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INVESTIGATIONS OF WATER SOLUTIONS OF EUROPIUM CHELATES AS LASER MATERIALS

Semiannual Technical Summary Report

1 July 1965 - 31 December 1965

Issued: 31 December 1965

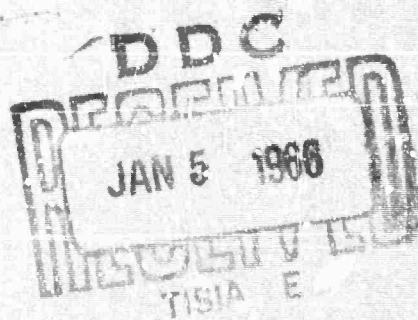
E. P. Riedel

R. G. Charles

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PITTSBURGH, PENNSYLVANIA 15235

Contract No. Nonr-5033(00)

ARPA Order No. 306



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ABSTRACT

Because heavy water should be a superior liquid laser solvent, studies of various systems soluble in heavy water have been emphasized.

In order to obtain materials which can be efficiently optically pumped in large volumes of practicable dimensions, two different approaches have been employed. The first is to form mixed ligand complexes in solution. This modifies the absorption band of the chelate directly. Two systems of this type are described. The second approach is that of utilizing intermolecular energy transfer in solution. We have demonstrated, for the first time, intermolecular energy transfer in heavy water solutions. Two systems of this type are described. The use of heavy water as a solvent and the use of intermolecular energy transfer to solve the problem of efficient optical pumping appears to be the most promising approach to the development of a high radiance liquid laser.

Studies of systems soluble in organic solvents have aided in the development of systems in heavy water. The organic cation has been shown to have an important effect on the laser threshold of solutions of europium benzoyltrifluoroacetate. A series of new europium chelates have been synthesized and some of their properties studied. Laser operation has been achieved with three of these new europium chelates in acetonitrile. The effects of scattering on laser performance are shown to be large for these systems soluble in organic solvents.

1. INTRODUCTION

The last report of liquid laser research at Westinghouse was the Final Technical Summary Report on contract Nonr-4573(00) issued 31 December 1964. This report summarized the work done at Westinghouse with both government and Westinghouse funds from 1961 up to the end of 1964. Since contract Nonr-4573(00) did not begin until 1 July 1964, most of this work was conducted with company funds. The present report summarizes the work done during 1965 with both company and government funds. Again, most of these studies have been performed with company funding.

There are two serious problems with existing liquid lasers. First, the cross section at the peak of the absorption bands of the chelates employed are too high to be utilized effectively in pumping many proposed laser systems. Secondly, existing liquid lasers employ organic solvents which have comparatively large values of refractive index change with respect to temperature, dn/dT . During optical pumping, this leads to severe light scattering effects within the laser material. Both of these problems were pointed out in the last report. As discussed in that report, it appears that the use of heavy water as the solvent for liquid lasers would result in a laser matrix with far better optical qualities than organic solvents and in fact, better than most crystalline materials as well. Basically, this is because changes in refractive index due to temperature and stress optical effects are essentially zero for heavy water near 6°C . For this reason, the goal of the liquid laser research at Westinghouse has been the development of a laser employing heavy water as a solvent. Studies of systems soluble in heavy water are described in Section 2 of the present report.

It appears that there are two basic ways of approaching the absorption band problem. These are discussed in Section 2.1.

2. SYSTEMS SOLUBLE IN HEAVY WATER

In order to develop systems with more suitable absorption properties for optical pumping purposes, the work discussed in Section 2 was performed. The studies described in Sections 2.2 and 2.4 were begun with Westinghouse funds. This work was finished under the present contract. The studies summarized in 2.3 were performed under the present contract.

2.1 Ways of Solving the Optical Pumping Problem for Liquid Lasers

As mentioned in the introduction, one of the two important problems with existing liquid lasers is the poor efficiency with which these solutions convert flash lamp light to europium ion population inversion. There appears to be two separate approaches to this problem. The first is to modify the europium-containing species in solution so that part of the molecule possesses absorption bands suitable for efficient laser pumping. This approach, although certainly a feasible one in principle, has proven to be quite difficult. Basically, this is because all of the laser requirements of high quantum efficiency, good solubility, good absorption characteristics, etc. are imposed on one species. While it is fairly easy to satisfy some of these requirements it is difficult to satisfy all of them simultaneously in one molecule.

The second approach is to utilize the process of intermolecular energy transfer in solution. Here one species (the sensitizer) absorbs the flash lamp light and transfers part of this energy to a separate lasing species (the activator). This approach has the fundamental advantage that it relaxes the requirements placed on the lasing species. That is, it no longer must possess satisfactory laser pump bands. In addition, the concentration of the sensitizer may be adjusted essentially independently of that of the activator. This allows one

to adjust the concentration of the sensitizer to a desirable level for its absorption cross section to efficiently absorb the flash lamp light. For example, if the laser solution diameter to be pumped is d and the cross section near the peak of the sensitizer absorption band is σ , the number of ions per unit volume of the sensitizer needed to make efficient use of the pump light is about $1/\sigma d$. The process of intermolecular energy transfer is known to be strongly dependent on the distance R between the sensitizer and activator. If the transfer process is of the dipole-dipole resonance type, the probability of transfer of energy⁽¹⁾ from the sensitizer to the activator is proportional to $(R_0/R)^6$ where R_0 defines the range for efficient transfer. In order to maximize the transfer process from this point of view, the concentration of activators should be adjusted so that every sensitizer has at least one activator within the sphere of radius R_0 . These requirements can be satisfied in solution. Efficient transfer has been shown to take place in organic solutions to rare earth ions⁽²⁾⁽³⁾.

