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

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Principal Investigator:

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

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Laser & Isotope Separation Office
Washington, D.C. 20545

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DISCLAIMER

I: INTRODUCTION:

The object of this work is the development of a system for the formation of excimers from their van der Waals ground states. Low temperatures obtainable in a free-jet expansion will be used to produce high steady-state concentrations of van der Waals dimers or oligomers. These will, in turn, be excited by low-energy resonant electron bombardment to yield excimers and exciplexes. The mechanism is as follows:

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

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

$$AB^{\ddagger} + M \xrightarrow{3} AB^{*} + M \qquad \text{(collisional de-excitation)}$$

It is proposed to prepare and study homo- and heteronuclear noble-gas excimers as well as excimers of noble-gas halides and oxides.

The experimental system for these studies is shown schematically in Figure 1. While the first quarter of this grant involved the evolution of design criteria, the second quarter has been devoted to the detailed design and acquisition of system components. In addition, calculations of expected ground-state van der-Waals dimer concentrations have been completed. The feasibility of using tuned lasers for resonant upward optical transitions of excimers has also been studied.

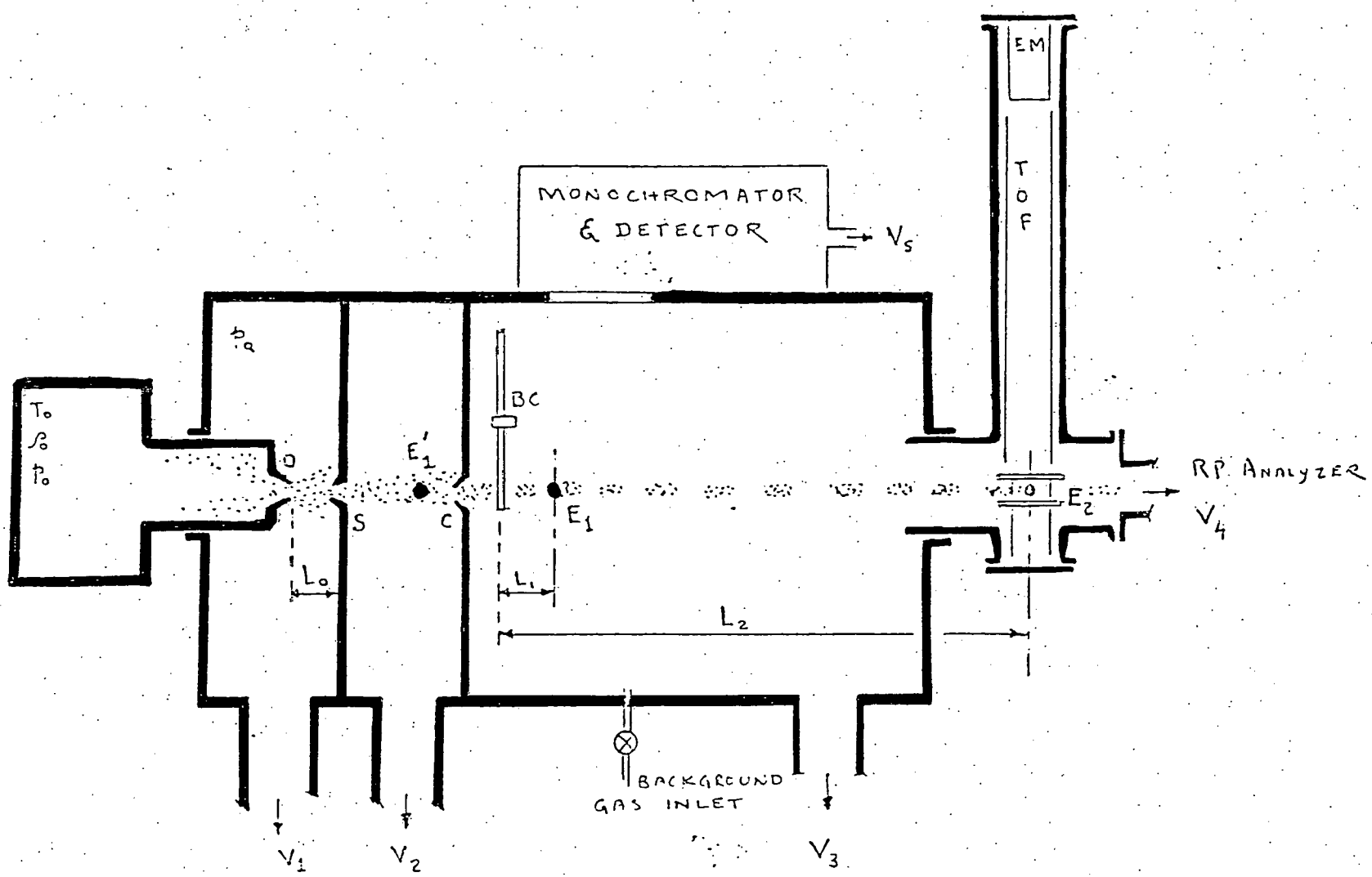


Figure 1. Experimental Apparatus

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.

II: THE STATUS OF THE APPARATUS.

For purposes of design, the experimental system was considered to be composed of twenty-three blocks which are labeled A-W in the Block Diagram, Figure 2. The status of each of these subsystems is as follows:

A: Gases

Quantities of OCS, Xe, Ne, Ar, CO, O_2 and N_2 are now on hand.

B: REGULATORS

With the exception of one adaptor, regulators are available for all the above gases.

C: GAS INLET SYSTEM

All major components are on order or are in the lab.

