

AD 721400

Molecular Beam Analyzer for Identifying Transient
Intermediates in Gaseous Reactions*

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ABSTRACT

When using a mass spectrometer to monitor free radical and atom intermediates in rapid gas-phase reactions, identification of the parent species of each ion is made difficult by fragmentation processes that occur at electron energies necessary for optimum ionization cross sections. Molecular beam analysis is a new approach to this problem whereby molecular beam measurements are used to characterize neutral species before they are ionized. Thus, the trajectory of a particle in an inhomogeneous magnetic field shows whether or not it has a large magnetic moment characteristic of a free radical, its motion in an inhomogeneous electric field indicates its symmetry and the magnitude of its electric dipole moment, and its velocity distribution determines its mass when the source temperature is known. Using these techniques, various atom, free radical and unstable molecular species have been identified in gases excited by microwave discharge or as products of atom-molecule reactions.

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INTRODUCTION

Research in gas phase reaction kinetics has been characterized by great duplication of effort resulting from uncertainties in reaction mechanisms. While measurements of reactant decay rates can provide precise determination of absolute rate constants and comparisons of relative product yields can provide relative rate constants, the conclusions of such work have often been invalidated by discovery of inaccuracies in the assumed reaction mechanism. Unequivocal mechanisms are best ascertained by methods that identify intermediates and measure their variation in concentration during the course of a reaction.

Progress in this direction has already been considerable, and techniques such as electron spin resonance, kinetic spectroscopy and mass spectrometry have contributed greatly to the development of gas phase kinetics. No truly general method for monitoring transients, however, has yet been developed. Electron spin resonance has been successful primarily with monatomic and diatomic intermediates, and spectroscopy has been limited to small species that produce simple, well-resolved spectra. Mass spectrometry, due to its universal applicability and great sensitivity, would appear to be most appealing for this purpose.¹ However, its use for the measurement of small free radical concentrations has

presented many difficulties, of which the elimination of interferences due to dissociative ionization processes has proved to be the most recalcitrant. Mass spectroscopists have followed two approaches, either subtracting out interferences that contribute at the free radical ion, or forming ions by bombardment with electrons of insufficient energy to induce any dissociative ionization process. The former approach is only applicable when the mole fraction of the radical is large, while the latter has resulted in greatly reduced ion intensities and has not been particularly effective in analyzing more complicated systems. In addition, it is often difficult to eliminate contributions from dissociative ionization of vibrationally excited species or interferences from the isotopic variations of the major reactants or products in the system. A key feature of mass spectrometers that have been most successful in analyzing for transients has been the molecular beam sampling system, i.e. a collisionless path between the source and the ionization region.² This modification eliminates destruction of unstable intermediates on surfaces of the apparatus and permits modulation of the beam to discriminate against ions formed from background gas in the ionization chamber.

We have been developing a new approach towards greatly expanding the applicability of mass spectrometry to this problem of

detecting and monitoring intermediates in gaseous reactions. Basically, our method is to employ a number of molecular beam techniques to measure properties of the transients before they are ionized in the mass spectrometer.³ Preselection of neutral species in the beam before ionization eliminates interferences at the parent peak of the transient species and thus obviates the necessity for using low energy electrons, with the resulting loss of ionization efficiency. In addition, beam measurements could be employed in cases where appearance potential discrimination would be ineffective due to the possibility of breaking very weak bonds or bonds containing appreciable vibrational energy. We have termed the use of molecular beam techniques for this purpose "molecular beam analysis".

Specifically, the properties measured in the molecular beam are velocity distributions and magnetic and electric dipole moments. For a molecular beam effusively sampled from a source with a definite translational temperature, the mass of the neutral parent of an ion may be determined from its velocity distribution.⁴ A rough measurement of the magnetic moment of the parent is given by its transmission through an inhomogeneous (hexapolar) magnetic field and signifies whether it is a paramagnetic free radical or a diamagnetic molecule. Finally, the electric dipole moment of the parent, as well as its symmetry, is indicated by its transmission through an inhomogeneous (quadrupolar) electric field.

APPARATUS DESCRIPTION

A schematic diagram of the molecular beam analyzer is shown in Fig. 1. Molecules effuse from a reactor into an apparatus composed of four chambers, the vacuum characteristics of which are listed in Table I. The detector chamber contains a high efficiency electron bombardment ionizer and a mass spectrometer. The latter is a 450, 15-cm radius magnetic sector instrument with variable entrance and exit slits, and is generally operated with a resolution of ca. 100. Ions are collected on a 12-stage DuMont electron multiplier (type SPM-02-402), which provides a gain of 10^5 when operated at 2.5 kV. This chamber is also fitted with a Granville-Phillips variable leak valve which permits controlled addition of background gas to the detector.

The beam ionizer, which is shown schematically in F. 2, is similar to one designed by Weiss.⁵ Ionization occurs between grids 1 and 2, which are electrically connected so that the potential distribution between them is established by the electron space charge. The space-charge potential has a minimum in two dimensions and is made to monotonically decrease in the third direction by increasing the separation between the grids toward the exit electrode. The ions are thus confined as they are accelerated out of the space charge. After further acceleration the ions are

Table I
Vacuum Characteristics of Molecular Beam Analyzer

Chamber	Source	Main	Buffer	Detector
Pump	285 liter/sec oil diffusion	1200 liter/sec oil diffusion	8 liter/sec ion	50 liter/sec, ion + 3600 liter/sec Ti sublimation
Typical* Pressure (Torr)	5×10^{-6}	1×10^{-6}	3×10^{-8}	2×10^{-9}
Beam path in chamber (cm)	3	45	20	20 (to ion- izer)

*With reactor at 1 Torr and using a .01-cm diameter circular sampling orifice.

deflected onto the entrance slit of the mass spectrometer. Weiss' original design has been modified by eliminating the grids from the entrance and exit electrodes to prevent reflection or adsorption of beam molecules, and by using a tetrode rather than a triode structure. An externally operated translational motion is employed to position the ionizer so that the maximum number of beam molecules are ionized.

