and silicon were much worse. Molten aluminum is extremely corrosive to almost all substances; molybdenum has limited resistance to attack. It took only 15 minutes at 1700° K for the aluminum to destroy the crucible. Recommended materials are boron nitride and an intermetallic composite of titanium diboride and boron nitride. Both are expensive; the former material would be unable to withstand the thermal stress in our arrangement while the latter is extremely difficult to machine or form into a particular shape. Silicon required a temperature of 2300K. A graphite crucible was filled with a 3:1 mixture of silicon carbide and silicon¹³ and sealed with a press fit. The oven reached 2000K before it shorted out; we surmised, upon inspection, that as the two heating coils expanded inward, they came close enough together to effectively heat shield one another, causing them to melt (molybdenum melts at 2883 K). The graphite crucible escaped unscathed and we felt that if the oven design were suitably modified, the crucible would successfully have served its purpose. The story of tin, mirabele dictu, will be told in the last chapter.

2. Supersonic Nozzle

The advantages of using a supersonic nozzle as a beam source include intensities which are orders of magnitude greater than an effusive source and near mono-energetic velocity distributions.

The basic theory of nozzle flow assumes that a stream of molecules will undergo an isentropic expansion when flowing out of an orifice under high pressures. The effective translational (and sometimes internal) temperature will decrease and all the molecules will travel with some local flow velocity v_s . If H_o is the original enthalpy and H the internal beam enthalpy after expansion:¹⁴

$$H + \frac{1}{2} m v_s^2 = H_o$$

To an approximation:

$$v_s^2 = \frac{2}{m} C_P (T_o - T)$$

where T_o and T are the source temperature and final expansion temperature. This final temperature T which is generally less than one-tenth of T_o means that the molecules travel along with a very narrow speed distribution around that of the flow velocity. The heat capacity, C_P , will include rotational and/or vibrational contributions if they are relaxed in the expansion. Our experience is that for small molecules with large vibrational frequencies ($h \nu \gg kT$) only rotational modes are relaxed. Noticeable relaxation of vibrational modes was measured for di-iodomethane which has low bending mode frequencies associated with the heavy iodine atoms. This lowered effective temperature also causes increased flow along the axis of the beam accounting for the smaller angular divergence. If the expansion is totally efficient in putting all available energy into the flow velocity ($T = 0$), then the speed enhancement over an effusive flow source is:

$$v_s = \alpha_o \left(\frac{C_P}{R} \right)^{1/2}$$

where α_o is the most probable number density velocity of a Maxwell-Boltzman distribution ($\alpha_o = (\frac{2RT_o}{m})^{1/2}$). Since the expansion usually produces a flow temperature of 10-30 K, the expression for the velocity distribution is:

$$F(v) = \frac{v^2}{\alpha_s^2} \exp - [(v - v_s)^2 / \alpha_s^2]$$

where v_s is the flow velocity and α_s is equal to:

$$\alpha_s = (2RT/m)^{1/2}$$

where T is the effective flow temperature. This derivation is usually presented in terms of Mach numbers and the ratio of C_P to C_V .

The Mach number is defined as:

$$M^2 = v_s^2 / c^2$$

where:

$$c^2 = \gamma RT/m$$

c is the local velocity of sound in an ideal gas and γ is the ratio C_P/C_V .

Thus one obtains:

$$\frac{T}{T_o} = [1 + (\gamma - 1) M^2 / 2]^{-1}$$

The higher the Mach number, the lower the effective flow temperature.

One should note that if $C_P = 4R$ (relaxation of all three rotational modes of a non-linear molecule) then the flow velocity will approach twice that of the most probable velocity of an effusive flow source and an effective spread in velocities will result as follows:

$$\frac{\Delta v}{v} = \frac{\alpha_s}{v_s} \approx \frac{1}{2} \left(\frac{T}{T_0} \right)^{1/2}$$

which is typical.¹⁵

The nozzle is composed of a source chamber with a small opening ($\sim .008''$) and a skimmer. The source chamber contained a tantalum heater and chromel-alumel thermocouple so that elevated temperatures could be reached (which can be important in changing the vibrational distribution of reactants). The molecules expand out of the orifice and the expansion is "frozen" downstream before they reach the skimmer. The skimmer is a stainless steel cone with an orifice ($\sim .040''$) cut in the pointed end. It is supposed to "skim out" those molecules not directly along the axis of the beam and prevent them from disrupting the nearly mono-energetic beam. Once the molecules reach the skimmer it is assumed that they no longer interact with one another or essentially collision-free conditions exist. The nozzle-skimmer mount allows for the variation of source-skimmer distance while the experiment is in progress. The characteristics of the beam change with this parameter and usually the distance was set to maximize intensity. Complete details along with alignment procedures have been described by R. Behrens, Jr.⁷

The gas delivery line to the nozzle source is shown in Figure II-5. We show this rather familiar diagram so as to describe our "seeding" technique. The gas line was entirely constructed of $3/8''$ o.d. stainless steel tubing connected using Swage-or-Gyro-lock fittings. The leak valves were Granville-Phillips Series 203, the shutoff valves were Hoke forged needle valves, and the manometer a Texas Instrument Model 141 fused quartz pressure gauge. Glass was not used due to use of pressure of several atmospheres and to avoid breakage. In order to obtain greater translational

SIDE CHAMBER I GAS LINE

L.V. LEAK VALVE
 T.C. THERMOCOUPLE GAUGE
 MAN SPIRAL QUARTZ MANOMETER
 TRAP LN_2 COLD TRAP
 ⊗ SHUT-OFF VALVE

Figure II-5. Side Chamber I Gas Line

velocities in a nozzle source, a heavy gas in low concentration can be mixed with a light gas such as helium. If they mix completely, the resultant gas will have a mass and heat capacity equal to that of the original gases weighted by their respective mole fractions. Since mass is the overriding factor in the flow equation the heavy beam component becomes much faster. One can vary mixtures to vary the speed and even seed with a heavier gas to slow the beam. The simplest way to prepare a seeded gas is to fill a large ballast tank with the wanted mixtures at high pressures and then use this as a source. This was rejected as unwieldy and perhaps unsafe when using poisonous and corrosive gases. Such gases as chlorine, bromine, and hydrogen chloride corroded and contaminated our stainless steel line in normal use. Any attempt to reuse a ballast tank with a potentially reactive gas might cause an explosion. Another method is to use separate gas cylinders but carefully regulate the flow rates of each gas at the cylinder; this is difficult to do at the low flow rates we use.

Our solution was to bleed the heavy gas into the evacuated nozzle system until the desired steady state pressure was reached (for a 10% mixture of heavy gas 20 torr) as measured by the spiral quartz manometer. The seeding gas was then allowed in, raising the pressure to the final level (200 torr). The mixture was forced to go through a mixing chamber filled with borosilicate glass beads. The mixture was allowed to flow through the nozzle for 15 minutes and then the relative intensities of each species was recorded using the detector. After a few more minutes, this reading was checked and if the relative signals were steady, it was assumed that the beam was equilibrated. Due to uncertainties in ionization efficiencies and other experimental unknowns, the exact composition was

undetermined; but we felt that we had a reproducible standard which could be met at later dates. Since velocity distributions could be measured experimentally, we did not have to know the exact mixture to interpret our experimental results.