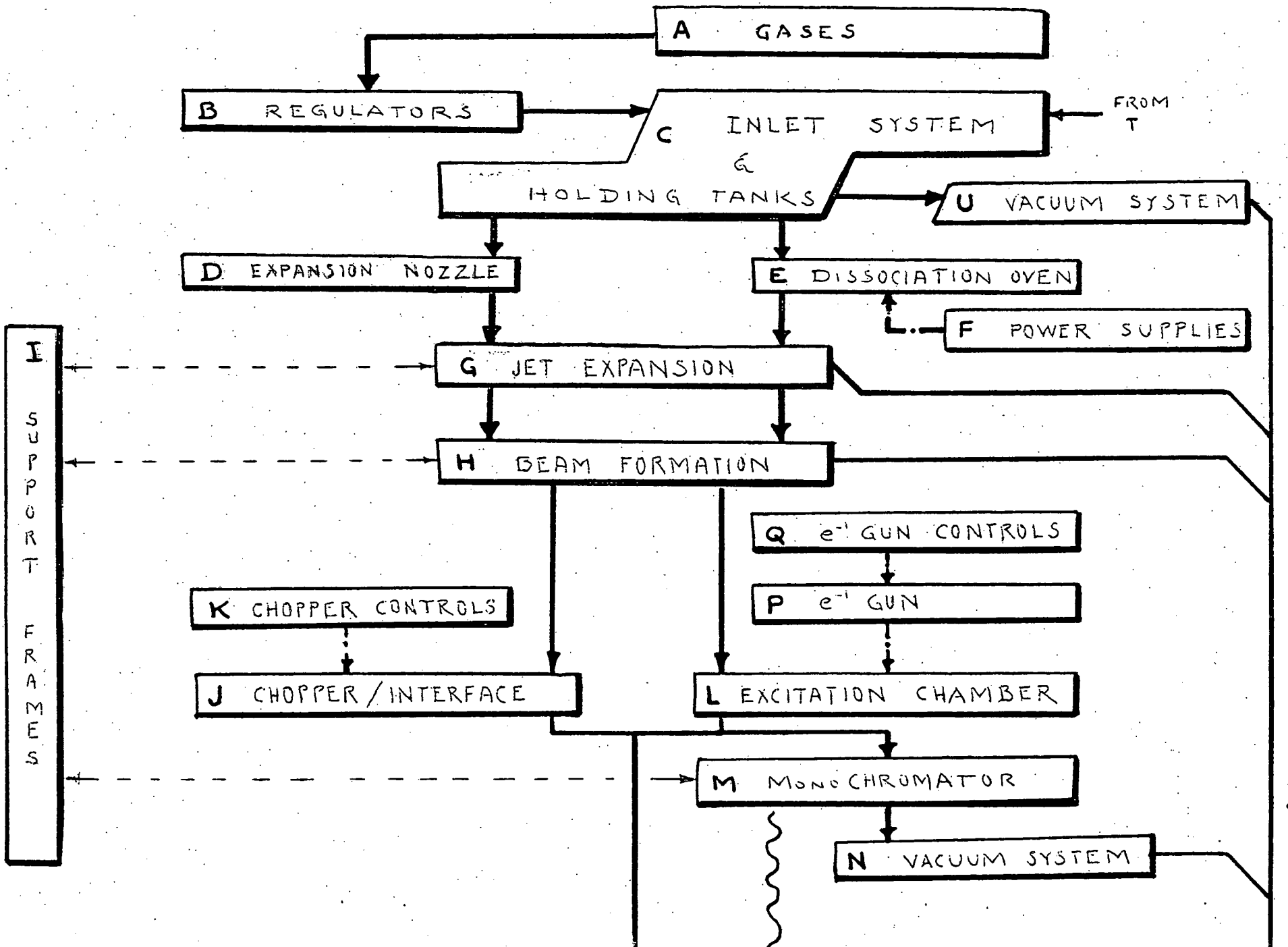
D: NOZZLE INLET

This will be a solenoid-operated pulsed nozzle source. The nozzle design is in our machine shop; the expansion orifices are to be delivered (Engelhard Industries) by the end of June. A coolant system to control the temperature of this stagnation source is to be obtained from Federal Excess Property.

The solenoid and its power supply must be designed or ordered.

E: DISSOCIATION OVEN

We are considering the conversion of a Knudsen Cell oven inlet


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⁻¹ GUN CONTROLS
P e⁻¹ GUN
K CHOPPER CONTROLS
J CHOPPER / INTERFACE
L EXCITATION CHAMBER
M MONOCHROMATOR
N VACUUM SYSTEM
BLOCK DIAGRAM

