COO-2810-10

MASTER

A LOW-PRESSURE APPROACH
TO
THE FORMATION AND STUDY
OF
EXCIPLEX SYSTEMS

Progress Report
Contract No. EY-76-S-02-2810. 003

Dr. George Sanzone
Department of Chemistry
Virginia Polytechnic Institute and State University
Blacksburg, Virginia 24061

November, 1977

REA

DISCLAIMER

Contents

I: INTRODUCTION

Continued fundamental studies are proposed on both the formation and properties of new materials for high-energy, gas-phase lasers. Attention will remain focussed mainly (but not wholly) on systems which have bound excited states but unbound ground states.[1] An important class of such excimer/exciplex systems has a van der Waals dimer/oligomer as its ground state. At the initiation of this work, a new technique for the preparation of excimers and exciplexes was presented in which van der Waals complexes are formed as intermediates. Candidate systems for study include the excited states of dimers, oxides, and halides of the inert gases, as well as rare-gas-mercury complexes.

The main purpose of a laser is to generate large numbers of coherent photons. Consequently, it is necessary to study both primary and secondary photoprocesses operating in laser systems.[2] It is the objective of this research to probe the relative rates of electron pumping of excited-state manifolds and (ultimately) the preferentially pumped vibronic states within each manifold. Reactive quenching of emission, resonant self-absorption of laser emissions as well as collision- and non-collision-induced intersystem crossing will also be considered. The system developed for these studies can also provide such additional data as appearance potentials for van der Waals ground states and photoionization cross sections of excited states of such complexes.

II: THE LOW-PRESSURE APPROACH

Although our laser candidates will be used at very high pressures, the rapid collisional quenching present at those pressures complicates the study of excitation processes and radiative lifetimes. Instead of going to high pressures, the approach being taken is to use the low temperatures obtained in a free-jet expansion to produce a high steady-state concentration of van der Waals dimer or oligomer. These are to be excited by low-energy resonant electron bombardment to yield excimers or exciplexes, probably in excited vibrotational states. The formation mechanism is thus:

(1) $A + B \xrightarrow{1} AB$ (in free jet expansion)

(2) $AB + e^{-1} \xrightarrow{2} AB^{\ddagger} + e^{-1}$ (e^{-1} beam excitation)

In these reactions, A might be a noble-gas atom while B could be another noble gas atom, an oxygen atom or a halogen atom. The procedure is based upon the known ability to form dimers and oligomers in the first steps of condensation in a jet expansion.[3] It assumes that excitation by electron bombardment is a "vertical" process. Once formed, an excimer can suffer a number of fates, as represented by the following paths for excimer depletion:

(3) $AB^{\ddagger} + M \xrightarrow{3} A + B + M$ (reactive quenching)

(4) $AB^{\ddagger} \xrightarrow{4} A + B + h\nu$ (radiative dissociation)

(5) $AB^{\ddagger} + M \xrightarrow{5} AB^{*} + M$ (collisional de-excitation to the vibrotationally unexcited excimer AB^{*})

(6) $AB^{\ddagger} \xrightarrow{6a} A + B + h\nu$

$h\nu + AB^{\ddagger} \xrightarrow{6b} AB^{**}$ (resonant self absorption)

In addition, the vibrotationally unexcited AB^{*} can itself undergo reactive quenching, radiative dissociation and resonant self absorption. The total mechanism embodied in the above equations is shown schematically in Figure 1.

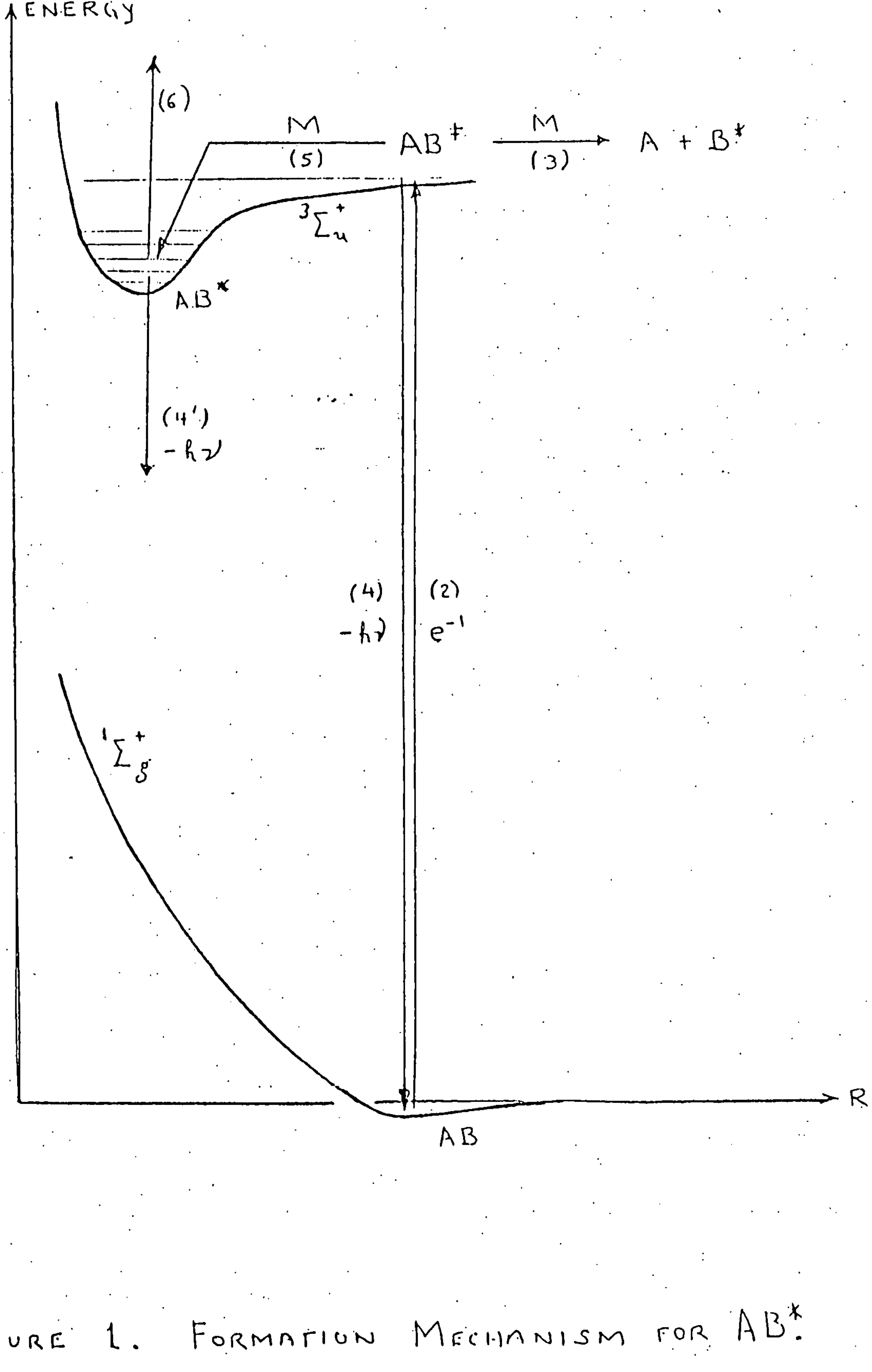


FIGURE 1. FORMATION MECHANISM FOR AB*.
VAN DER WAALS COMPLEX AB IS
PRODUCED IN A FREE JET EXPANSION.

III: STATUS OF PRESENT CONTRACT

The present, short-term goals of this work included the development and construction of an experimental system to study excited-state kinetics of excimers, and the demonstration of the validity of the low-pressure approach outlined in the initial proposal. The apparatus is composed of the following principal components:

a) Cluster-molecular beam source of van der Waals dimers;

b) Modulated-beam mass spectrometer;

c) Low-energy electron beam for the production of excimers;

d) Vacuum-UV to Visible detection and photon-counting system to monitor excimer emission;

e) Flash-excited tunable laser for studies of resonant self absorptions.

Progress on the evaluation of the proposed experiments will be represented by completion of the following experiments:

a) The formation of Ar_2 in its van der Waals ground state;

b) Low-energy electron-beam excitation of Ar_2 to form Ar_2^* (and $Ar_2^{\ddagger}$);

c) Fluorescence studies of Ar_2^*

d) Photon-absorption studies of Ar_2^*

A schematic of our apparatus is shown in Figure 2. The experimental system, composed of 25 major subsystems, is outlined in the Block Diagram of Figure 3. The apparatus is in use at this time. (Complete check-out of the laser system is awaiting the delivery of safety goggles and power/energy meter.)

Ar_2 has been detected and the proper performance of the cluster molecular beam has been verified. Difficulties have been experienced in the development of an excitation electron gun with high emission and low energy bandpass. An indirectly-heated-cathode gun is now under development while a well-focussed gun (but with only 100 microamp beam) from another project is being used to push the work forward. The fluorescence studies of Ar_2^* should be completed by the end of the present contract period.