3. Hydroxyl Radical Source

Production of atomic free radicals associated with diatomic molecules (H, F, Cl, O, etc.) is fairly commonplace;¹⁵ a source for molecular free radicals is much more difficult to design. The only such free radical used in a crossed molecular beams experiment was the methyl radical.^{6, 16} The hydroxyl radical is of great interest to scientists studying pollution and upper atmosphere chemistry; almost nothing is known of its behavior in bi-molecular reactions, including mechanisms and even the products of such events. It is thought that it is more important than oxygen atoms in combustion chemistry.¹⁷

Two approaches to the construction of a source of hydroxyl radicals were taken. The first was the pyrolysis of hydrogen peroxide which is described by Tim Parr.⁸ Unfortunately this method required the use of ninety-eight percent peroxide which is extremely corrosive, potentially explosive, and requires special handling. As a backup system, it was decided that the thermal dissociation of water at temperatures above 2000 K was a reasonable method. At 2200 K, one torr pressure of water dissociates gave ten percent hydroxyl radical. About the only material resistant to oxidation at these temperatures is the precious metal iridium. Utilizing technology learned in constructing the high temperature oven, we decided that the simplest approach would be to pass an electrical current through an iridium tube while water was effusing through a slit in the tube.

Since high source pressures reduced percentage yield, it was decided to use the existing oven mount so that the source would be as close to the collision zone as possible.

The iridium tube¹⁸ was 10 cm long, 0.37 cm in diameter and 0.05 cm wall thickness. The bottom end of the tube was capped off when made and the top end stuck through a hole in a copper block to which it was hard soldered. The gas inlet connection to the tube was made with a Cajon o-ring fitting. The copper block was water cooled and provided the electrical power connection. The electrical connection at the bottom provided a more difficult problem. Iridium softens at 2300 K, melts at 2727 K and has a vapor pressure of 10^{-4} torr at 2400 K. Thus a connection had to be made which allowed for thermal expansion (1 mm) yet put no mechanical stress on the softened tube. A water cooled copper block was suspended from the mount block (with the necessary Bakelite insulation) with stainless steel side supports. Bolted into the bottom block was a stainless steel crucible containing indium. The indium was melted with a torch while the source was assembled to allow the iridium tube to slide into the crucible. When current was passed through the tube causing it to heat up, the indium would melt (m. p. = 429 K) allowing the tube to freely float while making electrical contact. The proximity of the indium to the cold copper block would prevent it from becoming too hot and vaporizing (vapor pressure = 1 torr at 1520 K).¹⁹

The slit on the tube was 0.038 cm wide and 0.478 cm long. The source was attached vertically to the previously described oven mount with a similar beam flag arrangement. Only limited tantalum heat shielding was provided as only 300 watts of power (270 amperes at 1.1 volts) was needed to heat the tube to 2300 K; also, the corrosive nature of the source gas

would cause any such shielding to deteriorate with time. A trial run using oxygen was performed to check the performance of the source. It was found that a maximum pressure of six torr could be used before the diffusion pumps were swamped. We also calibrated our temperature readings with an optical pyrometer by measuring speed distributions of the beam at near-effusive pressures. We reached a temperature of 2100 K when the source failed. We discovered that the indium had attached the iridium tube and destroyed the walls of the tube where it dipped into the indium. The damage was irreparable and this method was abandoned due to time and expense considerations. The availability of a phase diagram would have predicted this catastrophe.

References

1. H. W. Cruse, P. J. Dagdigian, and R. N. Zare
Faraday Disc., 55, 277 (1973).
2. D. R. Herschbach, Advances in Chemical Physics,
Vol. 10(Interscience, New York, 1966) p. 319.
3. For example: J. B Anderson, R. P. Andres, and J. B. Fenn,
ibid, p 275.
4. R. W. Bickes and R. B. Bernstein, Rev. Sci. Instrum.,
41, 759 (1970).
5. Y. T. Lee, J. D. McDonald, P. R. LeBreton, and D. R. Herschbach,
Rev. Sci. Instrum. 40, 1402 (1969).
6. C. F. Carter, M. R. Levy, and R. Grice, Faraday Disc.,
55, 357 (1973).
7. R. Behrens, Jr. Ph.D. Thesis, University of California, Berkeley -
also issued as Lawrence Berkeley Laboratory Report LBL-3529 (1975).
8. T. P. Parr, Ph.D. Thesis (1976) University of California, Berkeley.
9. G. O. Brink, Rev. Sci. Instrum., 37, 857 (1966)
10. Industrial Tectonics, Ann Arbor, Michigan
11. Union Carbide Corporation
12. An unsuccessful attempt to use an unsupported, 0.010 wall thickness
tantalum tube as a mantle was made. After several cycles the tube
buckled where a hole was cut to allow the beam to pass through.
13. S. G. Davis, D. F. Anthrop, and A. W. Searcy
J. Chem. Phys., 34, 659 (1961).
14. H. Pauly and J. P. Toennies, Methods of Experimental Physics,
Vol. 7 (A), (Academic Press, New York, 1968)p. 237.

15. a) Y. T. Lee, P. R. LeBreton, J. D. McDonald, D. R. Herschbach
J. Chem. Phys., 51, 455 (1969) (Cl and Br atoms).
- b) T. P. Schaefer, P. E. Siska, J. M. Parson, F. P. Tully,
Y. C. Wong and Y. T. Lee, J. Chem Phys, 53, 3385 (1970)
(F atoms).
- c) J. Grosser and H. Haberland, Chem. Phys Lett., 7, 442 (1970)
(H and D atoms).
- d) D. D. Parish and D. R. Herschbach, J. Am. Chem. Soc.
95, 6133 (1973) (O atoms) .
- e) D. St. A. G. Radlein, J. C. Whitehead, and R. Grice
Mol. Phys., 29, 1813 (1975) (O atoms).
16. J. A. Logan, C. A. Mims, G. W. Stewart, and J. Ross,
J. Chem Phys., 64, 1804 (1976).
17. W. E. Wilson, Jr., J. Phys. Chem. Ref. Data, 1, 535 (1972).
18. Englehard Industries, Murray Hill, New Jersey
19. F. Rosebury, Handbook of Electron Tube and Vacuum Techniques,
(Addison Wesley, Reading 1965)
20. W. Kohl, Handbook of Materials and Techniques for Vacuum
Devices, (Reinhold, New York 1967).