2.2 Intermolecular Energy Transfer in Heavy Water: System I

We have shown intermolecular energy transfer to exist between the p-benzoylbenzoate anion $(p-BB)^-$ and europium ethylenediaminetetraacetate $Eu(EDTA)^-$ in heavy water solution. A paper which describes this system in detail has been accepted for publication in the Journal of Chemical Physics. This paper is included in this report as Appendix A. This system does not lase; presumably because of photodecomposition of $(p-BB)^-$. However, the system is important in that it demonstrates for the first time that efficient intermolecular energy transfer can take place in heavy water. When ultraviolet light is absorbed by the $(p-BB)^-$ ion, part of the absorbed energy is transferred to

$\text{Eu}(\text{EDTA})^-$. Narrow line fluorescence characteristic of the europium ion in $\text{Eu}(\text{EDTA})^-$ is then observed. The overall quantum efficiency of this process at room temperature has been shown to be as high as 20%.

2.3 Inter and Intramolecular Energy Transfer in Heavy Water: System II

The successful demonstration of intermolecular energy transfer in heavy water between p-benzoylbenzoate and $\text{Eu}(\text{EDTA})^-$ has encouraged the search for other materials which will sensitize $\text{Eu}(\text{EDTA})^-$. At first glance, materials which are known to form relatively insoluble complexes with Eu^{+3} in water might be excluded from such a search. The benzoyltrifluoroacetone anion $(\text{BTF})^-$ is such a material forming the relatively insoluble $\text{Eu}(\text{BTF})_3$ in water. However, if the absorption cross section of the sensitizer is high, the required concentration of the sensitizer for efficient laser pumping will be low. In fact, the required concentration may be so low as to be within the solubility limits of the system. For example, the molar absorption coefficient ϵ for the $(\text{BTF})^-$ anion at the peak of the absorption band at $3200\text{\AA}$ is about 1.5×10^4 . If the penetration depth, d , defined by $1/\alpha$ where α is the absorption coefficient at $3200\text{\AA}$ is to be one centimeter, then the concentration of $(\text{BTF})^-$ must be $1.8 \times 10^{16} \text{ cm}^{-3}$. We have investigated mixtures containing $\text{NaEu}(\text{EDTA})$ at a concentration of $6 \times 10^{18} \text{ cm}^{-3}$ and $\text{Na}(\text{BTF})$ at concentrations between 6×10^{18} and $6 \times 10^{16} \text{ cm}^{-3}$. Solubility is complete in this range of concentrations.

At a concentration of $6 \times 10^{16} \text{ cm}^{-3}$ in $\text{Na}(\text{BTF})$, intermolecular energy transfer takes place from $(\text{BTF})^-$ to $\text{Eu}(\text{EDTA})^-$. At this concentration in $\text{Na}(\text{BTF})$, the fluorescence spectrum of the mixture, shown in Fig. 1(a), is identical to that observed for $\text{Eu}(\text{EDTA})^-$ alone⁽⁴⁾. However, the excitation spectrum of the fluorescence of this mixture shown in Fig. 2(a) is not that of

