COO-2810-4

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

Progress Report

And

Research Renewal Proposal for Contract No. E(11-1)-2810

Submitted by

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DISCLAIMER

I: INTRODUCTION

Continued fundamental studies are proposed on both the formation and properties of new materials for high-energy, gas-phase lasers. As originally proposed, attention will be 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. In the original proposal for this work, a new method for the preparation of excimers and exciplexes was presented in which van der Waals complexes are formed as intermediates. Systems under study include the excited states of dimers, oxides and halides of inert gases.[2]

The assumption underlying our choice of systems is that high-energy gas lasers will operate at high pressures. The main purpose of a laser is to generate large numbers of coherent photons. Consequently, it is necessary to study both primary and secondary photo-processes operating in laser systems.[3] It is the object 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 as well as collision- and non-collision-induced intersystem crossing will also be considered. (Collision-induced crossing is particularly interesting in that an understanding of this process is not only important in such systems as rare-gas oxide lasers, but also to our understanding of the application of the Transition State and RRKM theories to systems such as N_2O which exhibit such crossing.[4])

While the original proposal focussed on the kinetics of excimer formation and on the study of reactive and radiative lifetimes, it is proposed to expand the scope of our work to include another source of depletion of excimer concentrations: namely, resonant self-absorption of laser emissions. This process, particularly at high pressures, could lead to a serious loss of excimers (and photons) through the production of more-highly-excited (perhaps Rydberg) states.

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.[5] 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.

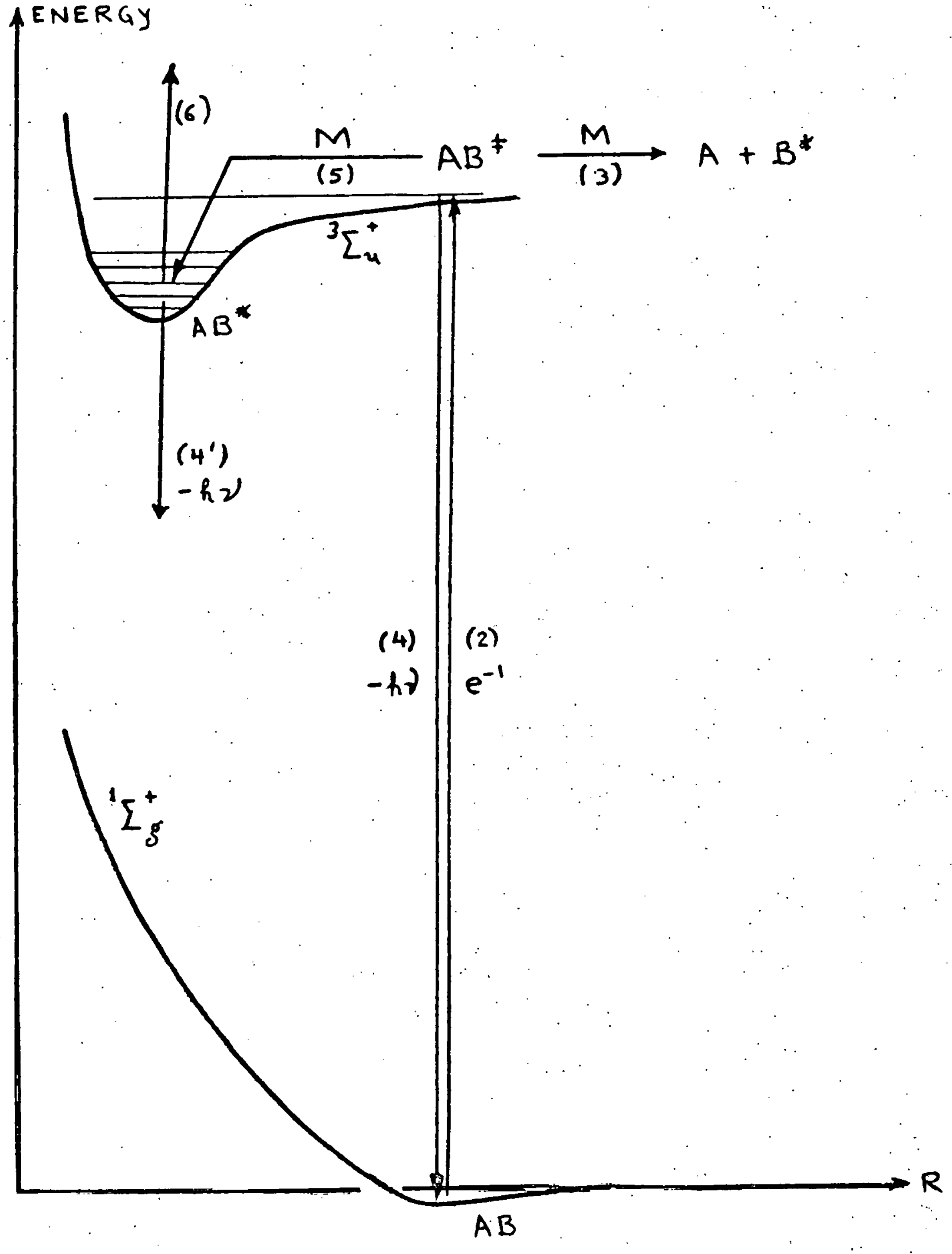


Figure 1. Formation Mechanism for AB*.
Van der Waals complex AB is
produced in a free jet expansion.

The use of resonant, low-energy electron pumping is not contingent on the production of a species in the expansion. Consequently, the same apparatus can be used to study excited states of stable species. It is planned to study the collisional and reactive lifetimes of excited-state free radicals, in particular CO*, CO_2* and CS*.

The experiments proposed are difficult. But they also have a reasonable probability for yielding much-needed fundamental <u>experimental</u> data on the spectra, lifetimes and reactivity of a wide class of materials. The experimental and theoretical tools for these studies are being assembled at this time. The system being built is shown schematically in Figure 2. This proposal requests funds to complete the preparations and to execute these experiments.

