AD-A050 579 CORNELL UNIV ITHACA N Y SCHOOL OF APPLIED AND ENGINE--ETC F/G 20/5
NOVEL CHEMICAL LASER SYSTEMS.(U)
NOV 77 T A COOL

UNCLASSIFIED AFOSR-73-2550
AFOSR-TR-78-0156 NL

1 OF 1
AD
A050579

END
DATE
FILMED
3-78
DDC

AD A050579

DDC FILE COPY

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: AFOSR-TR-78-0156	2. GOVT ACCESSION NO.
3. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle): NOVEL CHEMICAL LASER SYSTEMS	5. TYPE OF REPORT & PERIOD COVERED: Final rept. 15 Jun 74 - 31 Mar 77
	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s): Terrill A. Cool	8. CONTRACT OR GRANT NUMBER(s): AFOSR-73-2550
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Cornell University, School of Applied & Engineering Physics, Ithaca, NY 14853	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: 61102F, 2303/B1
11. CONTROLLING OFFICE NAME AND ADDRESS: Air Force Office of Scientific Research/NC, Bolling AFB DC 20332	12. REPORT DATE: Nov 77
	13. NUMBER OF PAGES: 17 (12 40p.)
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report): UNCLASSIFIED
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

DDC RECEIVED MAR 1 1978 F

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Chemical Laser
Metal-Oxidizer Reactions
Electronic Transition Lasers
Yttrium Chloride
Excimers

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Chemiluminescence spectra were recorded for a variety of metal-oxidizer reactions and measurements of fluorescence rates were performed for molecular bonds and atomic emissions. Dissociation reactions to produce large concentrations of meta atoms on a short time scale were carried out by means of thermal, electrical and electron beams procedures. Nearly all systems studied had low fluorescence rates for product metal oxide or metal halide molecules. Laser action was observed for over 40 new wavelengths from 17 metal atoms formed from the dissociation of metal halides, hydrides, alkyls and carbonyls. These wavelengths were in the near IR

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

407 244

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

20. ABSTRACT (Continued)

from 1.152 to 14.54 microns and were identified with transitions in the atoms: As, Bi, Cd, Fe, Ga, Ge, Hg, In, Ni, Pb, Sb, Se, Sn, Te, Tl, V and Zn. Electronically excited YCl was formed from the reaction of chlorine with Y metal; chemiluminescent spectra from the excited YCl species were recorded in a shock tube-driven supersonic mixing flame. Strong emission was noted near 4000Z and weaker bands at longer wavelengths believed to arise from triplet states of chemically formed YCl. This reaction system is of interest because of a high photon yield, a high degree of specificity in energy disposal among product states and the possible existence of laser transitions of appropriate radiative lifetimes for chemical laser operation. Electrical discharges is PH3/N20 leads to strong visible chemiluminescence from an excited (PO)2 species. The chemiluminescence is continuous from about 3200A to beyond 2 micron with a broad maximum near 7500A. The emission is believed to arise from the (PO)2 excimer and may lead to a chemically pumped laser capable of broad band tuning throughout the visible spectral region.

FINAL SCIENTIFIC REPORT

NOVEL CHEMICAL LASER SYSTEMS

Air Force Office of Scientific Research

Grant AFOSR 73-2550

For The Period June 15, 1974 Through March 31, 1977

Submitted to:

Dr. Robert A. Osteryoung
Directorate of Chemical Sciences
Air Force Office of Scientific Research

Submitted by:

Dr. Terrill A. Cool
School of Applied & Engineering Physics
Cornell University
Ithaca, New York 14853

November 9, 1977

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH (AFSC)
NOTICE OF TRANSMITTAL TO DDC
This technical report has been reviewed and is approved for public release LAW AFR 190-12 (7b).
Distribution is unlimited.
A. D. BLOSE
Technical Information Officer

I. INTRODUCTION

During the past 3 years a large number of reactions have been studied at several laboratories as possible candidates for electronic transition chemical lasers. At present only two or three reaction systems appear to provide the high photon yields, the desired specificity of excitation of product states, and reaction products of suitably long radiative lifetimes. For this reason we have chosen to study the $Y + Cl_2 \rightarrow YCl^* + Cl$ atom-exchange reaction and a second reaction system which leads to chemically formed $(PO)_2^*$ excimer molecules. Sections II and III of this report summarize the present status of studies of the yttrium chloride (YCl) molecular system; Section IV discusses work on a potentially efficient chemically pumped $(PO)_2^*$ excimer system. This report is intended to summarize progress made under AFOSR Grant 73-2550 for the period June 15, 1974 through March 31, 1977. Research on these reaction systems is being continued under AFOSR Grant 77-3358.

II. SHOCK TUBE STUDIES OF THE Y + Cl_2 → YCl^* + Cl REACTION

Tables I and II summarize some recent photon yield measurements for several reactions which produce diatomic metal oxide or metal halide reaction products. Most of the reactions for which data are available, both at high and low pressures, exhibit a low photon yield at low pressure (ca, 10^{-3} Torr) and a high yield at high pressures (ca. 1 Torr). In some cases the photon yields are remarkably high (e.g., SmF and SnO), exceeding 50% at high pressures. In general, these reactions do not produce a high degree of specificity of excitation either at low or high pressures. The chemiluminescence from Sm + O_3, illustrated in Figure 1, indicates the typically broad featureless emission observed for many of the reactions investigated to date. These reactions include Sm, Eu, and Yb with oxidizers Cl_2, F_2, N_2O, O_3, and NO_2.[1,2] Spectra observed at high pressures are very similar to the low pressure spectra for these systems.

The most extensively studied reactions to date are the Ba + O_3 → BaO + O_2 and Ba + N_2O → BaO + N_2 reactions. These reactions give similar spectra. At high pressures the emission is dominated by $A^1\Sigma^+ \rightarrow X^1\Sigma^+$ bands which are responsible for the high photon yields of Table II. Careful studies by several groups, Field, et al.,[3] Palmer, et al.,[4] and Eckstrom, et al.,[5] have established that the $A^1\Sigma^+ \rightarrow X^1\Sigma^+$ emission results from energy transfer from one or more precursor states. The BaO($a^3\pi$) state and high vibrational levels of the BaO($X^1\Sigma^+$) state have been suggested as such possible primary reservoir states for the energy release of chemical reaction.

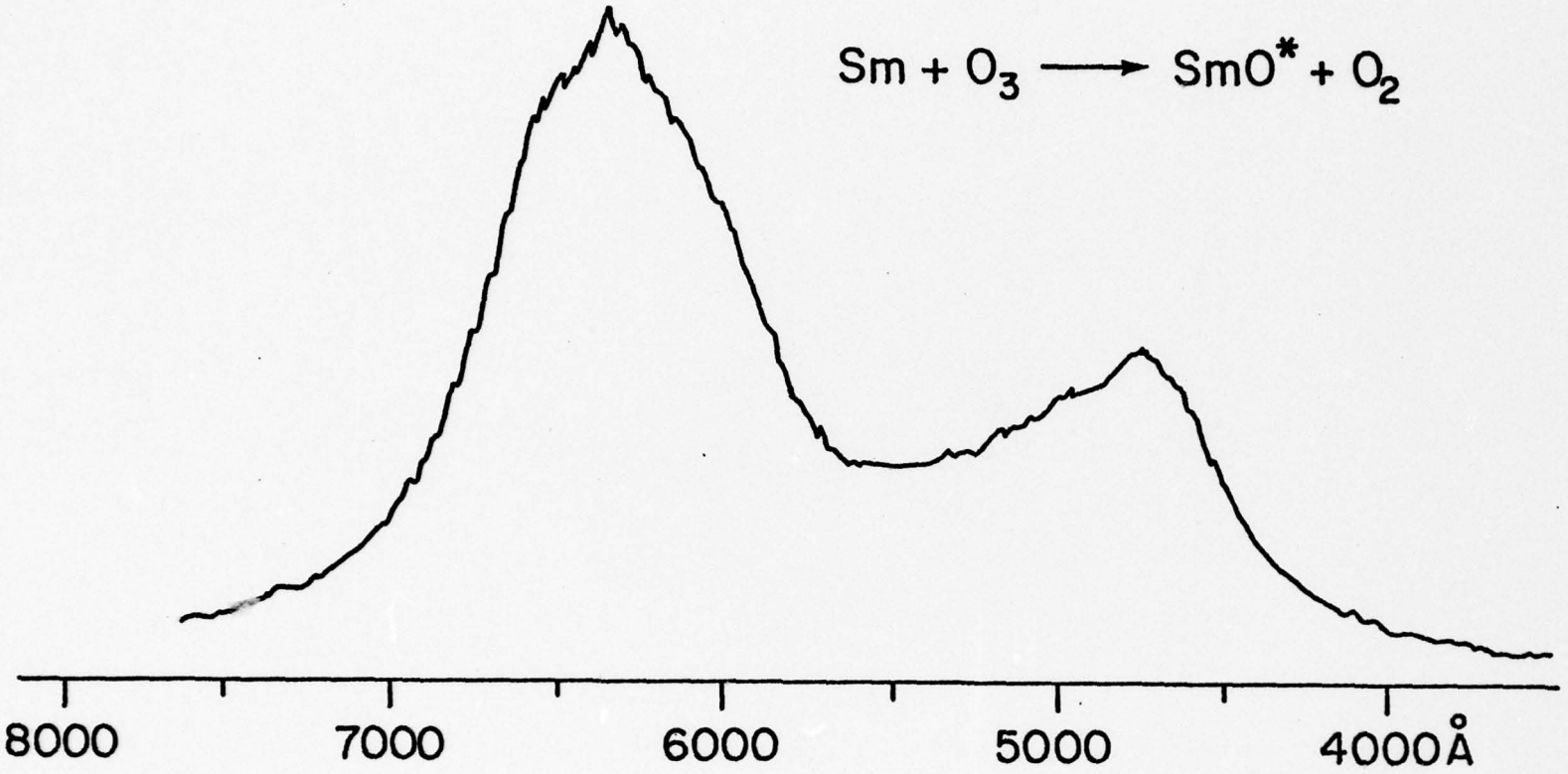


Figure 1: Visible Chemiluminescence from the Reaction $Sm + O_3 \rightarrow SmO + O_2$ Under Single Collision Conditions. C.R. Dickson and R.N. Zare, Chem. Phys. 7, 361 (1975).