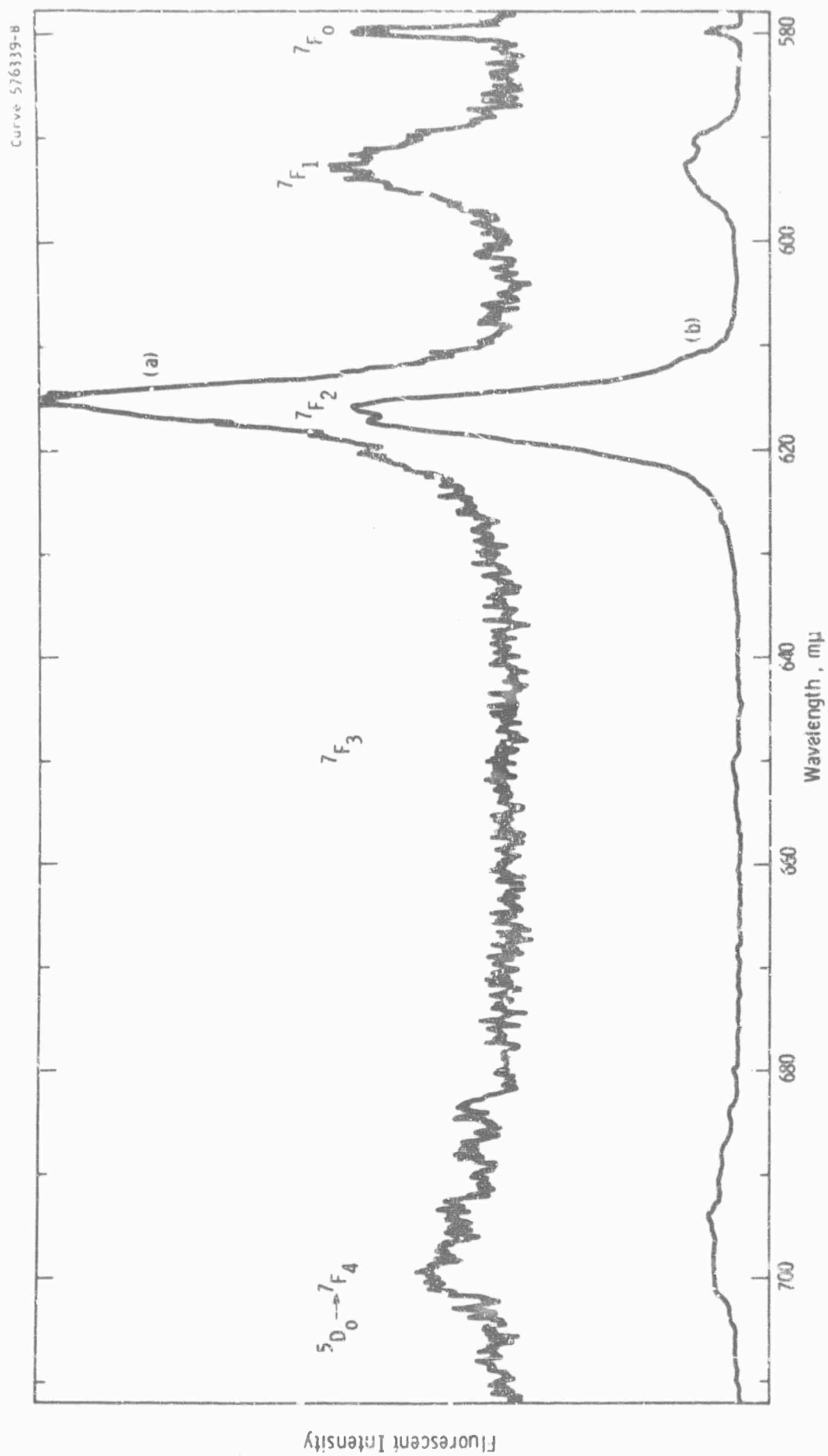


Fig. 1--Room temperature fluorescence spectra in D_2O
 (a) Nd^{3+} EDTA, 0.01M; NaBTF, 0.0001M
 (b) Nd^{3+} EDTA, 0.01M; NaBTF, 0.01M
 Resolution: 3 Å, excitation: near 3400 Å

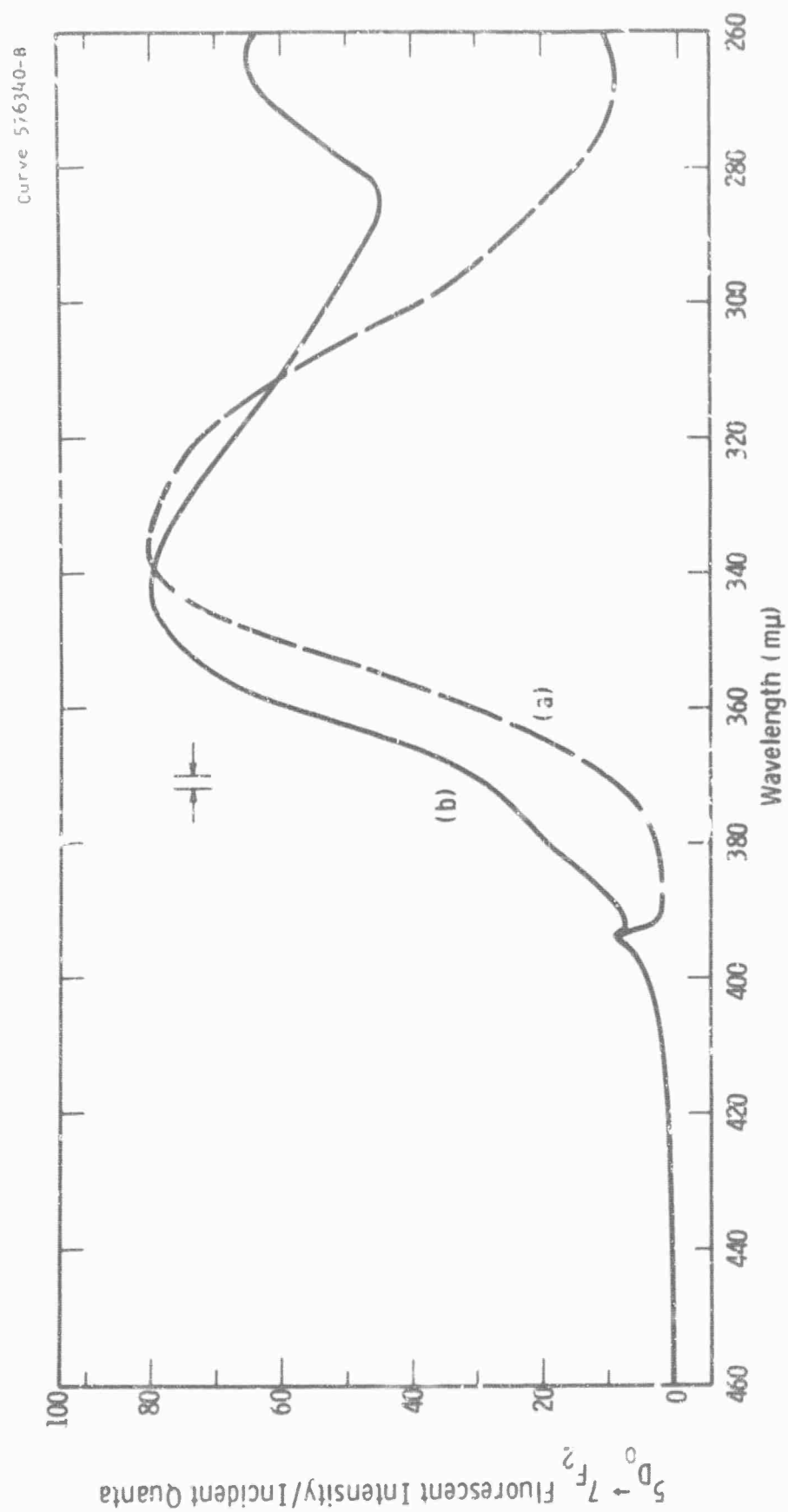


Fig. 2—Room temperature excitation spectra in D₂O
 (a) NaEu EDTA, 0.01M; Na BTF, 0.0001M
 (b) NaEu EDTA, 0.01M; Na BTF, 0.01M
 (curves have been normalized to the same height)

$\text{Eu}(\text{EDTA})^-$ alone⁽⁵⁾. The broad-band excitation spectrum shown in Fig. 2(a) must therefore be due to the presence of $(\text{BTF})^-$. The fact that absorption of light by $(\text{BTF})^-$ leads to fluorescence is evidence only of energy transfer. The fact that the observed fluorescence is identical to that of $\text{Eu}(\text{EDTA})^-$ alone in solution is strong evidence that the transfer is intermolecular in character.