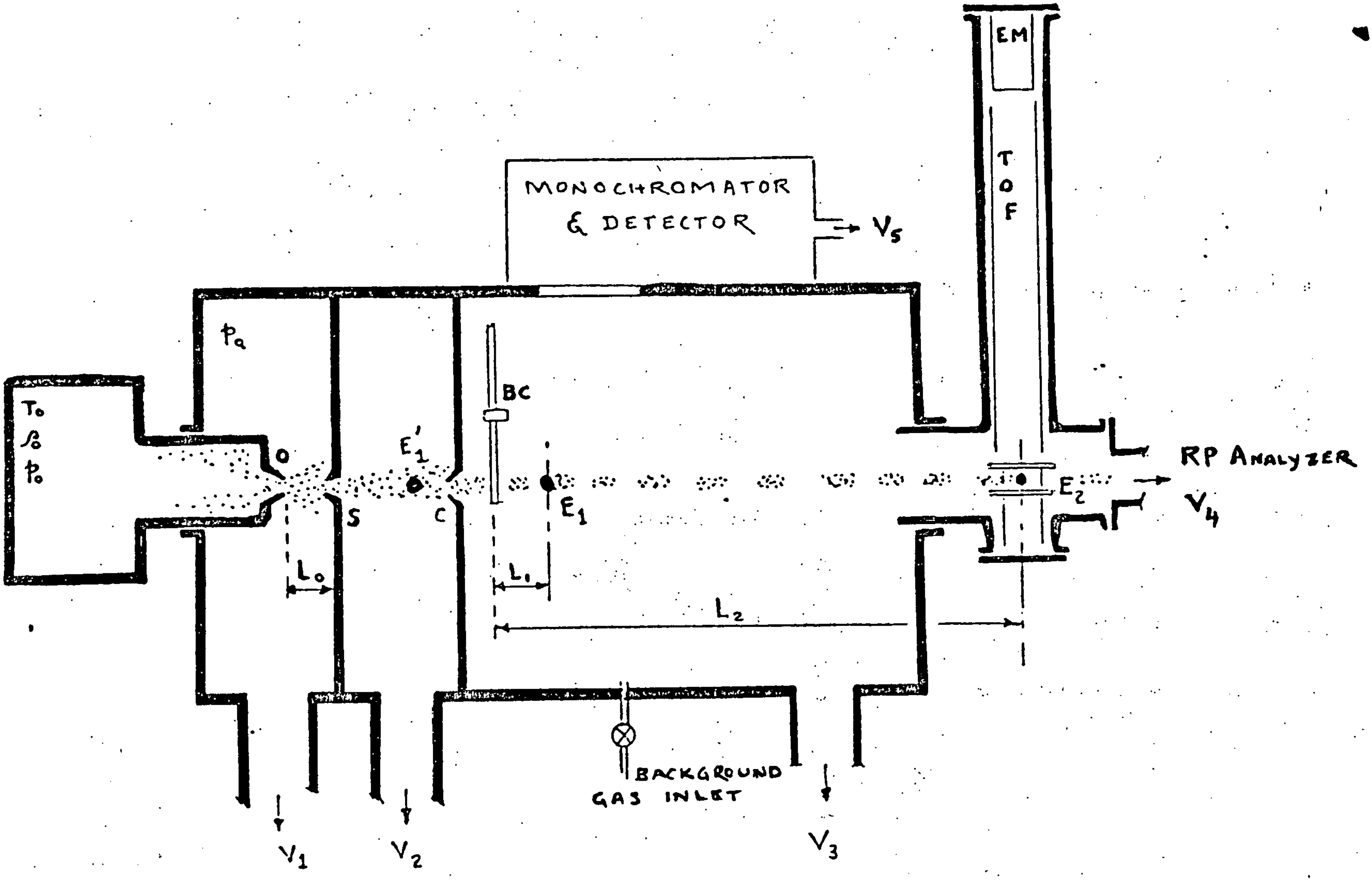


Figure 2. Experimental Apparatus

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.

III: DIMER & OLIGOMER 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. Design equations and criteria were developed and were reported in our first quarterly progress report (March, 1976).[6] One additional equation should be added, that for the maximum flow angle of the Prandtl-Mayer expansion:[7]

$$(7) \quad \phi = \frac{\pi}{2}\left(\frac{\gamma+1}{\gamma-1}\right)^{1/2} - \frac{\pi}{2}$$

An important result of the development of the design criteria was the recognition that jet geometry is virtually independent of conditions in the stagnation chamber but is determined principally by system pumping speeds.[6] This led to the decision to develop a <u>pulsed</u> 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. More-to-the point, variation of stagnation chamber conditions has been given real meaning in terms of the control of cluster size.[8]

In addition to the variation of the pulsed-nozzle duty cycle, the concentrations of selected oligomers will also be optimized by controlling the following parameters:[9]

Skimmer-to-nozzle distance (L_o),
Orifice diameter (D),
Stagnation pressure (p_o),
Stagnation temperature (T_o).

Beam composition will be monitored with a modulated-beam mass spectrometer. Dimers and higher oligomers which form in the initial expansion can be monitored as a function of the phases of modulated species arriving at the mass spectrometer. Beam modulation with lock-in detection will also help to eliminate problems of high background pressure in the excitation and mass-analysis chambers. The modulated-beam spectrometer is being built in-house. (But see section VII of this proposal).

Mass spectrometry of cluster beams is in its infancy. The problem is the lack of any standards for cluster size distributions. The combined use of retarding-potential ion energy analysis and of mass analysis in an alternate-cycle beam-monitoring system should provide a new standard for size-distribution measurements. Consequently, 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 beam monitoring technique represents an important improvement over the originally proposed simple mass analysis; it should be most valuable in our study of heteronuclear excimer systems.

III. 1: Inert-Gas Dimers

The formation of inert gas dimers will involve the free expansion of a single-component/two-component gas to obtain homonuclear/heteronuclear dimers.

III. 2: Inert-Gas Oxides

Ground-state van der Waals complexes of inert-gas oxides can be made in expansions of inert gas and oxygen atom mixtures. Oxygen atoms have been produced by thermal dissociation in a tubular iridium oven;[10] 90% dissociation, for example, has been obtained at 2300K.

The originally planned commercial oven is no longer available at a reasonable price. Consequently, a dissociation oven is under design. It will be either a modification of an available Knudsen cell or an iridium version of a tubular platinum oven reported in the literature.[11]

At the beginning of this work, our attention was directed to the XeO system. Of particular interest was where the potential energy curves arising from O(^{3}P) intersect the $1'\Sigma^+$ curve. Preliminary calculations of the Xe-O potentials were performed which showed no indication that intersection occurs within several kT of the well minimum of the $1'\Sigma^+$ curve.[12] Although refined calculations may not change this qualitative result, xenon oxide is certainly worthy of further study. It is planned to carry out some AB-initio calculations on this system to obtain more-meaningful potentials. (See section VII.2). Experimental values for some of the well-depths are available.[13]

III. 3: Inert-Gas Halides

Just as for the oxides, ground-state van der Waals complexes of inert-gas halides can be made in expansions of inert gas - halogen atom mixtures. Halogen atoms can also be produced by thermal dissociation. At 2000K, for example, the degree of dissociation is 51.8%, 85% and 98% for Cl_2, Br_2 and I_2, respectively. Rare-gas halide excimers might have considerable potential as bound-free ultraviolet systems.[14] Just recently, good theoretical potential energy curves for states of some of the rare-gas fluorides have become available.[15]

III. 4: Diatom-Rare Gas Atom Complexes

It is planned to study the properties of complexes of diatomic molecules and radicals with rare-gas atoms. The general approach will be to consider diatomics which are known to exhibit visible or ultraviolet lasing and to study the effects of bonding these species to rare-gas atoms. In effect, we will experimentally probe the perturbing effect of such bonding on the lifetimes (reactive and radiative) of the lasing excited states of the diatom. Two candidates have been selected for initial study: N_2 and CN; the latter will be obtained via the dissociation of cyanogen. The complexes will be formed in expansions of binary mixtures of the diatomic species and selected rare gases.

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 energy distribution in the photodissociation products of HeI_2 has been discussed.[16] But this species has a relatively long-lived excited state (10^{-7} sec) so that reactive quenching at the pressures used provided the dominant kinetics.

Supplementing the experimental work, AB-initio calculations of the potential energy surfaces of several atom-diatom (and diatom-diatom) systems are planned. These will employ either configuration interaction or spin-projected unrestricted Hartree-Fock theory with good basis functions.[17] The latter theory has already been found to provide a useful alternative to configuration-interaction treatments for the calculation of electronic spectra. Initially, the NeN_2 and NeCN systems will be investigated.