III. Data Analysis

A. General Formulation

The basic scattering equation is known as Beers Law:

$$I_A = I_0 \exp(-n_B l Q) \quad (1)$$

where I_A is the unscattered flux, I_0 the original intensity of species A, n_B the number density of the scattering particle, l the length over which scattering takes place, Q the cross section of the event. If the exponent is much less than one, the equation reduces to (after some rearrangement):

$$S(\text{no/sec.}) = V n_A n_B g Q \quad (2)$$

where S is the scattered signal, V is the intersection volume, g the relative velocity of A and B, and n their number densities. One notes that this is just a bimolecular rate equation where the rate constant k is:

$$k = Q g. \quad (3a)$$

In fact, the usual thermal rate constant is just this microscopic rate constant¹ averaged over the speed distribution of the particles:

$$k(T) = \int_0^{\infty} Q(g) g F(T, g) dg \quad (3b)$$

where $F(T, g)$ is the usual Boltzman distribution. The cross section thus contains all the information concerning the scattering event, i. e. - the absolute probability (in units of area) that a system will evolve from one quantum state to another. Thus the perfect experiment would involve measuring Q as a function of reactant and product quantum states. This is of course impossible, but total reactive cross sections as a function of relative translational energy have been measured² and reactant internal

state selection performed.⁵ Relative cross sections for evolution to product internal states is measured using electromagnetic fields³ and laser induced fluorescence.⁴

Our interest in reactive scattering involves investigating the dynamics of a scattering event. If two particles collide and react to give two new species, what is the motion of these species with respect to the reactants? Generally we can propose a mechanism of reaction if we can answer that question. The simplest way to "map out" the dynamics in the center of mass (CM) is to use spherical coordinates and obtain relative probabilities of a particle scattering into some solid angle w to $w + dw$, with a velocity u to $u + du$ or differential cross section, $I(\theta, \phi, u)$, defined as follows:

$$Q = \int_0^{\infty} \int_0^{2\pi} \int_0^{\pi} I(\theta, \phi, u) \sin \theta \, d\theta \, d\phi \, du. \quad (4)$$

This differential cross section is actually reduced to a two dimensional problem (θ, u) since in our experiments there is cylindrical symmetry around the relative velocity axis allowing one to simply integrate out the ϕ dependence.

Unfortunately, one measures scattered signal at some laboratory angle Θ and velocity v . Molecules do not recognize that they are traveling at right angles with respect to one another and the data must be transformed into the center of mass (CM) coordinate system. The general formulation can be found in the literature and will be summarized here.^{6,7} If two beams of particle masses M_1 and M_2 collide at a given angle defining an intersection volume, their relative velocity $\vec{g}$, collision energy E , and CM velocity $\vec{C}$ are given by:

$$\vec{g} = \vec{v}_1 - \vec{v}_2 \quad (5)$$

$$C = (M_1 v_1 + M_2 v_2)/M$$

$$E = \mu g^{2/2}$$

where

v_1 = velocity of beam 1

v_2 = velocity of beam 2

$$M = M_1 + M_2$$

$$\mu = M_1 M_2 / M$$

The result is easily shown graphically (Figure III-1) for which the name "Newton Diagram" was coined. Note the relationship between lab and CM coordinates; there are generally two (θ, v) which correspond to the same CM coordinates due to the symmetry around the relative velocity vector $\vec{g}$. The Jacobian for this transformation which preserves the total flux is:

$$S_{\text{flux}}(\theta, v) = I(\theta, u) v^2 / u^2 \quad (6a)$$

Since electron bombardment ionization efficiency is inversely proportional to particle speed, one measures a number density distribution which has been divided by a factor of v :

$$S_{\text{no. density}} = I(\theta, u) v / u^2 = I(\theta, u) J(\theta, u, \theta, v) \quad (6b)$$

This expression is used in all further analysis.

This analysis assumes that the beams are monoenergetic and only one "Newton Diagram" describes the transformation. Unfortunately

Fig. III-1. Laboratory-CM Transformation Diagram (Newton Diagram). Vector OE represents a Laboratory point at angle Θ and velocity V . Notice that it corresponds to the same CM coordinates as Vector OF.

there are distributions in beam velocities which lead to a distribution in Newton Diagrams and CM coordinates which contribute to scattering at a given lab coordinate. The information relating to CM coordinates is therefore somewhat scrambled and at times difficult to recover. The signal measured in the lab (within some not easily determined coefficient), S , is related to $I(\theta, u)$ by:

$$S(\theta, v) = \int_0^{\infty} \int_0^{\infty} I(\theta, u) P(v_1, v_2) J dv_1 dv_2 \quad (7a)$$

$$S(\theta) = \int_0^{\infty} S(\theta, v) dv \quad (7b)$$

where v_1 and v_2 are the beam speeds and

$$P(v_1, v_2) = g F(E) \rho_1(v_1) \rho_2(v_2) \quad (8)$$

is the probability of a Newton diagram contributing to a scattering event, $F(E)$ is the reactant energy dependence of the total cross section, and ρ is the beam speed distribution (J is defined by equation 6b). There is an implicit reactant energy dependence in $I(\theta, u)$ which is ignored here since $P(v_1, v_2)$ is a rather narrow function of energy when a nozzle source is being used. Sometimes, though, $I(\theta, u)$ is assumed to have such a dependence (transition state theory predicts this to occur).

B. Experimental Procedure

Molecular beam experiments are designed to collect data which can be used to solve equation 7 of the preceding section; i. e. - laboratory angular and velocity distributions of the scattered product and velocity distributions of the reactant beams. Velocity resolution of both reactants

and products were obtained using time-of-flight techniques which are described in detail in an appendix. Angular distributions of the product are obtained first (the equivalent of integrating equation 7a over lab velocity) at fine resolution over a wide range of angles (2.5° - 5.0° intervals from -8 to 108° in the lab). TOF data are then collected at several selected angles and for the reactant beams.

The lab angular distribution is time normalized using the program NORM. During an experiment, a reference measurement at a particular angle is taken periodically. If the drift in signal at this reference angle is not statistically significant, then no correction is made. If the drift is large, it is assumed that the signal varied linearly with time (due to long term drift in beam intensities) and corrected using the following equations:⁸

$$S_m(\Theta) = S(\Theta) \cdot I_R(1) / [I_R(i) + (I_R(i+1) - I_R(i)) \cdot C]$$

$$C = (t_m - t_i) / (t_{i+1} - t_i) \quad (9)$$

where the reading, $S_m(\Theta)$, measured at time t_m between reference readings at times t_i and t_{i+1} with intensities $I_R(i)$ and $I_R(i+1)$ give the normalized signal $S(\Theta)$. The standard deviation for each point, neglecting cross terms is:

$$\begin{aligned} \sigma(\Theta) = & \sigma_m(\Theta)^2 \left[\partial S(\Theta) / \partial S_m(\Theta) \right]^2 + \\ & \sigma_{R(1)}^2 \left[\partial S(\Theta) / \partial I_R(1) \right]^2 + \\ & \sigma_{R(i)}^2 \left[\partial S(\Theta) / \partial I_R(i) \right]^2 + \\ & \sigma_{R(i+1)}^2 \left[\partial S(\Theta) / \partial I_R(i+1) \right]^2 \end{aligned} \quad (10)$$

The standard deviations, σ , are just the square root of the total number of counts recorded in the computer locations corresponding to the data point.

The peak of the angular distribution is arbitrarily set equal to 8.0 (for plotting purposes).