TABLE I

SUMMARY OF SOME RECENT (%) PHOTON YIELD MEASUREMENTS UNDER SINGLE COLLISION CONDITIONS (ca. 10^{-4} Torr)

Metal	Oxidizers				
	N_2O	NO_2	O_3	F_2	Cl_2
Ba	2.3[b]	0.2[b]	--	--	--
Eu	0.2[a]	0.007[a]	0.3[a]	0.9[a]	--
Sc	--	--	--	$\gtrsim$10[c]	--
Sm	0.3[a]	0.07[a]	0.9[a]	11.8[a,b]	--
Y	--	--	--	--	$\gtrsim$5[c]

---

[a] C.R. Dickson and R.N. Zare, Chem. Phys. 7, 361 (1975).

[b] C.R. Dickson, S.M. George, and R.N. Zare, J. Chem. Phys. 67, 1524 (1977).

[c] J.L. Gole, Electronic Transition Lasers II, L.E. Wilson, S.N. Suchard, and J.I. Steinfeld, Editors, Proceedings of the Third Summer Colloquim on Electronic Transition Lasers, Snowmass-in-Aspen, Colorado, Sept. 1976. (MIT Press, 1977) pp. 136-165.

TABLE II

SUMMARY OF SOME RECENT (%) PHOTON YIELD MEASUREMENTS

AT HIGH PRESSURES (ca. 1 Torr)

Metals	Oxidizers						
	N_2O	NO_2	O_3	O_2	F_2	NF_3	Cl_2
Ba	25[a]	--	36[a]	8[a]	4.4[a]	50[a]	0.6[c]
Ca	--	--	--	--	0.3[c]	--	--
Eu	20[a]	--	5[a]	2.5[a]	2.5[a]	--	--
Ge	0.15[b]	0.05[b]	--	0.2[b]	0.07[b]	--	10^{-3}[b]
Mg	--	--	--	--	0.02[c]	--	--
Sm	38[a]	--	8[a]	9[a]	64[a]	70[a]	--
Sn	6.7[d] (50[e])	--	--	0.08[d]	0.3[d]	--	$<10^{-2}$[d]
Sr	--	--	--	--	0.1[c]	--	--

---

[a] D.J. Eckstrom, S.A. Edelstein, D.L. Huestis, B.E. Perry, and S.W. Benson, J. Chem. Phys. 63, 3828 (1975).

[b] G.A. Capelle and J.M. Brom, Jr., J. Chem. Phys. 63, 5168 (1974).

[c] D.J. Eckstrom, S.A. Edelstein, and S.W. Benson, J. Chem. Phys. 60 2930 (1974).

[d] G.A. Capelle and C. Linton, J. Chem. Phys. 65, 5361 (1976).

[e] W. Felder and A. Fontijn, Chem. Phys. Lett. 34, 398 (1975).

The several reactions of Tables I and II which exhibit a strongly pressure-dependent photon yield apparently conform to a simple mechanistic explanation.[1] A large fraction of the energy release of reaction is divided in a nearly satistical fashion among the various accessible internal product states. These states include high vibrational states of the ground electronic state and somewhat lower vibrational states of several electronically excited states. Communication between these electronic and vibrational states is maintained by rapid collisional processes. At low pressures the primary contributions to the photon yield come from directly excited states with relatively short radiative lifetimes. At higher pressures electronic states of long radiative lifetimes and high vibrational levels of the ground state are coupled to one or more electronic states of short radiative lifetimes to provide an efficient path for radiation as a major energy loss mechanism.

In contrast to all other reactions studied to date, the reactions forming ScF and YCl have a high degree of specificity and high photon yields under single collision conditions. Chemiluminescent spectra observed by Gole, et al.,[6,7] for the $Y + Cl_2 \rightarrow YCl^* + Cl$ reaction are shown in Figure 2. The narrow emission feature near 3950 Å from YCl^* is thought to arise from transitions from a $^3\Sigma^+$ upper state to the $X^1\Sigma^+$ ground state. Although very little is presently known concerning electronic states in YCl, the low-lying electronic energy levels for ScF should be similar; these are indicated in Figure 3. Fairly complete spectroscopic analysis of the singlet bands $E^1\pi \rightarrow X^1\Sigma^+$, $C^1\Sigma^+$, and $B^1\pi \rightarrow X^1\Sigma^+$ exists.[8]

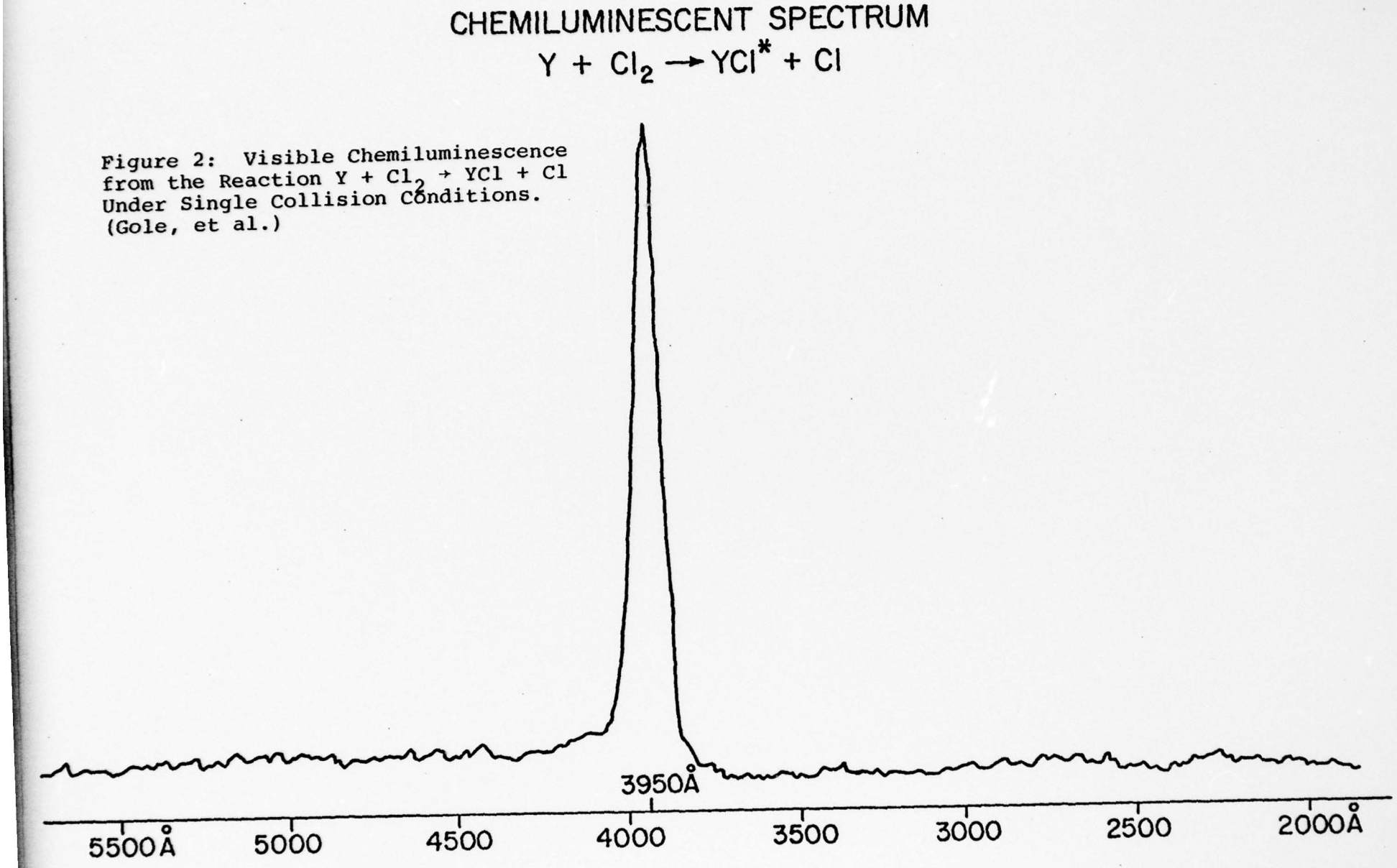


Figure 2: Visible Chemiluminescence from the Reaction $Y + Cl_2 \rightarrow YCl + Cl$ Under Single Collision Conditions. (Gole, et al.)