IV: 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.[18] 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.[19] Refined calculations which include metastable contributions to the dimer mole fraction have now been completed and the results are shown in Figures 3, 4, and 5. 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 heteronuclear dimers (and so excimers) of Xe, Kr and Ar should be most easily studied. The results of these calculations will be presented at an ACS regional meeting.[20]

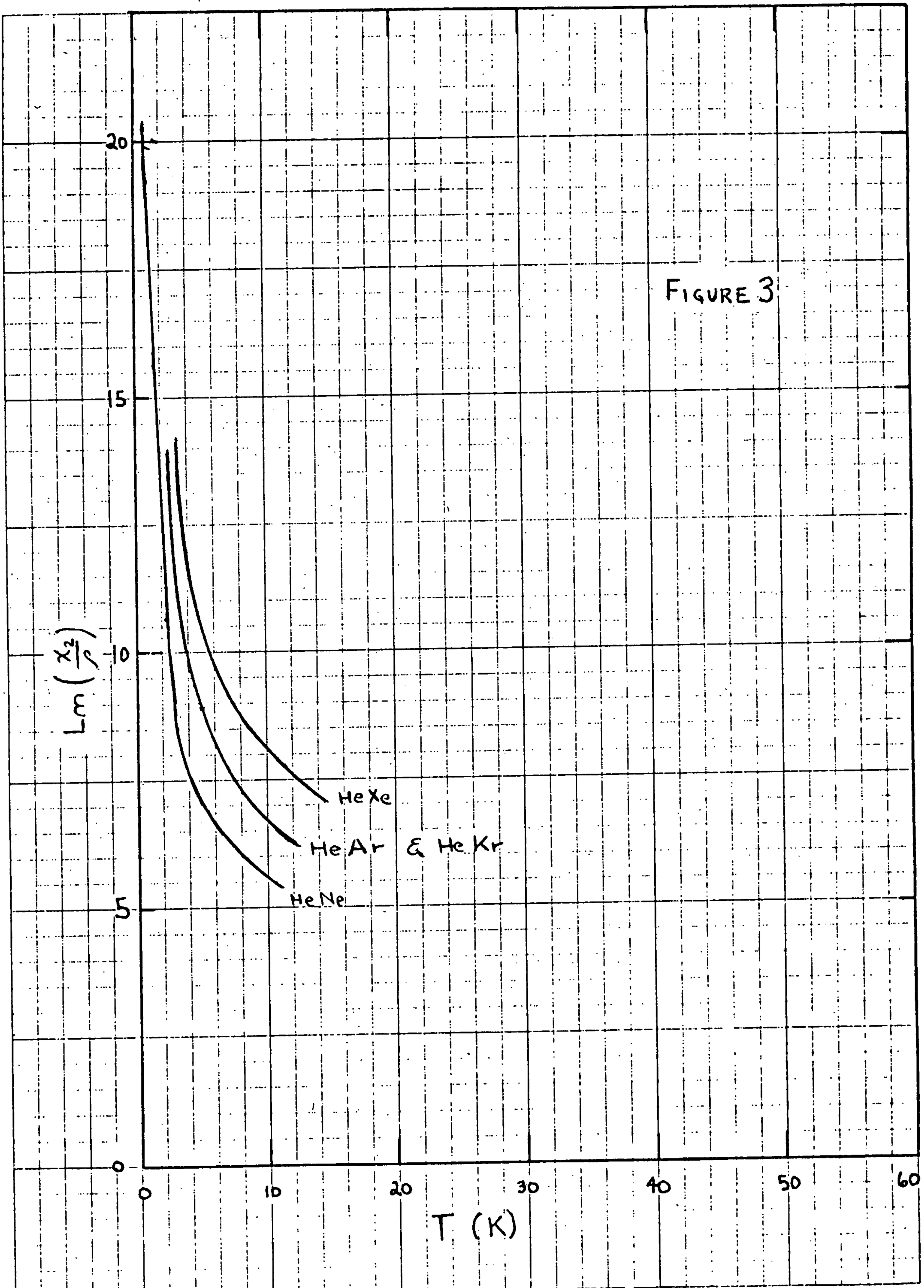


FIGURE 3

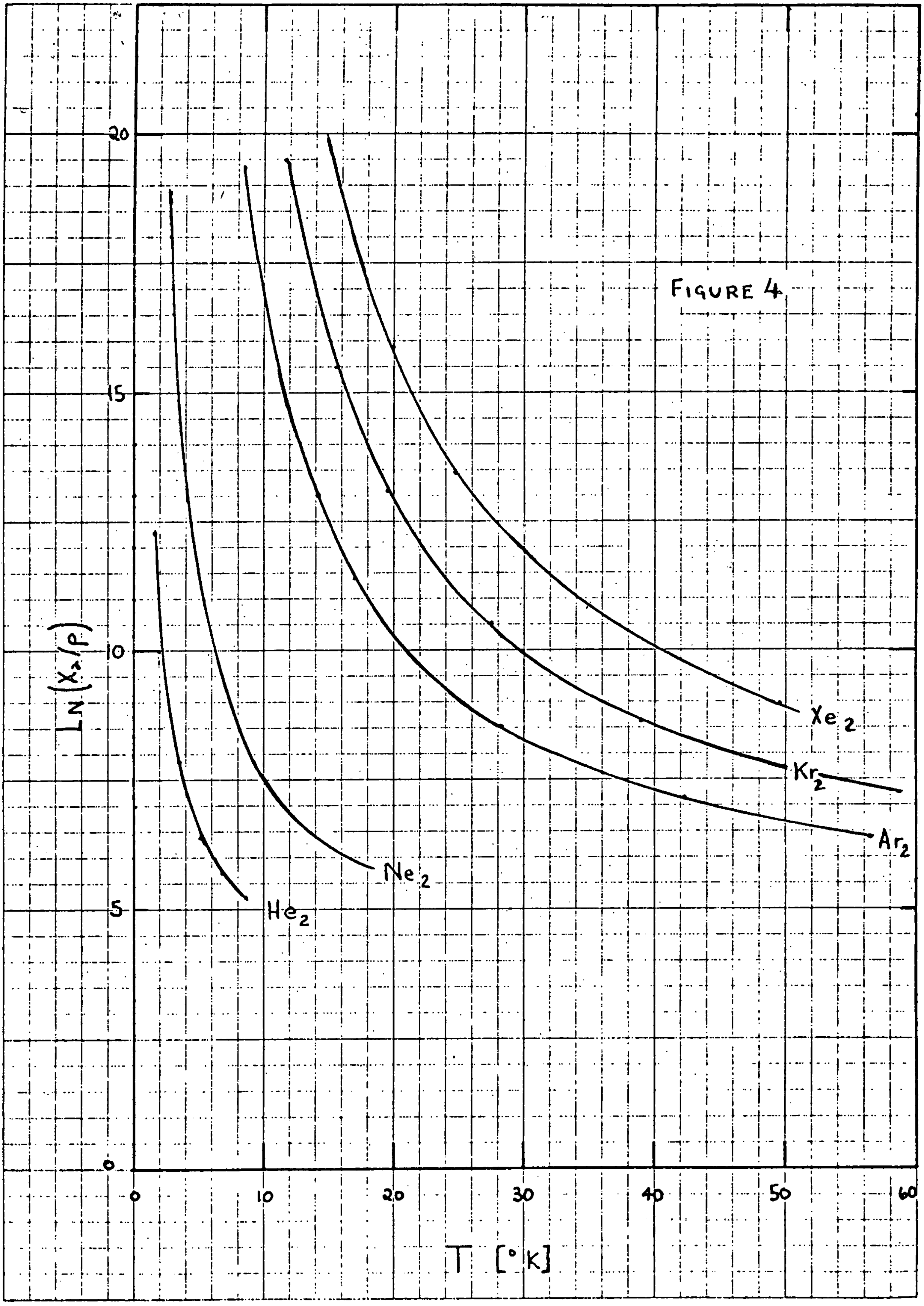


FIGURE 4

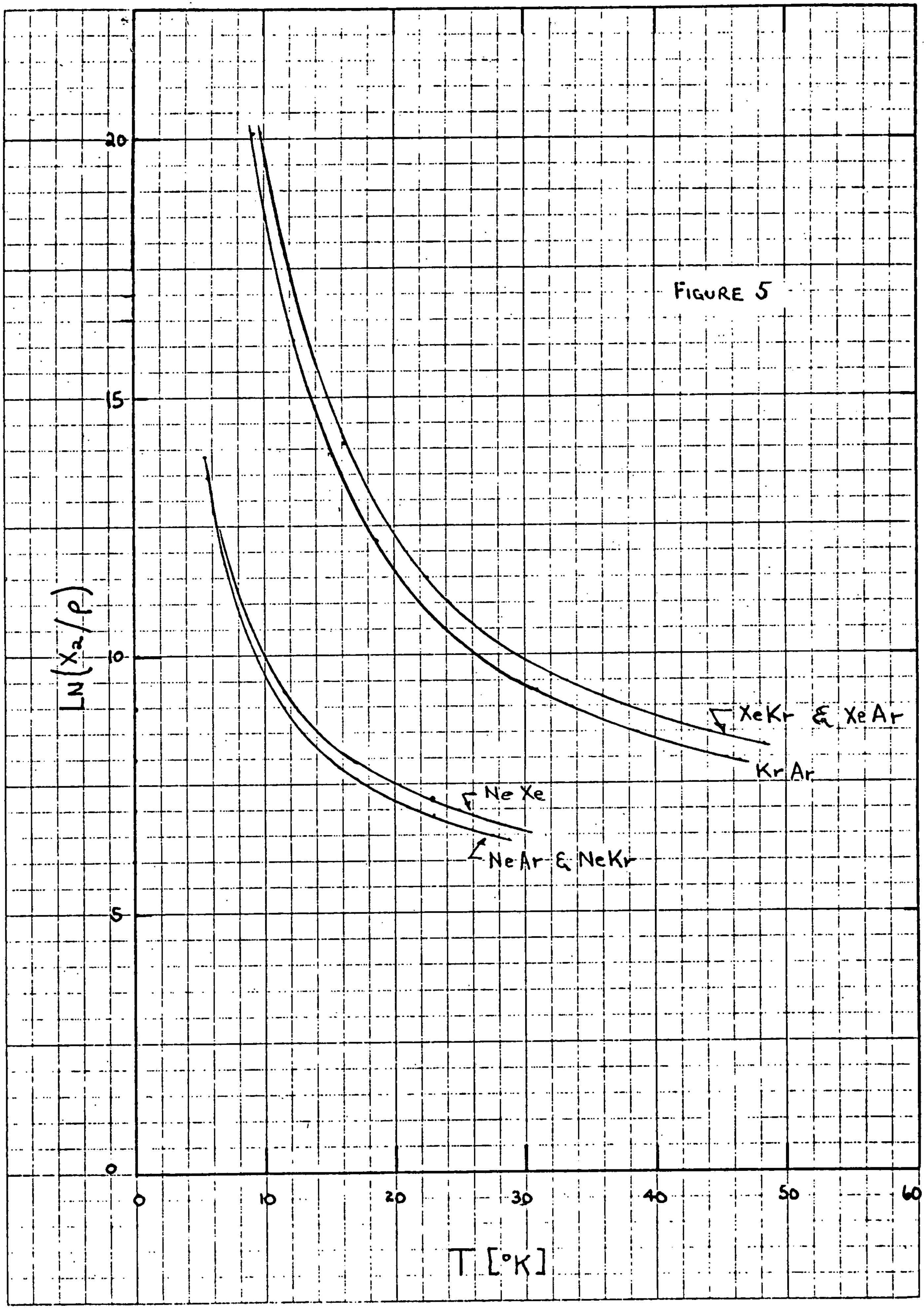


FIGURE 5
LN(X₂/ρ)
0
5
10
15
20
0
10
20
30
40
50
60
T [°K]
XeKr & XeAr
KrAr
NeXe
NeAr & NeKr

V: FORMATION & STUDY OF EXCIMERS & EXCIPLEXES

V.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 $AB^{\ddagger}$ 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 $Xe_2^{\star}$ is about an electron volt.(21)

The formation rate of $AB^{\ddagger}$ is given by

$$\frac{d[AB^{\ddagger}]}{dt} = k[AB]n_e, \tag{8}$$

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.[22] For the production of $Xe_2^{\ddagger}$, we should form in excess of 10^9 excimers per second.

If we assume a radiative lifetime for $AB^{\ddagger}$ 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.(23) 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.

V.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 in the introductory section I will involve five 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.(2,13)

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

$$(9) \quad AB + e^{-1} \longrightarrow AB^{\ddagger} + e^{-1}$$

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 conditions 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(24) (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.(25)