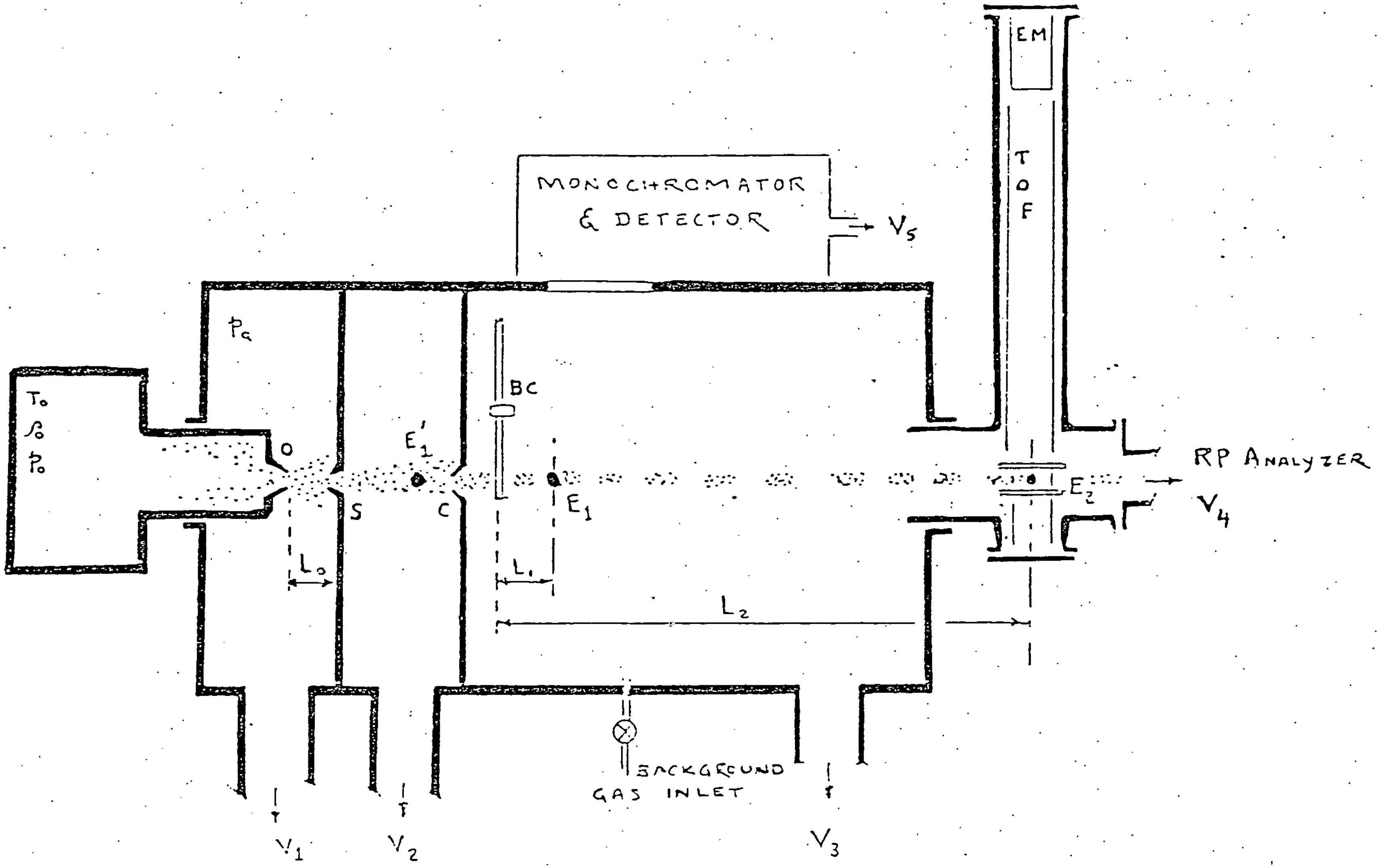
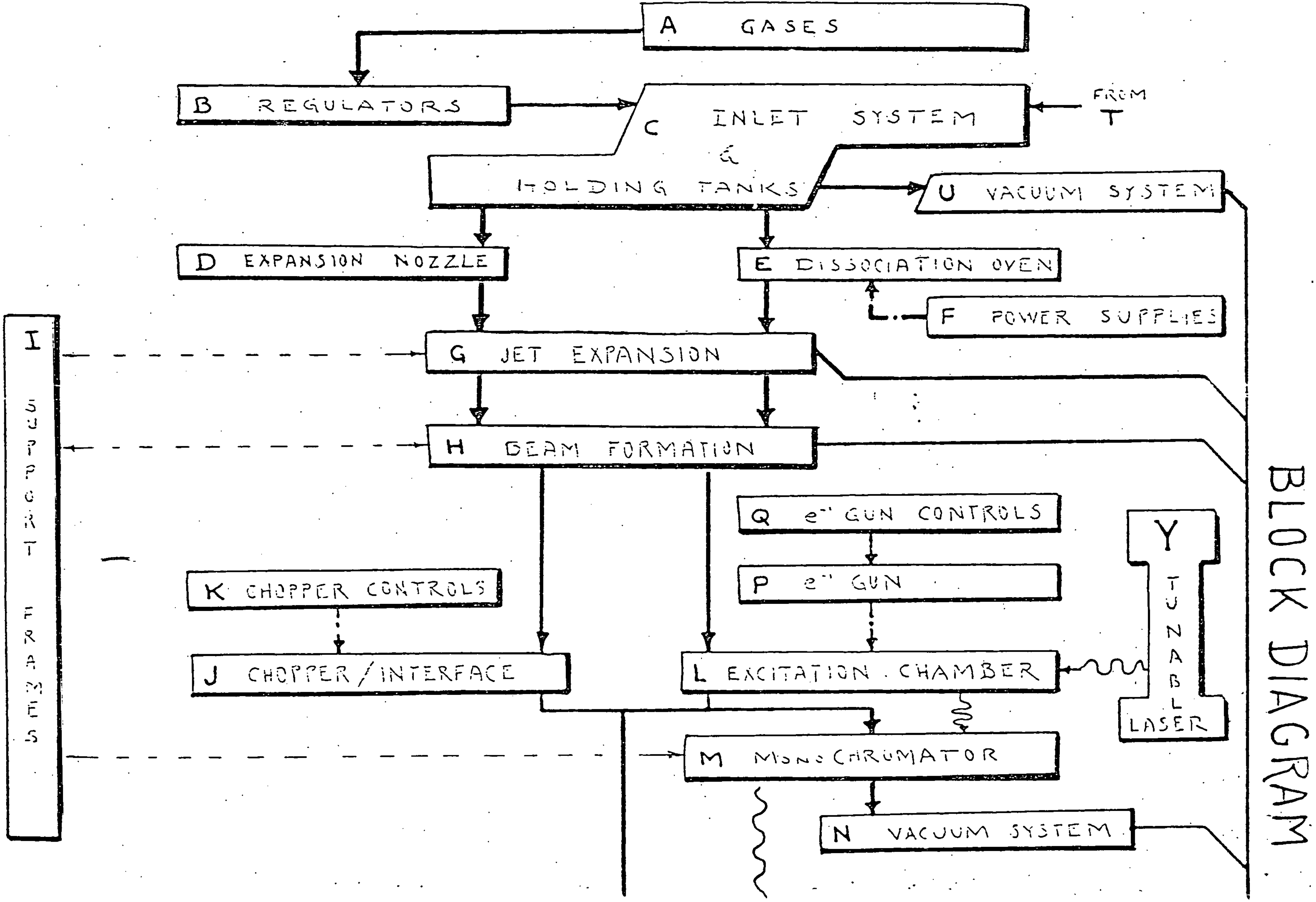
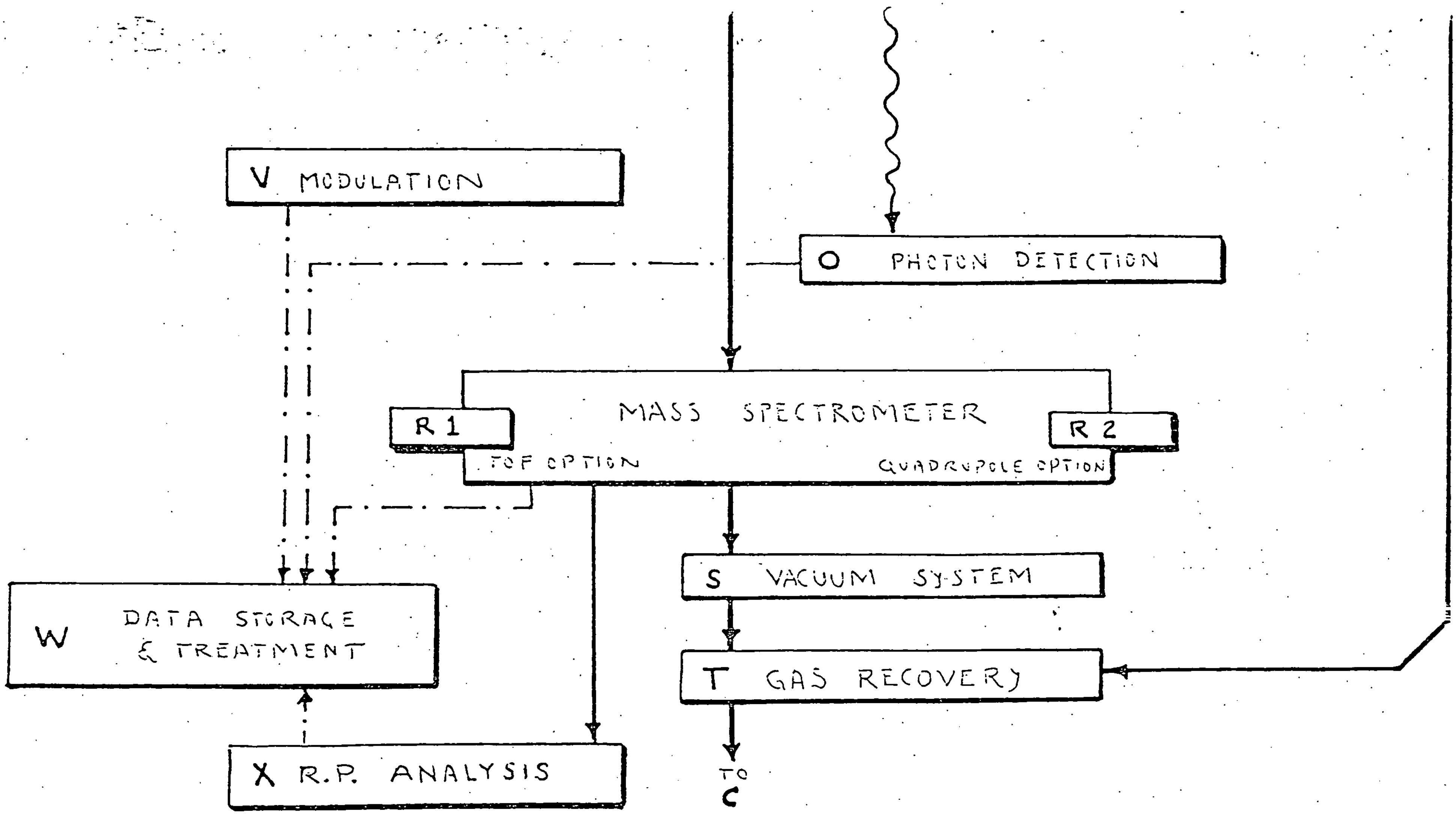