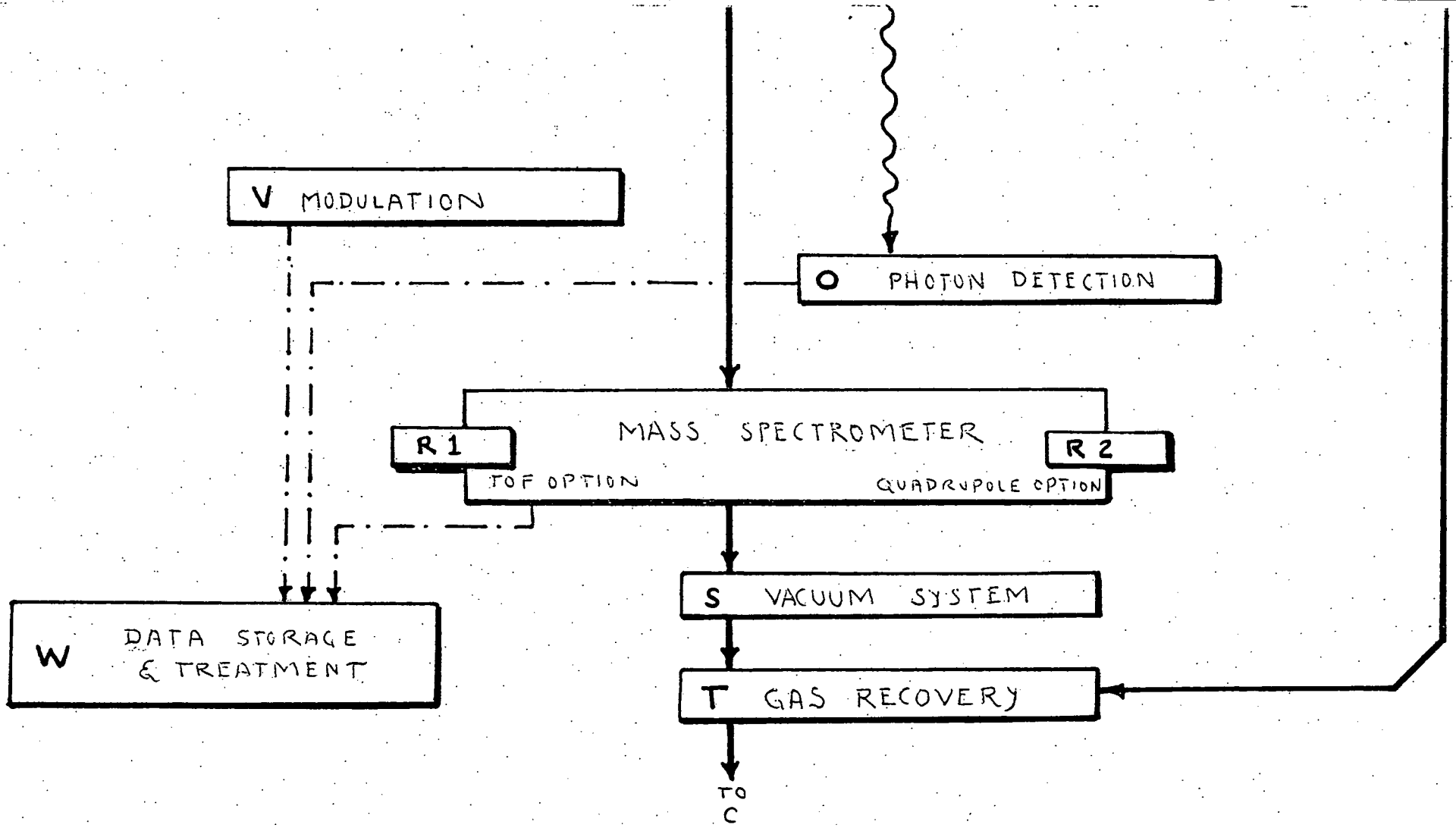


FIGURE 2 BLOCK DIAGRAM

to this application. The commercially available oven is too expensive.

F: DISSOCIATION OVEN POWER SUPPLY

We are looking into the modification of a Knudsen Inlet power supply for this application.

G: JET EXPANSION CHAMBER

All principal components are either on hand or on order. Fabrication of this system is underway.

H: MOLECULAR-BEAM FORMATION CHAMBER

Same status as item G.

I: SUPPORT FRAMES

These are required for Blocks G, H and M. Same status as item G.

J: BEAM MODULATION CHAMBER

Same status as item G.

K: CHOPPER CONTROLS

Major components are on order. Detailed circuits need to be designed.

L: BEAM EXCITATION CHAMBER

Under fabrication in our machine shop.

M: MONOCHROMATOR

This block was described in the Quarterly Progress Report COO-2810-2 of 29 Feb., 1976. Delivery has not yet occurred, but the supplier has promised a mid-June arrival.

N: MONOCHROMATOR VACUUM SYSTEM

Major components have been assembled or ordered.

O: PHOTON DETECTION SYSTEM

Same status as Block M.

P: EXCITATION ELECTRON GUN

Now under design.

Q: ELECTRON-GUN CONTROLS

All electronics except one major power supply has been ordered. Our electronics shop will specify this unit after circuits for excimer lifetime studies have been designed.

R: MASS SPECTROMETER

We still have not decided which of two options (Time-of-Flight or Quadrupole) will be exercised. A TOF has been obtained from EPA as Federal Excess Property while a quadrupole is on loan from NASA.

S: MASS SPEC VACUUM SYSTEM

Same status as Block N.

T: GAS RECOVERY SYSTEM

Major components have been assembled or ordered but detailed design of this system remains to be done.

U: INLET-SYSTEM VACUUM SYSTEM