The electron emitting filament is a thoriated tungsten strip, 5cm x 4mm x .02 mm, cataphoretically coated with ThO_2 and $\text{Th}(\text{NO}_3)_4$ to increase its emission. It is spotwelded through platinum foil to tungsten leaf springs which hold it taut when it expands thermally. Molybdenum screws position the filament to a uniform distance of ca. 1-2 mm from grid 1. No short circuits or broken filaments have occurred with this mounting and emission has been stable over many months of constant operation. Typical operating conditions are shown in Table II.

A small buffer chamber and a directional entrance⁶ enable the detector to be maintained in the low 10^{-9} Torr range, while sampling from reactors at pressures near 1 Torr. The directional entrance is a copper EMI honeycomb grid structure, 1-cm long and composed of 217 parallel thin-walled passages in an 0.3 cm^2 area. It is better than 80% transmitting for a molecular beam travelling along its axis, but has a conductance for background gas of only

Table II
Typical Ionizer Operating Conditions

Voltage drop across filament and leads	5.4 V
Filament heating current	14.0 A
Filament voltage	- 100 V
Electron current to grid 1	100 mA
Electron current to grid 2	100 mA
Electron current to anode	150 mA
Entrance electrode voltage*	+ 330 V

Exit electrode and shield are electrically connected and their voltage is varied to maximize the ion current.

*Voltages are with respect to grids 1 and 2 and the anode, which are electrically connected and floating on an ion accelerating voltage of ca. 2000 volts.

0.2 liter/sec. The directional entrance is mounted between two flexible metal bellows, so that it can be oriented for maximum beam transmission. A Granville-Phillips straight through (type S) valve permits the buffer and detector chambers to be isolated while the remainder of the apparatus is opened to the atmosphere.

In the main chamber provision is made for determining velocity distributions and magnetic and electric dipole moments. The beam, after collimation, encounters a rotating disk, which has one of the three shapes shown in Fig. 3. The left-most wheel modulates the beam for conventional phase sensitive detection. The center disk provides short pulses of beam. By recording the time required for particles to travel from this pulser to the ionizer, we obtain their time-of-flight (TOF) distribution, which is proportional to the distribution of v^{-1} . A disk containing two 1.6 mm slots and rotating at 50 cps produces beam pulses ca. 200 μ sec in duration, 10 msec apart. The right-most wheel modulates the beam in a pseudorandom manner, the modulation sequence repeating after 255 intervals. The TOF distribution can be extracted from the signal produced in such a manner by using correlation techniques.⁷ The advantage of this method of determining the TOF distribution is that the beam duty cycle is 50%, as compared with 1½% when employing the pulsed-beam technique. The correlation

method provides dramatic improvements in signal-to-noise in cases where there is appreciable background at the m/e of interest. The disks are either made of soft steel or contain a soft steel insert so that a magnetic pick-up (Electro Products, type 3080) positioned near their circumference generates a reference signal.

The motor for rotating the disks is located outside the vacuum system, and the rotary motion is transmitted through the source flange by an NRC rotary feedthrough (No. 1234-808). A Barden BarTemp bearing supports the rotating shaft within the vacuum system. For phase-sensitive detection or random modulation, a synchronous motor and 10:7 speed reducer are used, so that a highly constant rotation speed is maintained. For the pulsed-beam method of measuring TOF distributions, constancy of rotation speed is not as important, and it is found advantageous to employ a d.c. motor and speed controller, in order to avoid harmonics of line current.

A few cm past the rotating disk, a moveable obstacle may be inserted into the beam path, geometrically shadowing the entrance to the ionizer. Under perfect molecular beam conditions (i.e. all molecules moving in straight line paths), this would completely eliminate the detected beam. However, in our instrument this insertion only reduces the signal to about 2% of its straight-through value. This residual signal results from scattering of

beam molecules by background gas and various surfaces of the apparatus. The obstacle is a 1.5 mm diameter wire, mounted off center on the end of a rod. By rotating the rod, the wire can be positioned for minimum beam transmission.

With the obstacle in place, magnetic or electric inhomogeneous fields can be used to deflect species into the detector, if they possess appreciable magnetic or electric dipole moments, respectively. The percent magnetic or electric focusing at a given m/e is defined as the increase in current when the field is applied, divided by the current with the field and obstacle removed, $\times 100$. The inhomogeneous electric field is constructed from four stainless steel circular rods of 4.75 mm diameter and 9.2 cm length. A boron nitride insulator at each end holds the rods in a quadrupole configuration with their centers equally spaced on a circle of 9.5 mm diameter. The high voltage for the quadrupole is provided by a Spellman 0-30 kV power supply (model PN-30) and enters the vacuum system via an Alite high voltage terminal (No. 3-5-ID). A $3 \times 10^8 \Omega$ resistor in series with the supply helps to prevent damage to the field from sparks which occasionally occur at voltages above 20 kV. Voltages are measured by a Keithly 6-10C electrometer with a 6-103A high-voltage divider probe.

A magnetic hexapole field may be substituted for the electric quadrupole. The magnet (Hewlett Packard Co., part No. 349654) is 7.5 cm long with opposing poles 3 mm apart. The field near the pole tips is ca. 7000 gauss. Since it is a permanent magnet, comparisons of beam intensity with the field on and off must be performed by lifting the magnet out of the beam path. A kinematic mount is used so that each time the magnet is lowered, it is automatically realigned on the beam axis.

The source chamber contains the reactor being sampled. Most of the studies to date have been performed on flow systems excited by an electric discharge (see Fig. 4). Gases flow with a linear speed of ca. 1 meter/sec through a microwave discharge (50-100 watts of 2450 MHz power in an Evenson-type cavity⁸). The products of the discharge may be mixed with other gases at varying distances from the sampling orifice using a moveable inlet that passes into the flow system via an O-ring sealed Teflon connector. Sampling orifices are generally circular holes of .02-0.2 mm diameter, produced by sandblasting (with an S.S.White, model F machine). This process erodes a cone into the wall of the tube, so that the thickness of the glass at the hole is comparable to its diameter, as is required for effusive flow sampling. To make holes of diameter less than 0.1 mm, the sandblasting is

discontinued before piercing the wall, and the hole is completed with a spark from a Tesla coil.⁹ Some work has been performed using slit (ca. .05 mm x 3 mm) rather than circular hole orifices. These are prepared by sandblasting a V-groove that almost penetrates the wall of the tube and then completing the slit by rubbing abrasive slurry back and forth in the groove using a wire or razor blade. The slit orifice greatly increases beam intensity but somewhat aggravates the problems caused by scattered beam. They have been successfully employed only at low (below 100 micron) pressures.