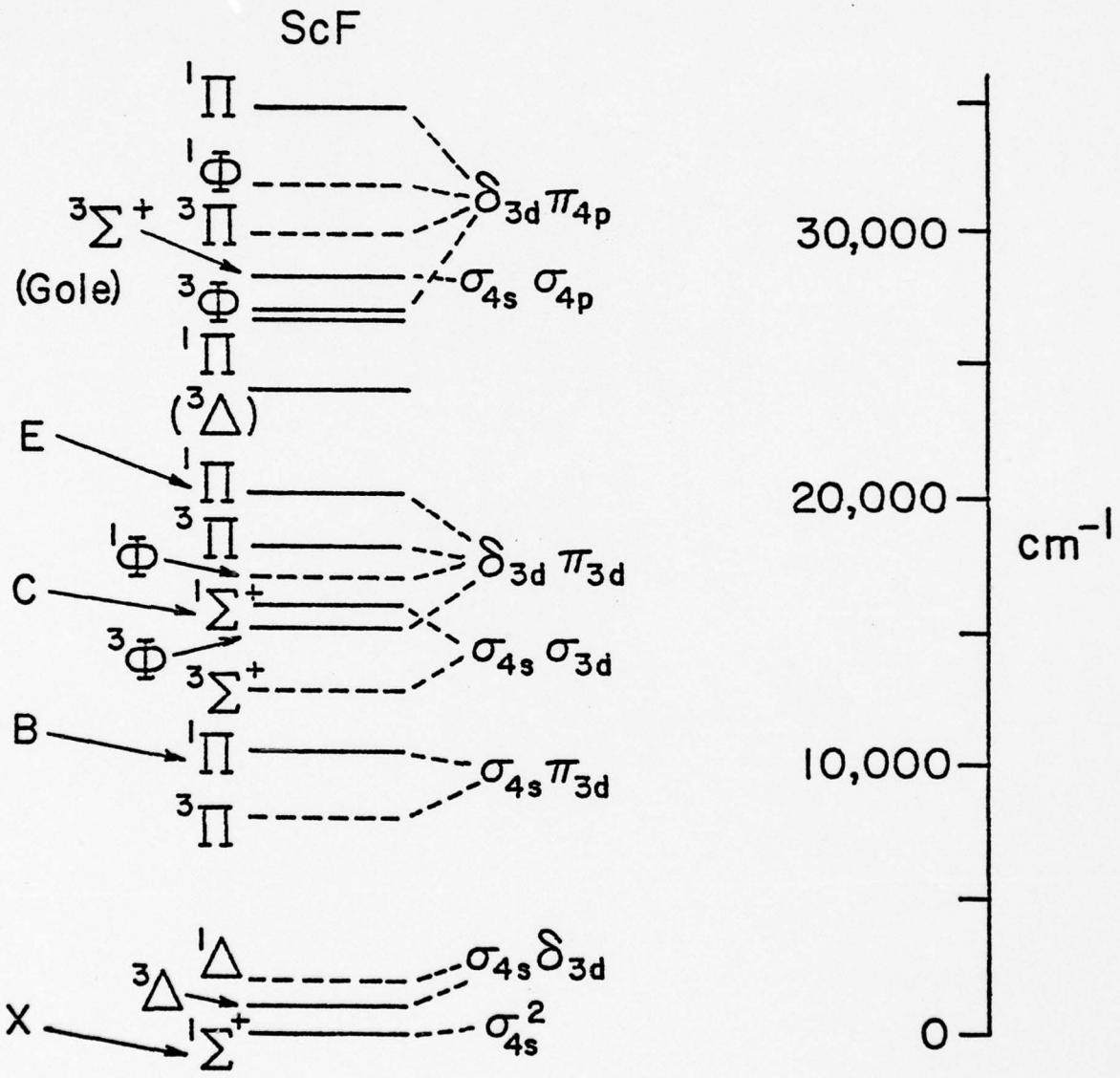


Figure 3: Low-lying Electronic Energy Levelsfor ScF (adapted from C.J. Cheetham and R.F. Barrow, Advances High Temp. Chem. 1, 7 (1967).

The $^3\Sigma^+ \rightarrow X^1\Sigma^+$ transition near 350 Å observed by Gole, et al.,[6,7] may be the band previously observed at 3360 Å in a neon matrix at 4°K.[9] The molecular orbitals to which the two 4s electrons in the Sc atom are promoted are given for several of the excited states of ScF in Figure 3. At present the only measured radiative lifetime for ScF bands is that of the $E^1\pi \rightarrow X^1\Sigma^+$ band which is approximately 1.1×10^{-4} sec.[8] The lifetime for the $C^1\Sigma^+ \rightarrow X^1\Sigma^+$ band is probably shorter, on the order of 10^{-5} sec. As illustrated in Figure 3, low-lying molecular orbits of ScF are similar in character to corresponding atomic orbitals in Sc.[10] Transitions between electronic states in ScF may be thought of as essentially two-electron transitions between atomic orbitals in Sc. Such transitions are of sd → ss, dd → ss, dd → sd, for sd → sd character, and would not be expected to have large transition probabilities. It seems likely that most of the transitions in the singlet and triplet manifolds of ScF have radiative lifetimes of the order of 10^{-3} to 10^{-5} seconds.

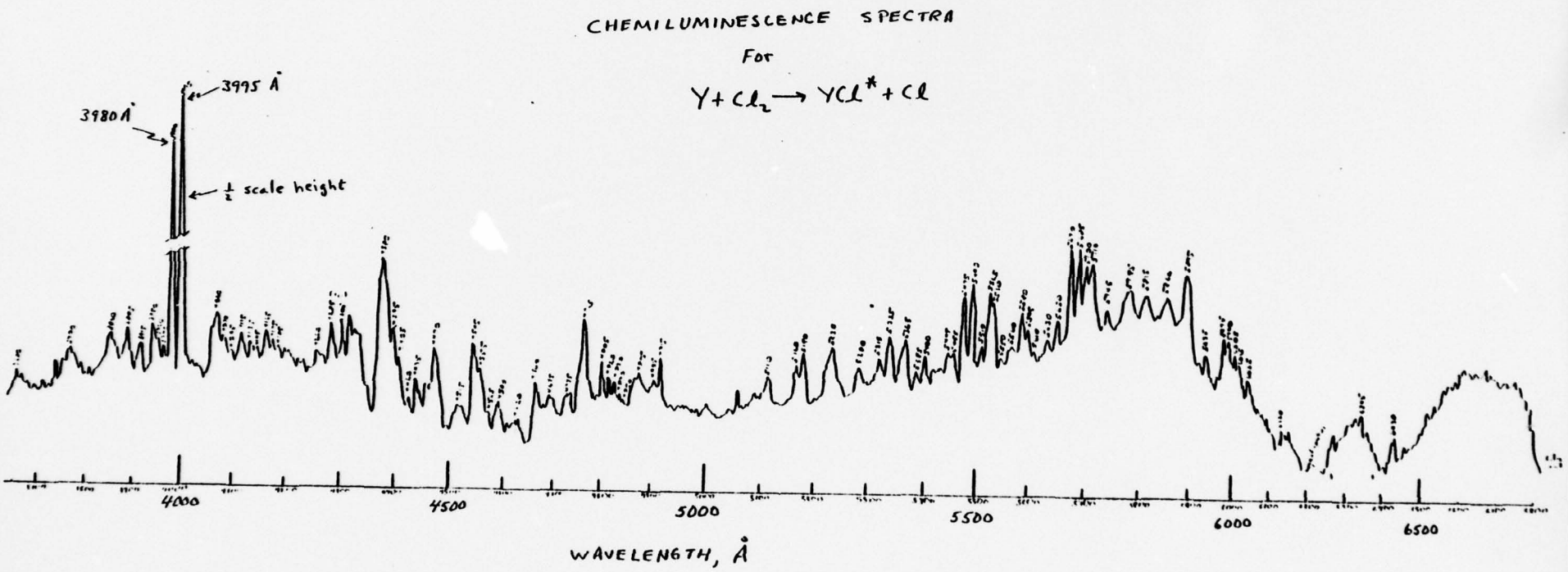
These considerations suggest that the reaction of Figure 2 has the desired specificity and leads to reaction product states of long radiative lifetimes. A third desirable characteristic of these reactions, a high photon yield, has been confirmed in recent studies of Gole and co-workers.[7] Their measurements indicate a photon yield of 4.8%, under single collision conditions, for the 3500 Å $^3\Sigma^+ \rightarrow X^1\Sigma^+$ band of ScF^* and a comparable photon yield for the corresponding band of YCl^* at 3950 Å. Even though, at present, nothing is

known concerning the collisional quenching of ScF^* and YCl^*, these molecules appear to be favorable candidates for electronic transition chemical lasers.

Figure 4 schematically illustrates the experimental apparatus we employ for studies of the reactions $Sc + F_2 \rightarrow ScF^* + F$ and $Y + Cl_2 \rightarrow YCl^* + Cl$. A heated section of the shock tube permits vaporization of either $ScCl_3$ or YCl_3 in The presence of an argon diluent. The heated gases are initially confined between thin metal diaphragms which are ruptured by the passage of the shock wave. Shock wave heating accomplishes dissociation of the $ScCl_3$ or YCl_3 before the gases are accelerated through a supersonic nozzle array. This primary flow is then mixed with a secondary flow of either F_2 or Cl_2 through slots at the trailing edge of each nozzle blade. The desired reactions are initiated in the supersonic mixing zone immediately downstream of the nozzle array. The pressures and temperatures in this zone are typically about 5-20 Torr and 800-1200°K, respectively.

Figures 5 and 6 present chemiluminescence spectra for the $Y + Cl_2 \rightarrow YCl^* + Cl$ reaction observed over the wavelength interval 3700-6700 Å. The spectra are uncorrected for film response characteristics. Predominant features of the spectra are the intense bands at 3980 and 3995 Å which are believed to correspond to the emission peak recorded by Gole et al., near 3950° Å shown in Figure 2. The data of Gole, et al, were taken under single collision conditions at pressures of about 10^{-4} Torr. In contrast the data of Figures 5 and 6 were obtained at a pressure of about 10 Torr.

Figure 5: Shock Tube Chemiluminescence Data.