When the concentration of $\text{Na}(\text{BTF})$ is increased to 10^{-2}M , energy transfer still takes place but it is predominantly intramolecular in form. At this concentration a mixed ligand complex between $\text{Eu}(\text{EDTA})^-$ and $(\text{BTF})^-$ is formed. This is indicated by the change in the fluorescence spectrum from that shown in Fig. 1(a) to that shown in Fig. 1(b). The transfer of energy from the $(\text{BTF})^-$ ligands to the europium ion is again demonstrated by the excitation spectrum shown in Fig. 2(b).

2.4 Mixed-Ligand Complex Formation in Solution

As mentioned in Section 2.1, another way to enhance the absorption characteristics for laser purposes is to modify the rare-earth containing species so that part of the molecule possesses absorption bands suitable for laser pumping. One way to do this is to form a mixed ligand complex in solution between the rare-earth containing species and a second ion.

We have studied such mixed ligand complexes in solution between both $\text{Tb}(\text{EDTA})^-$, and $\text{Eu}(\text{EDTA})^-$ and the 5-sulfosalicylate ion, $(\text{SSA})^{-3}$. The $(\text{SSA})^{-3}$ ion forms mixed ligand complexes in heavy water with both $\text{Tb}(\text{EDTA})^-$ and $\text{Eu}(\text{EDTA})^-$. When ultraviolet light is absorbed by the $(\text{SSA})^{-3}$, energy is transferred intramolecularly to the terbium ion from which fluorescence occurs with high quantum efficiency. The quantum efficiency for this process in the europium complex is however very low. A paper which describes these systems in detail has been accepted for publication in the Journal of Nuclear Chemistry and is included in this report as Appendix B.

3. SYSTEMS SOLUBLE IN ORGANIC SOLVENTS

In the hope of obtaining information which would aid in designing systems for use in heavy water, the studies in Section 3 were performed. The work summarized in Section 3.1 was started under contract Nonr-4573(00), and finished with Westinghouse funds. The studies described in Section 3.2 were started with Westinghouse funds and finished under the present contract.

3.1 Some Effects Involving the Organic Cation in Europium Benzoyltrifluoroacetate, $\text{Eu}(\text{BTF})_4^-$, Solutions

It is of interest to determine the effect, if any, on the laser threshold of varying the organic cation while holding the lasing species constant. In this case, the lasing species was the $\text{Eu}(\text{BTF})_4^-$ anion in acetonitrile⁽⁶⁾⁽⁷⁾. Fifteen organic salts, $\text{BEu}(\text{BTF})_4$, were synthesized and the laser threshold studied.

Electrical conductivity measurements indicate that each of the salts in acetonitrile is dissociated to a large degree to the free cation B^+ and $\text{Eu}(\text{BTF})_4^-$. In addition, the flash lamp light absorbed by B^+ is in all cases negligible compared to that of $\text{Eu}(\text{BTF})_4^-$. One might expect therefore that the laser threshold of these solutions would be the same. Actually the threshold varies considerably from one salt to the other and, in fact, the quinolinium salt did not lase at all. In the case of the quinolinium salt, it was found that the presence of the quinolinium cation enhanced the dissociation of $\text{Eu}(\text{BTF})_4^-$ in solution to such an extent as to prevent laser operation. These studies showed therefore that the organic cation can be important in determining the laser characteristics of the solution. A paper containing further details of this study has been accepted for publication in the Journal of Applied Physics. A copy of this paper is included in this report as Appendix C.

3.2 A Series of New Europium Chelates: Laser Action in Three New Chelates

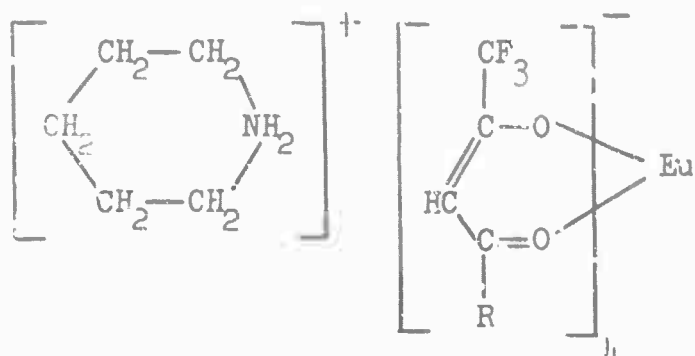
As discussed in Section 3.1, variations in the cation in organic salt solutions of $\text{Eu}(\text{BTF})_4^-$ can have an important effect on the laser properties of the solution. However, since the anion, $\text{Eu}(\text{BTF})_4^-$ is the lasing species, alterations in the structure of this ion should lead to an even more pronounced effect on the laser characteristics of the solution. This appears to be the case. We have synthesized a number of new europium chelates; all having different structures but all of the same basic tetrakis form. Some of the properties of these materials are summarized in Table I.

We have obtained laser action in three of these chelates dissolved in acetonitrile. These are α -naphthyl, the p-methoxyphenyl and the 2,5-dimethoxyphenyl compounds. The reasons for the failure of some of the other chelates to lase are not yet clear. Some chelates that do not lase have a higher quantum efficiency than those which do lase. The answer to this problem must await a more complete investigation.