The TOF distributions are normalized with respect to one another by requiring the sum of counts in the time bins at each angle to be proportional to the corresponding angular distribution intensity:

$$S(\Theta) = \text{FNORM} \sum_i S_i(\Theta, t_i) \cdot \Delta t \quad (11)$$

TOF data are then nominally transformed to velocity space by the following equations (using program VNOM):

$$v_0 = \bar{L}/t_0 \quad (12a)$$

$$S(\Theta, v_0) = S(\Theta, t_0) \bar{L}/v_0^2 \quad (12b)$$

where $\bar{L}$ is the average flight path, t_0 is the flight time measured from the center of the TOF chopping wheel pulse corrected for ion flight time in the detector, and $S(t_0)$ is the intensity at that time. This representation is graphically more explicit since it is independent of apparatus dimensions. The standard deviations of the nominal velocity points are given by (in the spirit of equation 10 and remembering that

$$S(v_0) = S(t_0) \cdot t_0^2 / \bar{L} :$$

$$\begin{aligned} \sigma_{v_0}^2 &= \sigma_{t_0}^2 \left[\frac{t_0^2 \cdot S(\Theta)}{\bar{L} \cdot \text{FNORM}} \right]^2 + \sigma_{S(\Theta)}^2 \left[\frac{S(t_0) \cdot t_0^2}{\text{FNORM} \cdot \bar{L}} \right]^2 \\ &\quad + \sigma_{\text{FNORM}}^2 \left[\frac{S(t_0) \cdot S(\Theta) t_0^2}{\text{FNORM}^2 \cdot \bar{L}} \right]^2 \end{aligned} \quad (13)$$

where σ_{t_0} is the standard deviation of the TOF point, σ_s of the angular distribution point calculated in NORM, and $\sigma^2_{FNORM} = \sum \sigma(t_i)^2$.

C. Determination of a Differential Cross Section

1. Program DECON

The purpose of analyzing the data is to infer the form of the CM differential cross section, $I(\theta, u)$. There is no unique solution to Equation 7 and methods of deconvolution are prone to numerical instability. One method of attack is to use an iterative approach developed for beam experiments by Siska⁹; a nominal inversion of the data to the CM system is made assuming mono-energetic beams and reinverted using equation 7. This in turn is employed in making a new guess as to the correct inversion and the process continues until the desired fit to the data is accomplished. This method has the advantage that there is no assumption of symmetry about the relative velocity axis and serves as a check on the experimental data. The major drawbacks include no systematic account of statistical uncertainties in the data and a need to smooth the data prior to analysis. A second approach is to represent the CM differential cross section as a set of ortho-normal functions with undetermined coefficients which are varied in order to fit the lab data. Program DECON as written by C. Sholeen¹⁰ has adopted this approach.¹⁹

The CM differential cross section has been expanded using Legendre polynomials to represent angular dependence and fourth order Laguerre polynomials for recoil velocity dependence:

$$I(\theta, u) = 4e^{-u/u_0} (u/u_0)^2 \sum_{i=0}^{n_P-1} \sum_{j=0}^{n_L-1} a_{ij} P_i(\cos\theta) L_j^{(4)}(2u/u_0) \quad (14)$$

where a_{ij} represents the undetermined coefficients. Both angular and velocity data points are fit according to equation 7 subject to energy conservation

$$E' + W' = E + W + \Delta D_0 \quad (15)$$

E = kinetic energy

W = internal energy

ΔD_0 = exoergicity

where primes denote the products, by numerical integration over both beam speed distributions (using the Zaremba method⁷), employing a least squares method to determine the unknown coefficients. The criterion for goodness of fit is the minimization of the quantity chi-squared:¹³

$$\chi^2 = \frac{1}{\nu} \sum_{i=1}^{N_s} (S_i - C_i)^2 / \sigma_i^2 \quad (16)$$

where the sum is over all data points, S_i , the calculated fit to the data point is C_i , the standard deviation of each point is σ_i , and ν is the number of degrees of freedom ($N_s - n_{PL}$). The number of polynomial terms used in the fit is determined according to the F-test.¹³ The F-value is defined as

$$F\text{-value} = \frac{(\chi^2 - \chi'^2) / (\nu - \nu')}{\chi^2 / \nu} \quad (17)$$

where primed terms correspond to the present iteration and unprimed terms to the previous iteration. If the F-value exceeds the F-test criterion for a 95% confidence level, then the latest polynomial term

added is considered to have significantly improved the fit. The parameter, u_0 , in the Laguerre expansion determines the peak of the exponential term and is set by the programmer after searching a wide range of values.

The above form of $I(\theta, u)$ makes no assumption about the separability of the cross section into angle and energy dependent functions and will henceforth be called COUPLED.

At times, one prefers to assume that $I(\theta, u)$ is separable:

$$I(\theta, u) = F(\theta) F(u) \quad (18a)$$

Historically this assumption has been made a priori in order to facilitate computation when recoil velocity data were not available (e. g. -reference 16).

More pragmatically, the COUPLED fits require more velocity data in order to prevent numerical blowup since the COUPLED equations provide many more degrees of freedom. The UNCOUPLED fits are generally well behaved even with a minimum of information and provide a check

on the COUPLED fits since they should not differ drastically in form

although χ^2 may suffer. Equation 14 is usually just uncoupled to:

$$I(\theta, u) = \left[4 \sum_{i=0}^{n-1} b_i P_i(\cos\theta) \right] \left[(u/u_0)^2 e^{-u/u_0} \sum_{j=0}^{L-1} c_j L_j^{(4)}(2u/u_0) \right] \quad (18b)$$

A second function for the velocity dependence is expressed in terms of reaction collision energy, E , and product recoil energy, E' , as (labeled TST):

$$P(E') = A(E, E') \left[\Delta D_0 + \langle W \rangle + E - E' \right]^y / \left[\Delta D_0 + \langle W \rangle + E \right]^{y+1} \quad (19)$$

where: $F(u) = P(E') (dE'/du)$

$\langle W \rangle$ = average reactant internal energy

$A(E, E') = \text{minimum of } 1, 0 \text{ or } (E'/BE)^x$

This is the appropriate expression when testing transition state theory and will be discussed in a subsequent chapter. When using either a COUPLED or UNCOUPLED fit, one can impose symmetry around 90° in the CM by using only even Legendre terms which will be known as COMPLEX.

One can also assume a reactant energy dependence of the cross section or an activation energy. The various dependencies and their labels are:

a.	$F(E) = E^{-1/3}$	ORBITTING	(20)
b.	$= 1$	FLAT	
c.	$= h(E-E^*)$	STEP- E^*	
d.	$= \left(\frac{E-E^*}{E} \right) h(E-E^*)$	LINE OF CENTER- E^*	

where $h(x)$ represents the Heaveside function and E^* is an activation energy. The first case is relevant for a collisional orbiting model assuming a r^{-6} potential for the reactant interaction.¹² The second assumes no energy dependence; the third assumes a step function with some minimum energy, E^* . The fourth assumes an activation energy, E^* , which must be surpassed along the line of centers of two molecules which are approaching with some impact parameter.¹

Standard linear least squares methods were used to solve the COUPLED case. The matrix inversion was accomplished using the Householder method¹⁴ which minimizes the Euclidean norm of $\|B - A\hat{X}\|$ where $\hat{X}$ represents the coefficients. A more typical inversion technique as described in reference 13 proved to be numerically unstable. The UNCOUPLED equations were solved using a subroutine, ZXPOWL, based on Powell's algorithm for finding a local minimum of a real function in this case χ^2 . In either case, available computer storage allowed DECON

to handle 225 data points and up to seven Legendre and seven Laguerre terms. Once the coefficients were determined, the lab angular and velocity distributions were backcalculated and plotted by a Cal Comp incremental plotter. An option, LUMAX, allowed the calculation of the fit to terminate at some maximum CM velocity; this was employed to prevent contributions from CM coordinates where the cross section was negative (a feature due to the functional form of the expansion).