The flow tube passes through the source chamber via O-ring sealed "quick-connects". This arrangement, along with the mounting of the external gas handling equipment on a laboratory cart, allows the rapid interchange of the system being studied. The source flange also incorporates a sight tube on the beam axis for telescope alignment of the apparatus.

The various methods of processing the output signal from the electron multiplier are diagrammed in Fig. 5. For dc recording of the mass spectrum on a Heath recording electrometer, multiplier load resistors of 10^7 , 10^8 or $10^9 \Omega$ are switch selected. Modulated beams may be phase-sensitive detected (Princeton Applied Research model 220 lock-in amplifier and model 210 selective

amplifier, with Tektronix type 122 low-level preamplifier) in order to greatly reduce the contribution of background gas in the detector chamber to the mass spectrum. Measurement of time-of-flight distributions with either the pulsed or randomly modulated beam is achieved by using a digital memory signal averager (Intertechnique Didac 800 Physioscope), which is synchronized to the signal by a pulse from the magnetic pickup. When recording TOF curves the multiplier load resistor is reduced to $1.5 \times 10^5 \Omega$, in order to maintain a sufficiently fast time response.

For low level signals it is difficult to eliminate all spurious pickup from the TOF curves, and the counting of individual multiplier pulses with multiscaling is generally more successful than signal averaging an analog signal. In this mode, the individual pulses from the multiplier are amplified (Hewlett Packard, 5554A charge-sensitive preamplifier, and Ortek, model 485 pulse amplifier), and pulses with greater than a preset height are selected by a discriminator (Ortek, model 421), for counting by the signal averager. For further processing of TOF data and for correlating the signal produced by the pseudo-random chopper, the memory content of the averager may be punched on cards by a link to an IBM model 526 card punch.

RESULTS AND DISCUSSION

Our early attempts to measure velocity distributions by the TOF method gave results grossly distorted from the beam-modified Maxwellian distribution ($dN \propto v^3 \exp(-mv^2/kT)dv$) that is usually the first approximation to a molecular beam velocity distribution. Relative to the Maxwellian, the data was enhanced at low velocity, showing that the difficulty could not be due to scattering, which would preferentially remove slow molecules from the beam. We suspected that ion trapping in the space charge of the ionizing electrons was delaying the ions, since such effect had been reported in the literature.¹⁰ A number of approaches were employed in attempting to eliminate this distortion. These included: reducing the space charge by lowering the filament emission by a factor of 5 (with a concomitant loss of ionization efficiency), applying negative voltage pulses to the exit electrode, applying a steady positive (repeller) voltage to the entrance electrode, and adding background gas to the detector chamber. Best results were obtained with a combination of the latter two techniques. Usually the entrance electrode was operated at + 330 volts with respect to the grids, and He was bled into the detector chamber to raise its pressure to ca. 2×10^{-6} Torr. At this pressure the background gas evidently provides sufficient ions to largely

neutralize the electron space charge. He is appropriate for this purpose since it produces ions at only a few peaks in the mass spectrum and does not interfere with the electron emission from the ThO_2 coated filament. (The emission actually increases slightly when the He is added.) Fig. 6 shows TOF curves for O_2 at its parent ion taken with these detector conditions which minimize ion trapping. When allowance is made for the finite duration of the beam pulse and length of the detector (the entrance and exit "slits" of the TOF spectrometer), reasonable agreement with a $v^3 \exp(-mv^2/2kT)$ distribution is obtained.

A quick indication of the mass of the progenitor of an ion can be obtained from the time to the peak of the TOF curve for that ion. Fig. 7 demonstrates that there is a linear relation between this time and the square root of the molecular weight of the parent, as is predicted by the beam-modified Maxwellian distribution. It is not important that the line does not extrapolate to the origin, since the signal from the magnetic pickup is not exactly synchronized with the beam pulse. In fact, this extrapolation is usually used to define $t=0$ for our curve fitting procedures.

Table III lists atomic, free radical and unstable molecular intermediates that have been detected by molecular beam analysis. This is the first reported mass spectrometric observation of the

Table III

Transient Intermediates Identified by Molecular Beam Analysis

Species	Estimated Partial Pressure (microns)	System	Total Pressure (Torr)
H	250	discharged* H ₂	2.5
N	120	discharged N ₂	3.0
O	150	N + NO	4.0
F	30	discharged CF ₄ or SF ₆	1.0
Cl	30	discharged Cl ₂	1.8
Br	80	discharged Br ₂	0.8
I	20	O + CF ₃ I	1.9
SO	40	discharged SO ₂	1.2
ClO	20	discharged Cl ₂ +O ₂ mixture	4.0
BrO	10	O + Br ₂	1.0
IO	10	O + CF ₃ I	2.4
OH	10	H + NO ₂	1.6
S ₂ O	5	discharged SO ₂	0.5
CH ₃	20	H + CH ₃ I	4.5
CF ₃	5	O + CF ₃ I	1.1

*50-100 watts of 2450 MHz microwave power.

very reactive radicals BrO and IO. Also noteworthy is the detection of CH_3 and CF_3 at ca. 0.5% concentration in the presence of much larger concentrations of reactants that give the parent ions of these radicals. The paramagnetic species were all identified by magnetic focusing at their parent ions, checking that there were no other species present that could give this response (e.g., BrO_2 and IO_2 in the case of BrO and IO). Magnetic focusing is a somewhat stringent requirement, since insertion of the hexapole partially blocks the scattered beam. As a result, for diamagnetic particles, magnetic defocusing is observed.