Although Ar_2 is an example of a bound-bound excimeric system, it 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 laser emission 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. A tuned UV-Visible laser will be employed. Upward-bound optical transitions induced by the laser (which would be tuned to the excimer system's lasing frequency) will be monitored by the emission from the more-highly excited states formed in the process.

As was noted in our second progress report,(19) 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.(19) Commercial tuned flash-lamp excited lasers are available which are 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).

VI: KINETIC STUDIES WITH EXCITED-STATE BEAMS

As mentioned in section II, a species need not be produced in the expansion for it to be resonantly pumped by our low-energy beam. A number of studies of reactions of beams of metastables with a background gas mixture may be possible. For these experiments, the excitation electron beam (E_1' in Figure 2) will be positioned to produce metastable species in a beam prior to its impingement on a controlled background gas. In this case, the expansion may be tailored to minimize the production of associative complexes. Although the background pressures can now be considerably higher (than in the above-described experiments), the concentrations of beam metastables will be less-quantitatively known.

VI. 1: Metastable Rare-Gas Reactions

Metastable states of heavy rare-gas atoms act both physically and chemically(26) much like alkali atoms. Consequently, reactions of these species can be used to produce chemically a number of bound-free emission systems. For example, in reactions such as

$$A^* + RX \rightarrow AX^* + \ldots.$$

$$A^* + CS \rightarrow AS^* + \ldots.$$

$$A^* + OCS \rightarrow AX^* + \ldots.$$

$$A^* + CO_2 \rightarrow A + CO_2^*$$

we can produce excimers of rare-gas halides and sulfides by reactions of metastable rare-gas atoms on backgrounds of organic halides (RX), carbon mono-sulfide, carbonyl sulfide, etc.

