63-3-1

(11) (Rept. no. 8657-6006-RU000)

(1)

(6) LIQUID LASER RESEARCH

(7) BIMONTHLY PROGRESS REPORT NO. 5

Nov. 1 ~~to~~ Dec. 31 ~~1962~~

SPACE SYSTEMS DIVISION

AIR FORCE SYSTEMS COMMAND

(9) 31 Dec 62, (10) 9p. incl. Tables

(12) Contract ~~No~~. AF 04(695)-97

(13) NA

(8)

Maurice W. Windsor

Prepared by:
Maurice W. Windsor
Section Head

R. B. Muchmore

Approved by
R. B. Muchmore
Division Director

Quantum Chemistry Section
QUANTUM PHYSICS LABORATORY
Physical Research Division

819510 (5) Space Technology Laboratories, Inc.
One Space Park
Redondo Beach, California

$1.10

I. Research Summary

Research Work was performed in the following areas: ~~carried out during this period can be summarized under four headings:~~

(1) Laser Experiments in Low-Temperature Organic Glasses,
(2) Quantum Yield Measurements,
(3) Solvent and Environmental Effects, and
(4) Preparation of New Chelates.

A. Laser Experiments in Low-Temperature Organic Glasses

High intensity flash experiments on solutions of europium and terbium chelates in frozen organic glasses at 77°K have been continued. The previously described llaser cell with confocal dielectric-coated mirrors was used. It has been shown that the double-peaked emission curves, illustrated in Figures 9 and 10 of the Semi-Annual Progress Report and tentatively attributed at that time to stimulated emission, are probably caused by oscillations in the light output from the xenon flash lamp used to pump the sample. At a given filling pressure (2cm of Hg say) a second peak becomes apparent in the light output at a certain critical energy (say about 6000 joules). The size of the second peak increases as the energy input to the lamp is increased. The critical energy for appearance of the second peak depends on the pressure in the lamp and the temperature. At lower pressures and lower temperatures, (e.g. 77°K), the second peak appears at lower energy; at 6cm pressure and room temperature, on the other hand, no second peak is detectable, even at the highest energies employed (11,000 joules). The light oscillations may be connected with shock-wave phenomena occurring in the lamp at low gas densities.

Although the majority of the observations can be accounted for by the above phenomenon, there remain a few experimental results which cannot entirely be explained along the above lines. For example, in one experiment with Terbium chelate the size of the second peak progressively decreased with repetitive flashes of equal

energy. Subsequent examination showed the glass to be full of small bubbles. This behavior is suggestive of laser action, followed by progressive spoilage of the cavity Q as bubbles are formed, thus leading to a decreased output. In all experiments since that time, the flash lamp output has been monitored with a separate photocell, so that it may be compared directly with the emission from the sample under study.

Dielectric coated mirrors of high reflectivity and which are not soluble in the organic solvents used in our work, have been obtained from Keim Mirror Inc. Mirrors with maximum reflectivity at 4450A (benzophenone) 5450A (terbium) and 6250A (europium) are now on hand.

In order to verify the optical quality of the confocal laser cavity at 77^{o}K, an unsilvered ruby was mounted in the brass jig, using confocal dielectric mirrors which had been aligned at room temperature. The cavity was then cooled to liquid nitrogen temperature with an air gap between the mirrors and the ruby. Stimulated emission was observed with a threshold of 6,000 joules. The ruby was then embedded in various low temperature glasses. The threshold for stimulated emission increased to about 7,200 joules. This rather small increase may be attributed to birefringence and bubbles in the low temperature glasses, since the ruby took up only 4cm of the 8cm path length between the confocal mirrors, the remaining path being through the frozen glass. The above experiment is important in showing that the frozen organic glasses are of fairly good optical quality. Studies are presently being conducted using crossed polaroids to detect and minimize strains. In addition, degassed solutions are being used, in order to retard the formation of bubbles upon flashing.