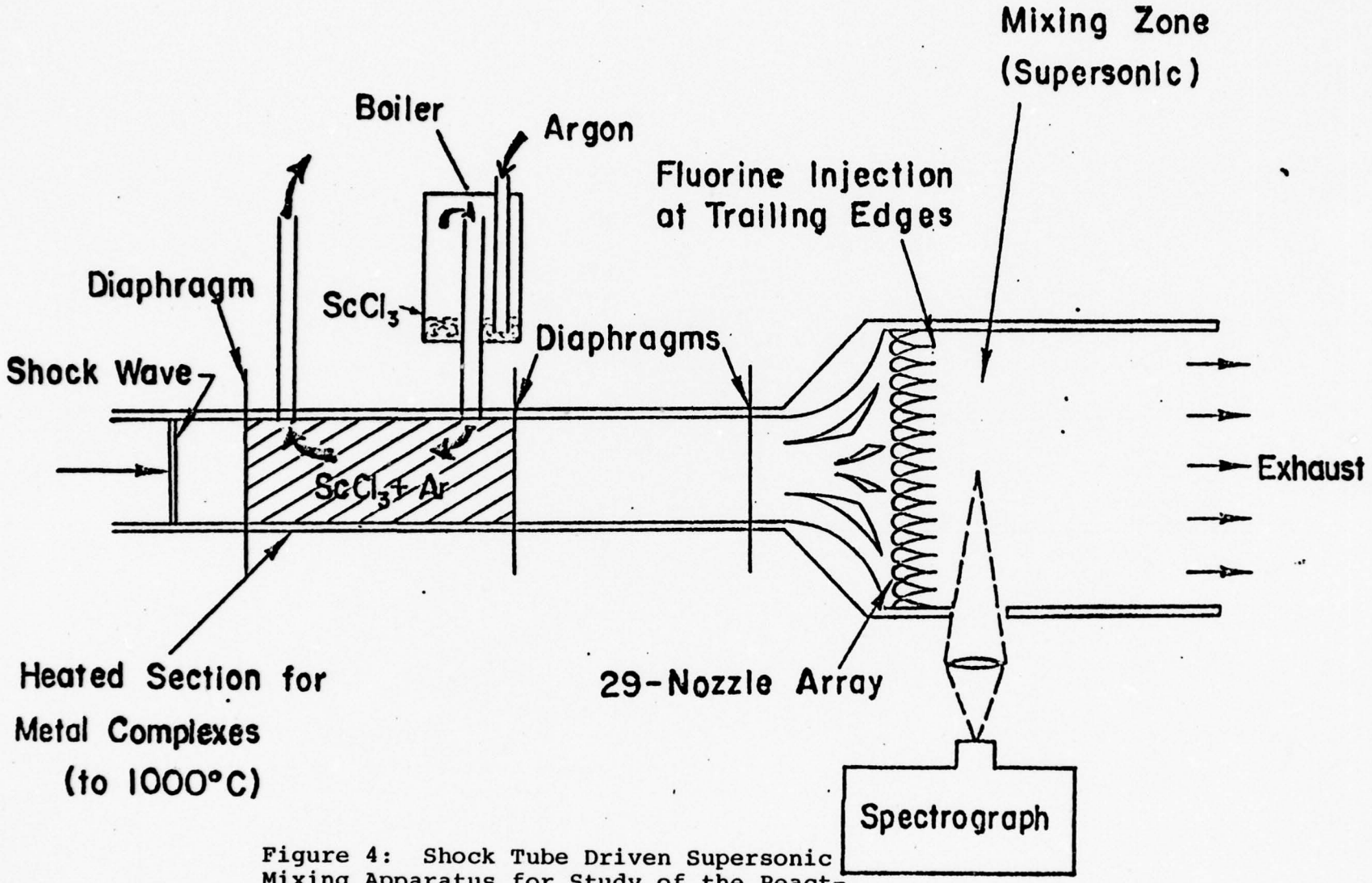
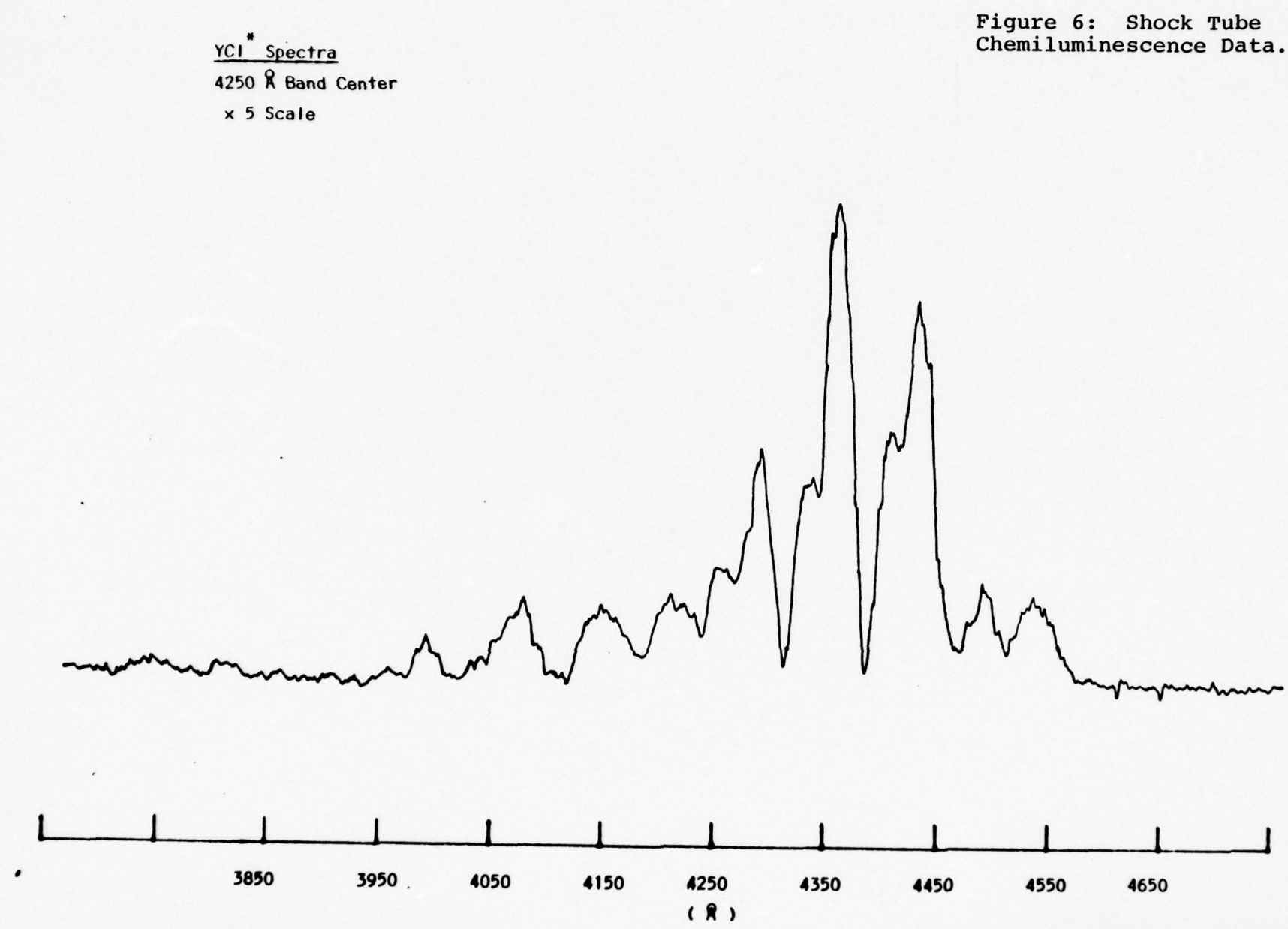


Figure 4: Shock Tube Driven Supersonic Mixing Apparatus for Study of the Reaction $Sc + F_2 \rightarrow ScF + F$ and $Y + Cl_2 \rightarrow YCl + Cl$.

Figure 6: Shock Tube Chemiluminescence Data.



The complex band sequences at longer wavelengths have yet to be analyzed, but are believed to be both singlet-singlet and triplet-triplet bands of YCl. Figure 6 indicates a set of bands near 4300 Å which may be $^3\pi \rightarrow {}^3\Delta$ or $^3\Delta \rightarrow {}^3\Delta$ bands. To our knowledge none of the bands of Figures 5 and 6 have been previously observed.

It seems likely that direct chemical formation of the $^3\Sigma^+$ state as suggested by Gole, et al., is a precursor to the appearance of the longer wavelength bands we observe at high pressure. These additional bands may be excited by energy transfer processes originating from the $^3\Sigma^+$ state. If this situation in fact exists the prospect for population inversions among several states situated below the $^3\Sigma^+$ state appear to be good.

Additional experiments are currently underway with the shock tube apparatus of Figure 4. Attempts are in progress to observe laser action in the near infrared part of the spectrum. An optical cavity consisting of hole-coupled gold-coated mirrors oriented transversely to the flow direction is used. A Ge-Cu high speed infrared detector with spectral sensitivity from about 1-25 microns is employed to detect laser output.

Potential laser transitions include triplet-triplet, singlet-singlet, and triplet-singlet transitions at wavelengths beyond 1 μ and vibration-rotation transitions for the ground electronic state near 25 microns.

III. LASER INDUCED FLUORESCENCE STUDIES OF YCl

Much additional information is needed to evaluate the potential of YCl as a chemical laser molecule. Spectral analysis of only one band system of YCl is currently available[8] and molecular constents have only been determined for the ground state and one electronically excited state. As many as 6 additional excited states may be identified from complete analysis of the spectra presented in Figures 5 and 6. The energies and identities of these states need to be determined. Moreover, radiative lifetimes and collisional quenching data are necessary for these several states.

The question of how energy is coupled by collisional processes from the nascent chemically pumped states to other radiating states must be answered before estimates of laser performance can be made.

In an effort to determine the molecular properties of excited electronic states in YCl we have designed and constructed apparatus shown schematically in Figures 7 and 8. A tungsten crucible located within a graphite furnace is heated to a temperature of 2200^{o}K to provide an effusive flow of yttrium vapor. Molecular chlorine is injected into the primary metal atom flow by means of a water cooled injector located 3 cm downstream from the effusive orifice. Pressures within the mixing and reaction zone can be varied from 10^{-3} to 10^{-1} Torr.

A pulsed tunable dye laser pumped by a 200 kW nitrogen laser at 10 Hz is used for excitation of molecular bands in