Figure 2. Experimental Apparatus

Orifice O; Skimmer S; Collimator C; Vacuum Pumps V_1, V_2, V_3, V_4, V_5; Beam Chopper BC; Excitation Electron Beam E_1 or E_1'; Analytical Electron Beam E_2; Electron Multiplier EM; Time-of-Flight Mass Analyzer TOF. Note: Distances L_0, L_1 and L_2 are variable.


A GASES
B REGULATORS
C INLET SYSTEM & HOLDING TANKS
FROM T
U VACUUM SYSTEM
D EXPANSION NOZZLE
E DISSOCIATION OVEN
F POWER SUPPLIES
I SUPPORT FRAMES
G JET EXPANSION
H BEAM FORMATION
Q e⁻ GUN CONTROLS
P e⁻ GUN
Y TUNABLE LASER
K CHOPPER CONTROLS
J CHOPPER / INTERFACE
L EXCITATION CHAMBER
M MONOCHROMATOR
N VACUUM SYSTEM
BLOCK DIAGRAM



BLOCK DIAGRAM
FIGURE 3

IV: DIMER FORMATION STUDIES

As indicated above, dimers (and oligomers) for these studies will be formed in a free-jet expansion. Because of this, a major experimental task has been the development of a nozzle-source cluster beam. An in-depth review of the literature revealed that, in general, the technology of cluster beams (beams with condensation nuclei) has lagged that of molecular beams. This required the derivation of a number of new relations, the validity of which had to be checked against the mass of existing experimental data. Table I includes a summary of design equations which have been collected or developed for a cluster beam.

A number of design criteria were developed, the most important of which are presented in Table II. An important result of the development of these criteria was a recognition that jet geometry is virtually independent of conditions in the stagnation chamber but is determined principally by system pumping speeds. This led to the decision to develop a pulsed cluster beam system. Although this approach added the mechanical design of a pulsed nozzle to our problems, it did add an important new control parameter: jet pulse duration. More important, the variation of stagnation chamber conditions has been given real meaning in terms of the control of cluster size.

Although nozzle shape is an important factor in conventional nozzle-beam design, it is unimportant for dimer studies. A study of cluster intensity for various nozzle shapes revealed that reported intensity increases were due to the formation of beams with larger average cluster size; the intensity of dimers, trimers and other lower-oligomers does not change with nozzle size. This led to the use of a sonic nozzle in our studies. With our pulsed, sonic

TABLE I: CLUSTER BEAM EQUATIONS

Property	Relation
1. Nozzle Knudsen No.	$K \equiv \frac{\lambda_o}{D}$
2. Skimmer Knudsen No.	$K_{skimmer} \equiv \frac{\lambda_+}{D_{skimmer}}$
3. Mach Disk Knudsen No.	$K_{MD} \equiv \frac{\lambda_+}{D_{MD}}$
4. Nozzle Maximum Mass Flow Rate	$\frac{dm}{dt} = \{\frac{2}{\gamma+1}\}^{\frac{\gamma+1}{2\gamma-2}} \rho_o \frac{\pi D^2}{4} \{\frac{\gamma R T_o}{M}\}^{1/2}$
5. Centerline Jet Density	$\rho = \{\frac{0.0678}{\gamma - 1}\}^{\frac{1}{\gamma-1}} \{\frac{D}{x}\}^2 \rho_o$
6. Location of Mach Disk	$X_{MD} = 0.67 D \{\frac{p_o}{p_+}\}^{1/2}$
7. Location of Virtual Source Point	$x_p \equiv D \{0.20 f - 0.56\}$
8. Mach Number of Flow	$Ma = \frac{5.43}{\gamma} \{\frac{X - X_p}{D}\}^{\gamma-1}$
9. Terminal Mach No.	$Ma_T = 1.17 K^{-0.4}$
10. Location of Onset of Background Penetration	$X_+ = 0.6 \frac{D}{K}$
11 Jet Expansion Chamber Background Pressure	$p_+ = \frac{2.86 p_o D^2}{S} \{\frac{T_o}{M}\}^{1/2}$
12. Jet Start-Up-Time	$t_{rise} = \frac{0.0304}{c_o} \frac{X_{BS}}{D_{BS}} D \{\frac{5.43}{\gamma}\}^{5/2} \{\frac{X}{D}\}^{\frac{5(\gamma-1)}{2}}$

TABLE I (Continued)

Property	Relation
13. Jet Decay-Time	$t_{fall} = \frac{X_{skimmer}}{c_+}$

Symbols Used In Table I:

ρ = Density
γ = Heat capacity ratio
λ = Mean free path
c = Speed of Sound

D = Diameter
m = Mass
M = Molar Mass
p = pressure

S = Pumping Speed
T = Kelvin Temperature
X = Distance From Nozzle Exit
f = Thermo degrees of Freedom

Subscripts:

o denotes stagnation chamber
\+ denotes jet-chamber background
BS denotes properties of jet barrel shock

TABLE II: DESIGN CRITERIA

For jet formation:

$$K \leq 0.3$$

For negligible skimmer interference:

$K_{skimmer} > 50$ is OK.

$K_{skimmer} < 1$ is OK.

$1 < K_{skimmer} < 50$ is NoK.

For negligible effect on Jet properties:

$$X_{skimmer} \lesssim \frac{1}{2} X_{MD}$$

For similar cluster intensity and size distribution, two scaling laws have been suggested in the literature:

$$\left\{ p_o \; D^{1/2} \; T_o^{-2.375} \right\} = \text{constant}$$

$$\left\{ p_o \; D \; T_o^{-2.50} \right\} = \text{constant}$$

nozzle, the important experimental variables for controlling dimer concentrations are:[4]

nozzle-to-skimmer distance,

nozzle diameter,

stagnation temperature, and

stagnation pressure.

The composition of our molecular beam has been monitored with a modulated-beam mass spectrometer. This home-built system employed a mechanically chopped beam with lock-in-amplifier detection. With the use of a pulsed nozzle source, the mechanical chopper was not required since detection could be synchronized with the nozzle opening. Moreover, by monitoring dimer ions as a function of time as produced in single-nozzle bursts, the contribution to dimer due to atomic-ion-background-atom recombination is eliminated. Single pulses of Ar_2^+ were first observed with storage-scope detection. Later, the storage scope was replaced with a Biomation transient recorder. The dimer of Ar_2 was monitored as a function of nozzle diameter, stagnation temperature, stagnation pressure and nozzle-to-skimmer distance. Formation kinetics of Ar_2^+ was shown to be third order in Ar pressure in the stagnation chamber. Moreover, it was found that Ar_2 formation in our system obeyed one of the laws of corresponding jets:

$$P_o DT^{-5/2} = \text{constant}.$$

See Figure 4. Data for nozzle diameter $D \gtrsim 0.5$ mm did not obey a law of corresponding jets. This is believed to be due to inadequate pumping speed for the jet-expansion chamber. The sonic nozzle profile used is shown in Figure 5. Figures 6 and 7 present the dependence of Ar_2 dimer concentration as functions of nozzle-to-skimmer distance and stagnation pressure.