The synergistic effect that can be achieved when TOF analysis is employed simultaneously with magnetic or electric focusing is illustrated in Fig. 8. These curves were taken at $m/e = 19$ (F^+) with 0.5 Torr of CF_4 in the source. With the discharge off (lower curve), the TOF distribution is characteristic of CF_4 . When the discharge is initiated (upper curve) the distribution shifts to earlier time, indicating a large contribution from a lighter species ($M < 25$). The response with the magnet and stopwire in place (center curve) shows that this light species is paramagnetic, and confirms the presence of a large concentration of fluorine atoms in the products of this discharge.¹²

An example where electric deflection was indispensable is the identification of S_2O in microwave discharges through SO_2 .¹³

In this system, with 15 kV applied to the quadrupole, ca. 50% electric focusing was observed at $m/e = 80$, the parent ion of S_2O . SO_3 , which has the same parent ion mass, might be predicted to occur in this system. It cannot, however, produce electric focusing, since it has a planar symmetric ground state and thus no permanent electric dipole moment. (No electric focusing was observed for reagent SO_3 , or for SO_3 formed by adding discharged O_2 to SO_2 .) If SO_3 contributed to this ion peak, it would dilute the electric focusing of S_2O . However, we would expect the focusing of S_2O to be very similar to that observed for $NOCl$, another nearly prolate symmetric top with a similar dipole moment ($\mu_e = 2.0$ Debye for $NOCl$ and 1.5 Debye for S_2O). Since $NOCl$ shows 53% electric focusing, we conclude that SO_3 cannot be the major contributor to the $m/e = 80$ ion current.

These preliminary experiments are intended to prove the feasibility and usefulness of molecular beam analysis. Although the ultimate sensitivity of the method has not yet been determined, some of the radicals reported were identified at less than 0.5% concentration in systems at total pressure of a few Torr. We believe that this new experimental approach will find an important role in identifying polyatomic intermediates in fairly complicated reactions, where considerable difficulty is generally experienced

using more conventional techniques.

ACKNOWLEDGEMENTS

We are grateful to A. Weisbrodt, B. Hertzler, J. Bozzelli and J. Abbotts for their aid in various parts of this work.

Footnotes

* Primary financial support for this work was received from the Office of Naval Research under contract N0014-67-A0151-0013. Also supported by Petroleum Research Fund Grant 1142-G2 and the Higgins and Shell Funds at Princeton University.

+ N.D.E.A. Graduate Fellow.

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11. Both sets of data were taken with wheel velocities of ca. 20 cps, which is considerably slower than is usually employed for the pulsed-beam method. At this velocity our best a priori estimate of the time resolution due to the duration of the beam pulse and length of the detector is 600 μ sec for the pulsed-beam mode and 450 μ sec for the random modulation mode. As can be seen in Fig. 6, data taken by the latter technique provides a slightly narrower TOF distribution.
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13. Since some slight sulfur deposits are formed on the walls, conditions are similar to those used to produce S₂O in D.J. Meschi and R.J. Meyers, J. Mol. Spectry. 3, 405 (1959); J. Am. Chem. Soc. 78, 6220 (1956).

Figure Captions

Fig. 1: Side view of molecular beam analyzer: A-electron bombardment ionizer; B-magnet pole tips; C-variable slits; D-electron multiplier, E-variable leak valve; F-directional entrance; G-flexible metal bellows; H-straight-through valve; J-pulser or modulator; K-magnetic pickup; L-motor; M-rotary motion feedthrough; N-bearing; P-moveable obstacle; Q-electric quadrupole field; R-high voltage terminal; S-reactor.

Fig. 2: Top view of electron bombardment ionizer.

Fig. 3: Left, disk for modulating the molecular beam; Center, disk for pulsing the molecular beam; Right, disk for random modulation of the molecular beam.

Fig. 4: Top view of beam source: A-microwave cavity; B-moveable inlet; C-teflon vacuum seal; D-sampling orifice; E-"quick-connects"; F-sight tube; G-collimator; H-light trap.

Fig. 5: Block diagram of signal processing electronics.

Fig. 6: Time-of-flight distributions for O_2 at $m/e=32$. \circ -- pulsed beam method, \bullet -- random modulation method. Line is best fit to a $dN \propto v^3 \exp(-mv^2/2kT)dv$ distribution convoluted with a 600 μ sec square wave.¹¹

Fig. 7: Dependence of time-of-flight curves on the molecular weight of the beam molecule: A-H₂, B-D₂, C-NH₃, D-H₂O, E-Ne, F-N₂, G-O₂, H-Ar(36), I-Ar(40), J-CO₂, K-NO₂, L-SO₂.

Fig. 8: Time-of-flight distributions at $m/e = 19$.

Source contains 0.5 Torr of CF₄ and is excited by a microwave discharge in the upper two curves.