Recent theoretical work of Boyd and Gordon (1) has shown that the field of a confocal resonator is, in the lowest order mode, largely concentrated along the axis of the cavity. Calculations for our system show that samples greater than about 1mm in diameter

waste pump power, since the field is very weak outside this diameter. Accordingly, several cylindrical glass and cross-linked plastic inserts have been fabricated. These have axial holes bored through them varying in diameter from 1mm to 3mm. These inserts will be used in future laser experiments, embedded in the organic glass between the confocal reflectors. In this way the majority of the pump light will penetrate to the narrow central core without being attenuated by absorption in the outer layers.

B. Quantum Yield Measurements

The construction of apparatus for measuring quantum yields has been completed and techniques have been developed for measuring absolute quantum yields of fluorescence. The method is based on that due to Weber and Teale (2). However, instead of glycogen, as in their work, a colloidal solution of silica (Ludox) in water is used as a scattering standard of unit yield. The subsequent experimental program has included checking the literature values for the quantum yields of solutions of fluorescein and anthracene. These results together with the previously unknown quantum yield of Europium benzoyl acetonate (EuB_3) in solution appear in Table I.

The agreement of our values of the quantum yield of fluorescein and anthracene with the literature establishes the accuracy of the method for medium and high values of quantum yield. The quantum yield of uranyl acetate will be measured and compared to the literature value of 0.04 to define the accuracy of our procedures for low values of quantum yields. This is especially necessary to confirm or disprove the surprisingly low quantum yield from EuB_3. The quantum yield of EuB_3 should also be measured at higher concentrations in solution by another method, to establish whether the low yield of fluorescence from EuB_3 is due to dissociation or decomposition of the chelate in dilute solutions.

TABLE I QUANTUM YIELD MEASUREMENTS

Fluorescent System (nondegassed and at 21°C)	Detector	STL Values Quantum Yield	Literature Values Workers	Quantum Yield
Fluorescein in 0.1N NaOH	Rhodamine integrating solution in front of photomultiplier.	0.97	Weber and Teale	0.92-0.93
Fluorescein in 0.1N NaOH	Calibrated photomultiplier	0.90	Weber and Teale	0.92-0.93
Anthracene in Benzene	Calibrated photomultiplier	0.236	Bowen	0.19
			Melhuish	0.216
Europium Benzoylacetonate in isopentane	Calibrated photomultiplier	0.022	--	None reported

Measurements of relative yields for EuB_3 have also been made in methyl-cyclohexane as a function of temperature. Results are as follows.

Temperature ^{o}K	Relative Yield
300	1
273	small increase
196	3
77	6

Thus, accepting the figure of 2.2% obtained above for EuB_3 in isopentane, we conclude that in a frozen isopentane glass at $77^{o}K$, the absolute fluorescence yield would be 13.2%.

C. Solvent and Environmental Effects

The relative intensities of chelate emission in various solvents have been measured for europium tris benzoylacetonate (EuB_3), europium tris dibenzoylmethide (EuD_3), terbium trisdibenzoylmethide (TbD_3), and terbium benzoylacetonate (TbB_3). For these solutions, 3650A light was used to excite the sample. In addition, several rare earth acetylacetonates(EuA_3, TbA_3, SmA_3 and DyA_3) have been procured recently and are presently being investigated. These latter chelates are excited with 3100A light. The recorded intensities are for oxygenated solutions, although some degassed samples were observed.

Table II summarizes the data taken at room temperature. The dibenzoylmethide compounds were not soluble in hydrocarbon solvents except cyclohexane. In comparable solvents, EuB_3 always gave a brighter emission than EuD_3. The terbium benzoyl acetonate gave no emission in any solvent at room temperature except mineral oil, and then only in low yield.

