ABSTRACT

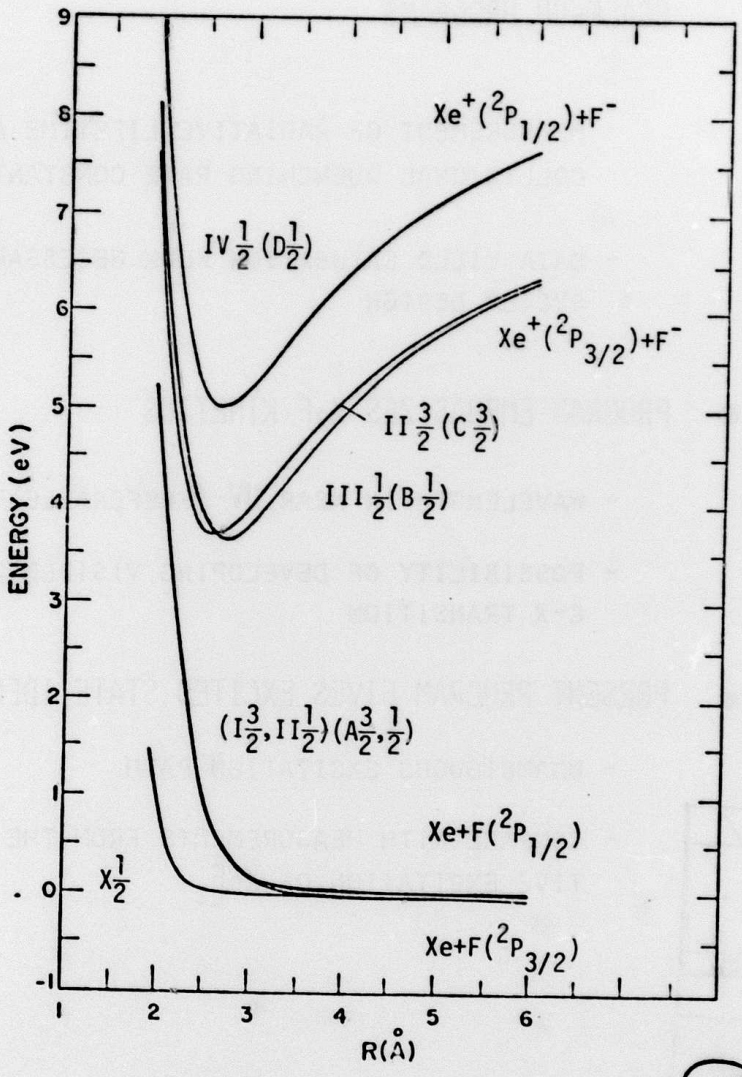
Title: Radiative Lifetime and Quenching Kinetics for the XeF (B 1/2) State, C.H. Fisher and R.E. Center, Mathematical Sciences Northwest, Inc.--A state-selective laser-induced-fluorescence technique has been used to determine the radiative lifetime and quenching kinetics for the XeF (B 1/2) excited state. Fluorine atoms are formed by flash dissociating a mixture of $UF_6$ and Xe in He. After a suitable delay to allow recombination of Xe and F atoms, ground state XeF molecules are excited to the XeF (B 1/2) state by passing a 3511 Å XeF laser beam through the cell. The fluorescence decay at 3533 Å is monitored perpendicular to the exciting light using a spectrometer-photomultiplier combination. Quenching rate coefficients for the collision partners He, Ne, Xe, $F_2$, and $NF_3$ have been determined. Fluorescence emission at 460 nm due to collisional transfer from the XeF (B 1/2) to the XeF (C 1/2) state has also been observed.
*Supported by DARPA Order No. 1806, ONR Contract No. N00014-76-C-1066.

## MSNW KINETICS PROGRAM--RARE GAS HALIDES

- BASIC KINETICS MEASUREMENTS IN SUPPORT OF DARPA SCALE-UP PROGRAMS
  - MEASUREMENT OF RADIATIVE LIFETIME AND COLLISIONAL QUENCHING RATE CONSTANTS
  - DATA YIELD SATURATION FLUX NECESSARY FOR SYSTEM DESIGN
- PROGRAM EMPHASIZES XeF KINETICS
  - WAVELENGTH IN NEAR UV (PREFERABLE TO KrF)
  - POSSIBILITY OF DEVELOPING VISIBLE LASER ON C-X TRANSITION
- PRESENT PROGRAM GIVES EXCITED STATE IDENTIFICATION
  - UNAMBIGUOUS EXCITATION PATH
  - COMPARE WITH MEASUREMENTS FROM THE DISSOCIATIVE EXCITATION OF $XeF_2$

# XeF POTENTIAL ENERGY CURVES

T. H. Dunning and P. J. Hay, to be published



## EXPERIMENTAL CONCEPT

- PRODUCE F ATOMS BY FLASH PHOTOLYSIS IN PRESENCE OF Xe

  e.g. $F_2 + h\nu \rightarrow 2F$

- WAIT FOR RECOMBINATION INTO GROUND ELECTRONIC STATE

  $Xe + F + (M) \rightleftharpoons X\,F(B\tfrac{1}{2}) + (M)$

  (DELAY TIME MUST BE LESS THAN TIME FOR F-ATOM RECOMBINATION OR LOSS BY DIFFUSION)