The properties of one of the three new chelates which lase have been investigated in more detail. This material is the piperidinium salt of europium tetrakis α -naphthoyltrifluoroacetate, $\text{PEu}(\alpha\text{-NTF})_4^-$ in acetonitrile. In solution this material has a somewhat lower quantum efficiency than $\text{Eu}(\text{BTF})_4^-$ and therefore lases at somewhat lower temperatures; laser action being observed at temperatures up to -10°C . The scattering loss due to index of refraction changes during optical pumping is high. At threshold this loss is about 30% per pass. In addition, the beam divergence of this laser is poor. Qualitatively, these results are consistent with the measurements made of time dependent scattering during optical pumping in organic liquids⁽⁸⁾. A paper containing a more detailed description of the spectroscopic, chemical and laser properties of $\text{Eu}(\alpha\text{-NTF})_4^-$ in acetonitrile is included in this report as Appendix D. This paper is being submitted for publication in the Journal of Chemical Physics.

Table I

Europium Chelates Derived from β -Diketones Related to Benzoyltrifluoroacetone



<u>R</u>	<u>Yield(%)</u>	<u>Elemental Analyses</u>		
		<u>%C</u>	<u>%H</u>	<u>%N</u>
2-thienyl	48	calcd. 39.6	2.5	1.3
		found 39.5	2.4	1.2
p-xenyl	89	calcd. 59.1	3.7	1.0
		found 59.5	3.9	1.0
α -naphthyl	96	calcd. 56.4	3.4	1.1
		found 56.3	3.5	1.5
β -naphthyl	98	calcd. 56.4	3.4	1.1
		found 56.1	3.2	1.2
p-fluorophenyl	94	calcd. 46.2	2.8	1.2
		found 46.8	2.5	1.2
p-methoxyphenyl	68	calcd. 48.3	3.6	1.2
		found 48.5	3.8	1.1
2,5-dimethoxyphenyl	96	calcd. 47.5	3.9	1.0
		found 47.7	4.0	1.0
o-methoxyphenyl	92	calcd. 48.3	3.6	1.1
		found 47.8	3.6	1.2
2-fluorenyl	98	calcd. 60.4	3.6	1.0
		found 60.4	3.6	0.7
3-phenanthrenyl	93	calcd. 61.7	3.5	1.0
		found 60.9	3.5	0.8

4. SUMMARY AND SUGGESTIONS FOR FUTURE WORK

Systems soluble in both organic solvents and heavy water have been studied. The work in heavy water has been emphasized because of the better optical homogeneity properties of that solvent for liquid laser applications.

Two different types of systems have been studied in heavy water. The work with both types of systems has been aimed at improving the optical pumping characteristics of materials in solution.

The first type of system is a mixed ligand complex in solution. The idea here is to modify an existing chelate by incorporating ligands having better absorption characteristics for laser pumping purposes.

The second type of system contains two different species in solution, a sensitizer and an activator. The process of intermolecular energy transfer is then used to excite the europium containing species (the activator). We have shown intermolecular energy transfer to take place for the first time in heavy water. Intermolecular energy transfer appears to show the greatest promise for efficient optical pumping of liquid lasers.

The work with chelates soluble in organic solvents may be divided into two general parts. The first part describes effects which show that the organic cation may have an important effect on the laser properties of a solution. The second part describes some effects associated with variations in the structure of the europium containing anion where the basic tetrakis form of the anion has been maintained. A number of new chelates of this type have been synthesized and studied. Three of these have been shown to lase. The effects of scattering in these lasers are however large since they employ an organic solvent.

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From the standpoint of the development of efficiently pumped high radiance liquid lasers, systems soluble in heavy water and employing intermolecular energy transfer in solution appear to hold considerable promise. Work along these lines should be intensified to take advantage of the fact that effects associated with change in refractive index with temperature and stress optic effects are both essentially absent in heavy water near 6°C. Except for water, which has certain undesirable characteristics, heavy water appears to be unique in this respect.

PAPERS PUBLISHED

1. R. G. Charles, E. P. Riedel and P. G. Haverlack, "Energy Transfer Between p-Benzoylbenzoate and Europium Ethylenediaminetetracetate in Water Solution", J. Chem. Phys., in press.
2. R. G. Charles and E. P. Riedel, "A Fluorescent Terbium Chelate System in Water Solution", J. Inor. Nucl. Chem., in press.
3. E. P. Riedel and R. G. Charles, "The Effects of Organic Cations on the Laser Threshold of Solutions of Europium Tetrakis Benzoyltrifluoroacetate", J. Appl. Phys., in press.
4. E. P. Riedel and R. G. Charles, "Spectroscopic and Laser Properties of Europium α -Naphthoyltrifluoroacetate in Solution", to be submitted for publication in J. Chem. Phys.

REFERENCES

1. D. L. Dexter, J. Chem. Phys. 21, 836 (1951).
2. A. Heller and E. Wasserman, J. Chem. Phys. 42, 949 (1965).
3. M. L. Bhaumik and M. A. El-Sayed, J. Phys. Chem. 69, 275 (1965).
4. See Fig. 3(b) of Appendix A.
5. See Fig. 4(b) of Appendix A.
6. H. Samelson, A. Lempicki, C. Brecher and V. Brophy, App. Phys. Lett. 5, 173 (1964).
7. E. J. Schimitschek, J. A. Trias and R. B. Nehrich, Jr., J. Appl. Phys. 36, 867 (1965).
8. E. P. Riedel, Appl. Phys. Lett. 5, 162 (1964).