2. Velocity Resolution

Program DECON, as originally written and modified, was designed to handle $S(\theta, v)$ which had already been corrected for the velocity resolution of the detector. As described earlier, our TOF data were nominally transformed to velocity space without correcting for resolution effects. Several molecular beam groups correct the TOF data before searching for a solution to the CM differential cross section using Siska's method of iteration;⁹ this requires extensive hand smoothing of the data and makes uncertain the statistical analysis we have employed.^{15, b, c} We have modified program DECON to accept the nominally transformed data in the following manner. A TOF data point, $S(\theta, t_0)$ represents a true lab velocity distribution $S(v)$ which has been convoluted with a detector response function G :

$$S(v_0) = \frac{\bar{L}}{v_0^2} S(t_0) = \frac{\bar{L}}{v_0^2} \int_0^{\infty} dv G(t_0, v) S(v) \quad (21)$$

$$\text{where } \int_0^{\infty} G(t_0, v) dt_0 = 1.0$$

But since $S(v)$ is given by equation 7, $S(v_0)$ is just:

$$S(\theta, v_0) = \frac{\bar{L}}{v_0^2} = \int \int \int dv_1 dv_2 dv P(v_1, v_2) I(\theta, u) G(t_0, v) J(\theta, v). \quad (22)$$

Thus the program had to be changed to accommodate the extra integration over the detector response function. From experience, it has been found that evaluating equation 22 for each data point involves too much computer time and/or storage. We have approximated it by:

$$S(\theta, v_0) = \frac{\bar{L}}{v_0^2} \sum_i G_i(t_0, v) \int \int dv_1 dv_2 P(v_1, v_2) I(\theta, u) J(\theta, v) \quad (23)$$

where v is no longer a continuous variable but a set number, i , of bins with particular intervals. The $G_i(t_0, v)$ are an integration of $G(t_0, v)$ over the entire velocity bin. In calculating G , the lowest velocity bin is assumed to extend to zero velocity while the highest velocity bin is assumed to extend out to 10^4 m/sec.

One would normally choose equal sized velocity bins but we decided that the intervals should reflect the bias of the data which corresponds to equal time bins and therefore unequal velocity bins. We selected these velocity bins by calculating the width of each experimental time bin in velocity space:

$$v_+ = \bar{L}/t_+ \quad v_- = \bar{L}/t_- \quad (24)$$

where $+$ and $-$ represent the upper and lower limits of the time bin (bin width is typically 40 usec). The number of bins was set equal to the number of data points at a given lab angle. This reflects the TOF data where resolution gained at low velocities is offset by large uncertainties in the recorded signal. Resolution at high velocities is poor but experimental error is small. Once the coefficients of the CM differential cross

section were determined, the lab data were backcalculated using equal sized velocity bins as a check on the self consistency of the approximation and plotted on the same figure as the data points. Slight discrepancies at high velocities are found when compared to the fit obtained in the original least squares routine; this is to be expected as using equally sized velocity bins gives one more resolution at high velocities than one started with. A complete description of the detector resolution will be found in the appendix.

Appendix: TOF Measurement

A. Introduction

Early molecular beam experiments involved measuring signal as a function of angle only:¹⁶

$$S(\theta) = \int_0^{\infty} S(\theta, v) dv \quad (25)$$

In order to analyze these results, the functional form of $I(\theta, u)$ was surmised using adjustable parameters, the integral over v , v_1 and v_2 performed, and the results compared to the experiment. Unfortunately, a large set of parameters provided an adequate fit to the data and many details of the reaction were lost.¹⁶ The next generation of experiments involved gaining velocity information by chopping the product flux with a series of rotating slotted discs which only transmitted a small interval of velocities chosen by the experimenter.¹⁰ These velocity selectors, though, are bulky and require fine alignment. The technique used in this series of investigations is time-of-flight (TOF) analysis which requires a minimum of apparatus in the vacuum chamber and simple mechanical technology.¹⁵ This appendix contains a description of this technique and the means by which obtained information is analyzed.

The scattered particles travel from a collision zone (see Figure III-2a) at some lab angle Θ and are chopped by a rotating wheel having N rectangular slots of width H which is turning with some angular speed and a period P between each slot. The pulse width, W, is the time needed for the wheel to turn a distance H. ($W = P \times \% \text{ transmission}$). As a slot passes the detector opening of width F, setting time equals zero, molecules enter the detector and travel to the electron bombardment ionizer, where a small fraction ($\approx .01\%$) are ionized. The ions then travel to the scintillation counter where they are detected. The time of flight of the detected particles is just:

$$t = \frac{L}{v} + \left(\frac{L}{v^2 + v_I^2} \right)^{1/2} + A'' \quad (26)$$

where L is some distance $L_1 \leq L \leq L_2$ traveled by the neutral particle, the second term a correction for ion flight time in the detector, and the third a correction for misalignment of the triggering mechanism of the computer which consists of a light bulb and photodiode (Figure III-2b) placed 180° out of phase with the detector opening. The two latter factors, combined in a term labeled A, are immediately subtracted as v_I is typically at least an order of magnitude greater than the neutral species velocity, v. This correction is discussed in a subsequent section.

One should note that the parameter t is defined by the time as read from the computer and is referenced to the point at which particles first enter the detector. The quantity t_0 used in the main body of this chapter contains a correction for the last two terms in equation 26 and is referenced to the middle of pulse of molecules transmitted by the

Fig. III-2.

- a. Detector Outline for TOF Analysis
- b. Chopping Wheel and Photodiode Pulse

chopping wheel. This change of reference point was made to facilitate the mathematical formulation of the problem. The relationship between the two is discussed in section D.

B. Response Function

The basic equation governing the signal intensity as a function of time for a number density detector is:

$$S(t, v, L)dt = A_x g_e N_e Q_i \mathcal{F} \frac{F(v)}{v} dv dL G'(t^*) dt^* \quad (27)$$

A_x = detector area

g_e = speed of electrons

Q_i = ionization cross section

N_e = number density of electrons

$\mathcal{F}$ = total flux density at the detector

$F(v)$ = flux density probability as a function of velocity

v = velocity of the particle

t = time measured in the experiment

t^* = dummy time variable related to t by:

$$t = t^* + \frac{L}{v} \therefore dt = dt^*$$

$G'(t^*)$ = response function

The variables t and t^* just arise from the fact that molecules of some velocity passing through the wheel slot for some time dt^* appear "downstream" in the detector at a time given by $\frac{L}{v}$ for a time interval dt equal to dt^* . The variables g_e , N_e , and Q_i can be summed up in an overall detector efficiency, ϵ , and is assumed constant for a given experiment and detected particle. Thus $S(t, v, L)dt$ is equal to the number of counts in time bin, t , with width dt , for a particular velocity,

flight path, and response function value. Experimentally one measures the signal without reference to v , L , or G :

$$S(t) = \epsilon \int \int dv dL \frac{F(v)}{v} G'(t^*) \quad \text{where } G'(t^*) = G'(t, L, v) \quad (28)$$

Notice that since $dt = dt^*$, both can be eliminated. The time, t , is that which is read from the computer. If the flight path were well defined, $G'(t, L, v)$ would be a delta function in L and the integral over dL would be eliminated. But experimentally, L is found to vary over a considerable range.

