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 UF₆ 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, F₂, and NF₃ 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.
MSN W 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 XeF₂
XeF POTENTIAL ENERGY CURVES

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

![Diagram showing potential energy curves for XeF]
EXPERIMENTAL CONCEPT

- **PRODUCE F ATOMS BY FLASH PHOTOLYSIS IN PRESENCE OF Xe**

  \[ \text{e.g. } F_2 + h\nu \rightarrow 2F \]

- **WAIT FOR RECOMBINATION INTO GROUND ELECTRONIC STATE**

  \[ \text{Xe} + \text{F} + (M) \rightleftharpoons \text{XeF}(B_2^1) + (M) \]

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

- **EXCITE XeF(X_2^1) BY XeF LASER ON B-X TRANSITION**

  \[ \text{XeF}_v(X_2^1) + h\nu \rightarrow \text{XeF}(B_2^1) \]

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

  \[ \text{XeF}(B_2^1) \rightarrow \text{XeF}(X_2^1) + h\nu \]

  \[ \text{XeF}(B_2^1) + M \rightarrow \text{XeF}(X_2^1) + M \]
SCHEMATIC DIAGRAM FOR THE OPTICAL SETUP FOR THE
LASER INDUCED FLUORESCENCE EXPERIMENT

XeF LASER
GRATING
FUSED SILICA FLAT

f = 10 cm LENS
f = 30 cm LENS

f = 2.5 cm LENS

0.25 m SPECTROMETER

PHOTOMULTIPLIER

PHOTO-DIODE

3500 Å INTERFERENCE FILTER

TO GAS HANDLING SYSTEM
353 nm FLUORESCENCE FROM
125 TORR He + 10 TORR Xe + 0.7 TORR UF₆

\[ \tau = 11.2 \text{ NSEC} \]
$XeF(B_2^1)$ FLUORESCENT LIFETIME MEASUREMENTS

$\tau = 18.7 \pm 1.4 \text{ nsec}$

![Graph showing decay frequency vs. pressure]
XeF(B1\textsuperscript{3}) QUENCHING BY F\textsubscript{2}

250 TORR He + 10 TORR Xe + 0.3 TORR UF\textsubscript{6}

SLOPE = k\textsubscript{F\textsubscript{2}} = 1.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}
SUMMARY OF XeF(B\textsuperscript{1}\textsubscript{2}) RADIATIVE LIFETIME
AND QUENCHING DATA

- XeF(B\textsuperscript{1}\textsubscript{2}) \( \tau_r = 18.7 \pm 1.4 \) nsec

- XeF(B\textsuperscript{1}\textsubscript{2}) TWO BODY QUENCHING RATE CONSTANTS

<table>
<thead>
<tr>
<th>MOLECULE</th>
<th>( k_q (\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}) )</th>
<th>PRESSURE RANGE (TORR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>2 \times 10^{-12}</td>
<td>75 - 750</td>
</tr>
<tr>
<td>Ne</td>
<td>\leq 1.4 \times 10^{-13}</td>
<td>75 - 750</td>
</tr>
<tr>
<td>Xe</td>
<td>6 \times 10^{-11}</td>
<td>5 - 80</td>
</tr>
<tr>
<td>F\textsubscript{2}</td>
<td>1.2 \times 10^{-10}</td>
<td>0.5 - 24</td>
</tr>
<tr>
<td>NF\textsubscript{3}</td>
<td>3 \times 10^{-12}</td>
<td>15 - 500</td>
</tr>
<tr>
<td>UF\textsubscript{6}</td>
<td>&lt; 1 \times 10^{-11}</td>
<td>0.3 - 2</td>
</tr>
</tbody>
</table>

*PRELIMINARY UPPER BOUND ESTIMATES*
XeF POTENTIAL ENERGY CURVES

T. H. Cunnnin; and F. J. Hay, to be published.
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 UF₆
EFFECT OF Ar CONCENTRATION ON 460 nm FLUORESCENCE