- EXCITE $XeF(X\tfrac{1}{2})$ BY XeF LASER ON B-X TRANSITION

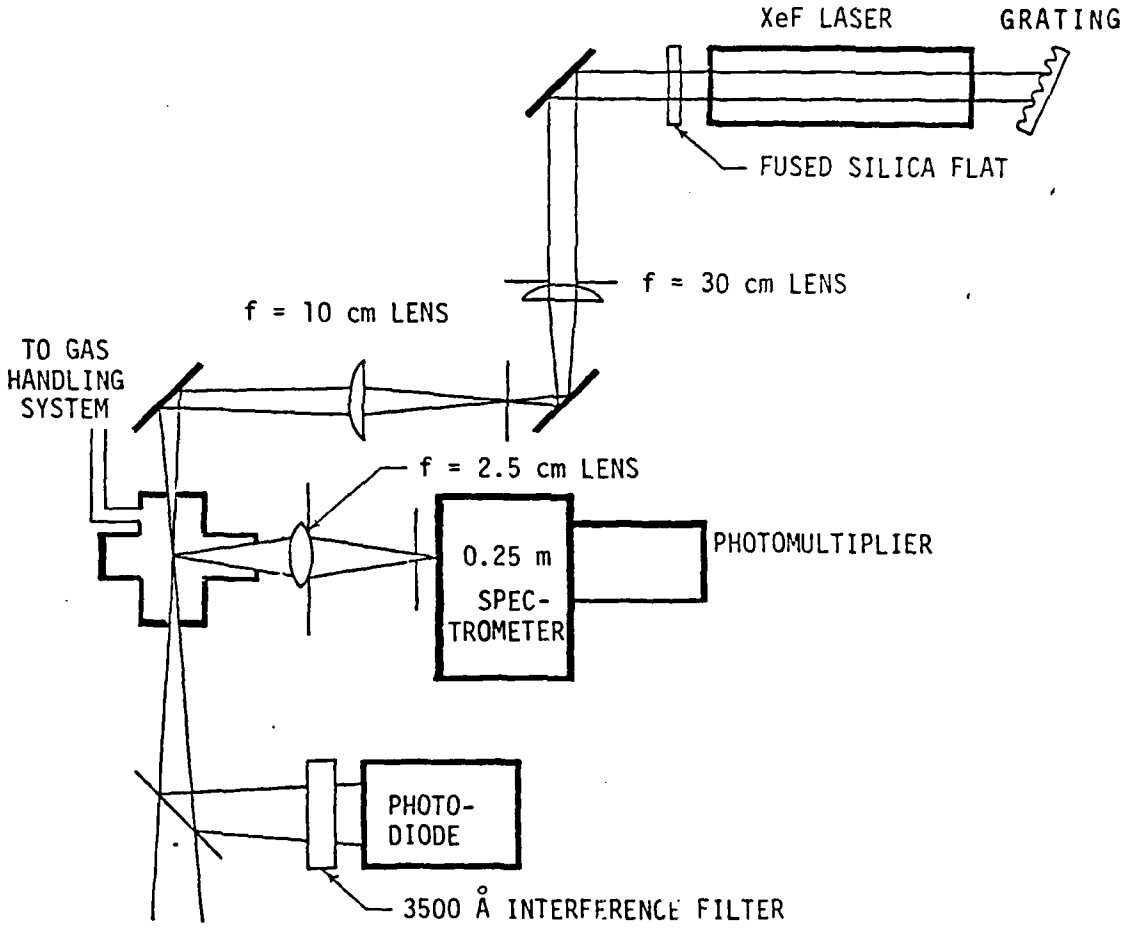
  $XeF_{v''}(X\tfrac{1}{2}) + h\nu \rightarrow XeF(B\tfrac{1}{2})$