The response function contains two factors. One is a shutter function which is just a scaling factor for the detector area as a function of time which arises from chopping the signal with a slotted wheel. The slot and detector opening have finite widths which cause the shape of the pulse of molecules not to be a delta function; the pulse is triangular if both are the same size, a square wave if one is much smaller than the other, and trapezoidal if one is somewhat larger. This causes an uncertainty in time zero since generally the pulse length of molecules is about ten percent of the flight time for reactive scattering and the length and shape of the pulse must be accounted for.

The second factor arises from an uncertainty in the flight path length which is equal to the distance from the chopping wheel to the point of ionization and extraction. This must be accounted for by integrating the shutter function over the length of the ionizer. If the entire ionizer is not utilized, integration over a smaller interval is performed. Thus $G'(t^*)$ is the probability that for a given flight path and shutter function, a particle of given velocity will appear in a given time bin t .

1. Physical Description

The chopping wheel and detector opening form a barrier to entry of particles into the detector. The effective area of the detector entrance is determined by the shutter function (See Figure III-5) with reference points A, B, C, and D. If the scattered signal is of constant flux, the number of particles entering the detector is proportional to that effective area. Assuming mono energetic particles which are all ionized at some distance L from the chopping wheel, signal will be recorded in the computer starting at some time t such that $t^* (= t - L/v) \geq A$ and continuing until $t^* = D$ with relative intensities determined by the shutter function. A further obfuscation is the variation in flight paths for the detected particles. This has an effect of "smearing out" the information even more. Figure III-3 shows the relative contribution of a given velocity to a time bin corresponding to some nominal velocity. The area under each curve is determined by the Jacobian v^2/L . The need to average over flight paths is dramatically shown, especially at low velocities, in Figure III-4. This illustrates that many time bins will contain contributions from particles with a particular velocity.

2. Mathematical Description

a. Shutter Function

The shutter function is just a trapezoid defined by a rectangular slit moving by a rectangular detector opening (Figure III-5) where:

A = delay time determined experimentally (see Section B-3)

$$B = W \cdot F/H + A$$

$$C = W + A$$

$$D = W(1 + F/H) + A$$

Fig. III-3. The Response Function, $G(t_0, v)$, multiplied by the pulse width W . $W=50$ 2sec, $F=H=.380$ cm. Arrows mark the nominal velocity, v_0 . This represents the actual probability of a particle with a given velocity, V , contributing to a time bin corresponding to a nominal velocity. The effect of the ionizer width is not so apparent due to the sharp triangular nature of the shutter function. The solid line represents flight paths of 17.32-21.32 cm (actual case) and the broken lines represent flight paths of 19.22-19.42 cm. Notice the effect of the Jacobian, v^2/L .

XBL 75I-5455

Fig. III-4. This figure shows the range of arrival times for particles with a given velocity. The relevant parameters are $F = .30$ cm $H = .44$ cm, $W = 74 \mu$ sec, and $L = 17.32 \rightarrow 21.32$. The peak of each curve is arbitrarily normalized to 1.0 (the areas under each curve should be 1.0). The effect of the ionizer width is quite apparent for the slower particle; the total pulse lasts for $W(1+F/H) = 125 \mu$ sec and the range of arrival times for the slower particle is 300μ sec but only 150μ sec for the fast particle.

Fig. III-5. Shutter Function. The total width is equal to $W(1+F/H)$. $B = F \cdot W/H + A$, $C = W + A$, $D = W(1+F/H) + A$

F = detector width (cm)

H = wheel slot width (cm)

W = pulse width (sec)

Here it is assumed that F is smaller than or equal to H. If not, F becomes the wheel slot width, H the detector opening, and the pulse width, W, refers to the detector opening. Thus nothing is gained by making the TOF wheel slot any smaller than the detector opening.

To facilitate computation, an analytic expression has been derived to describe the shutter function:¹⁷

$$SF(1) = (S/2)[(t^* - A) + |t^* - A|] \quad (29a)$$

$$SF(2) = (-S/2)[(t^* - B) + |t^* - B|]$$

$$SF(3) = (-S/2)[(t^* - C) + |t^* - C|]$$

$$SF(4) = (S/2)[(t^* - D) + |t^* - D|]$$

where $S = H/F \cdot W^2$ and $|\dots|$ denotes absolute value. The sum of these four functions defines the shutter function, which when summed up gives:

$$\begin{aligned} SF(t^*) &= SF(1) + SF(2) + SF(3) + SF(4) \\ &= (S/2)[|t^* - A| - |t^* - B| - |t^* - C| + |t^* - D|] \end{aligned} \quad (29b)$$

Notice that this expression is well defined for all time, t^* , whether less than A or greater than D.

b. Finite Ionizer Length

As was mentioned previously, the flight path of the scattered molecule is not the same for all molecules. The range of flight paths, L_1 to L_2 (Figure III-2a) depends on ionizer characteristics and the ionoptics which extract the charged particles. Even if a particle is ionized at the beginning of the ionizer, if it is not extracted until it reaches the end of the ionizer, its flight time will reflect the longer distance. We will now

integrate the response function over L, assuming equal probability of all flight paths between L_1 and L_2 ($\Delta L = L_2 - L_1$):

$$G(t_o) = \frac{L_2}{L_1} \int S/2 [|t^* - A| - |t^* - B| - |t^* - C| + |t^* - D|] dL / \Delta L \quad (30a)$$

Now if: $|X_i| = |t^* - K_i| = |t - L/v - K_i|$

$$dX = - \frac{1}{v} dL$$

$$dL = -vdX$$

$$\int |X| dX = \frac{|X| X}{2}$$

$$G(t_o) = \frac{Sv}{2\Delta L} \frac{L_2}{L_1} \int [|X_1| - |X_2| - |X_3| + |X_4|] dX \quad (30b)$$

$$= \frac{-Sv}{4\Delta L} [X_1 |X_1| - X_2 |X_2| - X_3 |X_3| + X_4 |X_4|] \frac{L_2}{L_1} \quad (30c)$$

$$\begin{aligned} G(t_o) = \frac{-Sv}{4\Delta L} [(t - \frac{L_2}{v} - A) \cdot |t - \frac{L_2}{v} - A| - (t - \frac{L_2}{v} - B) \cdot |t - \frac{L_2}{v} - B| \\ - (t - \frac{L_2}{v} - C) \cdot |t - \frac{L_2}{v} - C| + (t - \frac{L_2}{v} - D) \cdot |t - \frac{L_2}{v} - D| \\ - (t - \frac{L_1}{v} - C) \cdot |t - \frac{L_1}{v} - C| + (t - \frac{L_1}{v} - B) \cdot |t - \frac{L_1}{v} - B| \\ + (t - \frac{L_1}{v} - D) \cdot |t - \frac{L_1}{v} - D| - (t - \frac{L_1}{v} - A) \cdot |t - \frac{L_1}{v} - A|] \end{aligned} \quad (31)$$

One should note that whereas the shutter function is well defined, the response function, G, involves the computation of possibly small differences in large numbers and can cause problems in numerical computation on a computer. So far, this has not been a problem in calculating reasonable fits to beam TOF spectra.