LASER INDUCED FLUORESCENCE IN A MIXING FLAME

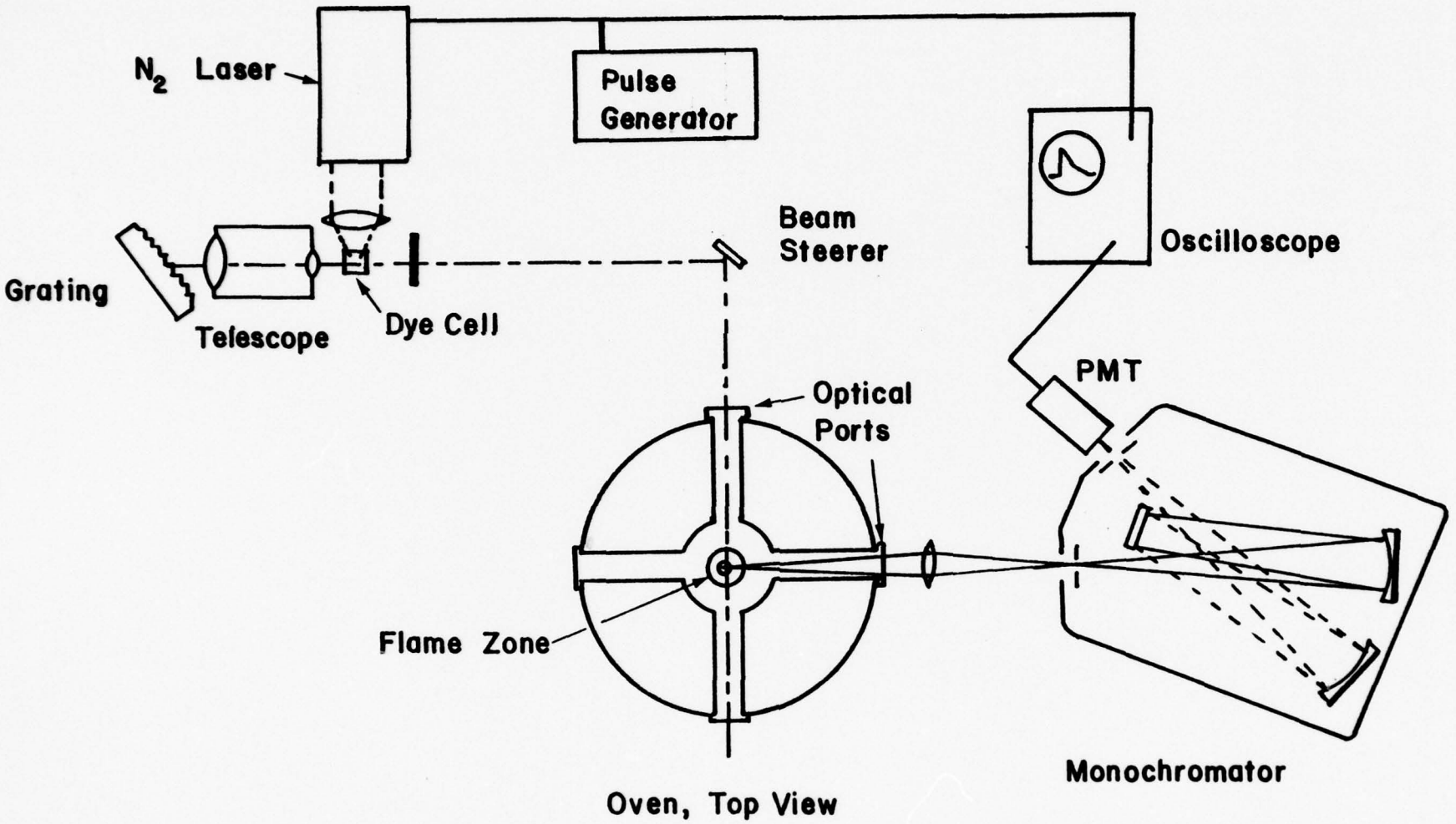


Figure 7

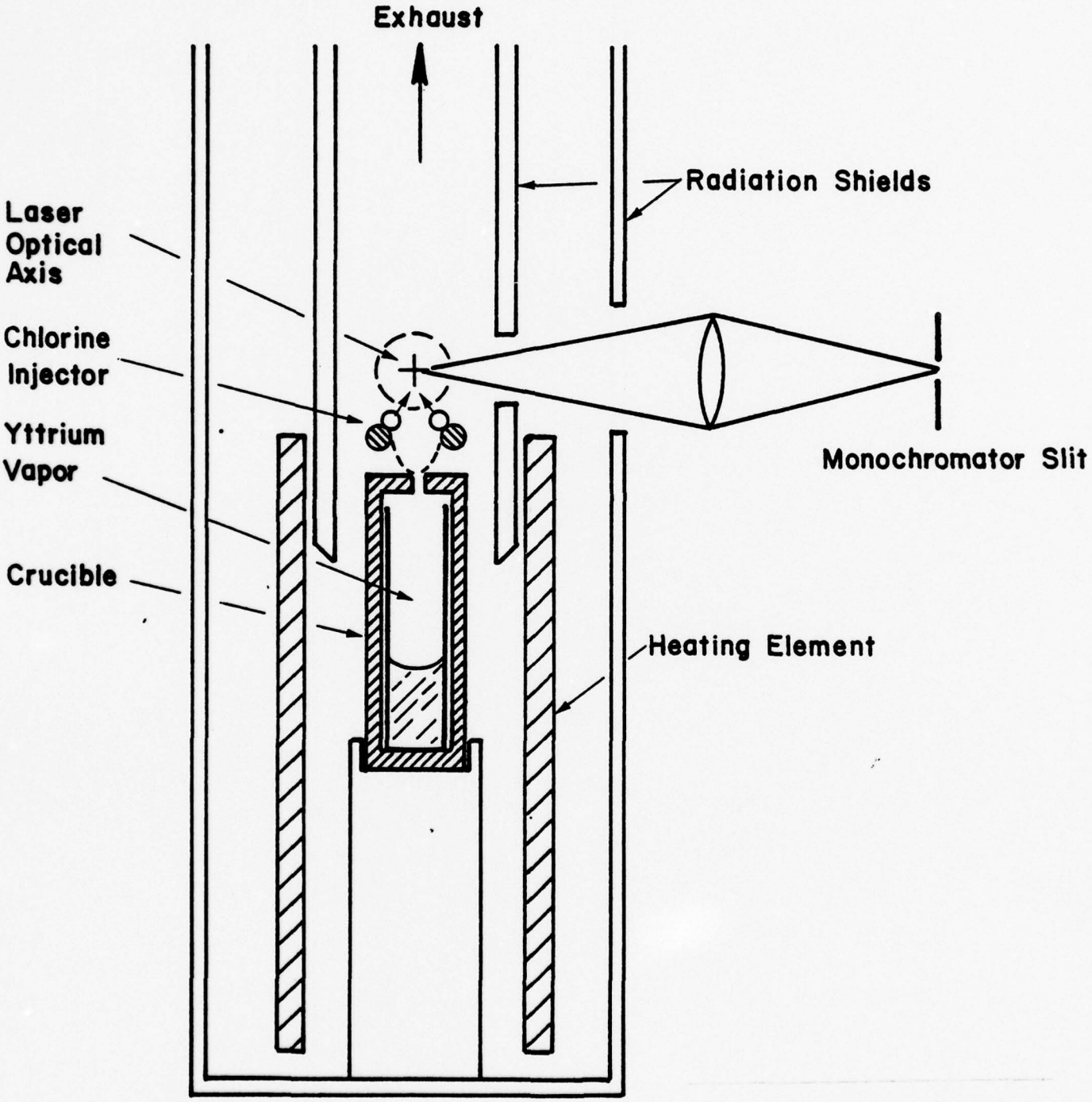


Figure 8: Flow Geometry for YCl Mixing Flame.

chemically formed YCl. Laser energies of about 10-20 μJ are available with use of various dyes covering the wavelength region from 4000-6000 Å. The dye laser is a conventional design with grating and telescope capable of 0.4 Å bandwidth in this spectral range.

The laser intensity and fluorescence signal are monitored with PM tubes. The PM tube signals are few into a dual channel boxcar integrator.

At present the apparatus is not completely operational because of some difficulties we encountered with the oven flow system. When modifications are completed we plan to make several types of measurements. The dye laser will be progressively tuned from 3800 to 6000 Å and excitation spectra from YCl recorded. The high resolution and reproducibility afforded with this method should permit identification of many of the YCl molecular bands (Figs. 5 and 6) observed in the shock tube studies.

Radiative lifetimes will be determined for selected molecular bands with measurements of the fluorescence decay times at low reaction zone pressures. Additional fluorescence decay measurements will be made as a function of the pressure of several additive gases to determine collisional quenching cross sections for YCl states of laser interest.

In some cases it may also be possible to measure energy transfer rates between states. An example of great interest would be a determination of energy transfer rates from the upper states of the 3980 to 3995 Å bands of Figure 5 to other

lower-lying states. The tunable dye laser affords the possibility of selective excitation of the 3980 and 3995 Å bands. A search will be made for fluorescence from other bands at longer wavelengths as the pressure of the reaction zone is progressively increased. Measurements of energy transfer rates will require observations of the decay times of the 3980 and 3995 Å fluorescence and fluorescence rise and decay times for the longer wavelength secondary fluorescences.

IV. AN IDEAL REACTION MECHANISM FOR AN EFFICIENT VISIBLE CHEMICAL LASER

The remarkably high photon yields observed for several of the reactions of Table II hold much promise for efficient chemical laser operation. These reactions demonstrate that radiant energy can be efficiently obtained from chemical reactions even when the released energy initially resides among nonradiating states. What is needed is a kinetic mechanism which acts to ensure that this radiant energy is emitted from the upper state of an inverted population.

An ideal mechanism of this type is illustrated in Figure 9. Given a chemically produced metastable atom or molecule A^*, suppose that an association reaction $A^* + BC \rightarrow (ABC)^*$ can occur to form an electronically excited excimer molecule $(ABC)^*$. If radiative transitions to a repulsive energy hypersurface account for the major source of decomposition of the excimer, then efficient laser action may be possible analogous to that of the recently developed rare gas-halide ultraviolet lasers.

An example of such a system which we are currently investigating consists of the reaction steps

$$P(^4S) + N_2O(X^1\Sigma^+) \rightarrow PO(^4\pi) + N_2(X^1\Sigma^+) \qquad (1)$$

$$PO(^4\pi) + PO(X^2\pi) \rightarrow (PO)_2^* \qquad (2)$$

$$(PO)_2^* \rightarrow h\nu + PO(X^2\pi) + PO(X^2\pi) \qquad (3)$$

A CHEMICALLY PUMPED EXCIMER LASER

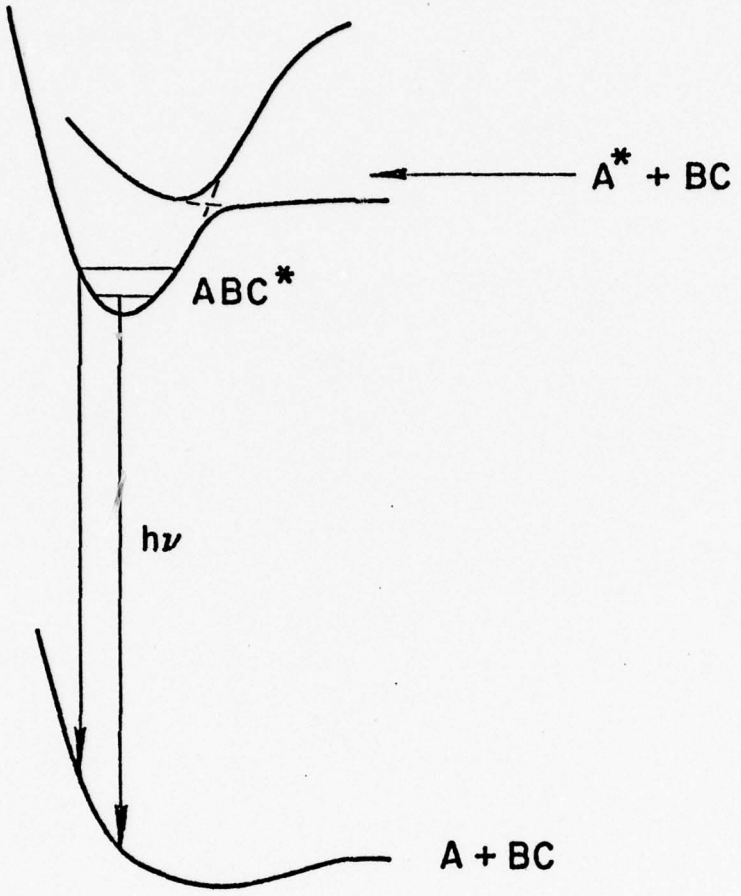


Figure 9

Reaction (1) is expected to lead to the efficient production of the metastable PO($^4\pi$) state illustrated in Figure 10. Precursor reactions of importance in the PH_3/N_2O system are listed in Table III. Studies of the chemiluminescence resulting from the discharge initiation of chemical reactions in mixtures of PH_3 and N_2O have revealed a strong continuous emission extending from about 3200 Å to beyond 2 μ with a broad maximum near 7500 Å. Chemiluminescence spectra are presented in Figures 11-13. The spectra of Figures 11 and 12 are uncorrected for film response. This emission is believed to arise from the $(PO)_2^*$ excimer emission of process (3), as indicated schematically in Figure 14. To data attempts to achieve laser emission from this system have been inconclusive, although photon yields for wavelengths from 3200 Å to 2 μ have been found to exceed 10^{-3} under favorable conditions.