- MONITOR FLUORESCENCE DECAY--COMPETITION OF RADIATIVE DECAY AND COLLISIONAL QUENCHING

  $XeF(B\tfrac{1}{2}) \rightarrow XeF(X\tfrac{1}{2}) + h\nu$

  $XeF(B\tfrac{1}{2}) + M \rightarrow XeF(X\tfrac{1}{2}) + M$

# SCHEMATIC DIAGRAM FOR THE OPTICAL SETUP FOR THE LASER INDUCED FLUORESCENCE EXPERIMENT

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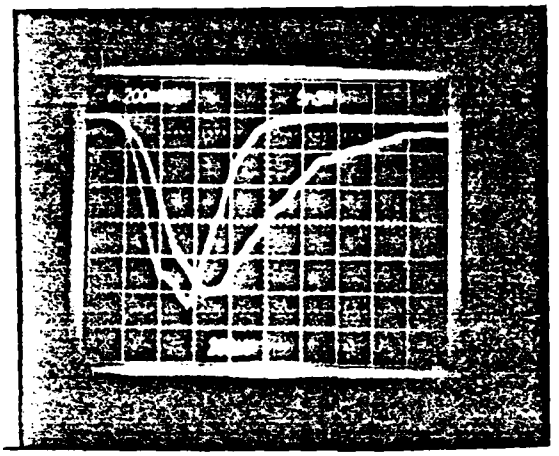
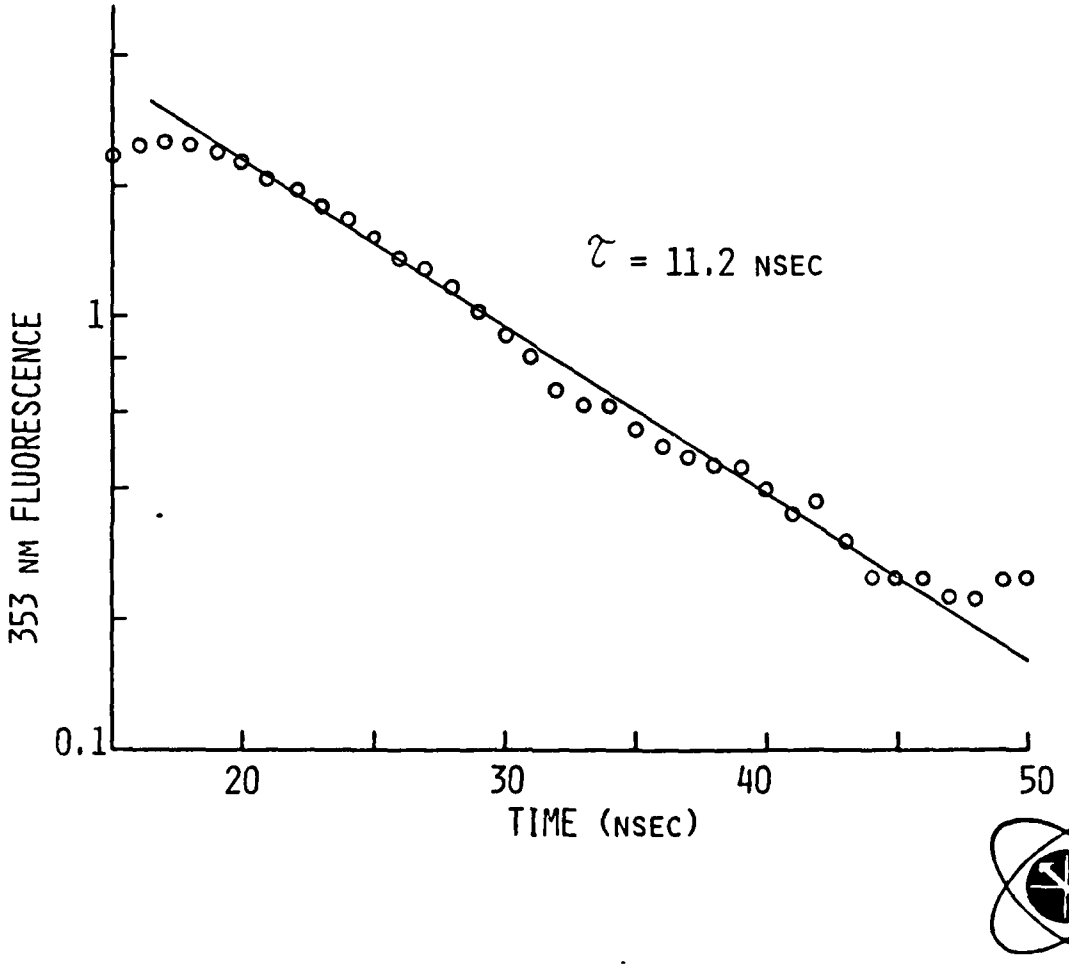
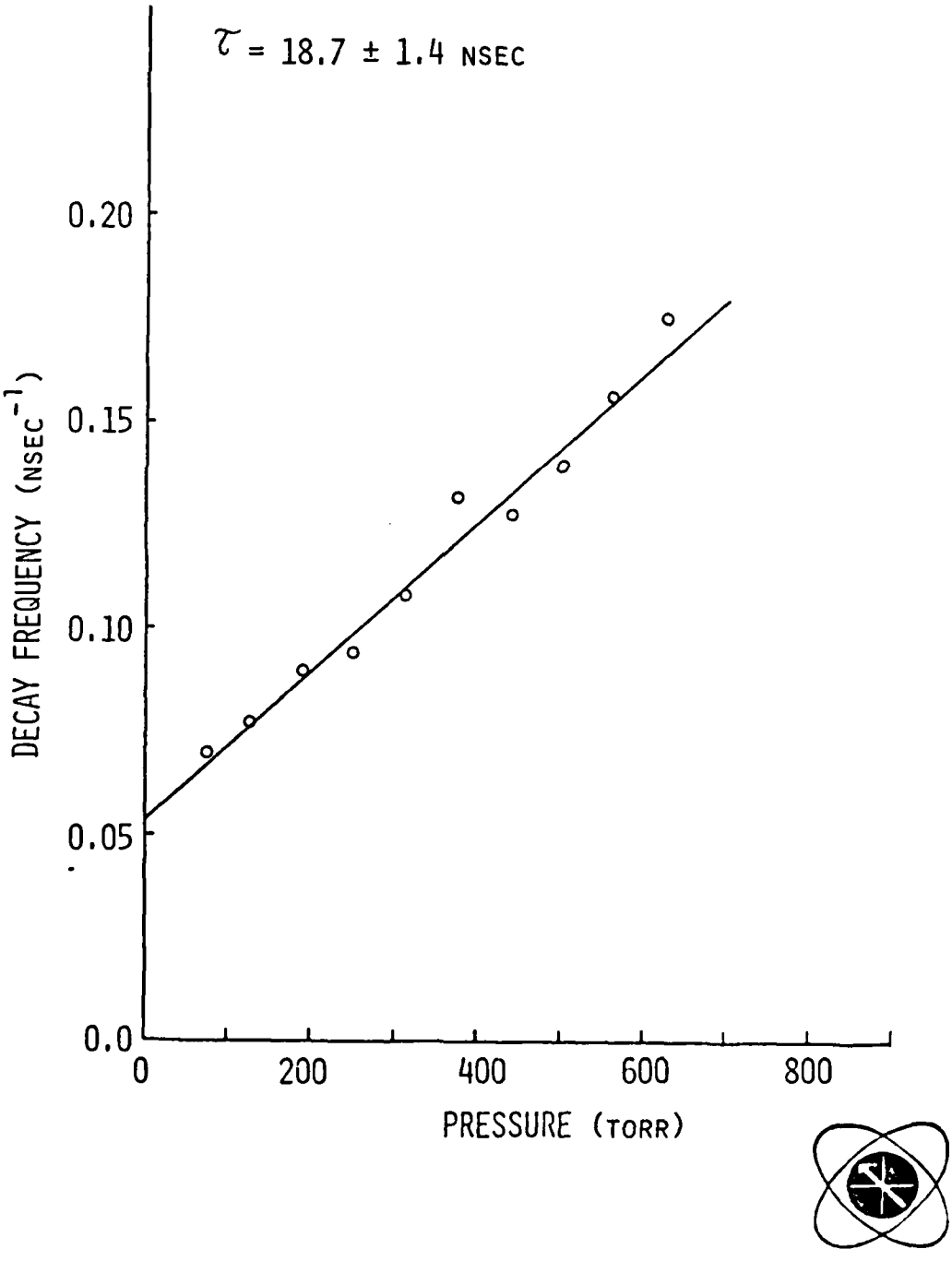
## 353 NM FLUORESCENCE FROM
## 125 TORR He + 10 TORR Xe + 0.7 TORR $UF_6$