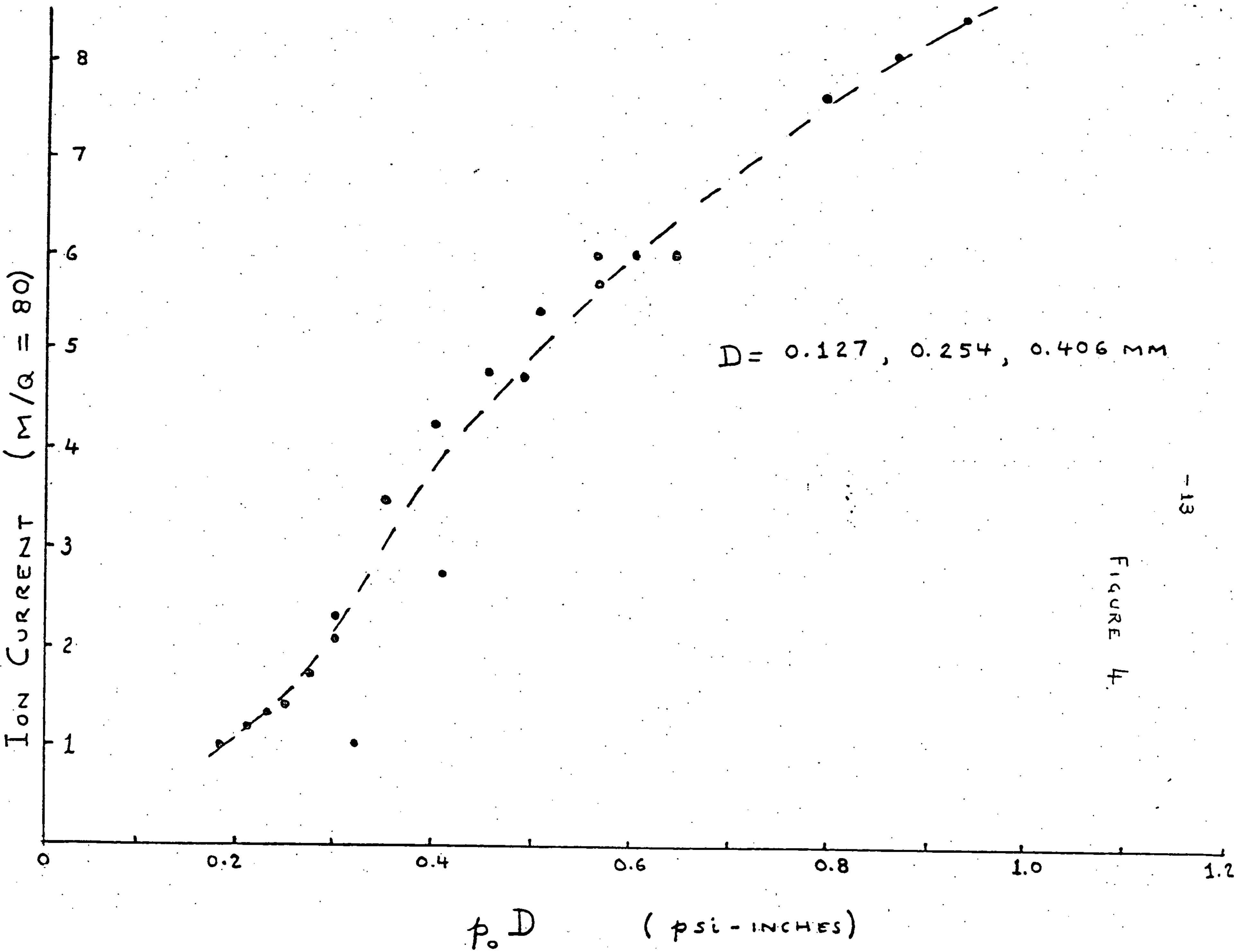
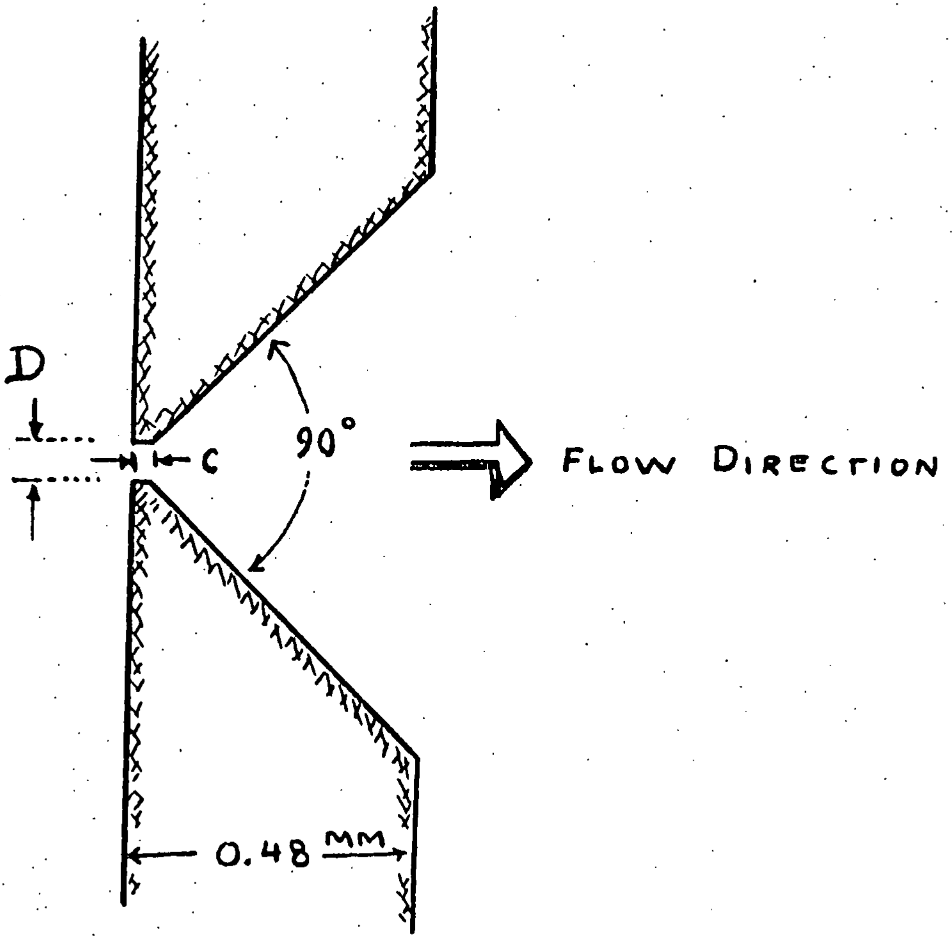

Ion Current (M/Q = 80)
1
2
3
4
5
6
7
8
0
0.2
0.4
0.6
0.8
1.0
1.2
$p_o D$ (psi - inches)
D= 0.127, 0.254, 0.406 MM

Figure 4.