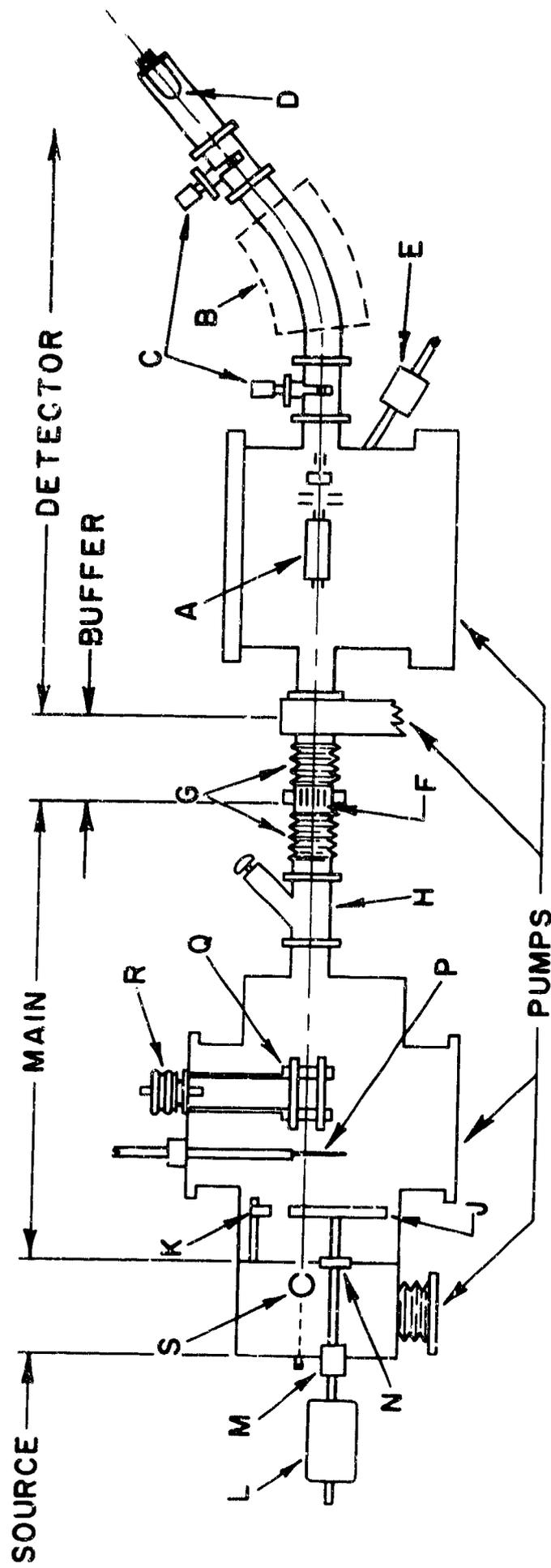


FIG. 1

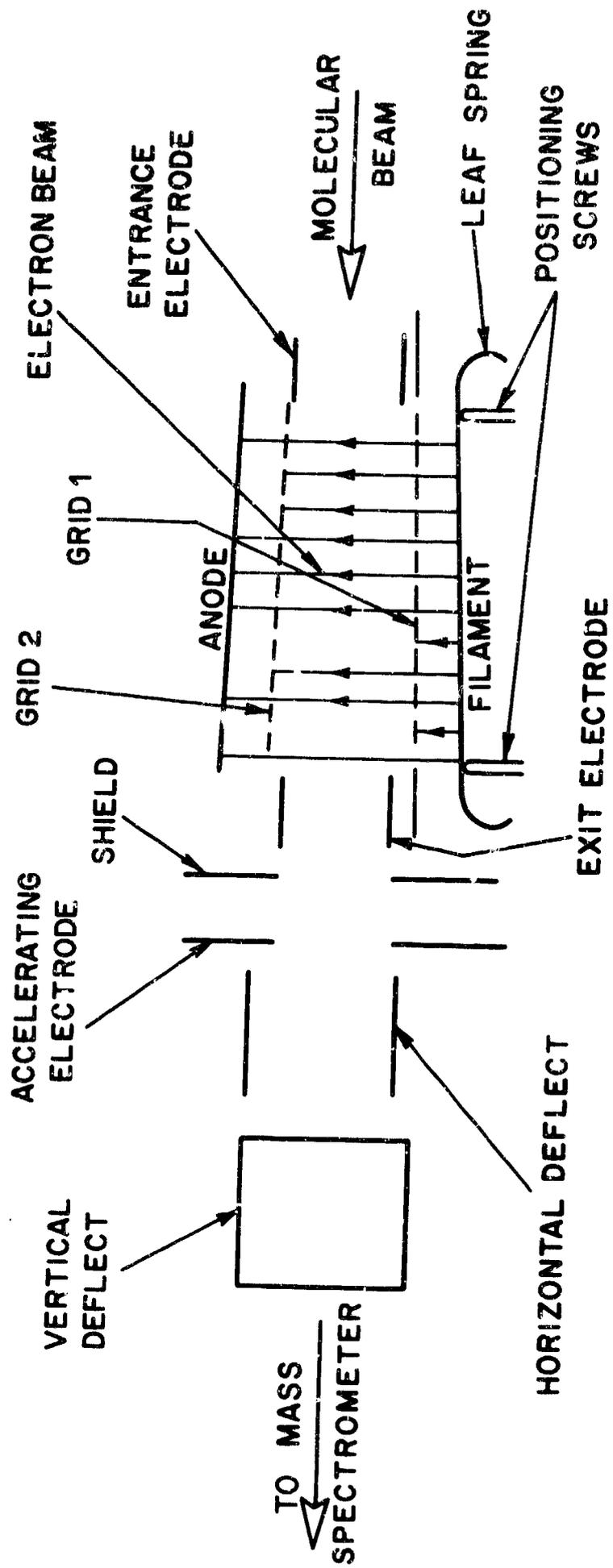


FIG. 2

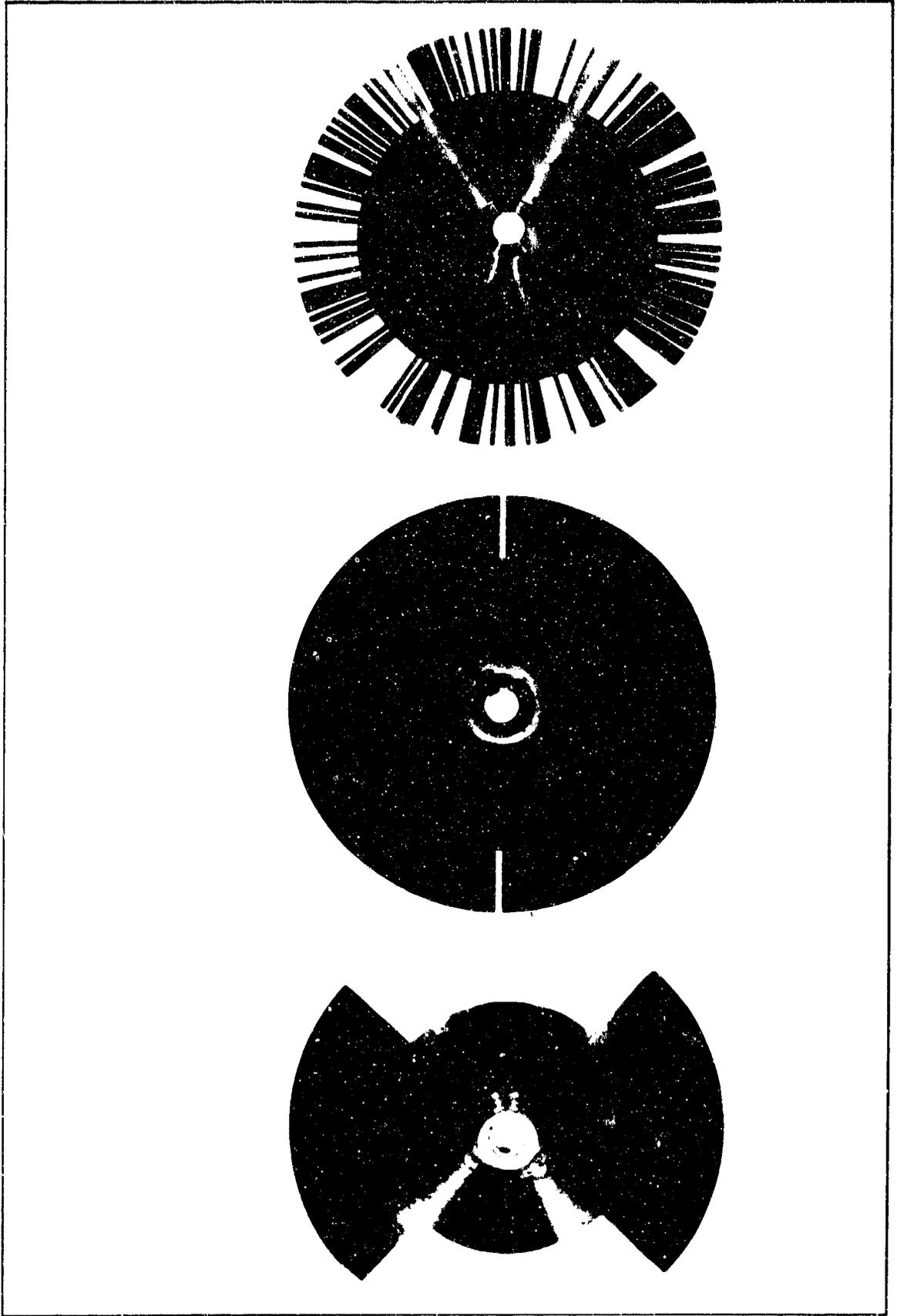


FIG. 3

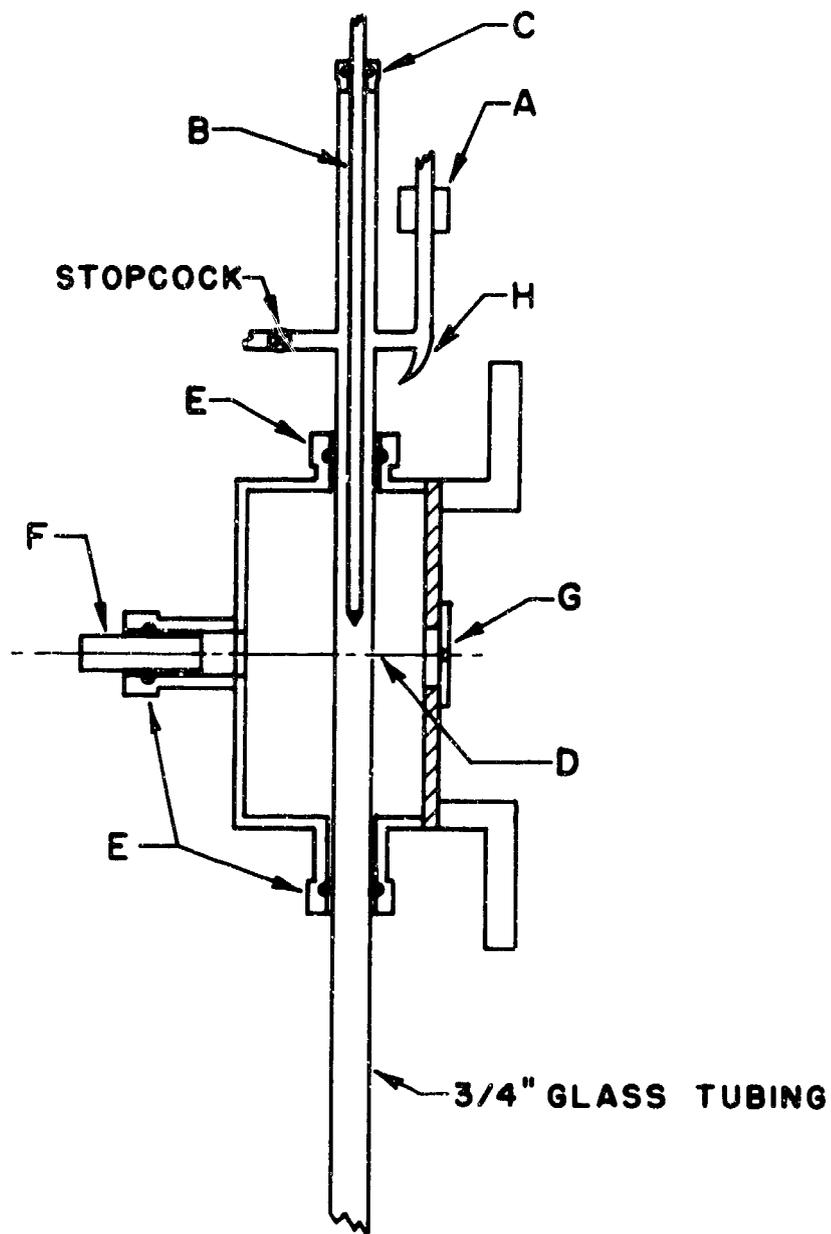


FIG. 4

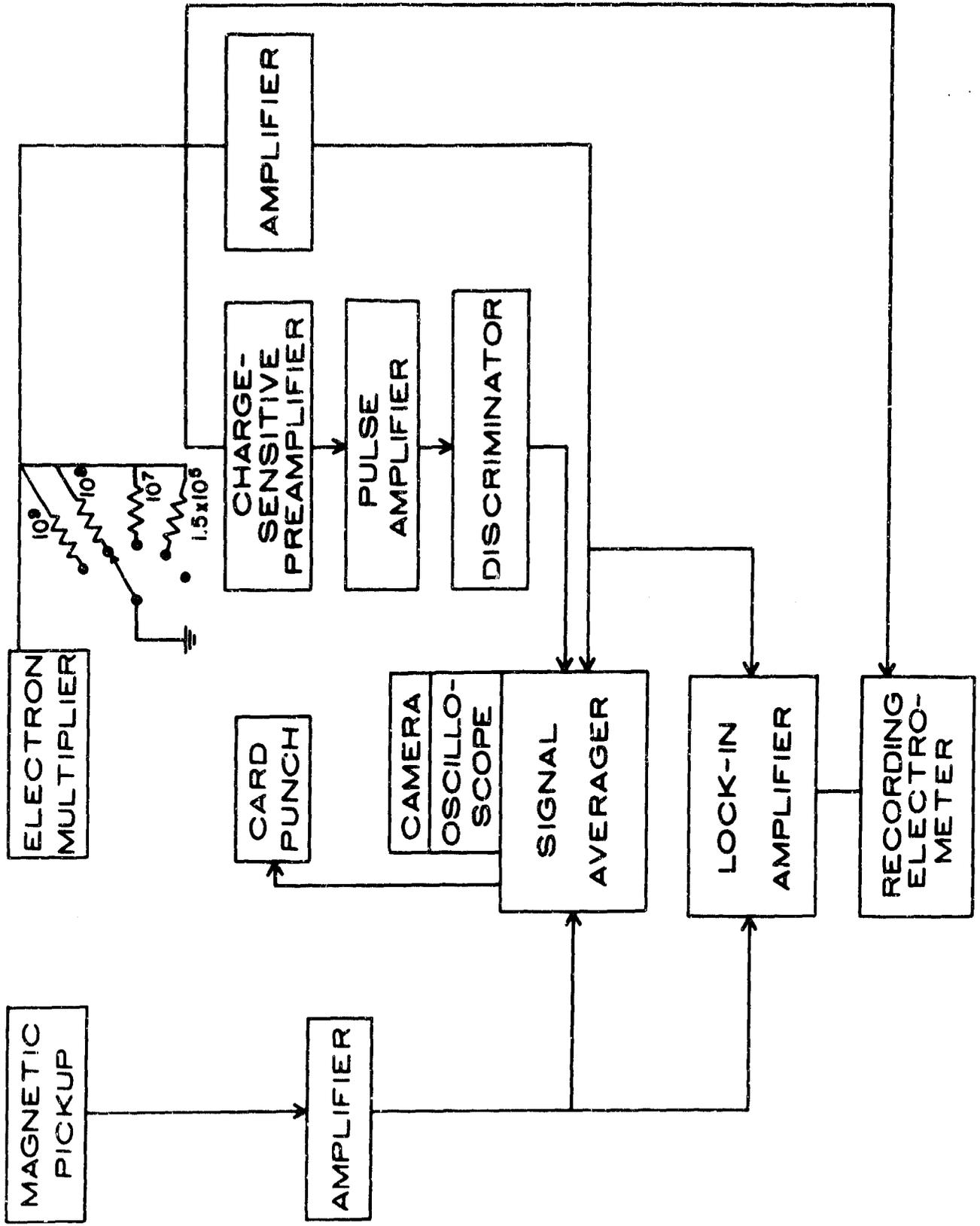


FIG. 5

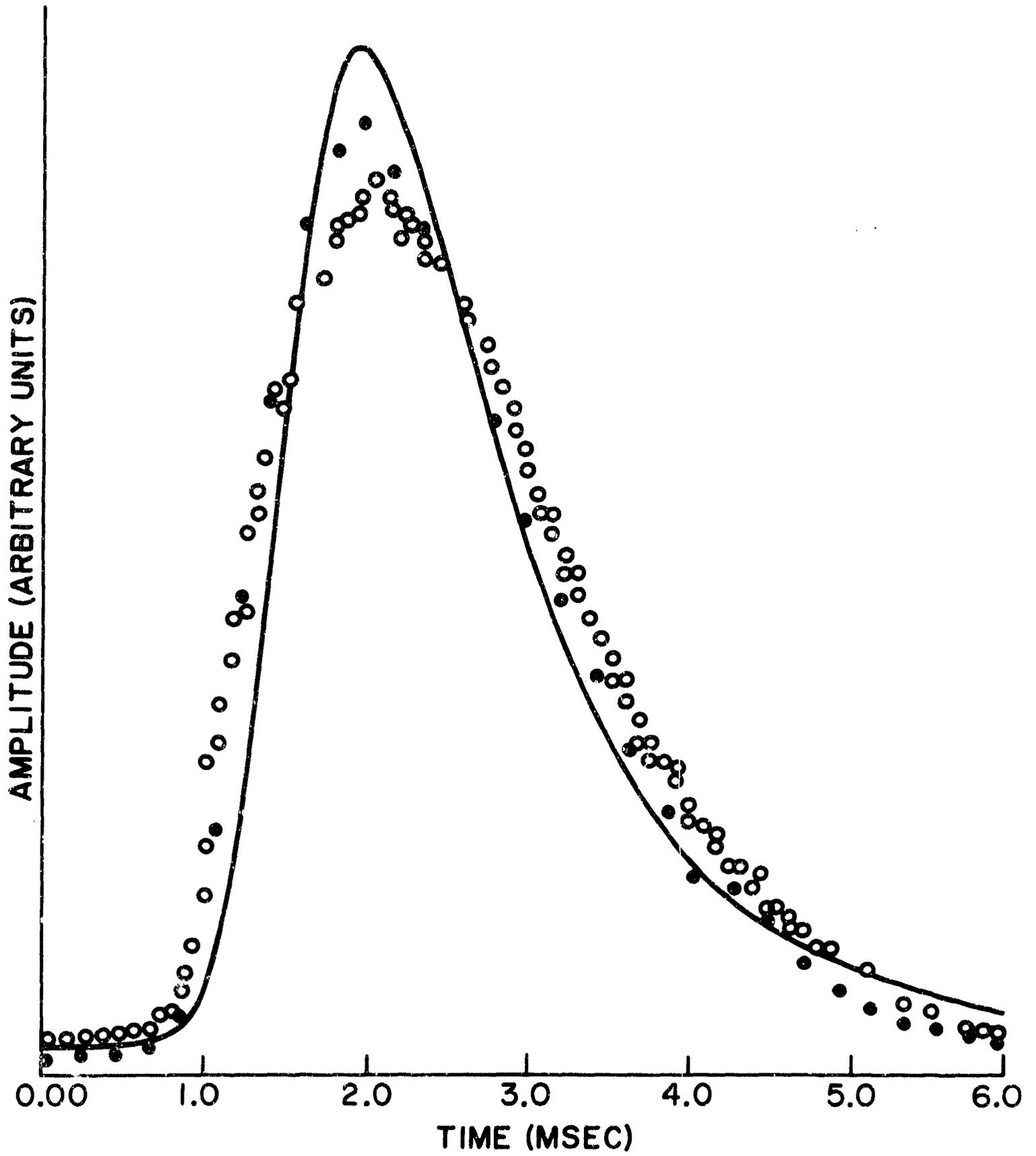


FIG. 6

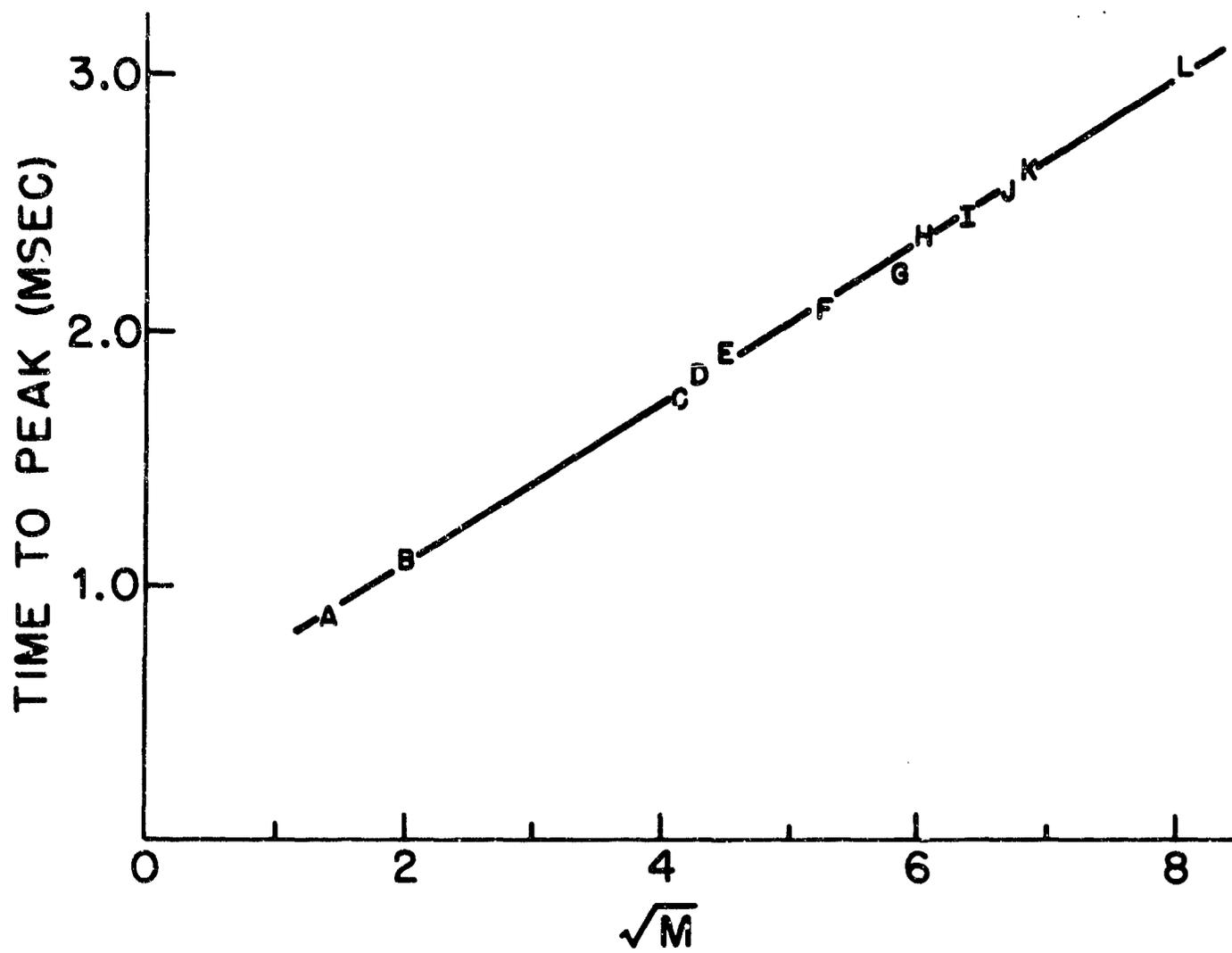


FIG. 7



- Discharge on
- Discharge on
obstacle and magnet lowered
- Discharge off

← 0.8 msec

FIG. 8

Unclassified

Security Classification

DOCUMENT CONTROL DATA - R & D

Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified

1. ORIGINATING ACTIVITY (Corporate author) Princeton University Princeton, New Jersey 08540		2a. REPORT SECURITY CLASSIFICATION Unclassified