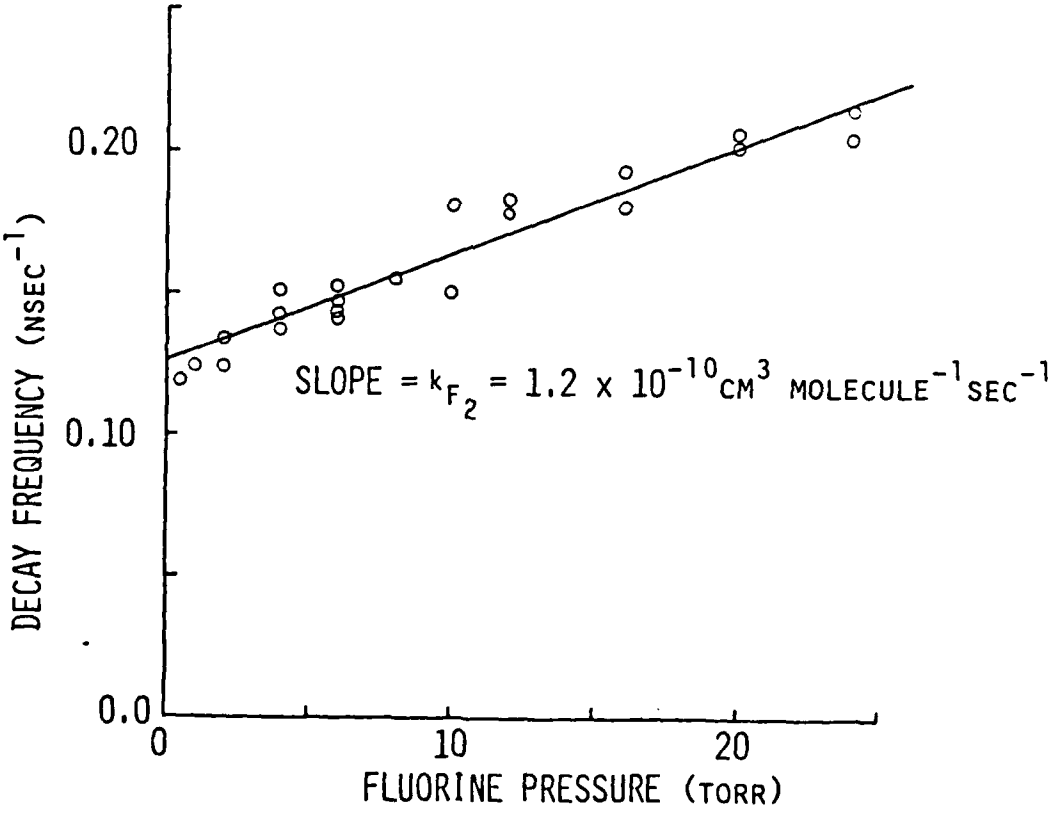


## XeF($B\frac{1}{2}$) FLUORESCENT LIFETIME MEASUREMENTS



## $XeF(B\frac{1}{2})$ QUENCHING BY $F_2$

250 TORR He + 10 TORR Xe + 0.3 TORR $UF_6$



# SUMMARY OF $XeF(B\frac{1}{2})$ RADIATIVE LIFETIME AND QUENCHING DATA

- $XeF(B\frac{1}{2})$ $\tau_r = 18.7 \pm 1.4$ NSEC

- $XeF(B\frac{1}{2})$ TWO BODY QUENCHING RATE CONSTANTS

| MOLECULE | $k_q$ ($CM^3$ $MOLECULE^{-1}$ $SEC^{-1}$) | PRESSURE RANGE (TORR) |
|---|---|---|
| He | $2 \times 10^{-12}$ | 75 - 750 |
| Ne | $\lesssim 1.4 \times 10^{-13}$ | 75 - 750 |
| Xe | $6 \times 10^{-11}$ | 5 - 80 |
| $F_2$ | $1.2 \times 10^{-10}$ | 0.5 - 24 |
| $NF_3$ | $3.2 \times 10^{-12}$ | 15 - 500 |
| ~~$UF_6$*~~ | ~~$< 1 \times 10^{-11}$~~ | ~~0.3 - 2~~ |

~~* PRELIMINARY UPPER BOUND ESTIMATES~~

# XeF POTENTIAL ENERGY CURVES

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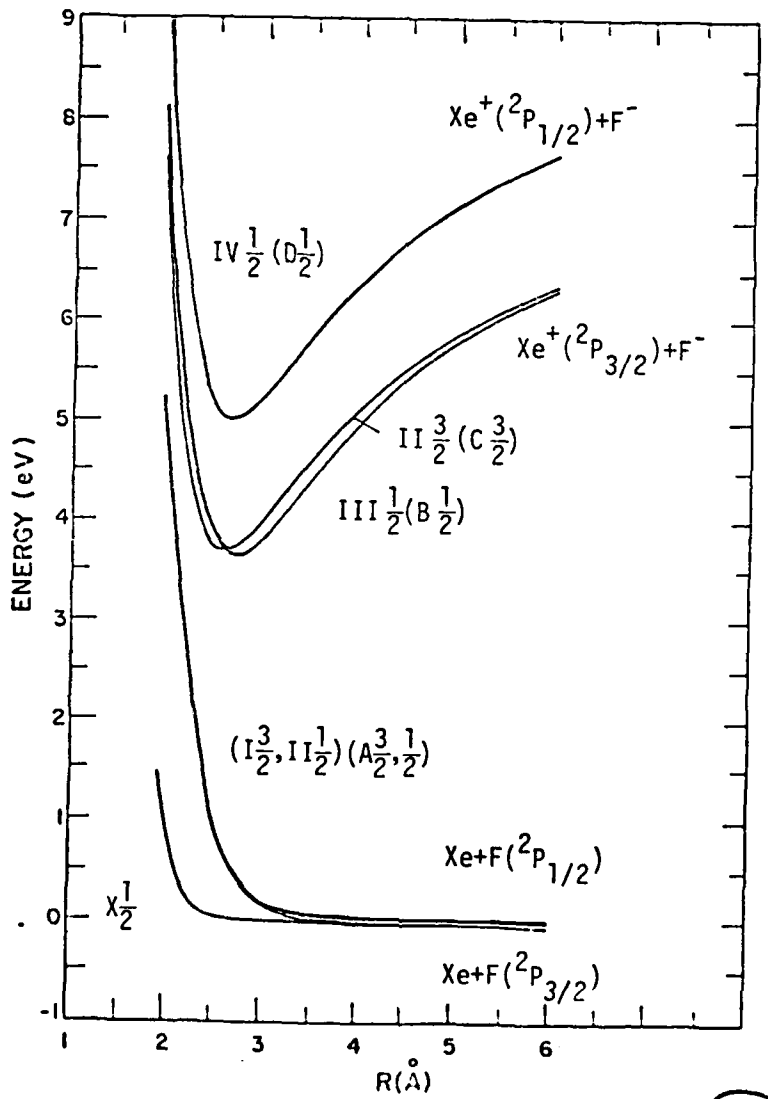
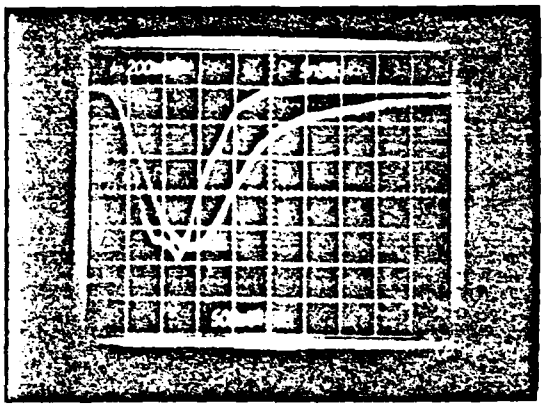
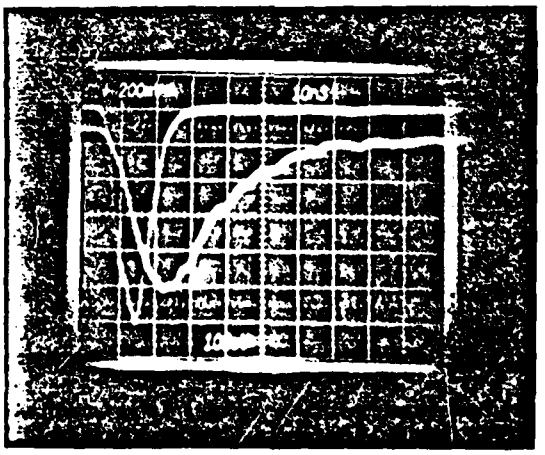