V. 2: Metastable Oxygen Atom Reactions

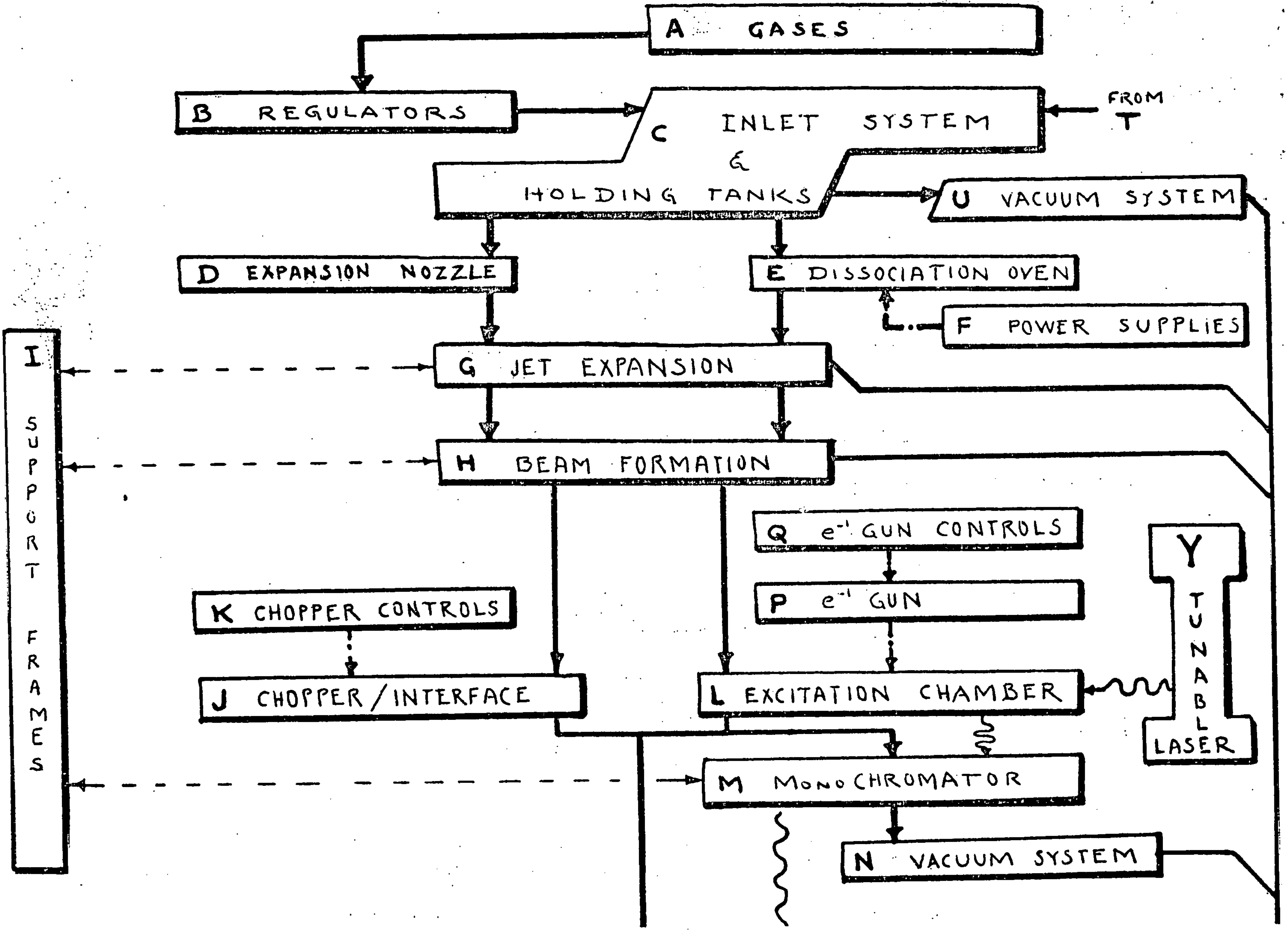
Oxygen atoms in the ground ^3P state can be selectively pumped to their ^1D and

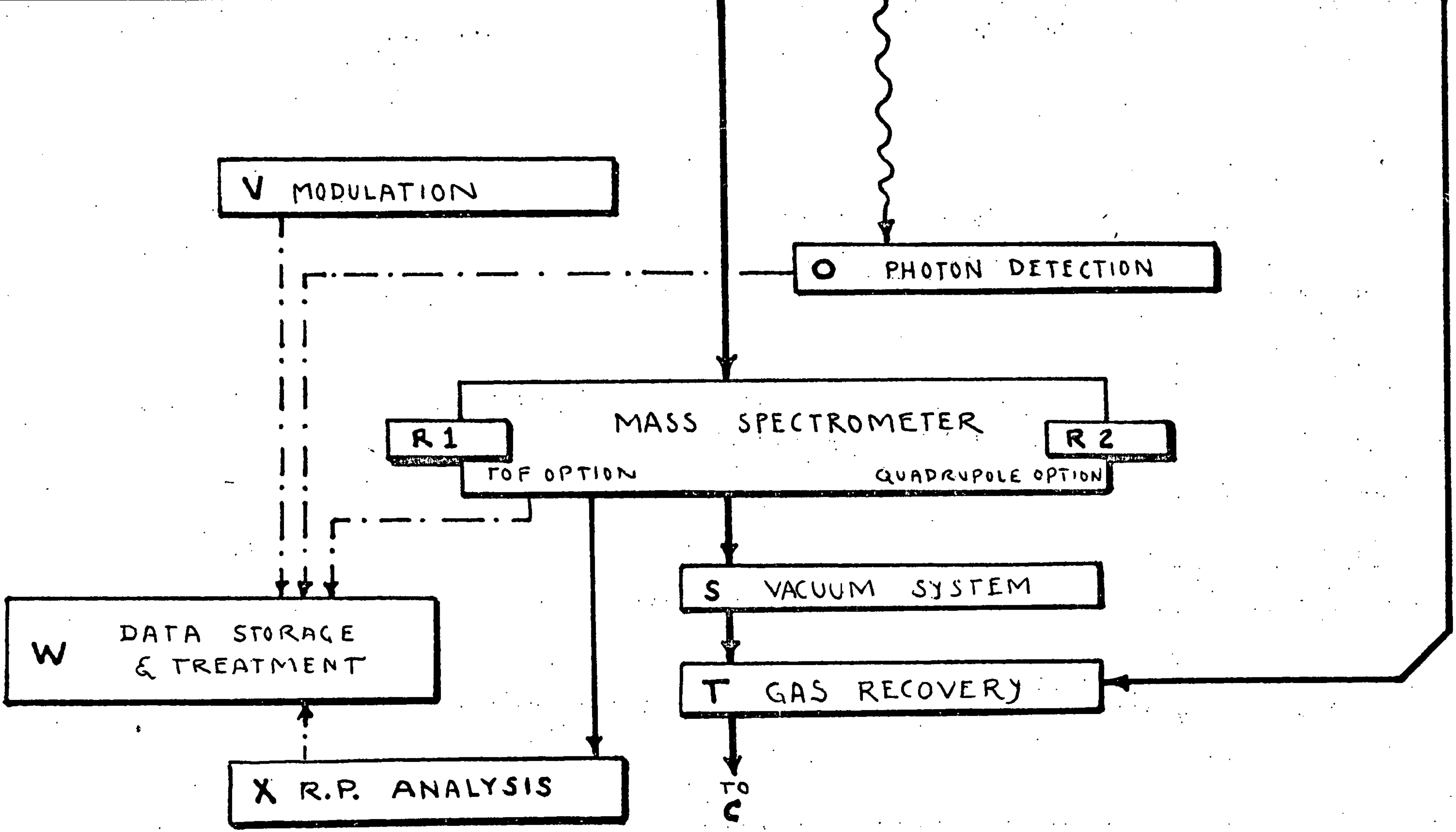
^1S states in a pure (thermally dissociated) oxygen beam. These can be reacted with background rare-gas mixtures. Such beam-gas reactions should complement the more quantitative experiments described in Section II and should contribute to our understanding of collisionally-induced intersystem crossing.