A flashlamp pumped dye laser has been used to measure the intracavity absorption spectra associated with the PH_3/N_2O emission over the wavelength range from 5000-6500 Å. Typical pulse shapes for the dye laser and excimer emission are given in Figure 15. Very little absorption occurs when the two profiles coincide as is the case in Figure 15. A strong molecular absorption is observable, however, when the dye laser is delayed with respect to the excimer emission.

Strong evidence in favor of the excimer hypothesis is given in Figure 16. Here the peak spontaneous emission intensity determined from emission profiles similar to the

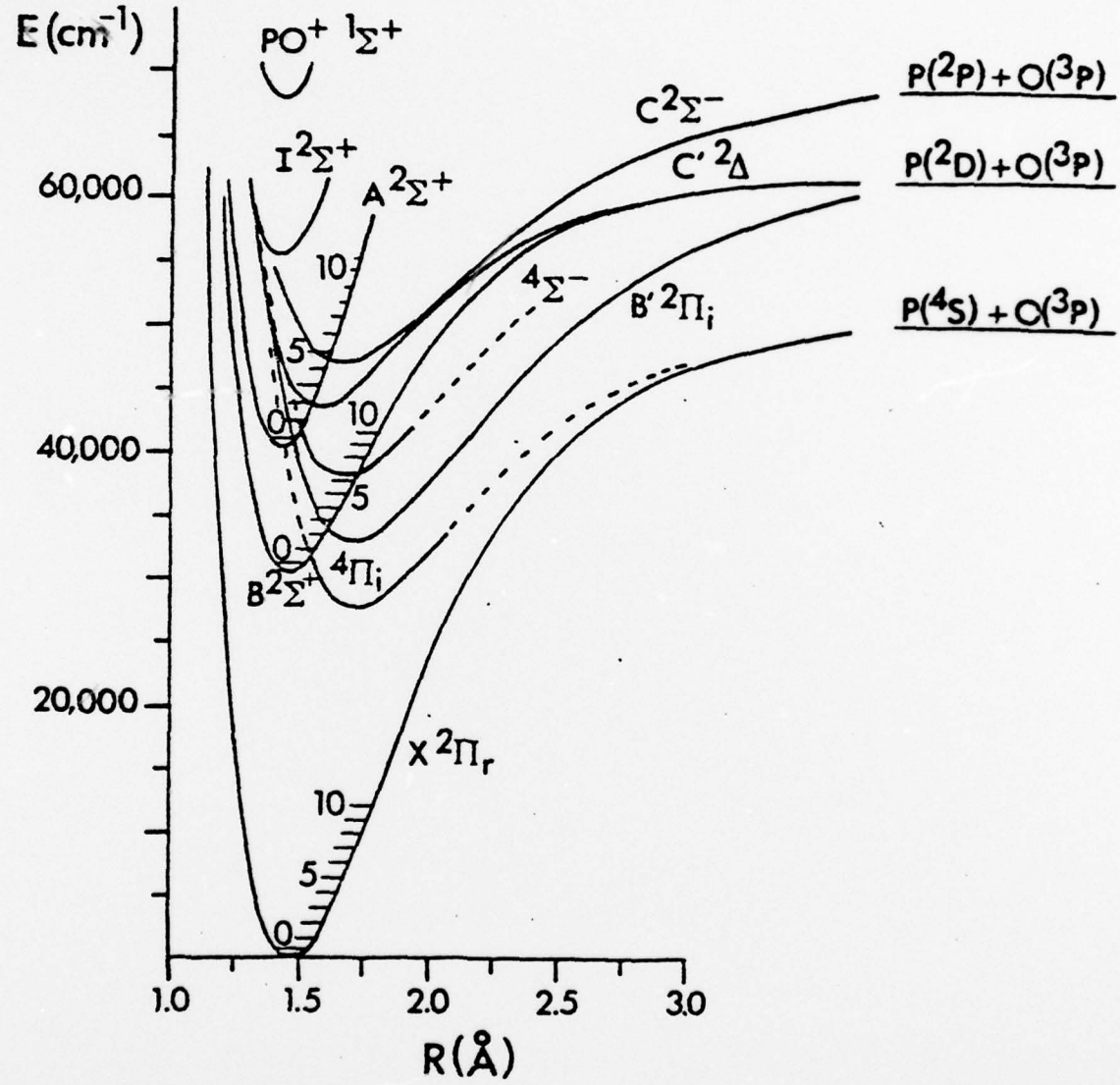


Figure 10: Low-lying Potential Energy Curves for PO Adapted from R.D. Verma, M.N. Dixit, S.S. Jois, S. Nagaraj, and S.R. Singhal, Can. J. Phys. 49, 3180 (1971).

TABLE III
Discharge-Initiated Reactions
in PH_3/N_2O Mixtures.

$$PH_3 \xrightarrow{e^-} PH_2 + H$$
$$N_2O \xrightarrow{e^-} N_2 + O$$
} initiation

$$PH_3 + H \rightarrow PH_2 + H_2$$
$$PH_3 + O \rightarrow PH_2 + OH$$
$$PH_3 + OH \rightarrow PH_2 + H_2O$$
} formation of PH_2

$$PH_2 + PH_2 \rightarrow PH + PH_3$$
$$PH_2 + X \rightarrow PH + XH \quad ; X = O, H, OH$$
} formation of PH

$$PH + N_2O \rightarrow HPO + N_2$$
$$PH + OH \rightarrow HPO + H$$
} formation of HPO

$$PH + O \rightarrow P + OH$$
$$PH + H \rightarrow P + H_2$$
$$PH + PO \rightarrow P + HPO$$
} formation of P

$$H + HPO \rightarrow PO + H_2$$
$$O + HPO \rightarrow PO + OH$$
$$P + N_2O \rightarrow PO^* + N_2$$
} formation of PO

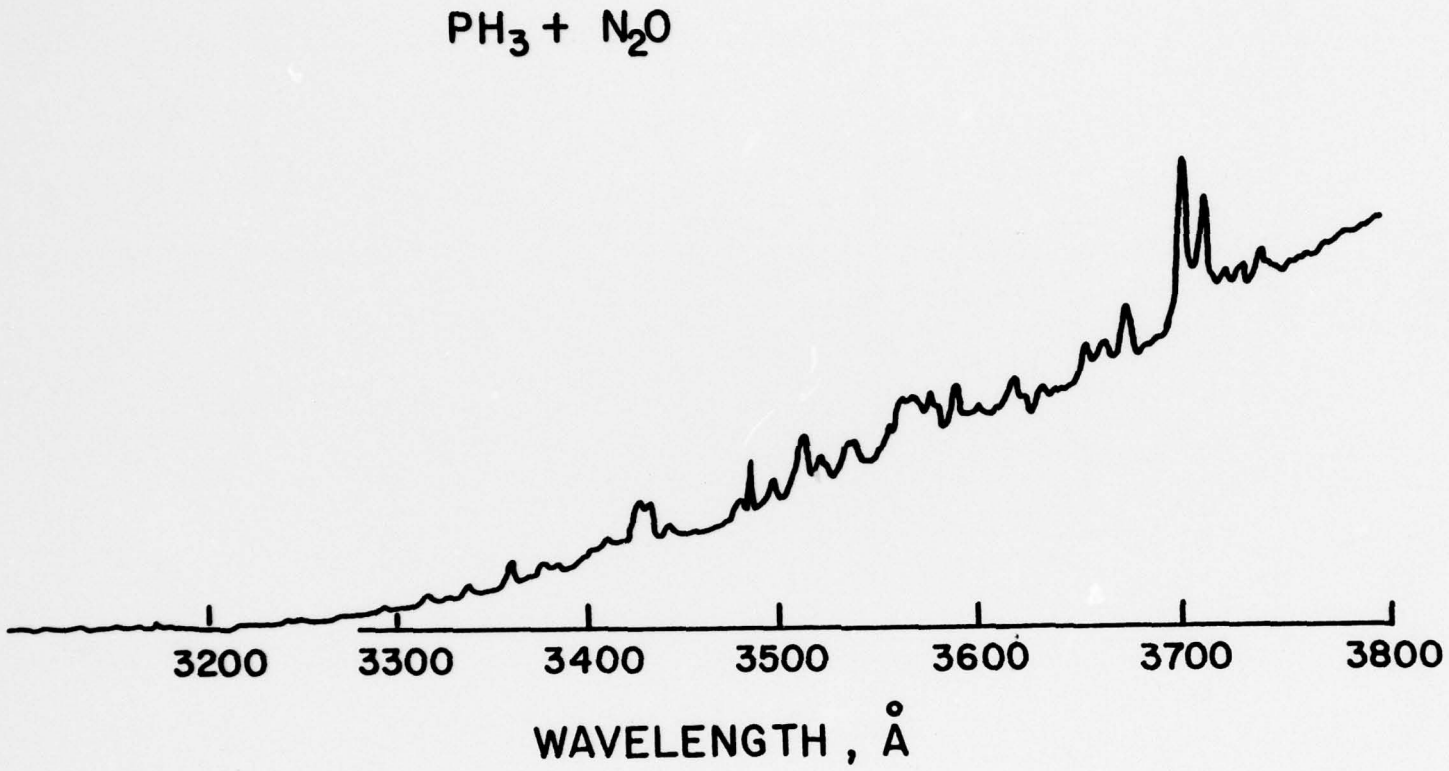


Figure 11: Chemiluminescence Spectra for PH_3/N_2O System.