SONIC NOZZLE PROFILE



C = 0.025 MM

FIGURE 5

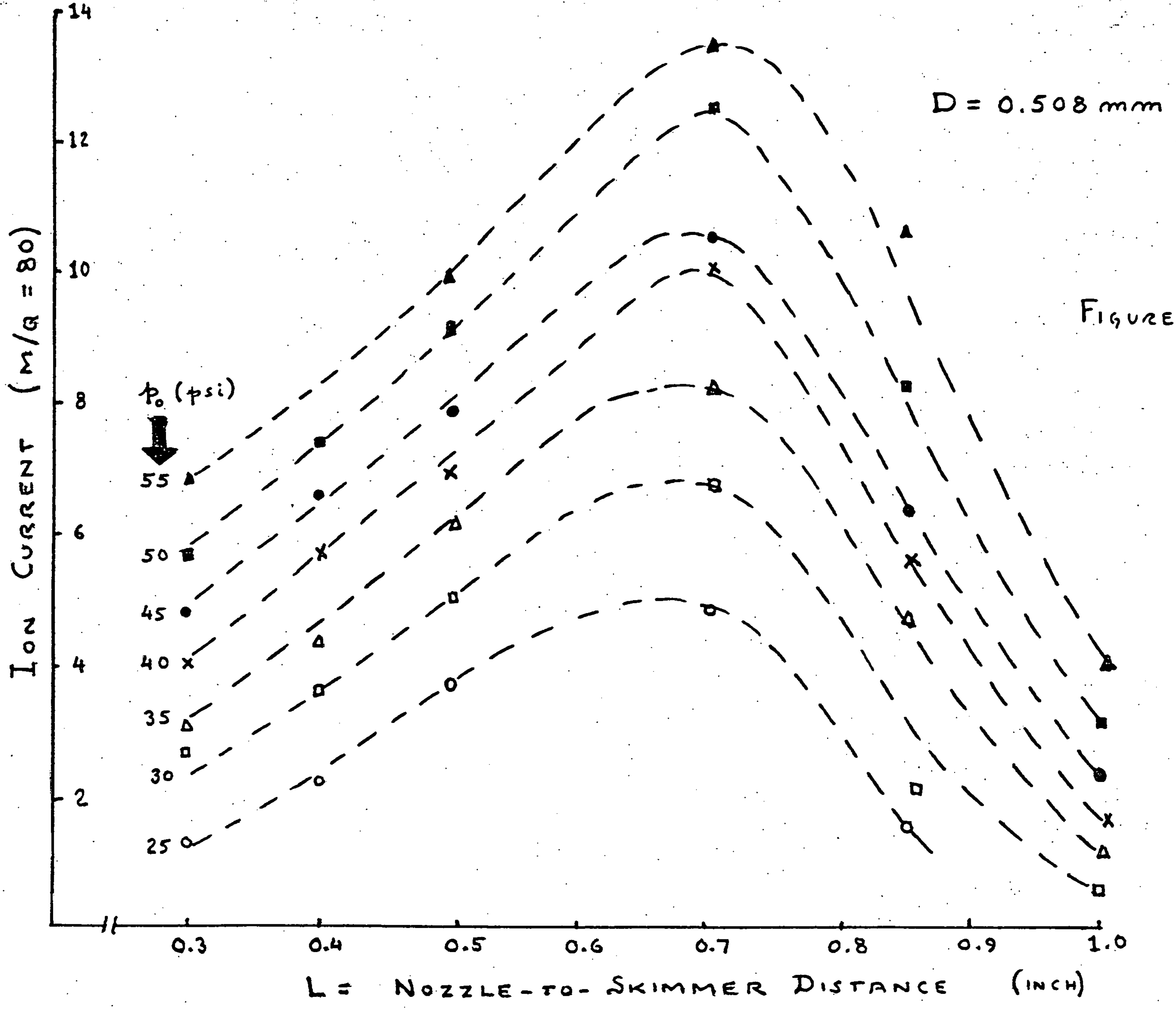

D = 0.508 mm
Ion Current (M/Q = 80)
p_o (psi)
55
50
45
40
35
30
25
14
12
10
8
6
4
2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
L = Nozzle-to-Skimmer Distance (inch)

Figure 6.

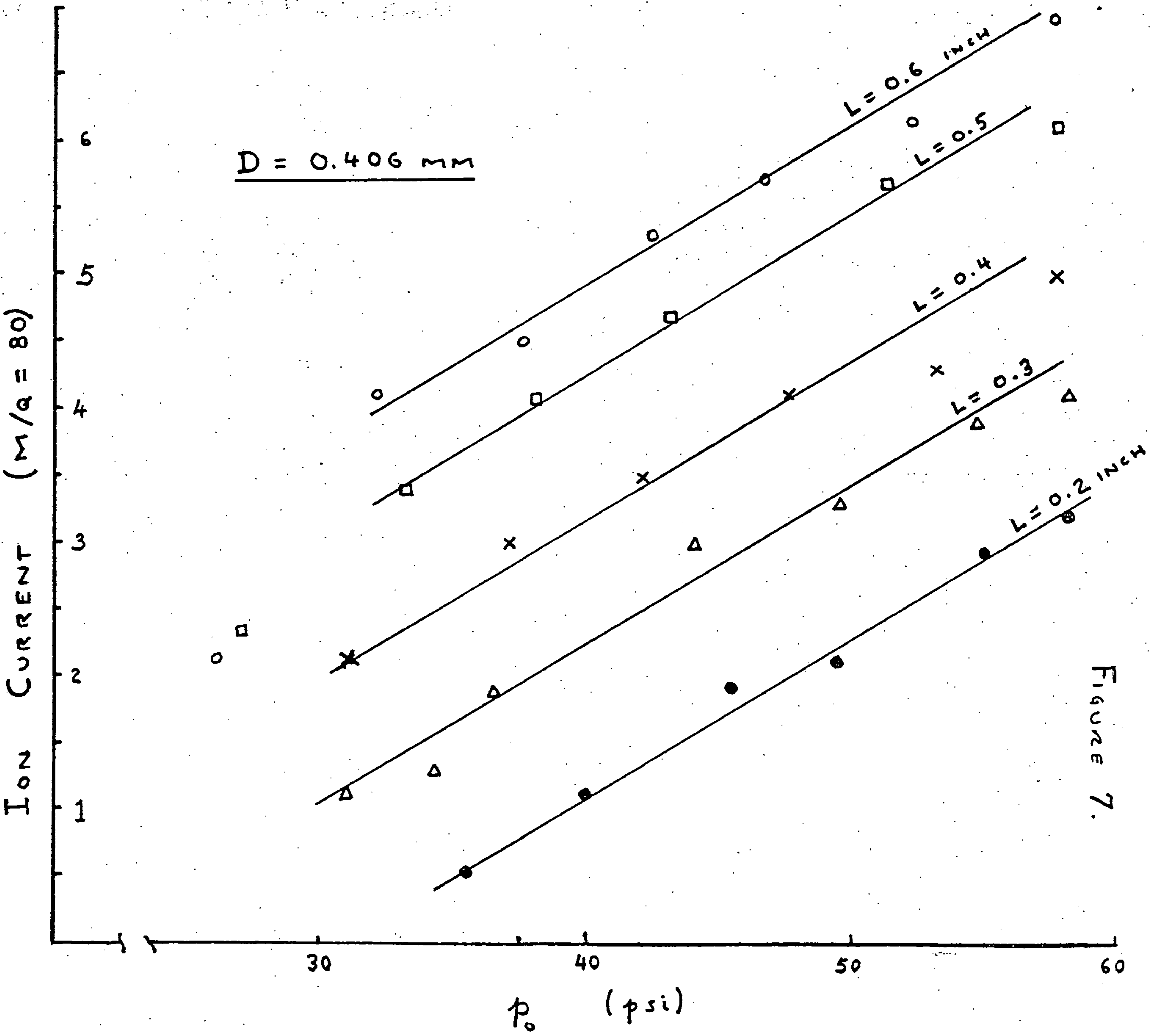

D = 0.406 mm
L = 0.6 inch
L = 0.5
L = 0.4
L = 0.3
L = 0.2 inch
Ion Current (M/Q = 80)
1
2
3
4
5
6
30
40
50
60
p_o (psi)

Figure 7.

IV.1: Retarding Potential Ion Energy Analysis

Mass spectrometry of cluster beams is in its infancy. The problem is a lack of standards for cluster size distributions. The combined use of retarding-potential ion energy analysis and of mass analysis in an alternate-cycle beam system should provide a new standard for size-distribution measurements. It is proposed to add a retarding-potential analyzer to our apparatus in line with the molecular beam but downstream of the mass spectrometer electron beam. The combined mass spectrometer/RP analyzer should be most valuable in studies of heteronuclear excimer systems.

IV.2: Rare-Gas Dimers

As for the case of Ar_2, the formation of other rare gas dimers will involve the free expansion of single-/two-component gases to obtain homonuclear/heteronuclear diatomics.

IV.3: Inert-Gas Halides and Oxides

Ground-state van der Waals complexes of inert-gas oxides or halides can be made in expansions of inert gas-oxygen atom or inert gas-halide atom mixtures. Oxygen atoms have been produced by thermal dissociation in a tubular iridium oven;[5] 90% dissociation has been obtained at 2300 K. Halide atoms can also be produced by thermal dissociation.[6] While the oxide systems appear to have too much gain, the rare-gas halide excimers could have considerable potential as bound-free ultraviolet systems. Experimental values for some well-depths are available;[7] good theoretical potential energy curves of some rare-gas fluoride states are also available.[8]

IV.4: Mercury and Mercury-Rare Gas Dimers

There is continuing interest in metal vapor excimer systems as candidates for lasers for laser fusion.[9] In particular, the lowest electronic levels in Group IIB elements are metastable with lifetimes of the order of 0.1 to 1.0 microseconds. The ground-state mercury dimer can be produced in the free expansion. There are some problems unique to work with metal vapors which will have to be solved. These are associated with maintaining high purity and the generation of high metal-vapor pressures. An inert-gas sweep-out technique could be employed for the formation of Hg_2. This technique would almost certainly be employed in the formation of mercury-rare gas dimers in the free-jet expansion. As noted below, the formation of ground state Hg_2 and HgA beams (A is any rare-gas atom) will allow a number of experiments on the excimers of these species, not the least important of which will be the photoionization cross sections of excited states.

The use of van der Waals molecules as photochemical prototypes has now been recognized. For example, the fluorescence excitation spectrum of HeI_2 has been studied and the distribution of energy in the photodissociation products of HeI_2 has been discussed.[10]

Supplementing the experimental work, calculations of expected rare-gas dimer concentrations have been carried out. These are reported in the following section. In addition, calculations of the Frank-Condon factors for the ionization of rare-gas dimers are in progress. These calculations will be helpful in the interpretation of the mass spectroscopy of rare-gas dimer systems.