VI. 3: Excited-State Free Radical Molecules

Free radical exciplex systems such as CS*, CO* and CO_2* could also be produced by electron bombardment of a nozzle beam of the stable ground-state species. These can, in turn, be made to impinge on a background gas of controlled composition. Of immediate interest would be the reactive and collisional lifetimes of the exciplexes as revealed by the quenching of their emissions.

BLOCK DIAGRAM





BLOCK DIAGRAM
FIGURE 6

VII: THE STATUS OF OUR APPARATUS

To date, we have been gathering or building the apparatus necessary for the successful execution of the proposed research. To a very great extent, then, the status of our research is directly mirrored in the status of the development of our tools.

VII.1: EXPERIMENTAL SYSTEMS

The experimental apparatus can, for the purposes of design and development, be considered to consist of some twenty five major subsystems which are labeled A through Y on the Block Diagram in Figure 6. The interrelationships among these subsystems are also shown in that figure.

The following subsystems are completed at this time:

A, B, K, M, O, Q, V.

The following subsystems will be completed by the end of the first year of this contract (by Dec. 1, 1976):

C, D, G, H, I, J, L,
N, P, R, S, T, U, W.

Two of these subsystems are required for the newly-proposed experiments described above:

X. Retarding Potential Analyzer
Y. Flash-Excited Tunable UV-Visible Laser.

Remaining systems E and F should be completed in the first quarter of the second contract year. Three of the subunits scheduled for completion in this first year require additional discussion.

T. Rare-Gas Recovery System

This system may require ongoing modification, depending upon which gas mixtures will be expanded.

P. Excitation Electron Gun

Actually two guns are involved. One, built of cathode-ray-tube components and suitable for the steady-state experiments, will be completed in this first contract year. The second, which requires very fast response times for the lifetime studies has not yet been designed. It will probably be patterned after a gun reported in the recent literature.(27)

R. Mass Spectrometer

Two working options have been kept open for this important part of our beam analysis system: Time-of-Flight or Quadrupole mass analysis. One of these has now been eliminated.

A Model 12 TOF mass spectrometer was obtained under a Loan Contract from EPA-Cincinnati and was later dedicated to this contract through an Excess Property transfer. This system is now a functioning mass spectrometer. It has a sensitivity around 0.1 amp per torr and a unit mass resolution of about 300.

Our quadrupole option is based on a loan from NASA-Langley Research Center of a Varian RGA of uncertain vintage and model number. Unmodified, this unit can detect partial pressures to 5×10^{-11} torr in a mass range from 10 to 250 amu. It was decided to increase the mass range to 600 amu and the circuitry to do this was rapidly developed. We now know, however, that unmodified this spectrometer has a unit resolution of only about 50! After modification (which involves a change in RF operating frequency), the unit resolution would be unusable in our studies (less than 35).

In order to meaningfully manipulate the cluster size distribution and so to optimize the production of van der Waals dimer in our cluster beam, we will need a unit mass resolution at about 600 amu. This is based upon our desire to see complexes up to at least the tetramer; ($^{134}Xe_4$ has a mass of 536 amu). Because of this, funds are requested with which to obtain a quadrupole spectrometer with unit resolution to about 1000 amu.

VII.2: AB-INITIO PROGRAMS

To date, all theoretical work in support of this program has been provided by VPI & SU. Two Fortran computer programs, "Gaussian 70" and "Polyatom" have been obtained from the Quantum Chemistry Program Exchange at Indiana University.(28) These are now operating on our computer. They perform ab-initio SCF molecular-orbital calculations with Gaussian-type orbitals. An algorithm has been written to perform spin projections(17) of the unrestricted Hartree-Fock wavefunctions which these programs generate for open-shell systems. This algorithm has been completely implemented and interfaced with the "Gaussian 70" program; interfacing with the "Polyatom" program should be completed in this first year of the contract.

Although only semi-empirical calculations have in the past been done with spin-projection of unrestricted Hartree-Fock functions, the results are sufficiently promising that we wish to perform some ab-initio calculations with this technique. The only results obtained to date are for the ground and first excited states of the N_2 molecule (using the limited 4-31 G basis provided in the "Gaussian 70" program). These results (see Table VII.2-1) are not outstanding, but they are promising and should be much improved when a better basis set is used. Some development of the present ab-initio programs is still required, however. In particular, it is necessary to modify the open-shell SCF subroutines to allow the treatment of higher excited states.

It will be desirable at least to compare some of our ab-initio calculations for atom-diatom and diatom-diatom complexes with the results of large configuration-interaction treatments. We are currently seeking a large CI program which will operate on our computer.

TABLE VII.2-1

Calculated Results for N_2 Molecule (R = 1.094 A; 4-31 G basis set)

State	Calculated Energy (au)
Ground (X)	-108.7539*
Unrestricted open shell ($\sigma \rightarrow \pi^*$)	-108.4444
Projected Triplet (${}^3\pi$)	-108.4820
Projected Singlet (${}^1\pi$)	-108.4238

Excitation Energies (ev)		Transition
Calculated	Experimental	
7.398	8.1	$x \rightarrow {}^3\pi$
8.982	9.3	$X \rightarrow {}^1\pi$

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* T. H. Dunning obtained -108.8967 au using a (9s, 5p) basis set contracted to (5s, 3p).(29)

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(b) D. H. Phillips and J. C. Schug, J. Chem. Phys. 61, 1031 (1974);

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IX: PERSONNEL

IX.1: PRINCIPAL INVESTIGATOR

George Sanzone
Associate Professor of Chemistry

Education

B.S. Engrg. Physics, Univ. of Illinois, 1965
M.S. Chemistry, Univ. of Illinois, 1967
Ph.D. Chem. Physics, Univ. of Illinois, 1969

Appointments

(1976-)	Associate Professor, VPI & SU
(1969-76)	Assistant Professor, VPI & SU Research Areas: Shock-Tube Chemistry, Charge Exchange in Gases, Mass Spectrometry, Molecular Beam Fluorescence of Excimers, Chemical Education.
(1965-69)	Research Fellow, University of Illinois Air Pollution Special Fellow, U.S.P.H.S. (1967-69)
(1963-66)	Mass-Spectrometer Engineer, Department of Chemistry, University of Illinois, Urbana, Illinois.
(1960-63)	Project Engineer, Bendix Corp., Cincinnati Division, Ohio. Designed Model 14-206 prototypes for current MAT Mass Spectrometer Series; invented the Bendix "Selected Ion Rejection Accessory" for GC-TOF Mass Spectrometry; designed first commercial T.O.F. Mass Spectrometer capable of chart recording both positive and negative ion spectra; designed first commercial T.O.F. with time-lag focusing capability.
(1959-60)	Designer, Burton-Rodgers TTA, Cincinnati, Ohio. Analog computer designs for jet-engine and cockpit-control flight simulators. These included a Cockpit Trainer for the Convair 880 and Weapons Trainer for the F4H.
(1955-59)	U. S. Navy