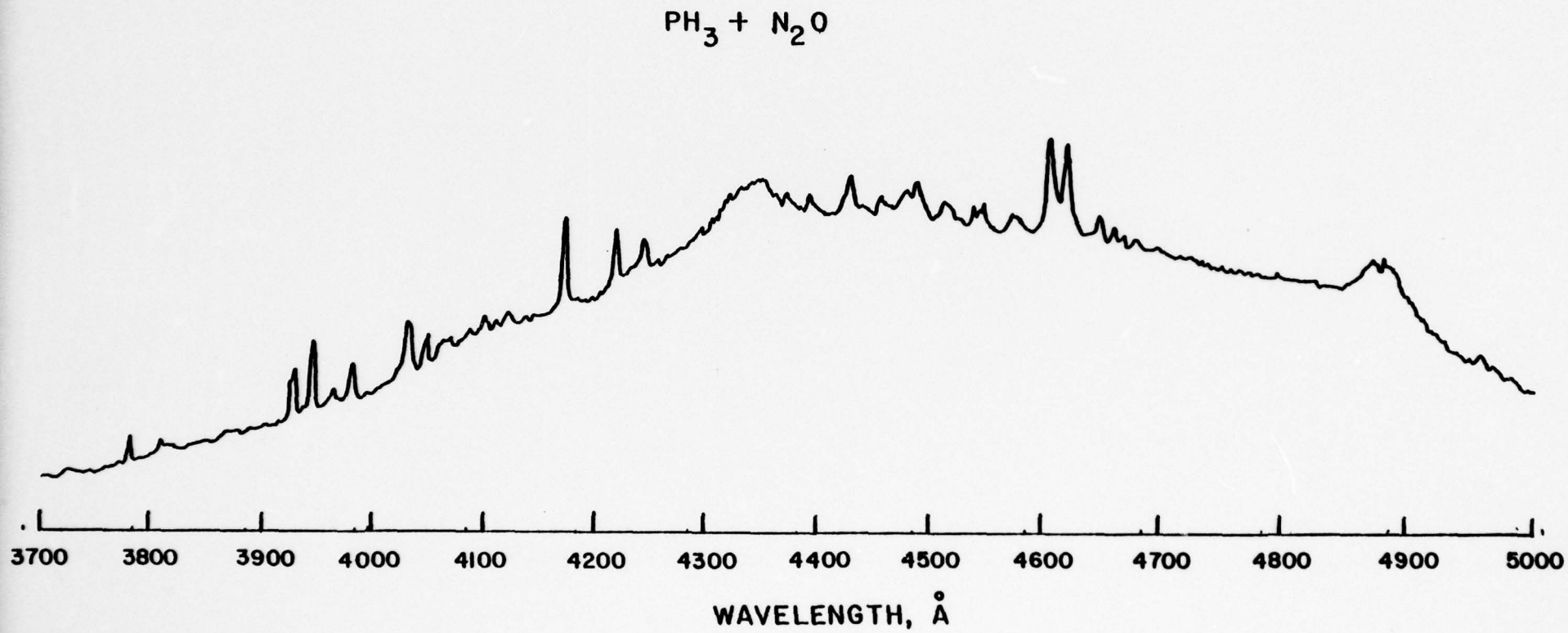


Figure 12: Chemiluminescence Spectra for PH_3/N_2O System.

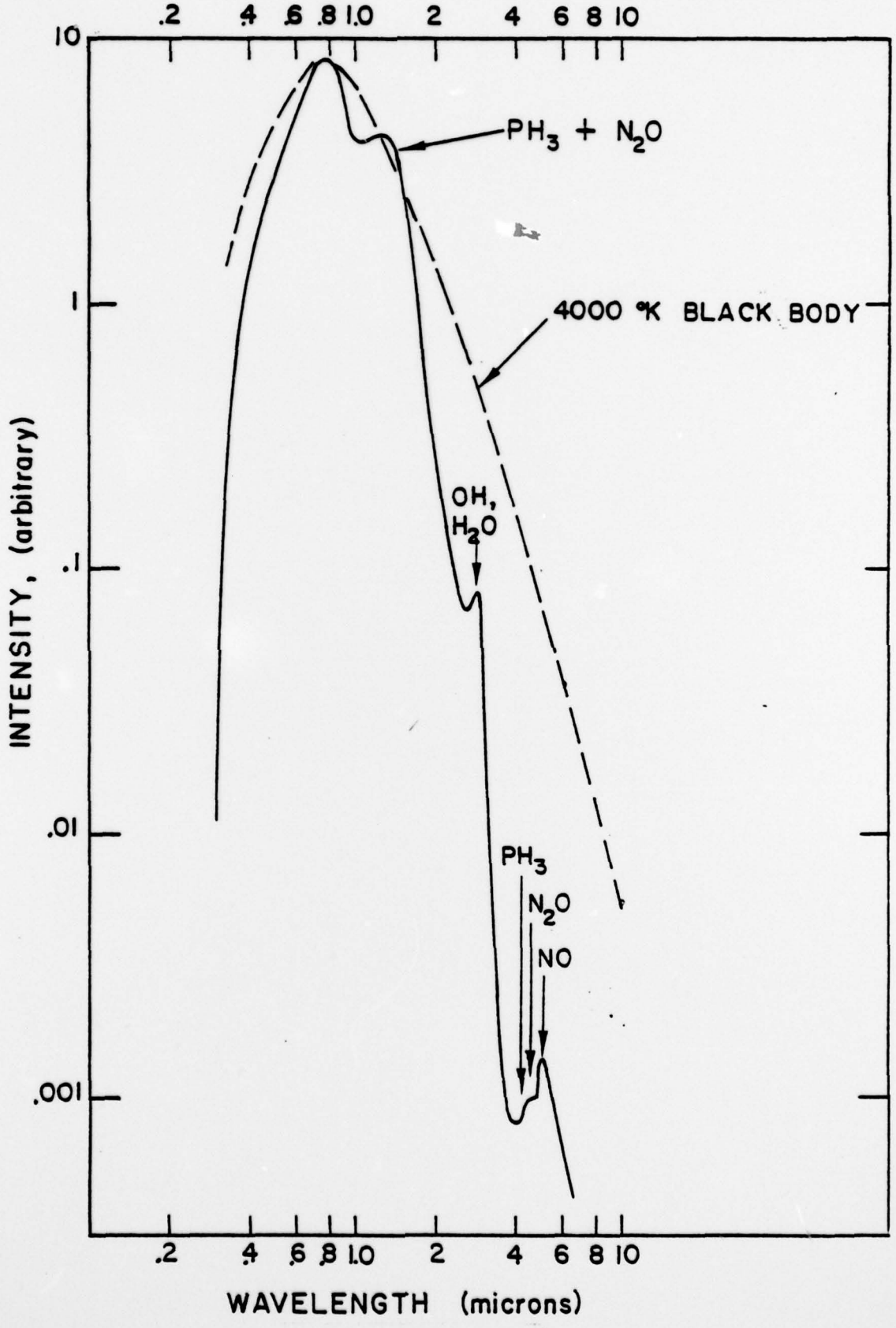


Figure 13: Absolute Emission Instensity Data for PH_3/N_2O System.

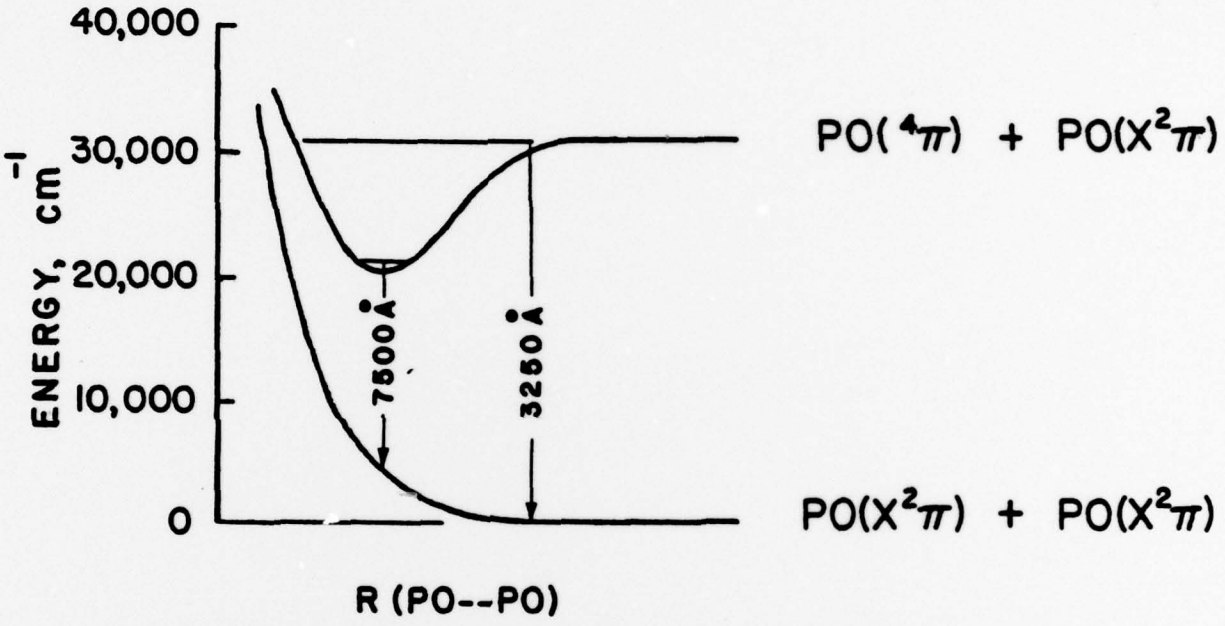


Figure 14: Schematic Cross Section of Potential Energy Hypersurfaces for $(PO)_2$ Dimer.

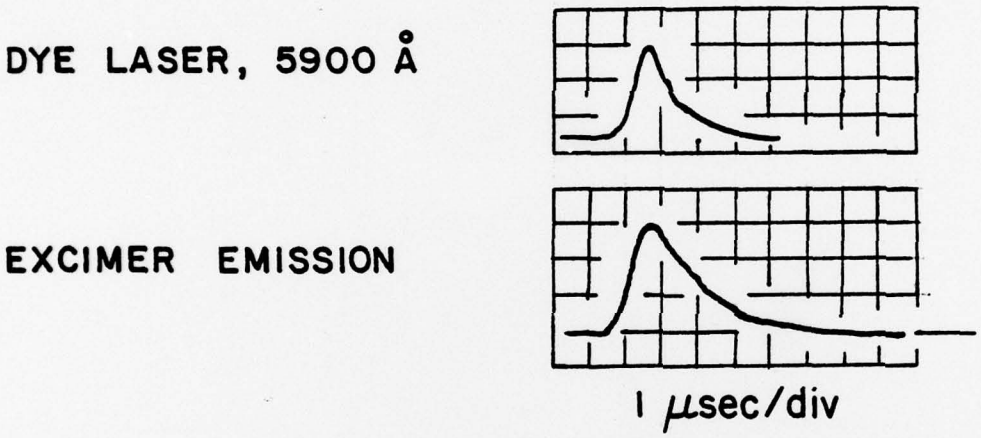


Figure 15: Temporal Profiles of Dye Laser Pulse and PH_3/N_2O Spontaneous Emission.