# COMPARISON OF XeF FLUORESCENCE AT 460 AND 353 NM



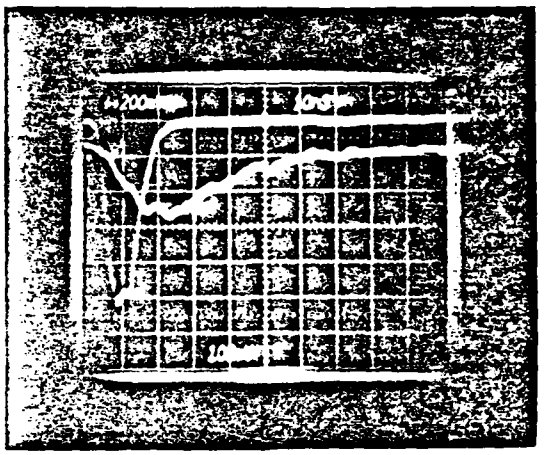
(A) 353 nm



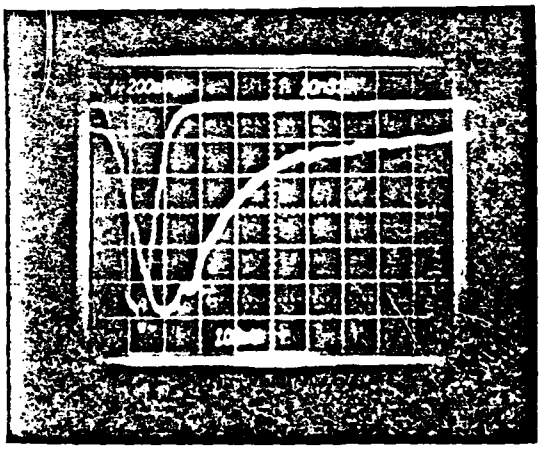
(B) 460 nm

1.5 atm He + 10 TORR Xe + 0.7 TORR $UF_6$

## EFFECT OF Ar CONCENTRATION ON 460 nm FLUORESCENCE



(A) 250 TORR Ar + 10 TORR Xe + 0.7 TORR $UF_6$



(B) 625 TORR Ar + 10 TORR Xe + 0.7 TORR $UF_6$

## DATA INTERPRETATION

$$XeF(B\tfrac{1}{2}) + M \rightarrow XeF(X\tfrac{1}{2}) + M \qquad (1)$$

$$XeF(B\tfrac{1}{2}) \xrightarrow{\tau_B} XeF(X\tfrac{1}{2}) + h\nu\ (353\ \text{NM}) \qquad (2)$$

$$XeF(C\tfrac{1}{2}) + M \rightarrow XeF(A\tfrac{3}{2},\tfrac{1}{2}) + M \qquad (3)$$

$$XeF(C\tfrac{1}{2}) \xrightarrow{\tau_C} XeF(A\tfrac{3}{2},\tfrac{1}{2}) + h\nu\ (460\ \text{NM}) \qquad (4)$$

$$XeF(B\tfrac{1}{2}) + M \underset{k_e'}{\overset{k_e}{\rightleftharpoons}} XeF(C\tfrac{1}{2}) + M \qquad (5)$$

PROCESSES (1 - 5) $\longrightarrow$ DOUBLE EXPONENTIAL DECAY WITH TIME CONSTANTS

$$\lambda_1, \lambda_2 (k_1,\ k_3,\ \tau_B,\ \tau_C,\ k_e,\ k_e')$$

IN LIMIT $k_e \longrightarrow 0$

(1,2) $\longrightarrow$ SIMPLE EXPONENTIAL DECAY FOR 353 NM

WITH $\lambda_1 = \frac{1}{\tau_B} + k_1 M$

(3,4) $\longrightarrow$ SIMPLE EXPONENTIAL DECAY FOR 460 NM

WITH $\lambda_2 = \frac{1}{\tau_C} + k_3 M$

IN LIMIT $k_e \longrightarrow \infty$

BOTH STATES DECAY WITH SAME TIME CONSTANT

$$\lambda_2 (\tau_B,\ \tau_C,\ k_e,\ k_i)$$

## LASER IMPLICATIONS

- SATURATION FLUX $\Phi_S = \frac{h\nu}{\sigma_{s.e.}} \left(\frac{1}{\tau_B} + \sum_i k q_i Q_i\right)$

FOR Ar + 1% Xe + 0.3% $F_2$ MIXTURES

$\Phi_S$ = 150 kW/cm$^2$ AT 1 ATM

$\Phi_S$ = 230 kW/cm$^2$ AT 2 ATM

- COMPARISION OF OPTICAL EMISSION PROPERTIES AT 351 NM AND 460 NM

| | | |
|---|---|---|
| WAVELENGTH (NM) | 351 | 460 |
| LIFETIME (NSEC) | 18.7 | 113* |
| BANDWIDTH (NM) | 2 | 47* |
| CROSS SECTION(CM$^2$) | $\sim 4\times10^{-16}$ | ~~$\sim 7\times10^{-18}$~~ |

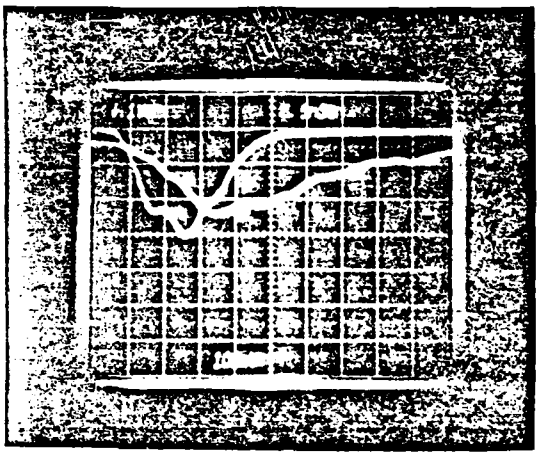
* FROM THEORETICAL CALCULATIONS BY T.H. DUNNING, JR. AND P.J. HAY.