3. Delay Time Determination

The delay time, A, is just a combination of the ion flight time from the point of extraction to the detector (flight path L') and a phase shift due to incorrect alignment of the triggering mechanism:

$$A = A' + A'' \quad (32)$$

$A' =$ phase shift

$A'' =$ ion flight time

We have assumed that L' (Figure III-2a) is a constant for all detected particles (it actually depends on the effective flight path L); it was set at the distance from the rear of the ionizer to the last exit lens before the ion reaches the aluminum cathode. It was then assumed that A'' could simply be calculated by assuming that the charged particle's velocity was solely determined by the ion energy setting of the detector:^{15c}

$$\frac{1}{2} mv^2 = eV$$

$m =$ mass of the particle

$e =$ electric charge

$V =$ ion energy (volts)

$$A'' = L' / v_I = L' \left(\frac{m}{2eV} \right)^{1/2} \quad (33)$$

We tested this assumption by measuring TOF distributions of bromine and sulfur hexafluoride beams. The SF_5^+ and Br^+ distributions were shifted to lower flight times with respect to SF_5^+ and Br_2^+ as predicted by the above equation.

If the triggering mechanism is perfectly aligned, the computer will start counting exactly as molecules first enter the detector. This occurs when the front edge of the slot in the wheel is aligned with the front edge of the detector opening. The phase shift, A' (in seconds) is just the amount of time the computer is turned on before or after the front edges of the wheel slot and detector opening are aligned.

If the computer turns on early, A' is defined as positive; if the computer is turned on late A' is negative. Measuring A' accurately requires a nozzle beam as a reference since it produces a sharp peak in the TOF spectrum. If one then measures the difference in peak time bins when turning the wheel in opposite directions, this is equivalent to measuring the difference in phase shifts. If one can analytically determine what this difference should be, the phase shift in each direction is easily calculated. If the computer turns on when the wheel is some distance D (Figure III-6) from the front edge of the detector opening, the phase shift, A' (seconds), is:

$$\begin{aligned} A' &= \frac{D}{O} & O &= \text{wheel velocity (cm/sec)} \\ &= \frac{D}{aR} & R &= \text{wheel radius (cm)} \\ & & a &= \text{angular velocity (rad/sec)} \end{aligned} \quad (34a)$$

If P is the measured period between the pulses and N is the number of slots on the wheel:

$$A' = \frac{D \cdot N \cdot P}{2\pi R} \quad (34b) \quad \text{where } a = \frac{2\pi}{N \cdot P}$$

Now the pulse width is just the time for the wheel to travel the distance of the slot, H , and is related to P by

$$W = \frac{NH}{2\pi R} \cdot P \quad (34c) \quad \text{notice } \frac{NH}{2\pi R} = \text{transmission of wheel}$$

Therefore combining equations 34a, b, c

$$A' = \frac{DN}{2\pi R} \cdot \frac{2\pi R}{NH} W = \left(\frac{D}{H}\right) W = \psi W \quad (34d)$$

All this amounts to giving the distance of misalignment in units of slot width, H , and realizing that the wheel turns the distance H in time W (pulse width). Once ψ has been determined, it is a constant for any wheel of the same slot width and one only needs to know the pulse width.

Fig. III-6. Phase Shift Determination

- a. The wheel is turning counterclockwise and F represents the detector slit width.
b. The wheel is turning clockwise and the new front edge is now a distance $2M$ from the above case.

The top diagram in Fig. III-6 depicts the wheel turning clockwise with a pulse width W , slot width H , and detector width F . The computer is being triggered early when the slot edge is some distance D (not to be confused with the shutter function) from the front edge of the detector opening. The trigger point has been artificially set at some distance M from a point 180° from the front edge of the slot. If the wheel is turned counter clockwise, one must realize that the front edges of the wheel slot and detector opening have been switched (they were the back edges). The triggering point has remained the same in space, but the front edge of the slot is now a distance $2 \cdot M$ past where it had been (Figure 6b). To this must be added the distance F (detector width) since the front edge of the detector has changed. Therefore:

$$D' = -(D + 2M + F) \quad (35a)$$

$$A'_{ccw} = \left(\frac{D'}{H}\right) W = - \left(\frac{D}{H} + \frac{2M}{H} + \frac{F}{H}\right) W \quad (35b)$$

$$A'_{ccw} = - \left(\psi + \frac{F}{H}\right) W - 2Z \quad (35c)$$

where D/H is just θ , and Z is $\left(\frac{M}{H}\right) W$ and is measured on the oscilloscope (Fig. III-2b). Z can be set on any point past the front edge of the pulse (corresponds to the front edge of the slot passing by the light bulb) but we normally trigger off the back edge. The negative sign arises from the fact that in the counter clockwise direction, we are triggering late.

Now the difference in the two measured TOF peaks of the nozzle beam is:

$$\Delta T_{\text{peak}} = A'_{\text{cw}} - A'_{\text{ccw}} = \psi W - [-(\psi + F/H)W - 2Z] \quad (36a)$$

$$= (2\psi + F/H)W + 2Z \quad (36b)$$

$$\psi = \frac{\Delta T - 2Z - (F/H)W}{2W} \quad (36c)$$

Once ψ is known, A is just:

$$A = \psi W + A'' \quad (37)$$

C. Normalization

The normalization of the response function requires that total flux be conserved and set to 1.0:

$$\int_0^{\infty} G(t, v) dt = 1.0 \quad (38)$$

This allows all relative normalization of data under varying experimental conditions to be determined using angular distributions. The area of the shutter function is just:

$$(S/2)(2F/H)W^2 = (H/2FW^2)(2FW^2/H) = 1.0$$

Thus:

$$\int_0^{\infty} G(t, v) dt = \int_{L_1}^{L_2} \int_0^{\infty} SF(t^*) dL dt^* / (L_2 - L_1)$$

$$\text{where } t^* = t - L/v \quad dt^* = dt$$

$$= \int_{L_1}^{L_2} 1.0 dL / (L_2 - L_1)$$

$$= \frac{L_2 - L_1}{L_2 - L_1}$$

$$= 1.0$$

(40)

Thus the probability that a particle with a given velocity will appear in the detector is normalized to one. Notice that this is independent of pulse width and ionizer length.

D. Calibration

Calibration of the TOF parameters (i. e. - L_1 and L_2) is usually performed by measuring the speed distribution of an effusive source which should be a Maxwell-Boltzmann distribution (completely characterized by the source temperature). Unfortunately in the old apparatus configuration, which included a collimation chamber, a measurable effusive beam could not be produced using the nozzle source. It was decided to go to the opposite extreme of supersonic flow conditions where the speed distribution is characterized by a Mach number and a parameter $\gamma(C_p/C_v)$.¹⁸ If the expansion is relatively complete ($M \simeq 8$) the peak of a measured speed distribution is solely determined by γ and L_1 and L_2 . A computer program, CONVOL, was written which performed the convolution of the response function, G , with the expected speed distribution:

$$S(t) = \int G(t, v) v^2 \exp\left[-(v - v_s)^2 / \sigma_s^2\right] dv \quad (41)$$

and plotted out the resulting TOF spectra. γ was set by including all translational and rotational modes. The values that fit a wide variety of this type of data (including mon-, di-, and triatomic gases) were

$L_1 = 17.32$ cm and $L_2 = 21.32$ cm. This corresponds to the full width of the Behrens' ionizer; this was expected as the ionizer was almost half as wide as it was long (1.5 cm compared to 4 cm) and the ion energy was set at 85 volts. Thus one would expect efficient extraction of the ions as they were produced in the ionizing region.