TABLE II

RELATIVE INTENSITITIES OF CHELATE EMISSION

IN VARIOUS SOLVENTS

Relative Intensity		EuB_3 (10^{-4}M)	EuD_3 (10^{-5}M)	TbB_3 (10^{-4}M)
10	Very Bright	Mineral Oil	---	
6	Good Emission	Isopentane n-hexane Cyclohexane Methylcyclohenone Toluene Benzene Glycerol	Toluene Benzene Cyclohexane	
1	Poor Emission	Xylene Ethanol Dioxane	Xylene Ethanol	Mineral Oil

The temperature dependence of fluorescence for both europium benzoylacetonate and terbium benzoylacetonate in mineral was measured from -30°C to room temperature. The terbium chelate shows a much greater increase in intensity with decreasing temperature than does the europium chelate.

Decomposition or dissociation of the chelates appears to occur in polar solvents such as ethanol, resulting in a pronounced drop in emission intensity. Slight decomposition over a period of several days occurs also in hydrocarbon solvents. This is reduced on degassing the solvent. In general the B_3 compounds are more stable than the corresponding D_3 compounds. It is expected that the A_3 compounds will show better stability still.

In conclusion, it appears that hydrocarbon solvents of high viscosity lead to the highest fluorescence yields, probably because of reduced collisional quenching of the triplet state in the viscous environment. Mineral oil should therefore be an early candidate as a solvent system for a liquid laser when suitable compounds have been discovered.

D. Preparation of New Chelates

Acetylacetonates of Eu, Tb, Sm and Dy have been prepared for us by Professor Crosby under his consultant agreement. These compounds are under evaluation as described above. Other new compounds which may be worthy of study are the bipyridyl and orthophenanthroline complexes. In addition, Crosby and coworkers have made lifetime measurements of the emission of the D_3 and B_3 compounds of Eu, Tb, Sm and Dy in several rigid glass systems at 77°K. Lifetimes vary from about 12μsec for DyB_3 to over 700μsec for TbB_3. Samples of NdB_3, NdD_3, SmB_3 and SmD_3 have also been obtained recently from a commercial source.

References

1. Boyd, G. D. and J. P. Gordon, Bell System Tech. Journal 489, (March, 1961).

2. Weber, G. and F.W.J. Teale, Trans. Faraday Soc., 53, 646 (1957).

II. Fiscal Information and Data (in K$)

	Current Period 11/5 - 12/30	Cumulative 12/30	Programmed Cost
Direct Labor	6.7	39.5	56.0
Overhead	6.5	37.9	56.0
Other Direct Costs	0.7	7.5	10.8
G and A	1.4	7.9	12.2
Total Costs	15.3	92.8	135.0
Fee	1.6	7.9	9.5
Costs + Fee	16.9	100.7	144.5

Man Hours 11/5 - 12/30	1456.8
Man Hours Cumulative	8206.8

III. Key Personnel

Dr. M. W. Windsor
Dr. W. R Dawson
Dr. J. L. Kropp
Mr. J. R. Novak
Mr. R. S. Moore
Professor G. A. Crosby (consultant)

DISTRIBUTION

STL

S. Altshuler
J. M. Andres
J. T. Bevans
R. C. Booton
R. Bromberg
W. Carlson
H. C. Corben
W. R. Dawson
J. M. Denney
A. S. Fulton
B. T. Haffey
J. Holland
A. Krausz
J. L. Kropp
D. B. Langmuir
W. Marrison
R. S. Moore
R. B. Muchmore
J. R. Novak
W. J. O'Sullivan
S. A. Pollack
A. F. Podlesak
W. A. Robinson
J. L. Rogers
F. E. Romie
A. Rosen
M. Silver
P. Staudhammer
D. Weber
R. M. Whitmer
M. W. Windsor
R. S. Witte
Patent Office

AEROSPACE CORP.

M. Birnbaum
T. S. Hartwick
V. Josephson
J. Munushian
M. T. Weiss
P. Kisliuk

SSD/AFSC

Capt. R. D. Eaglet (3 copies)

SCHOOL OF AEROSPACE MEDICINE

Col. J. E. Pickering (1 copy)

Professor G. A. Crosby
University of New Mexico