V: CALCULATED DIMER CONCENTRATIONS

Feasibility calculations in the original proposal for this work were based upon the properties of Argon. Since the success of our experiments depends so much on the validity of our estimates of obtained dimer concentration, it was considered important to refine our calculations on Argon and to extend the results to the other homo- and heteronuclear noble-gas diatomics. The quantity computed was the mole-fraction-per-unit-number-density as a function of the absolute (transverse) translational temperature in the beam. Following Stogryn and Hirschfelder, we assumed a Lennard-Jones (6-12) potential.[11] The calculations made use of conservative choices of experimental Lennard-Jones parameters. Preliminary calculations which ignored the contributions of metastably-bound double molecules were presented in our second quarterly progress report.[12] Refined calculations which include metastable contributions to the dimer mole fraction have now been completed and the results are shown in Figures 8, 9, and 10. As a guide, we note that in our system $T_{//}$ will freeze at about 10K but that transverse temperature $T_{\perp}$ will go lower. The results tend to confirm the rough estimates made in the original proposal and we note that homo- and hetero-nuclear dimers (and so excimers) of Xe, Kr and Ar should be most easily studied.

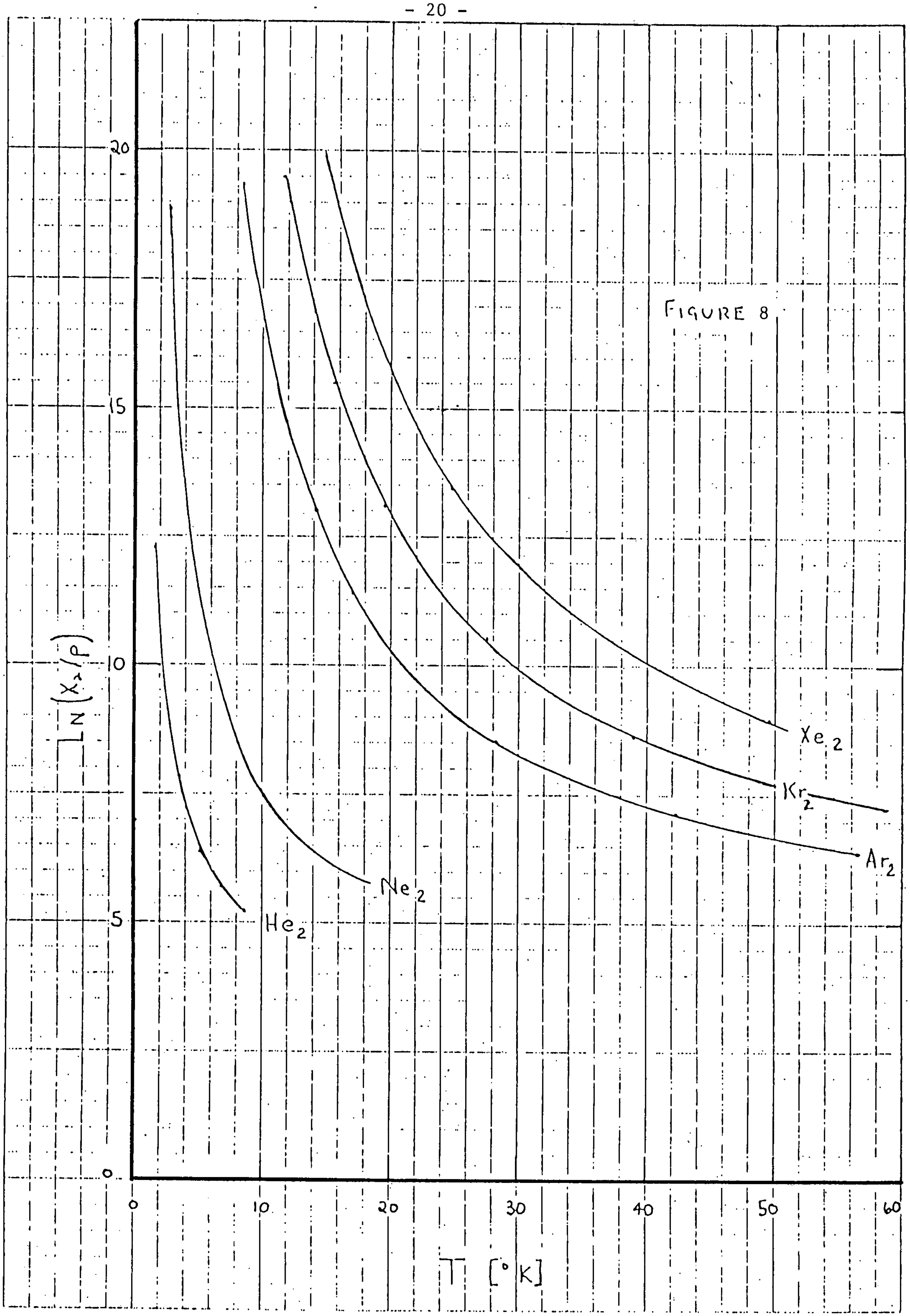


FIGURE 8
LN (X₂/P)
0
5
10
15
20
0
10
20
30
40
50
60
T [°K]
He₂
Ne₂
Ar₂
Kr₂
Xe₂

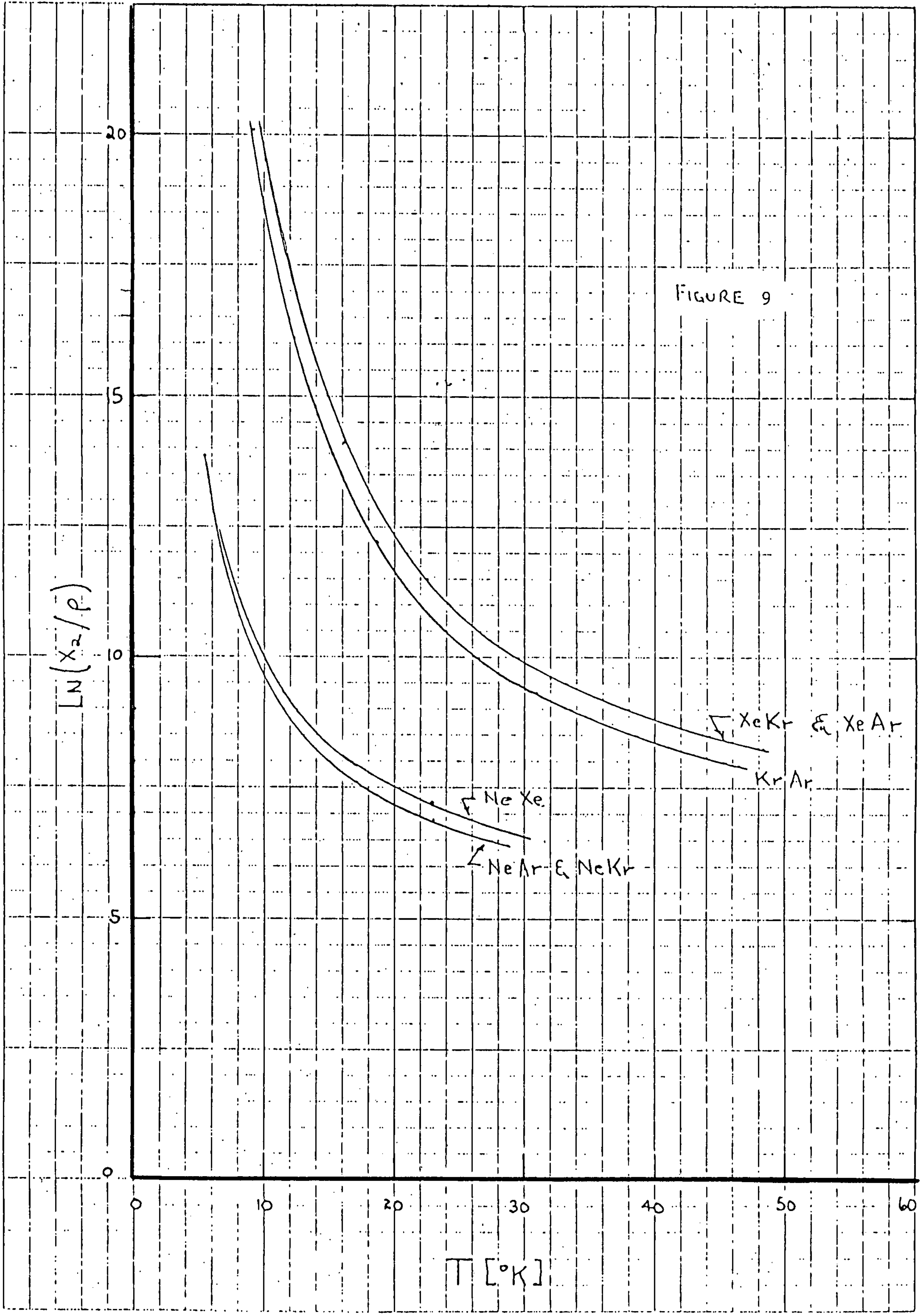


FIGURE 9
$LN(X_2/P)$
$T\ [°K]$
0
5
10
15
20
0
10
20
30
40
50
60
XeKr & XeAr
KrAr
NeXe
NeAr & NeKr