- FOR EFFICIENT 460 NM LASER, MUST FIND MOLECULE M SUCH THAT

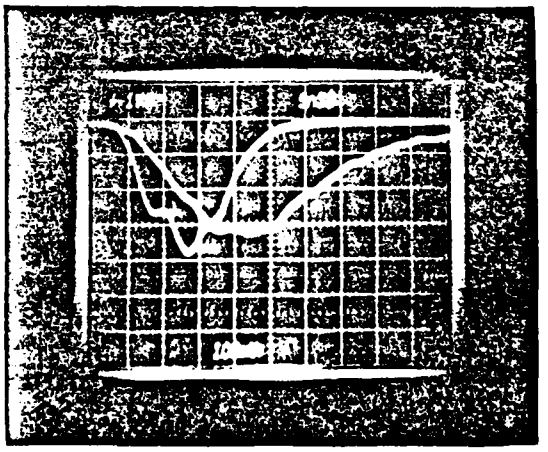
$$XeF(B\tfrac{1}{2}) + M \overset{k_e}{\rightleftharpoons} XeF(C\tfrac{3}{2}) + M$$

WITH $k_e[M] \cdots \frac{1}{\tau_B} + k_q^B Q$

## EFFECT OF XENON CONCENTRATION ON 460 nm FLUORESCENCE



(A) 250 TORR He + 20 TORR Xe + 0.7 TORR $UF_6$



(B) 250 TORR He + 30 TORR Xe + 0.7 TORR $UF_6$

## CONCLUSIONS

(1) Ne IS PREFERABLE TO Ar AS DILUENT

- SMALLER QUENCHING CROSS SECTION
- NO INTRINSIC ABSORPTION (NRL DATA)

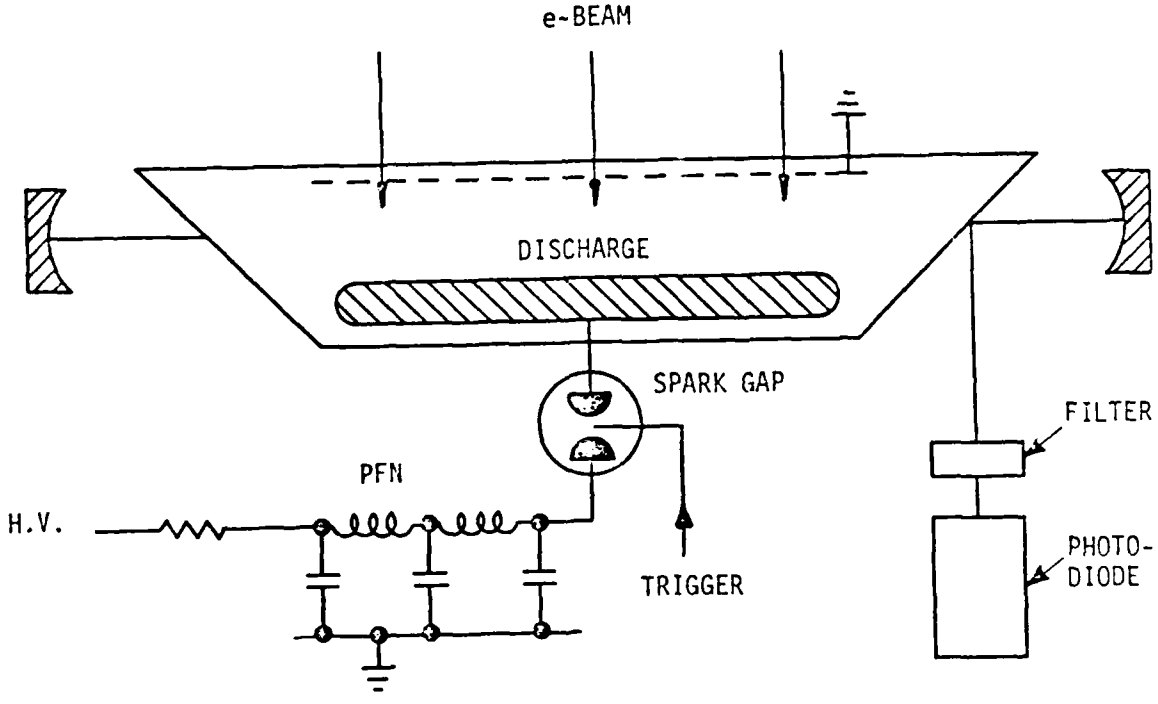
(2) STATE IDENTIFIED LIFETIME MEASUREMENT

