AD-A214 707

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY *(Leave blank)*

2. REPORT DATE
22 May 1981

3. REPORT TYPE AND DATES COVERED
Final

4. TITLE AND SUBTITLE
SPECTROSCOPIC INVESTIGATION OF LEAD MONOFLUORIDE

5. FUNDING NUMBERS
61102F
2303/B1

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8. PERFORMING ORGANIZATION REPORT NUMBER
AFOSR-TR- [illegible]
1652

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
AFOSR
BLDG 410
BAFB DC 20332-6448

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
AFOSR-80-0019

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release;
distribution unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

DTIC
ELECTE
NOV 29 1989
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14. SUBJECT TERMS

15. NUMBER OF PAGES
6

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT
unclassified

18. SECURITY CLASSIFICATION OF THIS PAGE
unclassified

19. SECURITY CLASSIFICATION OF ABSTRACT

20. LIMITATION OF ABSTRACT

NSN 7540-01-280-5500

1

Standard Form 298 (890104 Draft)
Prescribed by ANSI Std. 239-18
298-01

1652

[illegible] [redacted]

OBJECTIVE: The study of the state structure, lifetime and quenching of lead monofluoride produced in a flame of lead vapor and molecular by laser-induced fluorescence.

STATUS: The proposed research was directed toward the evaluation of PbF as an electronic transition chemical laser candidate. This study was initiated by the principal investigator during the 1978 USAF-ASEE Summer Faculty Research Program (1).

The proposed research consisted of (1) chemiluminescence studies, and (2) laser-induced fluorescence studies of the PbF $A^2\Sigma$ state.

(1) Chemiluminescence - The $A^2\Sigma$ excited state of PbF is of interest for a chemically-pumped laser because of its large ground state splitting (8270 cm^{-1}). Dickson and Zare observed chemiluminescence from the $A^2\Sigma \longrightarrow X^2\Pi_{\frac{1}{2}}$ transition but they reported no evidence for $A^2\Sigma \longrightarrow X^2\Pi_{3/2}$ emission in the beam-gas chemiluminescence spectrum (2). The proposed research was to concentrate on the observation of chemiluminescence from the $A^2\Sigma \longrightarrow X^2\Pi_{3/2}$ system. The PbF would be produced in an electronically excited state by the reaction of atomic Pb with F_2 gas. Atomic lead would be generated in an evacuated chamber by resistively heating lead metal in a tungsten crucible. Helium carrier gas would enter the reaction chamber around the outside of the crucible through a ring and carry the atomized Pb up through a throat where fluorine (mixed with diluent) would be injected through a concentric ring. Mixing would occur at the injection ring and a chemiluminescent flame would result. Chemiluminescence would be monitored through a viewing port with a scanning monochromator and a photomultipler.

(2) Laser-induced fluorescence - These studies were to utilize the previously described burner as a source of ground state PbF molecules.

Two types of experiments were planned: an excitation spectrum of PbF would be obtained and radiative lifetimes of the $A^2\Sigma$ state would be measured with time-resolved fluorescence spectroscopy. Lifetimes of the $A^2\Sigma$ state would also be determined for several pressures of added foreign gases and quenching rate coefficients would be evaluated.

A nitrogen laser-pumped dye laser would be used as the excitation source because of its short duration, high intensity, narrow linewidth, tunable output. Long sidearms with Brewster-windows would be attached to the reaction chamber for passage of the laser beam and laser-induced fluorescence would be monitored at right angles with a photomultiplier. The photomultiplier output would be amplified and fed to a boxcar signal averager for signal averaging and recovery of the fluorescence decay waveform. The curve would be displayed on a recorder.

The plan was to measure the lifetime of the $A^2\Sigma$ state while pumping transitions to excited vibrational levels from the lowest vibrational level in the ground state, $X^2\Pi_{\frac{1}{2}}$. The lifetime of the $A^2\Sigma$ state would also be measured while pumping from the $X^2\Pi_{3/2}$ ground state. Resolution of the laser-induced fluorescence in either case would also provide useful data.