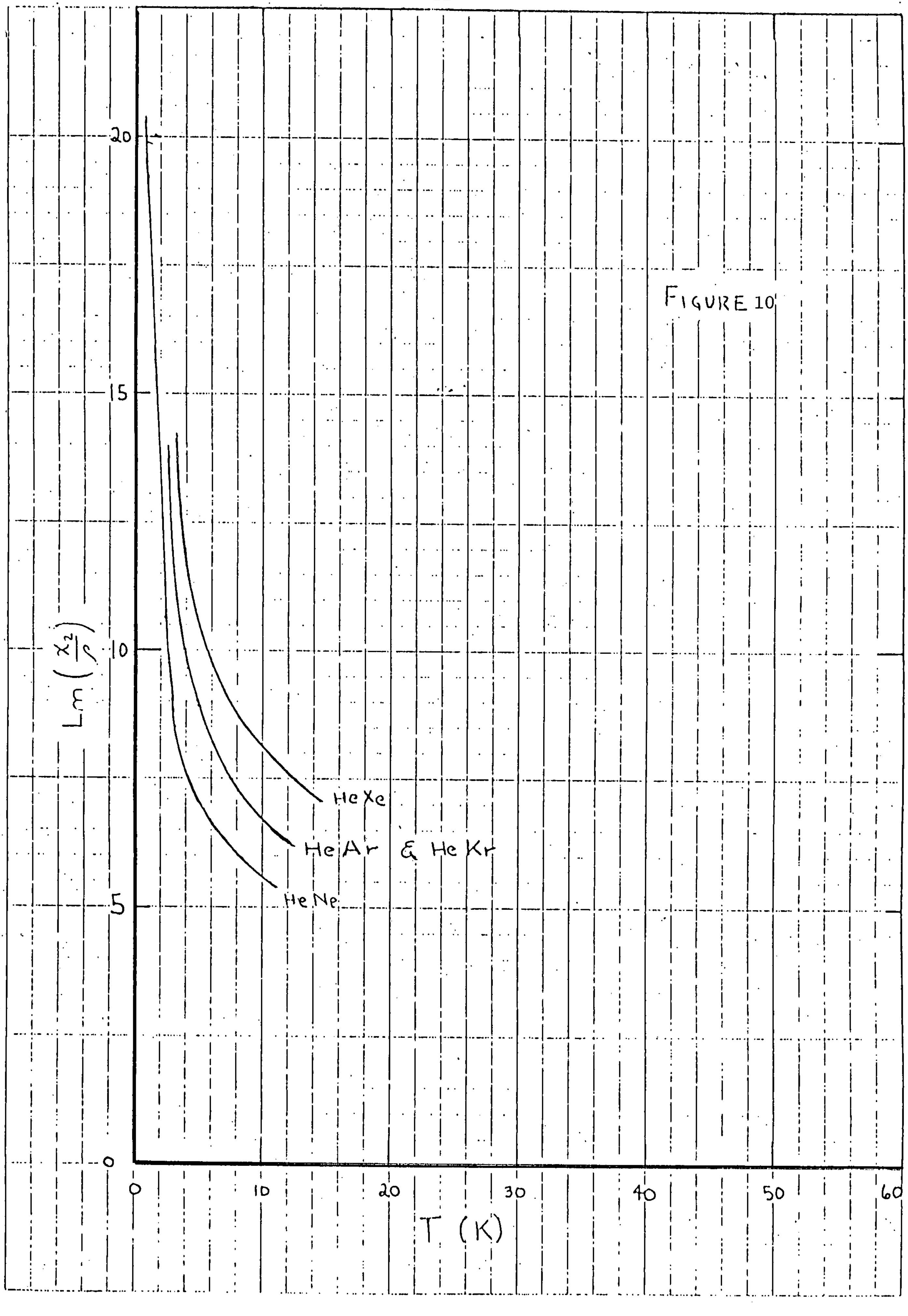


FIGURE 10
$\mathrm{Ln}\left(\frac{\chi_2}{\rho}\right)$
0
5
10
15
20
He Xe
He Ar & He Kr
He Ne
0
10
20
30
40
50
60
T (K)

VI: FORMATION & STUDY OF EXCIMERS & EXCIPLEXES

VI.1: FORMATION

Excimers and exciplexes will be produced by low-energy (typically 10 eV) resonant electron-beam pumping. Because electron-beam excitation is a vertical or Franck-Condon process, it is important that there exist vibrotational levels near the dissociation limit in the excited species AB at the internuclear configuration of the ground-state van der Waals complex. (See Figure 1.) The existence of such levels near dissociation is, however, reasonable. For example, Li and Stwalley found such states in the spectrum of Mg_2 at internuclear separations of 10 angstroms; for these states, the difference between the potential energy surface and the dissociation limit is about 0.050 eV. We note that the potential well depth for excimers like $Xe_2{}^*$ is about an electron volt.[13]

The formation rate of AB is given by

$$\frac{d[AB^{\dagger}]}{dt} = k[AB]n_e, \tag{7}$$

where n_e is the number of electrons in the volume of intersection of the dimer and electron beams. Rate constant k takes a value of about 3.6×10^{-10} cm^3/electron/second if the electron excitation cross section is assumed to be 2×10^{-18} cm^2 for 10 eV electrons.[14] For the production of Xe_2 , we should form in excess of 10^9 excimers per second.

If we assume a radiative lifetime for $AB^{\dagger}$ of about 20 NSEC, a beam velocity corresponding to the expansion terminal Mach number, and a reasonable value for the de-excitation cross section, then it is found that less than one percent of our excimers will be vibrotationally excited.[15] We should note, however, that a 20 nsec lifetime is probably too short for a high-energy laser material. Part of the objective of our research will be to find bound-free systems with longer radiative lifetimes.

VI.2: STUDIES OF EXCIMER/EXCIPLEX SYSTEMS

A very large number of systems can be studied. These will include the excimers of homo- and heteronuclear inert-gas dimers, of inert-gas oxides and of inert-gas halides as well as the atom-diatom exciplexes of systems such as $A \cdot N_2$, $A \cdot CN$ and $A \cdot Cl_2$, where A is a rare-gas atom.

Our attack on the problems outlined above will involve six basic classes of measurements.

A: Visible Vacuum Ultraviolet Spectra

The visible to vacuum ultraviolet regions of the spectrum will be monitored for each species studied. These emission spectra should help to characterize the wavelengths for potential new laser materials. Photon-counting will be employed when sensitivity requires. Low-pressure studies should yield well-resolved line spectra.[7]

B: Electron-Excitation Cross Sections

Steady-state emission intensity measured at very low background pressures in the excitation chamber can be used to deduce cross sections for electron-beam formation of excimers and exciplexes. The pumping electron-beam current will be monitored while the dimer concentration is obtained with the mass-spectrometer. From these data, the rate constant (and so the cross section) for the reaction

(8) $AB + e^{-1} \rightarrow AB^{\ddagger} + e^{-1}$

can be found. In addition, the dependence of this cross section on electron excitation energy can also be determined. It may be necessary to extrapolate measured cross sections to zero background pressure contitions in these studies. Absolute cross-sections will have large uncertainties, but relative cross-sections should be much more accurately determined.

C: Reactive Cross Sections

Total reactive cross sections for the collisional de-excitation and collisional dissociation of excimers can be obtained, once the cross sections for formation of excimers have been determined. Under the conditions of steady-state excimer formation, the data on reactive cross sections will be found by the simple process of varying the pressure as well as the composition of the background gas in the excitation chamber. Again, it is relative cross sections which can be obtained with the greatest accuracy.

D: Lifetimes

The effects of the variation in background pressure on emission spectra will provide a first probe of lifetimes. It is hoped that some of the new excimer/exciplex systems to be studied will have lifetimes of the order of collision times. Actual lifetimes will be measured in relaxation studies with pulsed electron-beam excitation followed by (variably) time-delayed photon counting. Newly available electron-bombardment-semiconductor devices[16] (Watkins-Johnson Corp.) allow the generation of very fast-risetime, high-energy pulses for the measurement of lifetimes shorter than 3 nsec. With an ability to measure lifetimes to 2 nsec, kinetic complexities can be probed. For example, the existence of two different lifetimes (5 and 40 nsec, respectively) for the singlet and the triplet manifolds of rare-gas excimers might be directly confirmed.

Ar_2 should provide a good system with which to develop our delayed-photon-counting and lifetime measurement techniques. The lifetime measurements are the most difficult experiments we have proposed.

E: Resonant Self Absorption

For high-pressure lasers, resonant self-absorption of lasing emissions could lead to a serious loss of excimers through the formation of more-highly-excited states. To study this process, the following experiment is proposed with our tunable UV-Visible laser. The population of excimers will be monitored by their steady-state fluorescence. Laser-induced transitions, i.e. absorptions, will be monitored as changes in the intensity of that steady-state fluorescence. Since the number of absorbing excimer states will not be large in our experiments, we will not be able to monitor the emissions from the more-excited states formed. Because of this, the total optical absorption cross sections of our excited states will be determined.