(A) 250 TORR Ar + 10 TORR Xe + 0.7 TORR UF₆

(B) 625 TORR Ar + 10 TORR Xe + 0.7 TORR UF₆
DATA INTERPRETATION

\[ \text{XeF}(B_2^1) + M \rightarrow \text{XeF}(X_2^1) + M \]  \hspace{1cm} (1)

\[ \text{XeF}(B_2^1) \xrightarrow{\tau_B} \text{XeF}(X_2^1) + h\nu \hspace{1} (353 \text{ NM}) \]  \hspace{1cm} (2)

\[ \text{XeF}(A_2^3, 1) + M \rightarrow \text{XeF}(A_2^3, 1) + M \]  \hspace{1cm} (3)

\[ \text{XeF}(C_2^1) \xrightarrow{\tau_C} \text{XeF}(A_2^3, 1) + h\nu \hspace{1} (460 \text{ NM}) \]  \hspace{1cm} (4)

\[ \text{XeF}(B_2^1) + \frac{k_e}{k_e} \xrightarrow{\tau_e} \text{XeF}(C_2^1) + M \]  \hspace{1cm} (5)

Processes (1 - 5) \rightarrow \text{DOUBLE EXPONENTIAL DECAY WITH TIME CONSTANTS}

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

In limit \( k_e \rightarrow 0 \)

(1,2) \rightarrow \text{SIMPLE EXPONENTIAL DECAY FOR 353 NM WITH} \ \lambda_1 = \frac{1}{\tau_B} + k_1M

(3,4) \rightarrow \text{SIMPLE EXPONENTIAL DECAY FOR 460 NM WITH} \ \lambda_2 = \frac{1}{\tau_C} + k_3M

In limit \( k_e \rightarrow \infty \)

Both states decay with same time constant

\[ \lambda_2 (\tau_B, \tau_C, k_e, k_1) \]
LASER IMPLICATIONS

- SATURATION FLUX $\Phi_s = \frac{h\nu}{\delta_{s.e.}} \left( \frac{1}{e_B^s} + \sum_i k_{q_i} Q_i \right)$

For Ar + 1% Xe + 0.3% F₂ mixtures
- $\Phi_s = 150$ kW/cm² at 1 ATM
- $\Phi_s = 230$ kW/cm² at 2 ATM

- COMPARISON OF OPTICAL EMISSION PROPERTIES
  AT 35/νM AND 460 NM

| WAVELENGTH (νM) | 351 | 460 |
| LIFETIME (NSEC) | 18.7 | 113* |
| BANDWIDTH (νM)  | 2   | 47* |
| CROSS SECTION (CM²) | $2 \times 10^{-16}$ | $7 \times 10^{-18}$ |

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

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

  $\text{XeF}(B^1) + M \rightleftharpoons \text{XeF}(C^3) + M$

  WITH $k_e[M] = \frac{1}{e_B^s} + k_B^e Q$
EFFECT OF XENON CONCENTRATION ON 460 nm FLUORESCENCE

(A) 250 TORR He + 20 TORR Xe + 0.7 TORR UF₆

(B) 250 TORR He + 30 TORR Xe + 0.7 TORR UF₆
CONCLUSIONS

(1) Ne IS PREFERABLE TO Ar AS DILUENT
    - SMALLER QUENCHING CROSS SECTION
    - NO INTRINSIC ABSORPTION (NRL DATA)

(2) STATE IDENTIFIED LIFETIME MEASUREMENT
    \( \tau = 18 \, \text{nsec} \) 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

- Ref. 3, R = 0.70, f = 0.2
- Ref. 6, R = 0.97, f = 0.5
- R = 0.70 (PRESENT WORK)
- R = 0.99 (PRESENT WORK)

Graph showing PUMP POWER DENSITY (W/cm² atm) vs. ft (nsec).
30 August 1977

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
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
General Services Manager

SAM:rk
ENC: 5

P.O. BOX 1887 BELLEVUE, WASHINGTON 98009 206-827-0460
RESEARCH ENGINEERING CONSULTING