APPENDIX A

Energy Transfer Between p-Benzoylbenzoate and
Europium Ethylenediaminetetraacetate in Water Solution

September 13, 1965

ENERGY TRANSFER BETWEEN p-BENZOYL BENZOATE AND
EUROPIUM ETHYLENEDIAMINETETRAACETATE IN WATER SOLUTION

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ABSTRACT

Ultraviolet radiation absorbed by the p-benzoylbenzoate ($p\text{-BB}^-$) ion in solution is transferred to an appreciable extent to the europium ethylenediaminetetraacetate (EuEDTA^-) ion and is reemitted as the visible red fluorescence characteristic of Eu^{3+} . Fluorescence intensity is greater in D_2O than in water. The fluorescence is quenched by dissolved O_2 . Although evidence for mixed ligand complexes involving $p\text{-BB}^-$ and EuEDTA^- was obtained, fluorescence seems to result from ultraviolet absorption by free $p\text{-BB}^-$ ions followed by intermolecular energy transfer to free EuEDTA^- ions. The analogous aqueous systems containing o- BB^- or m- BB^- are non-fluorescent, although all three of the solid hydrated salts Eu(o-BB)_3 , Eu(m-BB)_3 and Eu(p-BB)_3 fluoresce brightly at room temperature.

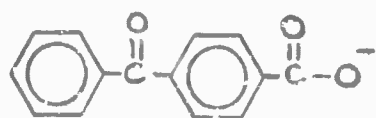
September 13, 1965

ENERGY TRANSFER BETWEEN p-BENZOYL BENZOATE AND
EUROPIUM ETHYLENEDIAMINETETRAACETATE IN WATER SOLUTION*

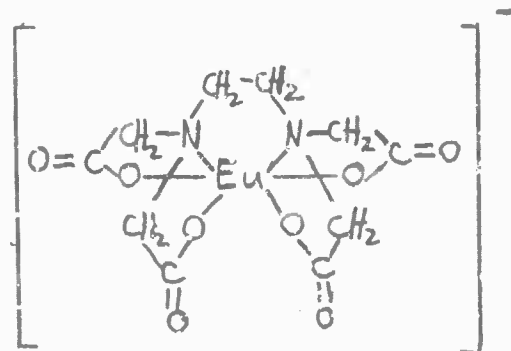
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INTRODUCTION

Several workers have observed energy transfer between aromatic ketones or aldehydes and trivalent europium in solutions of organic liquids¹⁻⁴. Such transfer has been suggested as a means of more efficiently converting pump light to europium ion fluorescence in liquid laser devices^{2,3}. We have been interested in analogous systems involving water-soluble ketone derivatives. Water, and especially heavy water (D_2O) have inherent advantages as liquid laser solvents, notably the small variation of refractive index with temperature near the freezing point^{5,6}. We have now observed significant energy transfer, in H_2O and in D_2O , between the p-benzoylbenzoate ion (formula I) and europium



I



II

*Part of this investigation was carried out under contract None-4573(00) as a part of Project DEFENDER under the joint sponsorship of the Advanced Research Projects Agency, the Office of Naval Research, and the Department of Defense.

in the form of its ethylenediaminetetraacetate chelate (EuEDTA^- , formula II). Interestingly enough, detectable energy transfer was not observed when the analogous o- or m-benzoylbenzoate ions were used.

EXPERIMENTAL

Materials

The salt $\text{NaEuEDTA} \cdot 8\text{H}_2\text{O}$ was prepared by reacting Eu_2O_3 with ethylenediaminetetraacetic acid and NaOH in water solution⁷. The product was purified by dissolving in water and reprecipitating with acetone. The purified salt was air-dried at room temperature.

p-Benzoylbenzoic acid was obtained from K and K Laboratories, Plainview, N.Y. The compound was recrystallized from ethanol. K and K Laboratories o-benzoylbenzoic acid was dissolved in dilute aqueous KOH and reprecipitated with HCl. The precipitated material was recrystallized from ethanol-water. m-Benzoylbenzoic acid was synthesized by the method of White et al.⁸. The product was purified by dissolving in toluene and precipitating with petroleum ether.

Solid europium salts of the three benzoylbenzoic acids were prepared as follows. The o-, m-, or p-benzoylbenzoic acid (0.01 mole) was stirred in a flask with a mixture of 100 ml water and 10 ml 1 M NaOH until dissolved. An aqueous solution of Lindsay 99.9 percent EuCl_3 (7.43 ml of 0.444 M) was then added dropwise to the stirred solution over a period of 5 minutes. A white precipitate formed throughout the addition. After stirring for an additional 1/2 hour the solid was filtered off, washed with water and dried in vacuo at room temperature. The products from the m- and p-benzoic acids were recrystallized

Spectroscopy

Absorption spectra of the sodium benzoylbenzoates were obtained with a Cary Model 14 spectrophotometer and 1 cm quartz cells. Solutions 10^{-4} to 10^{-2} M were prepared from the respective acids in 0.1 M NaOH as solvent. (In all experiments involving mixtures of benzoylbenzoates with EuEDTA⁻ only the stoichiometric quantity of NaOH was employed.) Concentrations of NaEuEDTA in water were in the range 0.01 to 0.05 M. Two mm. or 1 cm. quartz cells were used as required.

Fluorescence spectra were obtained with a 1/2 meter Jarrell Ash spectrometer with a dispersion of 32 Å per millimeter. A photomultiplier with an S-20 characteristic response was used to detect the signal. A Corning CS3-68 filter was placed between the sample and the entrance slit in order to remove scattered lamp light below 520 mμ. The fluorescent spectra are presented uncorrected for system sensitivity which is a factor of 2.1 greater at 580 than at 720 mμ and is approximately linear in this range. Illumination of the sample in a desired wavelength band was achieved by passing the light from an Osram (XBO-900) xenon arc lamp through a second 1/2 meter Jarrell Ash spectrometer (dispersion 32 Å/mm) with a Corning CS 5-58 filter placed between the exit plane and the sample in order to eliminate scattered light above 480 mμ.