Current Research Grants

ACS-PRF Grant No. 2516-G2 (1971-)
"A Critical Test of the Shock-Tube Mass Spectrometer Technique"

NASA Grant No. NSG 1020 (1974-)
"Determining Ion Kinetic Energies by a Method of Mass Spectrometer Peak-Shape Variation"

ERDA Contract No. E(11-1)-2810 (1975-)
"The Formation & Study of Exciplex Systems. A Low-Pressure Approach"

EPA Contract No. 5-03-6433A (1975-76)
"Analysis of Some Palladous Compounds"

Publications

1. "Electron Gun Performance Using a Modified Appearance Potential Technique". NASA STAR 4(20), 3982(1966). G. Sanzone
2. "Energy Resolution of the Conventional Time-Of-Flight Mass Spectrometer". Rev. Sci. Instr. 41, 741(1970). G. Sanzone
3. "The Mass Spectrometric Sampling of Shock-Tube Flows". Proc. 18th Annual Conf. Mass Spectrometry and Allied Topics. June, 1970. San Francisco, Calif. (Page B294). G. Sanzone and R. L. Belford.
4. "The Impulse-Focussed T.O.F. Mass Spectrometer". Proceedings of the 21st Annual Conf. Mass Spectrometry & Allied Topics. May, 1973. San Francisco, Calif. (Page 467). N. L. Marable and G. Sanzone.
5. "High Resolution Time-Of-Flight Mass Spectrometry. Theory of the Impulse-Focussed T.O.F. Mass Spectrometer". Internat. J. Mass Spectrom. Ion Phys. 13, 185 (1974). N. L. Marable and G. Sanzone.
6. "An Improved Laser-Schlieren System for the Measurement of Shock-Wave Velocity". Rev. Sci. Instr. 45, 949 (1974). J. A. Bander and G. Sanzone.
7. "The Measurement of Fragment-Ion Kinetic Energies by IFF Time-Of-Flight Mass Spectrometry". Proc. 22nd Annual Conf. Mass Spectrometry and Allied Topics. May, 1974. Philadelphia, Penns. (Page A3). T. A. Ligon and G. Sanzone.
8. "A Practical Ozone Generator". Va. J. Sci. 26, 5 (Spring, 1975). J. V. Banks, J. A. Bander and G. Sanzone.
9. "Shock-Tube Chemistry. I. The Laminar-to-Turbulent Boundary-Layer Transition". J. Phys. Chem. (in press). J. A. Bander and G. Sanzone.

IX.2: ASSOCIATE INVESTIGATORS

(A) John C. Schug
Professor of Chemistry

Education

B. Chem. Engrg., Cooper Union, 1957
M.S. Chem., Univ. of Illinois, 1958
Ph.D. Chem., Univ. of Illinois, 1960

Appointments

(1960-64)	Research Chemist, Gulf Research and Development Co.
(1964-67)	Assistant Professor of Chemistry, Virginia Polytechnic Institute & State University
(1967-73)	Associate Professor, VPI & SU
(1974-)	Professor, VPI & SU
(1965-)	Consultant to Philip Morris Research Center, Richmond, Va.

Publications

1. "Electron Coupling of Nuclear Spins. IV. Temperature Dependence in Substituted Ethanes", J. C. Schug, P. E. McMahon and H. S. Gutowsky, J. Chem. Phys. 33, 843 (1960).

2. "Note on Statistical Theory of Mass Spectra", J. C. Schug and N. D. Coggeshall, J. Chem. Phys. 35, 1146 (1961).

3. "Theory of Spin and Charge Distribution in Aromatic Ion-Radicals", J. C. Schug, T. H. Brown and M. Karplus, J. Chem. Phys. 35, 1873 (1961).

4. "Proton Chemical Shifts in Pi Complexes", J. C. Schug and R. J. Martin, J. Phys. Chem. 66, 1554 (1962).

5. "Spin Resonance Spectra of Substituted Aromatic Ions: Superposition Model", J. C. Schug, T. H. Brown and M. Karplus, J. Chem. Phys. 37, 330 (1962).

6. "Proton Chemical Shifts and Pi-Electron Distributions in the Hydroxy-Benzenes", J. C. Schug and J. C. Deck, J. Chem. Phys. 37, 2618 (1962).

7. "Spin Resonance Spectra of Substituted Aromatic Ions" Perturbation Model", T. H. Brown, M. Karplus and J. C. Schug, J. Chem. Phys. 38, 1749 (1963).

8. "Investigation of a Fragmentation Model for n-Paraffins", J. C. Schug, J. Chem. Phys. 38, 2610 (1963).

9. "Valence-Bond Theory of Resonance: Aniline, Phenol and Fluorobenzene", J. C. Schug, J. Chem. Phys. 39, 2798 (1963).

10. "Nature of Metastable Peaks in Mass Spectra", J. C. Schug, J. Chem. Phys. 40, 1283 (1964).

11. "Pi-Electron Valence-Bond Theory; Application to Vinyl Chloride", J. C. Schug, J. Chem. Phys. 42, 2547 (1965).

12. "Molecular Ionization Cross-Sections from the Classical Impulse Approximation", J. C. Schug, J. Chem. Phys. 43, 1426 (1965).

13. "Solvent Effects in Proton Magnetic Resonance", J. C. Schug, J. Phys. Chem. 70, 1816 (1966).

14. "Proton Chemical Shifts in Substituted Benzenes", J. C. Schug, J. Chem. Phys. 46, 2447 (1967).

15. "Proton Magnetic Resonance of Dimethyl Phthalates", J. C. Schug and B. P. Smith, J. Chem. Phys. 47, 849 (1967).

16. "Space-Charge Conduction in Insulators", A. C. Lilly, D. A. Lowitz and J. C. Schug, J. Appl. Phys. 39, 4360 (1968).

17. "Doublet Electronic States of the Benzyl Radical", J. C. Schug and D. H. Phillips, J. Chem. Phys. 49, 3734 (1968).

18. "Luminescence from Aromatic Polymers, Monomers and Dimers Under High-Energy Electron Excitation", D. H. Phillips and J. C. Schug, J. Chem. Phys. 50, 3297 (1969).

19. "Semi-empirical SCF Calculations for Substituted Benzenes", J. C. Schug and W. R. Carper, Mol. Phys. 18, 717 (1970).

20. "Optimum Parametrization in SCF Pi-Electron Theory", J. C. Schug, Mol. Phys. 19, 121 (1970).

21. "Intermolecular Interactions and the Weak Benzene-Halogen Complexes", E. G. Cook and J. C. Schug, J. Chem. Phys. 53, 723 (1970).

22. "Schottky Currents in Dielectric Films", J. C. Schug, A. C. Lilly and D. A. Lowitz, Phys. Rev. B1, 4811 (1970).

23. "Unrestricted Hartree-Fock Calculations on Some Hypothetical Molecules with Triplet Ground States", D. H. Phillips and J. C. Schug, Int. J. Quantum Chemistry, Symposium Volume 4, 221 (1971).

24. "Iodine-Induced Proton Chemical Shifts in Butyl Amines", J. C. Schug, W. M. Chang and M. J. Kogan, J. Magn. Res. 4, 25 (1971).

25. "Self-Association of Butylamines", J. C. Schug and W. M. Chang, J. Phys. Chem. 75, 938 (1971).

26. "Introductory Quantum Chemistry", by J. C. Schug (Holt, Rinehart and Winston, New York, 1971).