Calibrating the Extranuclear ionizer was made much easier by the fact that there was no collimation chamber present. Carbon dioxide was leaked into the side chamber (side chamber pressure $\sim 5 \times 10^{-5}$ torr) and allowed to effuse through the skimmer and a speed distribution measured. The values of L_1 and L_2 which corresponded to a Boltzman speed distribution at 298 K (room temperature) were 18.6 and 19.1. cm. This range correlated to the rear .5 cm of the ionizer. The ion energy was set at only 25 volts and the ionizer was designed to work in the space charge limit. Thus one would expect comparatively inefficient extraction of ions allowing them to drift through the ionizer with the same velocity until they were extracted as they reached the rear.

E. TOF Deconvolution

As mentioned in the main body of this chapter, the CM differential cross section deconvolution program had been set up to handle velocity data that had been corrected for detector resolution. Several groups 15 b,c have deconvoluted the TOF data before using it in a main data analysis program by using Siska's method.⁹ This approach recognizes that Equation 27 is a Fredholm integral of the first kind:

$$h(x) = \int_a^b dx' g(x, x') f(x') \equiv g * f \quad (42)$$

One recognizes that there are many oscillatory solutions for $f(x')$ ($= c(x') + d(x')$) such that $g + d = 0$, where $c(x')$ is the correct solution. Thus $f(x')$ is extremely sensitive to any noise in $h(x)$; also $g(x, x')$ can sometimes be a rather wide bandpass thus compounding the problem.

Siska's approach obtains a first guess at the solution by setting (using his notation):

Table III-1

TOF Parameters		
Parameter	Behrens' Ionizer	Extranuclear Ionizer
Flight Path		
L_1 (cm)	17.32	18.6
L_2	21.32	19.1
Detector Opening (F)		
large (cm)	.380	.318
small	.008	.008
Wheel Slot (H) ^a		
(cm)	.508	
	.380	.380
L' (cm)	12.5	27.4
Pulse Width (μ sec)	45 - 100	45
Ion Energy (volts)	65 - 85	20 - 30

^aThe first entry (.508 cm) corresponds to a wheel with $\sim 12.4\%$ transmission. The second entry (.380 cm) corresponds to a wheel with $\sim 3.7\%$ transmission.

$$f_0(x') = h(x) J(x, x') \quad (43)$$

which assumes that $g(x-x') \rightarrow \delta(x-x')J(x, x')$ where J is just the Jacobian of the transformation and δ is the delta function. Succeeding guesses are obtained by:

$$f_{n+1}(x') = f_n(x') [h(x)/g*f_n] \quad (44)$$

and continued until the average value of $[h(x)/g*f_n]$ reaches some pre-determined value. Some form of interpolation between data points is used to perform the convolution. Siska has had success in using this approach for the CM differential cross section determination (which is a similar problem where $P(E)$ is the bandpass). Upon using this method for deconvoluting TOF data, we found that the routine diverged when random noise produced undulations in the data with a frequency much higher than that of the detector bandpass; this was not unexpected as our detector response function was broad compared to our time resolution (at low velocities the bandpass extended over several time bins)

An ironic twist is that if spectra were taken with lower velocity resolution (by using larger time bins) the oscillatory nature of the data would have been reduced. Another way to ameliorate the situation is to decrease the response function width by using shorter pulse periods; unfortunately, this leads to "wrap-around" - low velocity particles appear in the first time bins of the next pulse.^{15a} This can be corrected for but again effectively smooths data accumulated for long flight times. We did not want to smooth our data so as to preserve the calculated statistical error bars.

Modifying DECON would allow the program to fit the scatter in the data as the statistics allowed. The TOF data were transformed by assuming a nominal time for a given time bin which corresponded to:

$$t_0 = t - (D+A)/2 \quad (45)$$

which is just the time corrected to the middle of the shutter function (This may just be considered an idiosyncrasy of our definition of the delay time, A).

References

1. M. Menzinger and R. Wolfgang, *Angewandte Chemie (Int. Edition)*, 8, 438 (1969).
2. e. g., M. E. Gersh and R. B. Bernstein, *J. Chem. Phys.*, 56, 6131 (1972).
3. e. g., R. Grice, J. E. Mosch, S. A. Safron, and J. P. Toennies, *J. Chem. Phys.*, 53, 3376 (1970).
4. c. g., P. J. Dagdigan, H. W. Cruse, A. Schultz, and R. N. Zare, *J. Chem Phys.*, 61, 4450 (1974).
5. e. g., a) P. R. Brooks, and E. M. Jones, *J. Chem. Phys.* 45, 3449 (1970).
b) R. J. Beuhler, R. B. Bernstein, and K. H. Kramer, *J. Amer. Chem. Soc.*, 88, 15331 (1966).
6. S. Datz, D. R. Herschbach, and E. H. Taylor, *J. Chem. Phys.*, 35, 1549 (1961).
7. T. T. Warnock and R. B. Bernstein, *J. Chem. Phys.*, 49, 1878 (1968).
8. R. Behrens, Jr., Report (June 1976) Ames Laboratory, Ames, Iowa.
9. P. E. Siska, *J. Chem. Phys.*, 59, 6052 (1973).
10. C. M. Sholeen and R. R. Herm, *J. Chem. Phys.*, 64, 5261 (1976).
11. M. Abramowitz and A. Stegun, Handbook of Mathematical Functions, (Dover, New York 1964).
12. H. S. Johnston, Gas Phase Reaction Rate Theory, (Ronald, New York 1966).
13. P. R. Bevington, Data Reduction and Error Analysis for the Physical Sciences, McGraw-Hill, New York 1964).
14. Golub, *Num. Math.*, 7, 206 (1965).
15. a) J. D. McDonald, P. R. LeBreton, Y. T. Lee, and D. R. Herschbach, *J. Chem. Phys.*, 56, 769 (1972).

15. (Cont'd)

- b) D. St. A. G. Radlein, J. C. Whitehead, and R. Grice, Mol. Phys., 29, 1813 (1975).
- c) J. A. Logan, C. A. Mims, G. W. Stewart, and J. Ross, J. Chem. Phys., 64, 1804 (1976).
- 16. S. M. Lin, C. H. Mims, and R. R. Herm, J. Chem. Phys., 58, 327 (1973).
- 17. R. Masel, Private Communication
- 18. H. Pauly and J. P. Toennies, Methods of Experimental Physics, Vol. 7(A) (Academic Press, New York, 1968)p. 237.
- 19. R. Behrens, Jr. modified the program to allow it to handle angular distribution points; he also rewrote the plotting routines. A. Freedman provided the velocity resolution correction. Joni Gray is gratefully acknowledged for her valiant efforts to represent the CM differential cross section using bar graphs instead of a polynomial expansion. For reasons unknown, this representation was extremely unstable.