Excitation spectra were obtained by scanning with the spectrometer used in illumination of the sample and setting the other spectrometer at the desired wavelength of the fluorescent spectrum to be monitored. The spectra are recorded and here presented reduced to constant quanta per unit wavelength interval of

the exciting beam. This was achieved by detecting with a photomultiplier the fluorescence of a rhodamine B quantum counter⁹ which was excited by a portion of the beam used to excite the sample. This signal was then ratioed with the signal from the sample fluorescence.

RESULTS AND DISCUSSION

Nature of the soluble europium species

Addition of sodium p-benzoylbenzoate (Na p-BB) to a water solution of NaEuEDTA produces a white precipitate at low molar ratios Na p-BB/NaEuEDTA. At higher ratios, a clear homogeneous solution is obtained. Elemental analyses for the white precipitate indicated no nitrogen content and were consistent with hydrated europium p-benzoylbenzoate ($\text{Eu}(\text{p-BB})_3$). The displacement of the europium from the very stable¹⁰ EuEDTA^- ion is apparently associated with the low solubility of $\text{Eu}(\text{p-BB})_3$ in water. Fig. 1, curve A, shows the fraction of the europium which is precipitated as a function of the amount of Na p-BB added. Redissolution of the $\text{Eu}(\text{p-BB})_3$, at higher ratios of Na p-BB/NaEuEDTA, is most readily explained by the formation of soluble mixed ligand complexes having both EDTA^{4-} and p-BB^- ions bonded to the same europium. The possibility of dissolution of $\text{Eu}(\text{p-BB})_3$ as ions such as $\text{Eu}(\text{p-BB})_4^-$ is ruled out by the results of curve B, Fig. 1. Here Na p-BB has been added to water solutions of EuCl_3 . The curve shows the formation of insoluble $\text{Eu}(\text{p-BB})_3$, without indication of the formation of soluble species in the presence of excess p-BB^- .

Bonding of the $p\text{-BB}^-$ ions to the europium, in mixed complexes, is undoubtedly through the carboxylate group. Simple complexes of the rare earth metals derived from carboxylic acids are well known¹⁰; and the alternate bonding possibility in the present instance, i.e. through the keto carbonyl group, does not seem likely in aqueous solution. Simple rare earth carboxylate complexes do not have high stabilities toward dissociation in solution¹⁰. It is likely, therefore, that mixed EuEDTA^- - $p\text{-BB}^-$ complexes would be in equilibrium with appreciable concentrations of free EuEDTA^- . The presence of free EuEDTA^- is indicated by the fluorescence results discussed below.

Light absorption and fluorescence properties

Figure 2 compares the ultraviolet absorption spectra of the three isomeric benzoylbenzoate ions with the spectrum of EuEDTA^- . The benzoylbenzoates absorb much more strongly throughout the ultraviolet than does EuEDTA^- . In solutions containing comparable molar quantities of benzoylbenzoate and EuEDTA^- , therefore, ultraviolet absorption is almost entirely through the BB^- . This was shown to be the case for a $(\text{Na } p\text{-BB})-(\text{NaEDTA})$ mixture ($p\text{-BB}^-/\text{EDTA}^- = 6$), the spectrum of which was indistinguishable from that of $p\text{-BB}^-$ alone.

The spectra of the BB^- ions show absorption at the longer wavelengths due to $n-\pi^*$ transitions associated with the keto carbonyl groups. These $n-\pi^*$ bands appear as shoulders on the more intense $\pi-\pi^*$ bands which peak at shorter wavelengths.

Solutions in H_2O or D_2O containing $p-BB^-$ and $EuEDTA^-$ gave the characteristic red fluorescence of Eu^{3+} when exposed to ultraviolet light. The corresponding aqueous systems containing $m-$ or $o-BB^-$ gave undetectable fluorescence (lower by at least a factor of 50) and they were not further studied.

The fluorescence spectrum of a D_2O solution containing $NaEuEDTA$ and $Na p-BB$ is given in Figure 3c. The fluorescence is found to be due entirely to transitions within the 4f shell of the bonded Eu^{3+} ion. Electronic transitions probably responsible¹¹ for the observed emission bands are shown on the Figure. The fluorescence spectrum of $NaEuEDTA$ alone, in D_2O was also obtained (Fig. 3b). Except for greatly decreased overall intensity (associated with the lower absorption of ultraviolet radiation, Fig. 2) the spectrum is identical with the fluorescence spectrum of the mixture¹². This evidence strongly suggests that the free $EuEDTA^-$ ion is the fluorescing species in $(p-BB^-)-(EuEDTA^-)$ mixtures. The weak $^5D_0-^7F_0$ fluorescence was examined at higher amplification and resolution for further evidence of the identity and number of fluorescing species present. These spectra are shown at the right in Fig. 3. Since theory predicts only a single emission band in this region of the fluorescence spectrum for trivalent europium, the presence of more than one band can be taken as evidence for more than one fluorescing species¹³. Surprisingly, the $EuEDTA^-$ ion under conditions of high resolution (Fig. 3b) shows definite splitting, possibly indicating the presence of more than one isomeric form of this ion. That the number of resolved $^5D_0-^7F_0$ bands is not increased in the $(EuEDTA^-)-(p-BB^-)$ mixture, is additional evidence that $EuEDTA^-$ is the sole fluorescing ion.

The emission spectrum of $EuCl_3$ in solution is shown in Fig. 3 for comparison. As expected, only a single $^5D_0-^7F_0$ band is observed. The relative

intensities of bands within the spectrum of EuCl_3 differ significantly from those of NaEuEDTA , illustrating the sensitivity of Eu emission spectra to changes in the local environment. The emission spectra of EuCl_3 and EuEDTA^- in D_2O agree well with those reported by Gallagher for H_2O solutions¹⁴. (Gallagher does not indicate, however, whether splitting was observed in the $^5\text{D}_0$ - $^7\text{F}_0$ region for EuEDTA^- .)