Experiments were planned to measure the thermalization of the ground state. The lowest vibrational level of the $A^2\Sigma$ state would be pumped out of successive vibrational levels of the $X^2\Pi_{\frac{1}{2}}$ ground state

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(i.e., $v'' = 0 \longrightarrow v' = 0$, $v'' = 1 \longrightarrow v' = 0$, $v'' = 2 \longrightarrow v' = 0$, etc.) in a series of experiments and the fluorescence intensity in each case would be measured. The fluorescence intensity measured in each experiment depends upon the lifetime of the excited state, the population of the lower transition state, and the Franck-Condon factors for the specific transition. Since the lifetime will be the same in all cases, the relative populations of the vibrational levels could be predicted if the Franck-Condon factors were known. The "vibrational temperature" of the ground state will be important information in the determination of the suitability of PbF for a chemical laser.

We planned to study the time evolution of fluorescence under a variety of conditions. Quenching rate coefficients for various gases are important if a PbF chemical laser is to be developed. Quenching coefficients can be evaluated from Stern-Volmer plots of lifetime data taken in various environments. First the total product quenching would be studied as a function of pressure. The pressure could be varied by choking the flow with a valve on the downstream side of the reaction chamber. The amount of quenching of the $A^2\Sigma$ state must be known for gases that may be produced or used in a chemical laser system. Quenching measurements would be made for helium, nitrogen, CO, and SF_6. Helium was to be used as the carrier gas for the Pb atoms and diluent for fluorine. Nitrogen might also be a possible carrier gas for a chemical laser and will be an atmospheric pollutant for an evacuated chemical laser. The molecules CO and SF_6 have many vibrational degrees of freedom and either may be used in a chemical laser as an energy sink to deplete higher vibrational levels to maintain the PbF molecule in the lowest ground state. Data from quenching studies would be useful in determining if the $X^2\Pi_{3/2}$ and $X^2\Pi_{1/2}$ doublet can be kept thermal under chemical laser conditions.

Several factors have prevented satisfactory progress on the proposed research. The construction of the experimental apparatus was 80% complete by February 1981. Earlier completion of the apparatus was delayed because the vacuum pump did not arrive until October 10, 1980. During this delay, inflation caused the price of supplies such as the fluorine/helium mixture to escalate much more than was anticipated in the budget. The fluorine mixture was not purchased sooner because of the safety considerations involved in storing toxic, reactive gases in a centrally-located campus laboratory. We submitted a proposal to the University of Arkansas during the Fall 1980 seeking internal funds to supplement the remaining money ($524.16) from the original starter grant. This request for $3000 for supplies and shop labor was subsequently rejected. In the interim, a University of Arkansas physical plant estimate for routing a 230 volt, 3-phase, 30 amp line into the lab for the vacuum pump was quoted at $2,200. At this point, the feasibility of completing this work became doubtful.

When I submitted this proposal for a starter grant, I recognized the possibility that the available funds would be inadequate. For this reason, the entire $10,000 grant was committed to the purchase of the necessary equipment and supplies. Even then, the work could only be completed with the loan of a nitrogen laser from Kirtland Air Force Base. We requested no salary for personnel to implement this project. It is now clear that the available funds were indeed inadequate to upgrade our facilities and complete the proposed research. After we had exhausted all reasonable possibilities which would have allowed timely continuation of the proposed work, we regrettably concluded that the interests of everyone concerned would be best served by termination of AFOSR 80-0019. This termination was mutually agreed to by all parties and was effective March 20, 1981.

REFERENCES:

1. R.B. Green, L. Hanko, and S.J. Davis, Chem. Phys. Lett. 64, 461 (1979).
2. C.R. Dickson and R.N. Zare, Opt. Pura Apl. 10, 157 (1977).

PUBLICATIONS: None

PERSONNEL: Principal Investigator - Robert B. Green

INTERACTIONS: None

DISCOVERIES, INVENTIONS, PATENTS: None

OTHER STATEMENTS: The vacuum pump, monochromator, and nitrogen laser were shipped to Kirtland Air Force Base on March 9, 1981 as instructed.