Same status as Block N.

V: MODULATION ELECTRONICS

A phase-lock amplifier and current probe have been ordered.

W: DATA HANDLING & STORAGE

Scopes, Scope cameras, recorders, a Biomation buffer memory and paper tape punch data logger are available from other projects.

III: 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 principal quantity to be computed is the mole fraction of dimers in the cluster beam. Since this quantity is directly proportional to gas density, it was decided to determine the mole-fraction-per-unit-number-density as a function of the absolute (transverse) translational temperature of the beam. This can be computed from the second virial coefficient with an assumed intermolecular potential. Following Stogryn and Hirschfelder[1], we assumed a Lennard-Jones (6-12) potential. To obtain conservative estimates without making detailed quantum corrections, we ignored the contributions of metastably-bound double molecules to the dimer mole fraction. The Lennard-Jones parameters used are given in Table I; They are conservative choices of Experimental results as tabluated by Kim and Gordon.[2]

Results of our calculations are given in Figure 3, 4 and 5. As a guide, we note that in our system $T_{//}$ will freeze at about 10 K but that transverse temperature $T_{\perp}$ will go lower. Insofar as our original estimates of mole fraction were based on Ar_2, we note that

homo- and heteronuclear dimers (and so excimers) of Xe, Kr and Ar should be most easily studied.

1. D. E. Strogryn & J. O. Hirschfelder, J. Chem. Phys. 31, 1531 (1959).

2. Y. Kim and R. Gordon, J. Chem. Phys. 61, 1 (1974).

TABLE I: LENNARD-JONES PARAMETERS*

Based on conservative choice of experimental values.

