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INVESTIGATION OF CONCEPT OF EFFICIENT SHORT WAVELENGTH LASER

QUARTERLY PROGRESS REPORT

1 August 1978 - 31 October 1978

L.G. Piper, R.H. Krech, E.R. Pugh and R.L. Taylor

1 December 1978

Prepared for
U. S. Department of Energy
Office of Laser Fusion
under Contract No. ES-77-C-03-4223-A002

PHYSICAL SCIENCES INC.
30 COMMERCE WAY, WOBURN, MASS. 01801

DISCLAIMER

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E&B

I. INTRODUCTION

Under this contract, Physical Sciences Inc. is investigating a concept for the development of an efficient short wavelength laser based on a class of endoergic molecules-azides. Because these latter compounds contain substantial chemical energy, they offer a potentially more efficient approach for the production of electronically excited molecules. During the past year we have acquired sufficient data and understanding of certain kinetic and spectroscopic processes to permit the design of two proof-of-concept experiments. In the present year's program, of which this is the second quarterly report, we will be concentrating upon these two proof-of-concept experiments, with some additional supporting measurements on the kinetics and spectroscopy of these azide laser media as required for data interpretation and analysis.

The first of these two laser-device experiments involves generating high concentrations of azide radicals in the thermal pyrolysis of solid, ionic azides, with the subsequent excitation of the $N_2(B^3\pi_g)$ state from azide-radical recombination. Laser action would then take place upon the $N_2(B^3\pi_g - A^3\Sigma_u^+)$, first-positive transition. The second laser-demonstration experiment involves creating a high density of $NCl(b^1\Sigma^+)$ state by uv photolysis of ClN_3. In this case laser emission is expected on the $NCl(b^1\Sigma^+ \rightarrow X^3\Sigma^-)$ transition at 665 nm.

During this reporting period preliminary experiments on both of these systems are underway. In the pyrolysis approach, initial emphasis has been placed on techniques to produce uniform, thin metallic films on ceramic substrates. In the photolysis experiment, considerable work has been performed on azide gas generation, handling, and purity. In addition, sensitive spectrometric diagnostics have been developed to detect $NCl\ (b^1\Sigma^+)$ fluorescence. These results are briefly described in this report.

II. SOLID AZIDE LASER DEMONSTRATION EXPERIMENT

In this laser demonstration experiment, high concentrations of azide radicals ($\sim 10^{17}$ mol-cm^{-3}) are to be generated by the rapid thermal pyrolysis of a thin ($\sim$1 micron) layer of sodium azide. This latter compound is coated on a metalized ceramic substrate. The rapid heating is provided by passing a pulse of current through the metallic film. Gas phase recombination of the N_3 radicals is expected to produce $N_2(B^3\pi_g)$ state, and laser action is anticipated on the $N_2(B^3\pi_g \rightarrow A^3\Sigma_u^+)$ first-positive transition.

In the previous quarterly report, we have described the apparatus constructed for the pyrolysis laser demonstration experiment, and the results of the initial tests of the thin-film metalized ceramic heater. In summary, the first heater, which consisted of a 12 micron layer of an 80% molybdenum/20% manganese sintered metallic coating on an alumina support ceramic, became severely pitted and fissured after several firings from arcing across surface irregularities and unevenness. Subsequently, it was decided that future plating attempts would be made by painting an organoplatinum solution on the ceramic substrate and air firing this coating at high temperature. This technique pyrolyzes the organic substitutants and produces platinum coatings with a bright mirror surface and a thickness of about 3000Å. Thicker films are made by multiple coatings and firings. The solution chosen for the plating is manufactured by Engelhard Minerals and Chemical Corporation of New Jersey and is commercially marketed as Platinum Bright 05X. It consists of a mixture of organoplatinum compounds and solvents containing 7-1/2% platinum by weight. Similiar solutions are used in the manufacture of the ceramic heating elements of electric ranges for home use. A 30" three zone tube furnace with a temperature rating of 1300°C has been obtained to perform

the firings. Initial testing of the platinized ceramic heater is expected to begin in the next quarter.