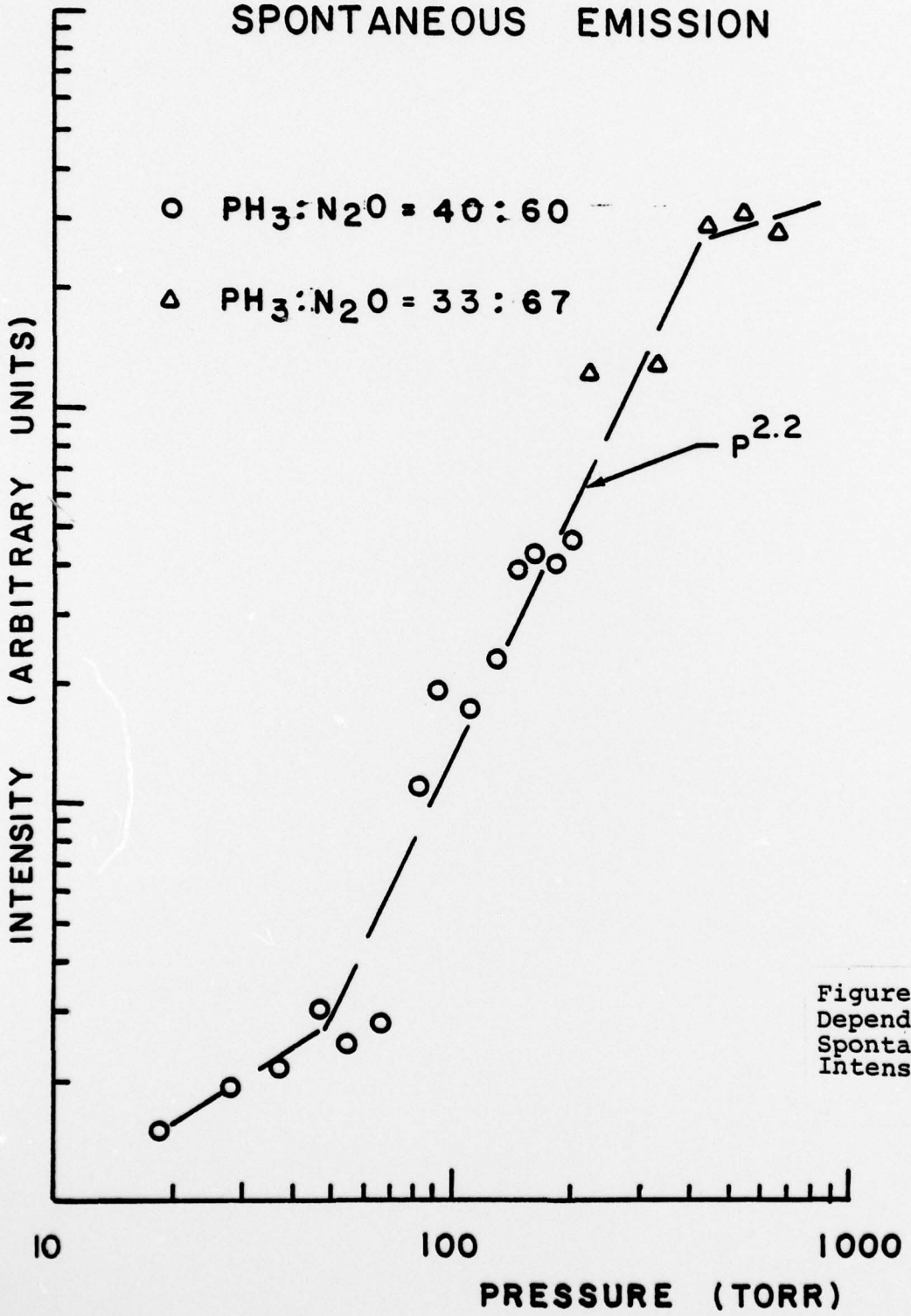


Figure 16: Pressure Dependence of PH_3/N_2O Spontaneous Emission Intensity.

lower trace of Figure 15 is plotted as a function of initial total reagent pressure. For pressures above about 20 Torr the temporal profile remains constant in duration, but the peak intensity varies approximately as the square of the pressure up to pressures of one atmosphere. Our cell is not designed for operation at higher pressures, but it is clear that quenching processes do not become dominant for pressures below one atmosphere.

Additional work on this interesting reaction system will be continued in an attempt to positively identify the emitter responsible for the strong radiation we observe.

REFERENCES

1. C.R. Dickson and R.N. Zare, Chem. Phys. 7, 361 (1975).
2. A. Yokozeki and M. Menzinger, Chem. Phys. 14, 427 (1976).
3. R.W. Field, C.R. Jones and H.P. Broida, J. Chem. Phys. 60, 4377 (1974); J. Chem. Phys. 62, 2012 (1975).
4. C. J. Hsu, W.K. Krugh, N.B. Palmer, R.H. Obernauf and C.F. Aten, J. Mol. Spectrosc. 53, 273 (1974).
5. D. J. Eckstron. S.A. Edelstein, D.L. Huestis, B.E. Perry, and S.W. Benson, J. Chem. Phys. 63, 3828 (1975).
6. C. Chalek, D.R. Preuss, and J. L. Gole, Electronic Transition Lasers, J. I. Steinfleld, Editor, Proceedings of the Second Summer Colloquium on Electronic Transition Lasers, Woods Hole, Mass., Sept. 1975 (MIT Press, 1976), pp. 50-55.
7. J. L. Gole, Electronic Transition Lasers II, L. E. Wilson, S. N. Suchard, and J. I. Steinfeld, Editors, Proceedings of the Third Summer Colloquim on Electronic Transition Lasers, Snowmass-in-Aspen, Colorado, Sept. 1976 (MIT Press, 1977(pp. 136-165.
8. S. N. Suchard, Ed., Spectroscopic Data I; Heteronuclear Diatomic Molecules, Parts A and B (IFI/Plenum, New York, 1975).
9. D. McLeod, Jr., and W. Weltner, Jr., J. Phys. Chem. 70, 3293 (1966).
10. L. Brewer and D.W. Green, High Temp. Science 1, 26 (1969).

PUBLICATIONS

A cumulative list of publications for work supported under Grant AFOSR-73-2550 is given below.

1. K. K. Hui and T. A. Cool, "Experiments Concerning the Laser Enhanced Reaction Between Vibrationally Excited O_3 and NO", to be published, J. Chem. Phys.
2. T. A. Cool, "Chemical Lasers", to be published as Chapter 5 in Dynamics and Energetics of Elementary Reactions, I. W. W. Smith, Editor, Plenum Publishing Company.
3. D. R. Fischell and T. A. Cool, "Spontaneous Emission from ScF in a Supersonic Mixing Flame", Proceedings of the Third Summer Colloquium on Electronic Transition Lasers, Snowmass, Colorado, September, 1976.
4. M. S. Chou and T. A. Cool, "New Metal Atom Transitions in As, Bi, Cu, Ge, Hg, In, Pb, Sb, and Tl", Proceedings of the Second Summer Colloquium on Electronic Transition Lasers, Woods Hole, Mass., September, 1975.
5. J. S. Whittier and T. A. Cool, "Initiation with an Electron Beam of Chemical Reactions of Interest for Visible Wavelength Lasers", Proceedings of the Second Summer Colloquium on Electronic Transition Lasers, Woods Hole, Mass., September, 1975.
6. J. A. McGarvey, N. E. Friedman, and T. A. Cool, "Vibrational Energy Transfer in Hf-HCN, DF-HCN, and H_2-HCN Mixtures from 240-450^{o}K", J. Chem. Phys., 66, 3189 (1977).

7. K. K. Hui and T. A. Cool, "Double-Quantum Vibrational Energy Transfer in the O_3-CO and O_3-OCS Systems", J. Chem. Phys. 65, 3536 (1976).

8. R. J. Pirkle and T. A. Cool, "Vibrational Energy Transfer for H_2-D_2 and H_2-HCl Mixtures from 220-450^{o}K", Chem. Phys. Letters, 42. 58 (1976).

9. T. A. Cool, "Transfer Chemical Lasers", Handbook of Chemical Lasers, John Wiley and Sons, Inc., p. 431.

10. M. S. Chou and T. A. Cool, "Laser Operation by Dissociation of Metal Complexes (II): New Transitions in Cd, Fe, Ni, Se, Sn, Te, V, and Zn", J. Appl. Physics, 48, 1551 (1977).

11. M. S. Chou and T. A. Cool, "Laser Operation by Dissociation of Metal Complexes: New Transitions in As, Bi, Ga, Ge, Hg, In, Pb, Sb, and Tl", J. Appl. Phys. 47, 1055 (1976).

12. R. N. Sileo and T. A. Cool, "Overtone Emission Spectroscopy of HF and DF: Vibrational Matrix Elements and Dipole Moment Function", J. Chem. Phys. 65, 117 (1976).

13. R. A. Lucht and T. A. Cool, "Temperature Dependence of Vibrational Relaxation in the HF-DF, HF-CO_2 , and DF-CO_2 Systems: II", J. Chem. 63, 3962 (1975).

14. R. A. Lucht and T. A. Cool, J. Chem. Phys. 60, 1026 (1974).

15. R. A. Lucht and T. A. Cool, J. Chem. Phys. 60, 2554 (1974).

16. K. K. Hui, D. I. Rosen, and T. A. Cool, Chem. Phys. Lett. 32, 141 (1975).

17. D. I. Rosen and T. A. Cool, J. Chem. Phys. 62, 466 (1975).

18. D. I. Rosen and T. A. Cool, J. Chem. Phys. 59, 6097 (1973).

PERSONNEL

Personnel, besides the principal investigator, who were supported entirely or in part under this Grant are listed below.

1. J. S. Whittier, Senior Research Associate
2. M. S. Chou, Postdoctoral Research Associate
3. R. J. Pirkle, Postdoctoral Research Associate
4. H. C. Brayman, Graduate Research Assistant
5. A. C. Erlandson, Graduate Research Assistant
6. D. R. Fischell, Graduate Research Assistant
7. N. R. Friedman, Research Assistant
8. D. R. Harris, Graduate Research Assistant
9. K. K. Hui, Graduate Research Assistant
10. R. A. Lucht, Graduate Research Assistant
11. J. A. McGarvey, Jr., Graduate Research Assistant
12. D. I. Rosen, Graduate Research Assistant