DIMER	σ [10^{-8} cm]	ϵ [10^{-12} erg]	REFERENCES*
He-He	2.65	23.5	J. Farrar et. al. J. Chem. Phys. 56, 5801 (1972)
Ne-He	23	2.64	D. Konowalow et. al. J. Chem. Phys. 57, 4375 (1972) R. Van Heijningen et. al. Physica (UTR) 37, 1 (1968)
Ar-He	34	2.98	D. Konowalow et. al. J. Chem. Phys. 87, 4375 (1972) R. Van Heijningen et. al. Physica (UTR) 38, 1 (1968)
Kr-He	33	3.13	R. Van Heijningen et. al. Physica (UTR) 38, 1 (1968)
Xe-He	50	3.32	R. Van Heijningen et. al. Physica (UTR) 38, 1 (1968)
Ne-Ne	63	2.73	P. Siska et. al. J. Chem. Phys. 55, 5762 (1971)
Ar-Ne	3.08	80	R. Van Heijningen et. al. Physica (UTR) 38, 1 (1968) J. Kestin et. al. J. Chem. Phys. 53, 3773 (1970) J. Parson et. al. J. Chem. Phys. 53, 2123 (1970)

Table I (Continued)

DIMER	σ [10^{-8} cm]	ε [10^{-12} erg]	REFERENCES*
Kr-Ne	3.16	80	R. Van Heijningen et. al. Physica (UTR) 38, 1 (1968) J. Parson et. al. J. Chem. Phys. 53, 2123 (1970) J. Kestin et. al. J. Chem. Phys. 56, 4086 (1972)
Xe-Ne	79	3.44	R. Van Heijningen et. al. Physica (UTR) 38, 1 (1968) J. Parson et. al. J. Chem. Phys. 53, 2123 (1970)
Ar-Ar	195	3.32	J. Parson et. al. J. Chem. Phys. 56, 1511 (1972)
Kr-Ar	214	3.41	J. Kestin et. al. J. Chem. Phys. 53, 3773 (1970) J. Parson, et. al. J. Chem. Phys. 53, 3755 (1970)
Xe-Ar	236	3.60	R. Van Heijningen et. al. Physica (UTR) 38, 1 (1968) J. Parson et. al. J. Chem. Phys. 53, 3755 (1970)
Kr-Kr	270	3.48	D. Konowalow et. al. J. Chem. Phys. 57, 4375 (1972)
Xe-Kr	223	3.82	R. Van Heijningen et. al. Physica (UTR) 38, 1 (1968)
Xe-Xe	342	3.85	J. Kestin et. al. J. Chem. Phys. 56, 4119 (1972). G. Davis B. Davis B.J. Chem. Phys. 57, 5098 (1972).

*Based on a literature search reported by Y. Kim and R. Gordon, J. Chem. Phys. 61, 1 (1974).