$\tau \simeq 18$ nsec FOR B STATE

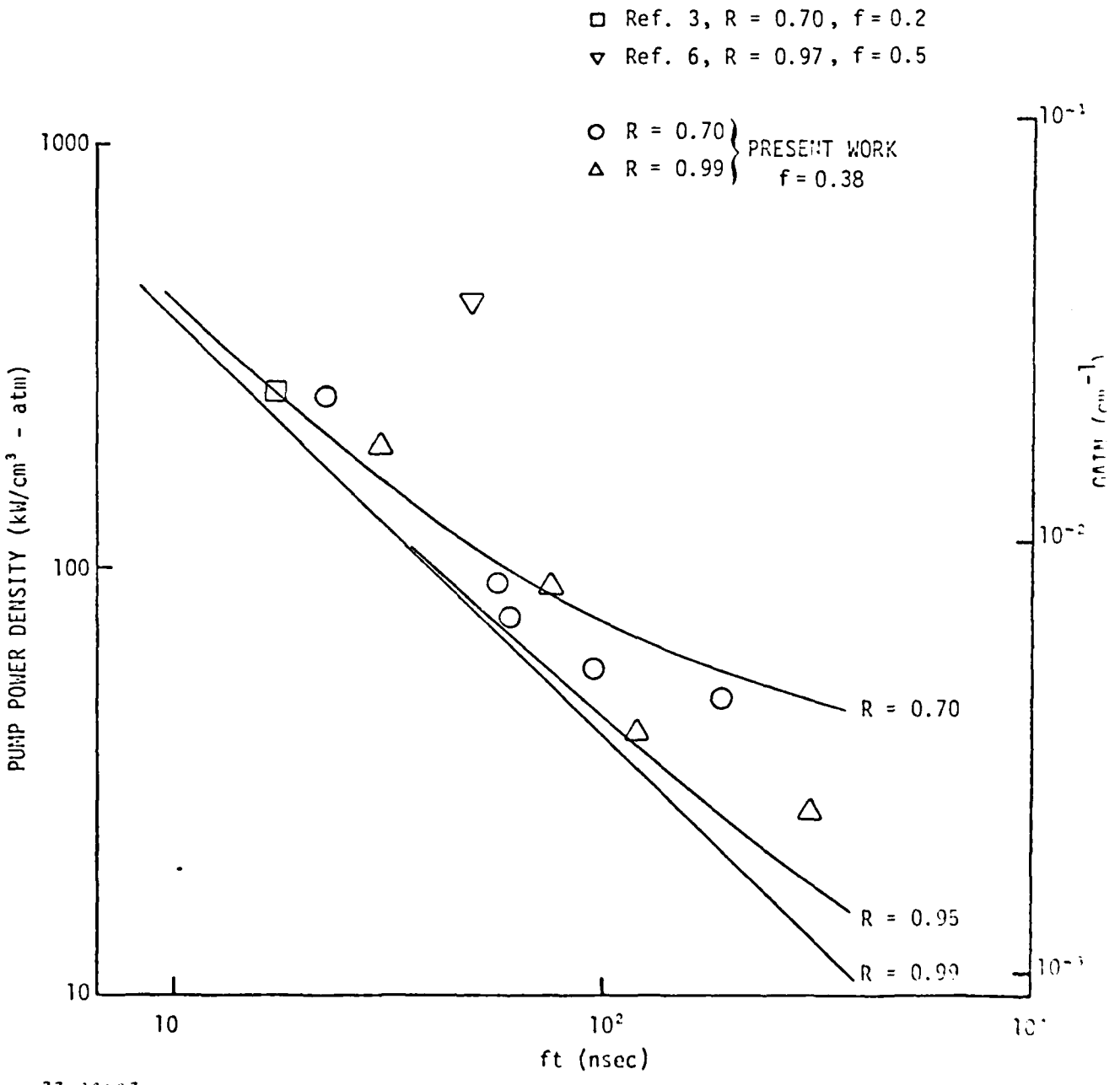
(3) REQUIREMENTS FOR POTENTIAL VISIBLE XeF LASER AT 460 nm

- RADIATIVE LIFETIME MEASUREMENT
- IDENTIFICATION OF EFFECTIVE COLLISION PARTNER TO POPULATE C STATE

# EXPERIMENTAL LAYOUT FOR KrF AND XeF THRESHOLD PUMPING MEASUREMENTS



# THRESHOLD POWER DENSITY MEASUREMENTS IN E-BEAM SUSTAINED DISCHARGES

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If OK prepare approval

Mr. R. H. Register
Contracting Officer
Office of Naval Research
Department of the Navy
800 North Quincy Street
Arlington, VA 22217

Dear Mr. Register:

N00014-76-C-1066 NR 395-568
MSNW Project 1062

Enclosed for your review are 5 copies of an abstract and viewgraphs entitled, "Radiative Lifetime and Quenching Kinetics for the XeF (B 1/2) State," by C. H. Fisher and R. E. Center. We request permission to submit this abstract and viewgraphs for presentation at the Thirtieth Annual Gaseous Electronics Conference, 18-21 October 1977. A paper would not be written for this presentation.

We would appreciate receiving your approval as soon as possible. Thank you for your assistance.

Sincerely yours,

MATHEMATICAL SCIENCES NORTHWEST, INC.

Sally Ann Mowrey

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