III. CHLORINE AZIDE LASER DEMONSTRATION EXPERIMENT

This approach is based on the photolysis of ClN_3 gas to efficiently produce NCl ($b^1\Sigma^+$) state, with lasing expected on the metastable NCl ($b^1\Sigma^+ \rightarrow X^3\Sigma^-$) transition at 665 nm. Previous experiments have shown that NCl ($b^1\Sigma^+$) state is generated from ClN_3 by uv photons, and therefore, a laser demonstration using dual coaxial flashlamp initiation has been assembled. Due to the endoergic nature of chlorine azide, a more efficient initiation technique such as multiphoton infrared photolysis can be developed. Recent experiments have demonstrated[1] that infrared multiphoton photolysis of HN_3 and DN_3 produces the electronically excited nitrenes, HN and DN.

The apparatus that has been assembled for this laser demonstration experiment was described in the previous quarterly report. Briefly, it consists of a dual coaxial flashlamp assembly with an active volume of 100 cm^3 and 50 cm arc length. Each of the lamps provides about 25 to 50 J of uv radiation in the 200 - 275 nm band pass which should be sufficient to completely photolyze 10 to 30 torr of ClN_3. A stainless steel gas generator and gas handling system is attached to the laser head. Experimental diagnostics include a fast response uv vacuum photodiode to monitor flashlamp output, a piezoelectric pressure transducer to measure the pressure history of the flash initiated ClN_3 explosion, a variable reluctance pressure transducer to measure initial and final static pressure in the laser cavity, a photoelectric monochrometer to observe NCl fluorescence, and a 1.26-meter SPEX spectrometer to record photographic spectra.

The technique selected for the generation of chlorine azide is due to Raschig[2] as modified by Gleu[3]. As an aqueous solution of NaN_3 and NaOCl is acidified, ClN_3 gas is evolved. The overall stoichiometry of the process can be represented as:

$$NaOCl + NaN_3 + H_2SO_4 \rightleftarrows ClN_3 + Na_2SO_4 + H_2O\,. \qquad (1)$$

The rate of evolution (and hence the pressure) of chlorine azide is easily controlled by adjusting the rate of acidification. In principle, the technique appears to be readily scalable for continuous generation of large quantities of pure ClN_3.

The initial experiments consisted of filling the laser cavity with 10 to 15 torr of ClN_3, flashing the lamps, and attempting to lase in a high Q cavity. Not surprisingly, these experiments failed, so the cavity was removed and a monochrometer installed to monitor the NCl fluorescence. Unfortunately, the only radiation observed in the vicinity of 665 nm was flash lamp self-emission. Additionally, the pressure measurements indicated only about a 50 to 75% increase in gas pressure after photolysis. The complete decomposition of ClN_3 into Cl_2 and N_2 should result in a doubling of the gas pressure. Chlorine azide is known to be a very unstable gas and once the decomposition is initiated, the entire volume is expected to decompose. The failure to observe nitrene fluorescence coupled with the smaller than expected pressure rise strongly suggests that the ClN_3 was not pure. Gaseous samples were taken and infrared spectra recorded. These were compared to the IR spectra of gaseous azides taken previously by Rice[4]. This comparison produced two facts: First, the amount of ClN_3 in the sample generally agreed with the pressure data which could indicate the presence of an unknown gas that does not have an identifiable IR spectrum (i.e., O_2 or Cl_2). Second, under some conditions, considerable HN_3 was found in the ClN_3 samples. It should be noted that HN_3 will also be photolyzed in the uv and lead to a pressure doubling, but, of course, it will not generate NCl.

At this point the ClN_3 preparation procedures were re-examined and after some effort, it has been determined that by starting with a basic solution of azide/hypochlorite (with more hypochlorite than azide) the generation of HN_3 is suppressed. The IR spectrum of the gas generated

under these conditions shows no HN_3, and upon photolysis the pressure rise indicates that the total gas purity was ≥ 85%. Due to certain dead volumes of gas remaining in the supply lines, greater accuracy from these pressure data is not possible. Mass analysis of the gas samples is now being performed to search for impurities such as Cl_2 and O_2.

While this analytical effort was underway, additional improvements to the diagnostics were also developed. A photographic spectrometer replaced the monochrometer. With greater spectral resolution and the potential ability to observe lines and bands on film in the presence of a background continuum, the spectrometer should help in locating the fluorescence emission from chloronitrene. Then, more quantitative measurements can be performed photoelectrically. One initial benefit that has already accrued from the spectrometer has been the ability to document the direct radiation from the flashlamps. By suitable improvements in the optical train, this continuum has been largely suppressed.

We are now in a position to resume the experiment with (i) a better technique for preparing pure chlorine azide, (ii) analytical techniques to monitor purity, and (iii) significant improvements in the optical diagnostics. Experiments to look for NCl fluorescence are currently underway.

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