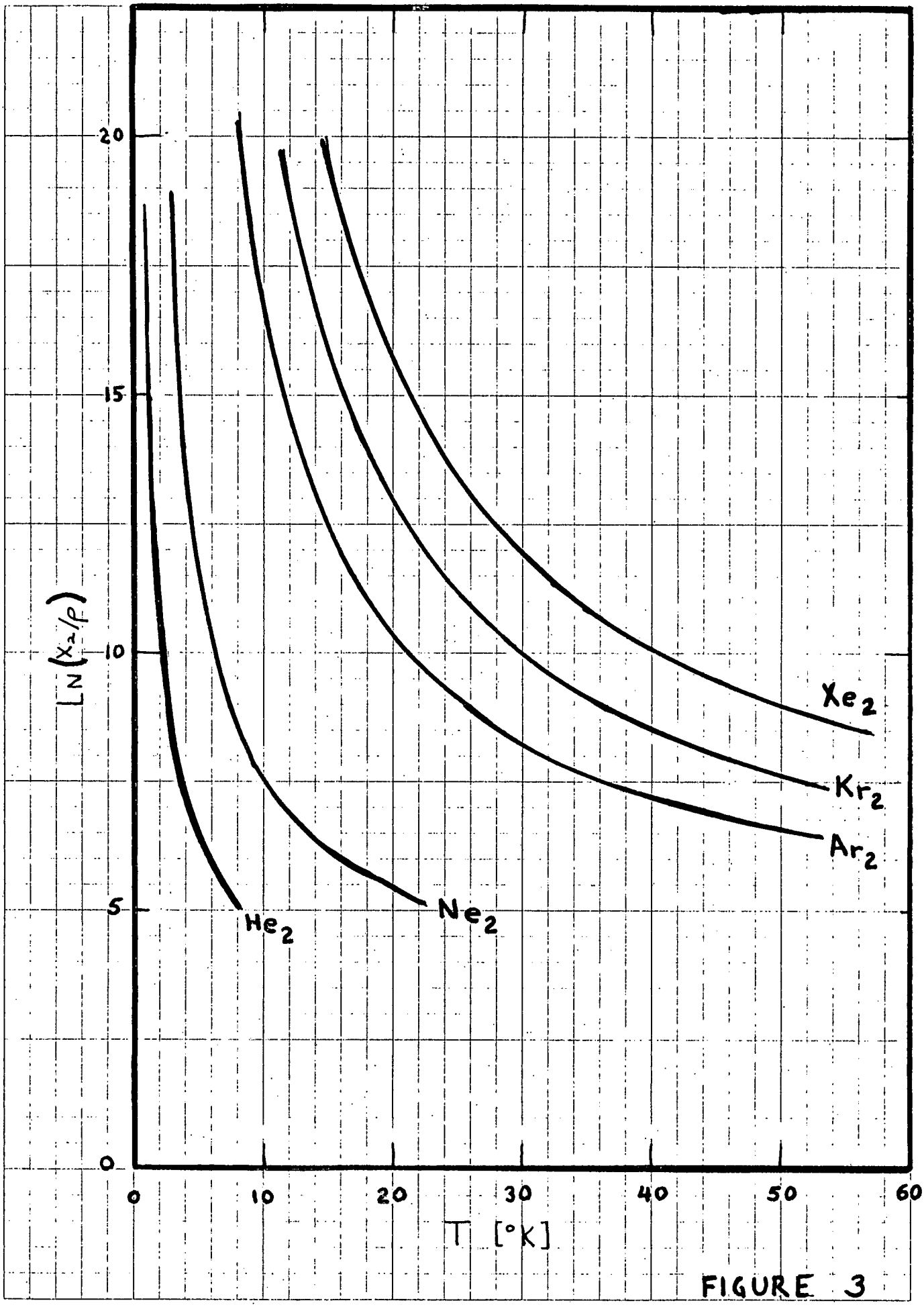


FIGURE 3

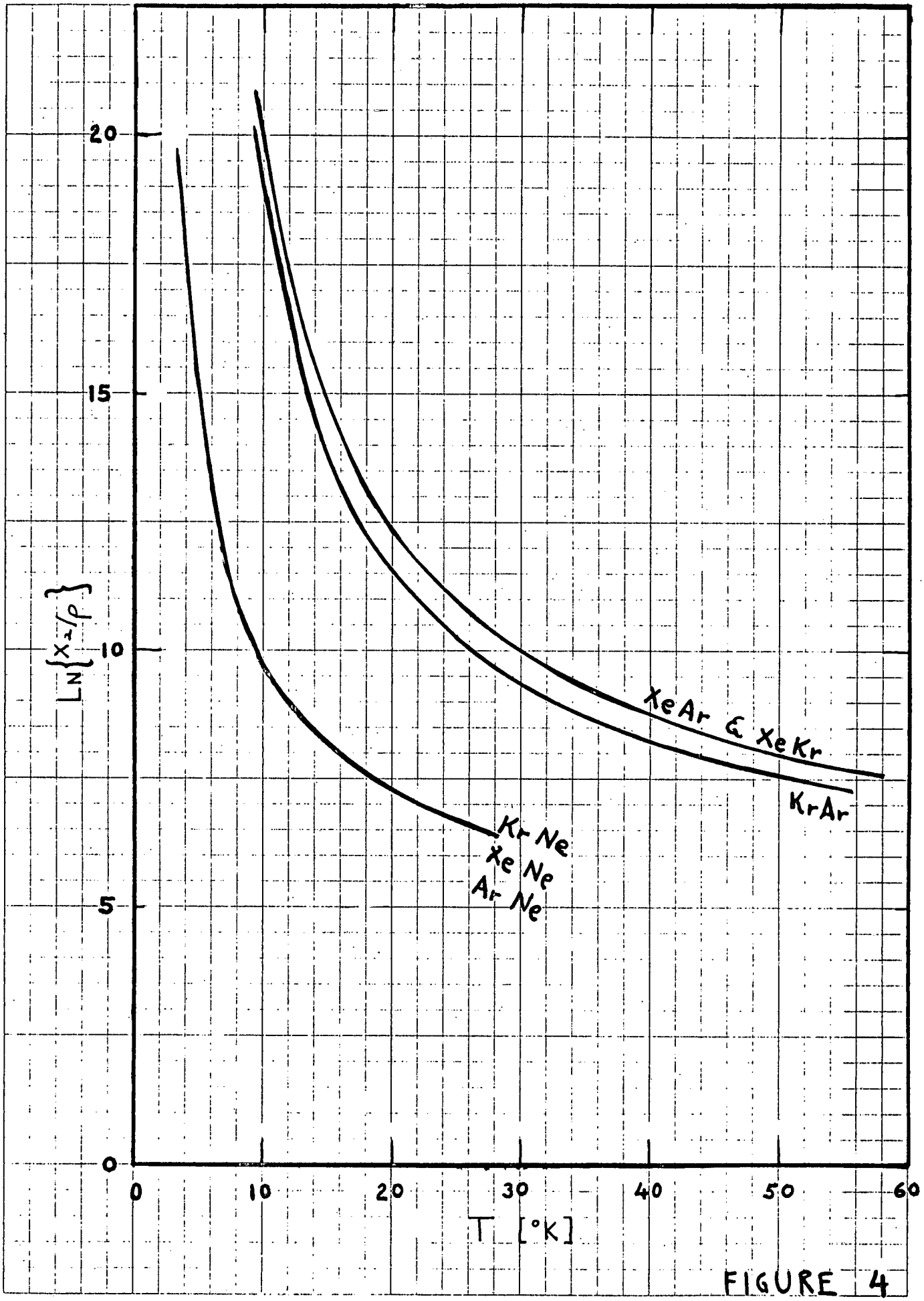


FIGURE 4

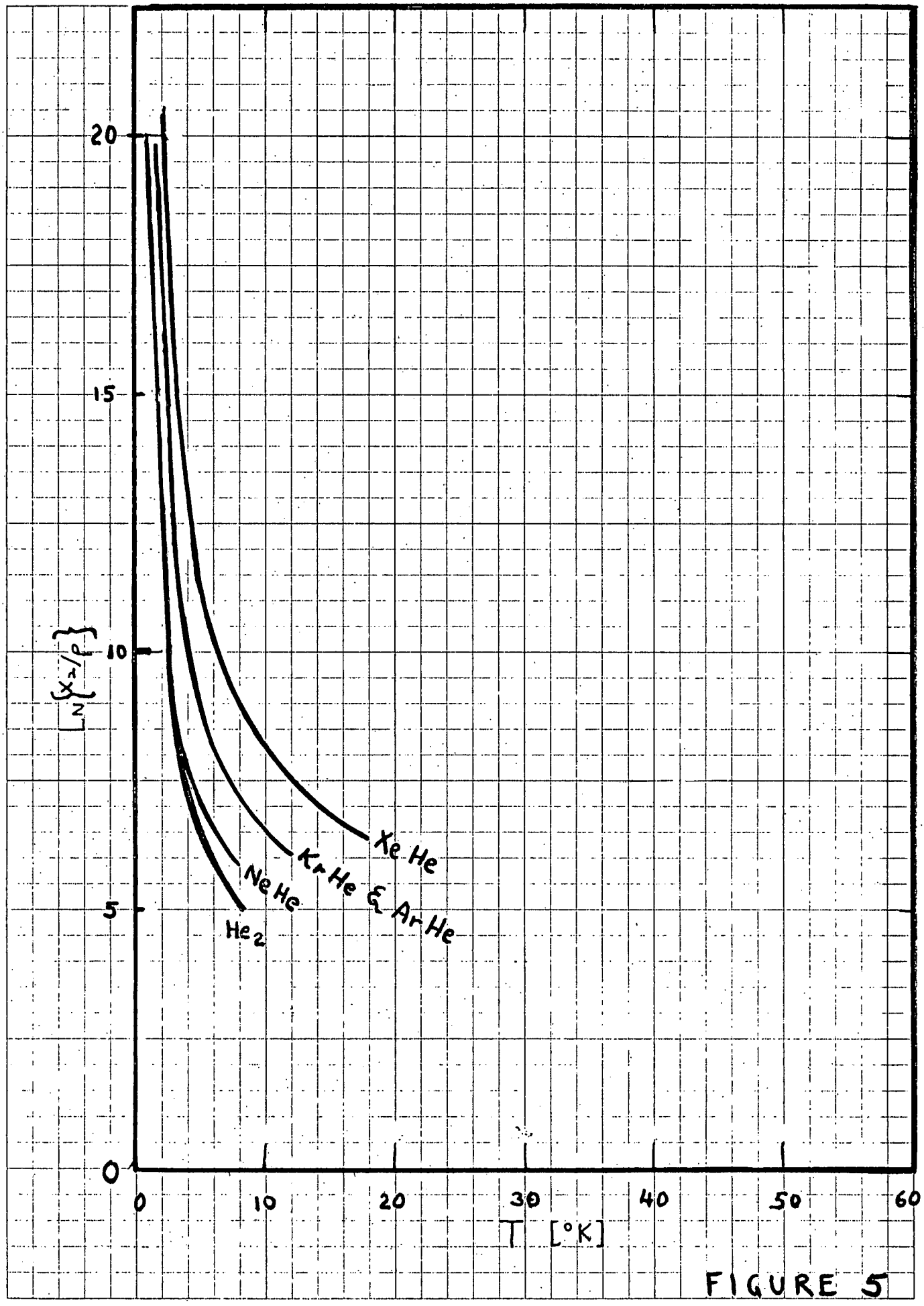


FIGURE 5

IV: UPWARD-BOUND TRANSITIONS.

The original proposal focussed on the kinetics of excimer formation and on the study of the reactive and radiative lifetimes of these species. Recent conversations with Hoff (of ERDA) and with Mies and Krauss (of NBS) have directed our attention to another source of the depletion of excimer concentration in the excimer laser: namely, resonant self-absorption of laser emissions. This process, particularly at high pressures, could lead to a serious loss of excimers through the production of more-highly-excited (perhaps Rydberg) states. To study this process, the following additional experiment is proposed.

A tuned UV-Visible laser would be employed to study the resonant absorption of excimers. Upward optical transitions induced by the laser could be monitored