This experiment is feasible only because of the extremely large resonant-absorption cross sections for visible light. The measurement of upward-bound resonant absorption cross sections would be complicated in the event that the minima in the potential wells of the excimer and van der Waals dimer occur at the same internuclear separation. Even this unusual case could be discovered by laser excitation studies of the ground-state dimer.

The experimental system has been designed to allow laser excitation studies either in the molecular beam or directly in the free-jet expansion. The tuned laser must deliver 64 MW of power for successful execution of these experiments. A commercial tuned flash-lamp excited laser is now available which is capable of 3 kw peak power at 90 MW average power, and which can operate at pulse repetition rates as high as 30 pulses per second. (Chromatrix CMX-4).

F: Photoionization of Excited States

Because a mass spectrometer is being used to monitor concentrations of beam species, another important (but difficult) class of experiment is possible. This is outlined in Figure 9. The dimer ion AB^+ produced by photoionization of beam species is monitored by the mass spectrometer which, with its electron beam off, acts as a passive ion detector. Structure in the photoionization efficiency curve for AB^+ which is induced by the beam-excitation electron electron gun is immediately interpretable in terms of the photo-ionization of excited states of the dimer. The mass spectrometer, using ion counting, provides a measurement of steady-state photo-ion current while photon counting of excimer florescence provides the steady-state excimer population. Monitoring of laser intensity could then allow the determination of photo-ionization cross sections. This type of data is seriously lacking for excimer-laser systems.

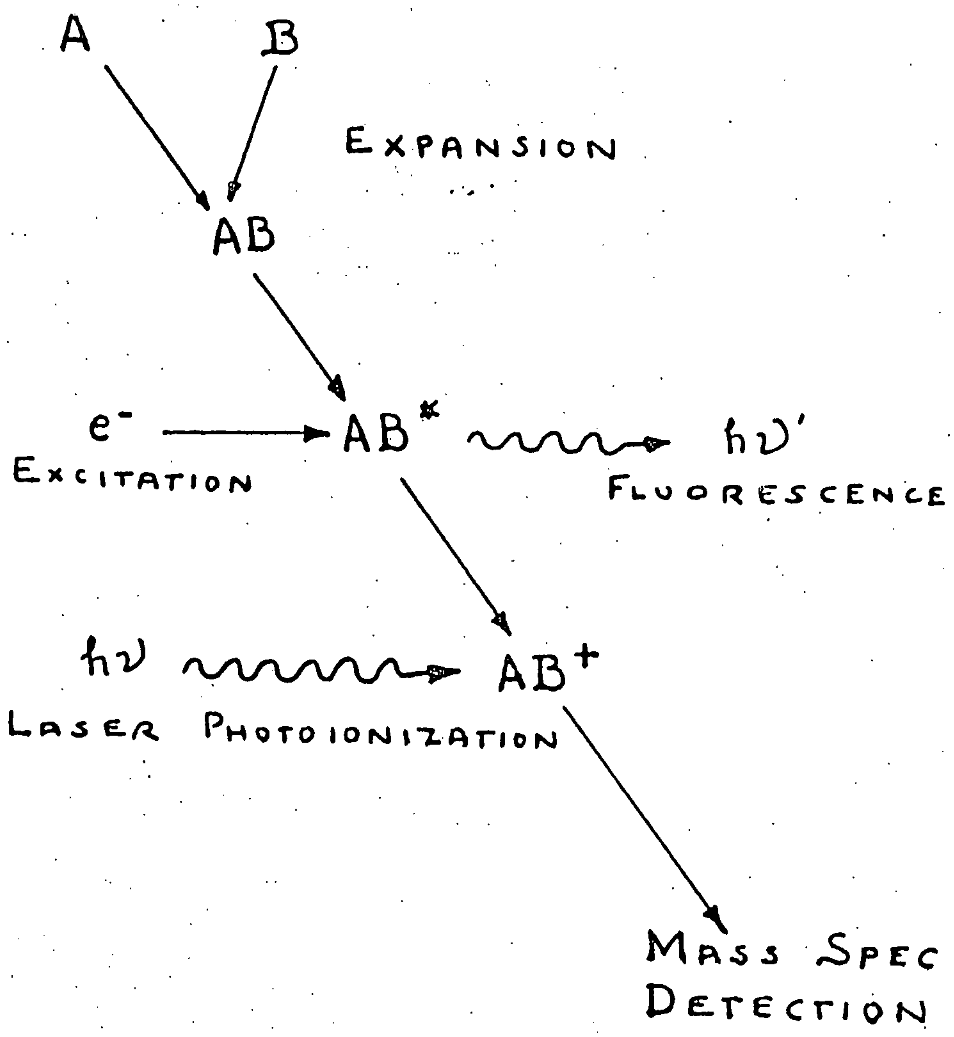


Figure 9.

Photo-Ionization of Excited States

VII: REFERENCES

1. (a) F. K. Houtermans, Helv. Phys. Acta 33, 933 (1960);
   (b) C. K. Rhodes, IEEE J. Quantum Electron. QE-10, 153 (1974).

2. G. A. West and M. J. Berry, J. Chem. Phys. 61, 4700 (1974).

3. (a) T. A. Milne and F. T. Greene, J. Chem. Phys. 47, 4095 (1967);
   (b) P. P. Wegener and J. Y. Parlange, NATO AGARD Publication AD 658-781, Vol. II, p. 607 (1967);
   (c) S. S. Lin, Rev. Sci. Instr. 44, 516 (1973);
   (d) Otto F. Hagena, in "Molecular Beams & Low-Density Gasdynamics," edited by P. P. Wegener (Marcel Dekker, Inc., N.Y., 1974), p. 93;
   (e) R. E. Smally, D. H. Levey and L. Wharton, J. Chem. Phys. 64, 3266 (1976);
   (f) C. B. Cosmovici, Rev. Sci. Instr. 47, 667 (1976);
   (g) C. A. Stearns, et al., NASA TM 73720, (NASA-Lewis Research Center, Cleveland, July, 1977).

4. (a) T. A. Milne and F. T. Greene, Adv. Chem. 72, 64 (1968);
   (b) J. P. Valleau and J. M. Dekkers, Can. J. Chem. 43, 6 (1965);
   (c) Also see Proceedings of Conferences on "Rarefied Gas Dynamics."

5. H. H. Lo, L. Kurzweg, R. T. Backman and W. L. Fite, Phys. Rev. 4, 1462 (1971).

6. (a) P. W. Hoff, J. C. Swingle and C. K. Rhodes, Appl. Phys. Lett. 23, 245 (1973);
   (b) H. A. Koehler, L. J. Ferderber, D. L. Redhead and P. J. Ebert, Phys. Rev. A9, 768 (1974);
   (c) S. K. Searles and G. A. Hart, Appl. Phys. Lett. 25, 79 (1974).

7. (a) M. A. Gardner, A. M. Karo and A. C. Wahl, J. Chem. Phys. 65, 1222 (1976);
   (b) C. K. Rhodes and P. W. Hoff, UCRL-74922 (Aug. 3, 1973);
   (c) H. T. Powell, J. R. Murray and C. K. Rhodes, Appl. Phys. Lett. 25, 730 (1974);
   (d) J. E. Valazco and D. W. Setzer, J. Chem. Phys. 62, 1990 (1975);
   (e) H. Askenas and F. S. Sherman, "Rarefied Gas Dynamics, 4th Symp.," (Academic Press, N.Y., 1966);
   (f) See also references 4 above;
   (g) D. L. Huestis, et al., Report AD-A009284 (NTIS, 31 Jan., 1975);
   (h) C. D. Cooper, G. C. Cobb and E. L. Tolnas, J. Molec. Spectry. 7, 223 (1961).

8. See reference 7(a).

9. (a) L. A. Schlie, B. D. Guenthe and R. D. Rathge, Appl. Phys. Lett. 28, 393 (1976);
   (b) R. E. Drullinger, M. M. Hessel and E. W. Smith, J. Chem. Phys. 66, 5656 (1977);
   (c) H. Komine and R. L. Byer, J. Chem. Phys.
   (d) Math. Sciences Northwest, Inc. Report 77-1077-1 (7 Oct., 1977);
   (e) J. R. Woodworth, J. Chem. Phys. 66, 754 (1977).

10. (a) M. S. Kim, R. E. Smalley, L. Wharton, and D. H. Levy, J. Chem. Phys. 65, 1216 (1976);
    (b) R. E. Smalley, D. H. Levy and L. Wharton, J. Chem. Phys. 64, 3266 (1976).

11. D. E. Stogryn and J. O. Hirschfelder, J. Chem. Phys. 31, 1531 (1959).

12. Quarterly Progress Report No. 2 (Mar-May, 1976) USERDA-COO-2810-3.

13. (a) K. C. Li and W. C. Stwalley, J. Chem. Phys. 59, 4422 (1973);
    (b) Reference 1(b).

14. M. J. Seaton, in "Atomic and Molecular Processes," edited by D. R. Bates (Academic Press, N.Y., 1962).

15. D. J. Bradley, M.H.R. Hutchinson and H. Koetser, Optics Comm. 7, 187 (1973).

16. A. Silzars, D. L. Bates and A. Ballonoff, Proc. IEEE 62(8), 1119 (1974).