		2b. GROUP
3. REPORT TITLE Molecular Beam Analyzer for Identifying Transient Intermediates in Gaseous Reactions		
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Technical Report - to be published in Chemical Instrumentation		
5. AUTHOR(S) (First name, middle initial, last name) Myron J. Kaufman and Charles E. Kolb		
6. REPORT DATE January 1971	7a. TOTAL NO. OF PAGES 32	7b. NO. OF REFS 21
8a. CONTRACT OR GRANT NO. ONR N0014-67-A0151-0013	9a. ORIGINATOR'S REPORT NUMBER(S) 2	
b. PROJECT NO. NR 092-531	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
c.		
d.		
10. DISTRIBUTION STATEMENT Distribution of this document is unlimited		
11. SUPPLEMENTARY NOTES New Method for Monitoring Transient Intermediates in Gas-Phase Reactions	12. SPONSORING MILITARY ACTIVITY Power Branch Office of Naval Research	
13. ABSTRACT When using a mass spectrometer to monitor free radical and atom intermediates in rapid gas-phase reactions, identification of the parent species of each ion is made difficult by fragmentation processes that occur at electron energies necessary for optimum ionization cross sections. Molecular beam analysis is a new approach to this problem whereby molecular beam measurements are used to characterize neutral species before they are ionized. Thus, the trajectory of a particle in an inhomogeneous magnetic field shows whether or not it has a large magnetic moment characteristic of a free radical, its motion in an inhomogeneous electric field indicates its symmetry and the magnitude of its electric dipole moment, and its velocity distribution determines its mass when the source temperature is known. Using these techniques, various atom, free radical and unstable molecular species have been identified in gases excited by microwave discharge or as products of atom-molecule reactions.		

Unclassified

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14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Mass spectrometer	10	3				
Free radicals	8,4	3				
Molecular beams	10	3				
Chemical kinetics	8,4	2				
Gas-phase reactions	5	2				
Electric discharges	10	2				

Unclassified

Security Classification