by the emission from the more-highly-excited states formed in the process. As we see below, this experiment is made feasible only because of the extremely large resonant absorption cross sections for visible light.

If τ is the radiative lifetime of the excimers produced in our experiment, then the number $N^{\ddagger}$ of excimers present after a time τ is given by:

$$(1) \quad N^{\ddagger} = \frac{dN^{\ddagger}}{dt} \{1 - \exp(-\frac{t}{\tau})\} \quad \tau$$

where $\frac{dN^{\ddagger}}{dt}$ is the steady-state rate of production of excimers. This rate will be about 10^9 excimers per second. If τ is taken to be

20 nsec, then

$$(2)\quad N^{\ddagger} = 20\ \{1 - \exp\ (-\tfrac{t}{\tau})\ \}\ .$$

Let P be the number of photons required to excite every excimer by resonant absorption. Then

$$(3)\quad P = \frac{N^{\ddagger}\ A}{\sigma_{RES}}$$

where A is the area of the target molecular beam (0.01 cm^2) and σ_{RES} is the resonant absorption cross section. The latter quantity is proportional to the square of the wavelength of the resonant transition. For a Breit-Wigner lineshape,

$$(4)\quad \sigma_{RES} = 0.477\ \lambda_o^{\,2}.$$

Taking λ_o to be 5000 Angstroms, we find that

$$(5)\quad P = 4 \times 10^8\ \{1 - \exp \tfrac{t}{\tau}\ \} \approx 1.6 \times 10^8 \text{ photons.}$$

This corresponds to a laser power of 64 mw. Commercial tuned flash-lamp-excited lasers are available which are capable of 3 kw peak power at 90 mw average power. (Chromatix mode CMX-4).

The experimental apparatus has been designed to allow the addition of an excitation laser beam.

V: PERSONNEL

The following individuals have constituted the Excimer Study Project Group during the report period.

EXPERIMENTALISTS

Dr. John C. Hassler

Dr. James A. Jacobs

Dr. George Sanzone (Principal Investigator)

Mr. Raymond W. Mattozzi (Graduate Student)

THEORETICAL SUPPORT

Dr. John C. Schug

Dr. Clayton D. Williams