27. "Amine-Iodine Interactions", J. C. Schug, W. M. Chang and M. C. Dyson, Spectrochim. Acta. 28A, 1157 (1972).

28. "Projected States of Open Shell Molecules. The Pi-Electron States of Cyclopentadiene Cation", D. H. Phillips and J. C. Schug, J. Chem. Phys. 57, 3498 (1972).

29. "Approximate Interaction Potentials for Benzene-Halogen Complexes", J. C. Schug and M. C. Dyson, J. Chem. Phys. 58, 297 (1973).

30. "The Nature of Iodine-Amine Solutions", J. C. Schug and M. J. Kogan, J. Magn. Res. 11, 406 (1973).

31. "Spin Contamination in Unrestricted Hartree-Fock Calculations", J. C. Schug and D. H. Phillips, J. Chem. Phys. 59, 1616 (1973).

32. "Fulvalene Ions. I. Calculations on Calicene Ions", M. A. Ogliaruso, J. C. Schug and S. C. Kitching, Tetrahedron 29, 4065 (1973).

33. "Approximate Spin Projection of Three-Component UHF Wavefunctions. The States of the Pentachlorocyclopentadienyl Cation and the Croconate Dianion", D. H. Phillips and J. C. Schug, J. Chem. Phys. 60, 1597 (1974).

34. "Spin Projection of Single Determinant Wavefunctions", D. H. Phillips and J. C. Schug, J. Chem. Phys. 61, 1031 (1974).

35. "Bonding in the Monohomocyclooctatetraene Anion Radical", D. A. Brewer, J. C. Schug, and M. A. Ogliaruso, Tetrahedron, 31, 69 (1975).

36. "Approximate Molecular-Orbital Studies of Organic Positron and Positronium Complexes", W. J. Madia, J. C. Schug, A. L. Nichols, and H. J. Ache, J. Phys. Chem., 78, 2682 (1974).

37. "CNDO Study of Chlorine-Benzene Complex", J. C. Schug and K. A. Levinson, Theor. Chim. Acta 37, 269 (1975).

38. "Calculation of Molecular Electronic Spectra by Projected-Unrestricted Hartree-Fock Theory", J. C. Schug, B. H. Lengsfield, and D. A. Brewer, Int. J. Quantum Chem. (in press).

(B) Clayton D. Williams
Associate Professor of Physics

Education:

B.A., Rice University (1957)
Ph.D., Washington University, St. Louis (1961)

Appointments

1961	Physics Department, Instructor, Washington University, St. Louis
1961-64	Physics Department, Assistant Professor, VPI & SU
1964-	Physics Department, Associate Professor, VPI & SU

Publications

1. "Ground-State Energy of Liquid Helium II", C. D. Williams and E. Feenberg, Proceedings of the Midwest Conference on Theoretical Physics, (West Lafayette, Indiana) p. 39 (1960).
2. "Solution of the Initial-Value Transport Problem for Monoenergetic Neutrons in Slab Geometry", R. L. Bowden and C. D. Williams, J. Math. Phys. 5, 1527 (1964).
3. "Temperature Dependence of the Nuclear Quadrupole Resonance Frequency of ^{79}Br in $NaBrO_3$ and $KBrO_3$", R. F. Tipsword, J. T. Allender, E. A. Stahl, Jr. and C. D. Williams, J. Chem. Phys. 49, 2464 (1968).
4. "Pressure and Temperature Dependence of the Nuclear Quadrupole Frequency of Na^{23} in $NaBrO_3$", C. J. Whidden, C. D. Williams and R. F. Tipsword, J. Chem. Phys. 50, 507 (1969).
5. "Asymmetry Parameters and the Temperature Dependence of the PQR Frequencies of ^{127}I in SnI_4", R. W. Ward, C. D. Williams and R. F. Tipsword, J. Chem. Phys. 51, 823 (1969).
6. "Pure Nuclear Quadrupole Resonance in Superconducting and Normal dhep ^{139}LaMetal", W. M. Poteet, R. F. Tipsword and C. D. Williams, Phys. Rev. B1, 1265 (1970).
7. "Pressure and Temperature Dependence of the Nuclear Quadrupole Resonance of ^{79}Br in $NaBrO_3$", D. D. Early, R. F. Tipsword, and C. D. Williams, J. Chem. Phys. 55, 460 (1971).
8. "Temperature & Pressure Dependence of the NMR Transition Frequencies of ^{27}Al in $LiAl(SiO_3)_2$, Spodumene", S. F. Harley, C. D. Williams, and R. F. Tipsword, J. Chem. Phys. 64, 4815 (1976).

IX.3: OTHER INVESTIGATORS

(A) James A. Jacobs
Professor of Physics

Education

B.A., State University of Iowa, 1937
M.S., State University of Iowa, 1940
Ph.D., State University of Iowa, 1941

Appointments

(1942-45)	Physics Department, Assistant Professor, State University of Iowa
(1941-45)	Physics Department, Technical Director, Phys. Engr. Dev. Proj., State University of Iowa
(1945-60)	Physics Department, Professor, State University of Iowa
(1960-73)	Physics Department, Prof. and Chairman of Physic Dept., Virginia Polytechnic Institute and State University
(1973-)	Physics Department, Professor, Virginia Polytechnic Institute and State University

Dr. Jacobs is acting as a consultant to this group on experimental matters.

(B) John C. Hassler
Assistant Professor of Chemical Engineering

Education

Ph.D. Chemistry, Kansas State Univ., 1966

Appointments

(1966-68)	Research Associate of Prof. J. C. Polanyi, Univ. of Toronto.
(1968-71)	Research Associate of Prof. P. D. Coleman, Univ. of Illinois
(1971-72)	Assistant Professor, Electrical Engineering, Univ. of Illinois
(1972-)	Assistant Professor, Chemical Engineering, VPI & SU

Dr. Hassler's experience in spectroscopy and dye lasers, as represented by over twenty publications, will be particularly useful in this portion of the proposed research.

X: FACILITIES

Although the proposed work will be done in the Chemistry Building of VPI & SU, the project will be supported by facilities and personnel from three departments: Chemistry, Chemical Engineering and Physics. In these departments, available for this research, are very good Glassblowing, Machine, and Electronics Shops, a "small computer" laboratory for on-line data processing, as well as synthesis and analytical laboratories.

University-wide research facilities available include additional machine and electronics shops and a computer center with an IBM 370 system, including two Model 158's.

In addition to providing machinists' time, the Physics Department has contributed several large vacuum components (pumps and traps). To the system described in this proposal, the following equipment are available from the principal investigator's laboratories:

CEC Vacuum Leak Detector
Bendix Model 12 TOF Mass Spectrometer
Transistorized Electronics Package for TOF
4" dia Pyrex Shock Tube (with Mass Spec Detection)
3" dia Stainless Shock Tube
2" dia Aluminum Shock Tube (with IR Detection)
1" dia copper Shock Tube (with TOF Detection)
Beckmann DU Recording UV-Vis Spectrometer
Perkin Elmer 301 Far-IR SPectrometer
CEC 21-620-A Trochoidal Mass Spectrometer

Beckman GC-4 Gas Chromatograph

30-Channel Analog Computer Laboratory

Scopes, Recorders, Etc.

The experimental system is being assembled in a new laboratory which was created from office space. The lab has been air conditioned and provided with the usual services (water, power, etc.).