The absolute quantum efficiency for the conversion of absorbed ultraviolet radiation to total Eu^{3+} fluorescence was measured for an air-equilibrated D_2O solution 0.2 M in p-BB⁻ and 0.01 M in EuEDTA^- . A room temperature value of 15% was obtained. When air-equilibrated H_2O was substituted for D_2O , the fluorescence efficiency dropped to 2%. Kropp and Windsor¹⁵ have noted a similar enhancement of fluorescence intensity for simple rare earth salts in D_2O as compared with solutions in H_2O . For both H_2O and D_2O , the quantum efficiency of the present system was practically independent of temperature in the range 5° to 26°C.

The observed quantum efficiency was found to be measurably sensitive to the presence of dissolved O_2 . When the above solution in D_2O was flushed with argon for 1/2 hr., the fluorescence quantum efficiency increased to 20%. When the solution was flushed with pure O_2 , the quantum efficiency decreased to 5%. The sensitivity to oxygen is further evidence¹ that energy transfer occurs intermolecularly between free p-BB⁻ ions and the fluorescing species EuEDTA^- .

The fluorescent intensity at room temperature of an air equilibrated D_2O solution 0.2 M in p-BB⁻ and 0.01 M in EuEDTA^- decayed exponentially with a decay time of 2.0 msec. The same result was observed for a 0.01 M solution of EuEDTA^- alone. The identical decay times is additional evidence that the fluorescing species is EuEDTA^- in solutions containing both EuEDTA^- and p-BB⁻.

In Fig. 4 the excitation spectrum of a (EuEDTA^-)-(p-BB⁻) mixture is compared with those of EuEDTA^- , alone, and with Eu^{3+} . In agreement with the

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In Fig. 4 the excitation spectrum of a (EuEDTA^-)-(p-BB⁻) mixture is compared with those of EuEDTA^- , alone, and with Eu^{3+} . In agreement with the

results of Gallagher¹⁴, the latter two ions are excited only within the weak absorption bands of trivalent europium, itself. The (EuEDTA⁻)-(p-BB⁻) mixture, however, is excited throughout that portion of the ultraviolet spectrum absorbed by p-BB⁻ ions (Fig. 1)¹⁶. The excitation spectrum, 4c is conclusive evidence for energy transfer between p-BB⁻ and europium, but does not, in itself, distinguish between inter- and intramolecular transfer in solution.

Solid europium benzoylbenzoates

In view of the differing behaviors of the three benzoylbenzoate isomers in exciting EuEDTA⁻ fluorescence in solution, it was of interest to extend our studies to the solid salts Eu(BB)₃. Each of these salts was obtained as an insoluble hydrate by the reaction between EuCl₃ and the sodium benzoylbenzoate in water solution. In contrast to the solution results, all three of the solid benzoylbenzoates show bright red fluorescence at room temperature when exposed to ultraviolet radiation. Figure 5 shows the fluorescence, in each instance, to be due entirely to Eu³⁺ transitions. Differences between the three spectra indicate that there are differences in symmetry and ligand field strength about the bonded europium in the three compounds.

The relative fluorescence brightness of the three solid europium salt hydrates at room temperature (2537 Å excitation) decreased in the order: p-(0.55) > m-(0.25), o-(0.25)¹⁷.

Figure 6 shows excitation spectra for the three solid benzoylbenzoate hydrates. Pronounced excitation throughout the ultraviolet, for all three

compounds, is definitive evidence that fluorescence occurs by ultraviolet absorption in the organic portion of the salt, followed by intramolecular transfer of energy to the bonded europium. At the longer wavelengths, there are superimposed on the curves of Fig. 6, small peaks corresponding to direct absorption by the bonded europium cation. At these wavelengths the benzoylbenzoate portion of the salt does not absorb efficiently and such fluorescence as does occur proceeds through direct excitation of Eu^{3+} .

The results obtained with the solid europium benzoylbenzoates show that there is no inherent impediment to transfer of energy between o- or m-benzoylbenzoate and europium. The lack of such transfer in solution, with EuEDTA^- , most probably indicates that the o- and m-isomers have a greater tendency than does the p-isomer to dissipate energy to the environment, by nonradiative means, before it can be transferred to the EuEDTA^- anion.

ACKNOWLEDGMENTS

The writers are grateful to Dr. R. C. Ohlmann for helpful discussions on the recording of excitation spectra and to Mr. R. Williams for aid in the experimental portion of this work.

Table I

Composition of Solid Europium Benzoylbenzoates

Compound	Yield %	% C	% H	% Eu	% H ₂ O ^c
(o-C ₁₄ H ₉ O ₃) ₃ Eu·4H ₂ O	89 ^a	calcd. 56.1	3.96	17.8	8.0
		found 54.8	3.96	17.8	8.5
(m-C ₁₄ H ₉ O ₃) ₃ Eu·2H ₂ O	85 ^b	calcd. 58.4	3.63	17.6	4.2
		found 58.1	3.72	18.0	4.0
(p-C ₁₄ H ₉ O ₃) ₃ Eu·2H ₂ O	95 ^b	calcd. 58.4	3.63	17.6	4.2
		found 58.4	3.74	17.4	4.0

^aNot recrystallized.

^bRecrystallized.

^cWeight loss on thermobalance to 150°C.

References and Footnotes

1. A. Heller and E. Wasserman, J. Chem. Phys. 42, 949 (1965).
2. E. Matovich and E. K. Suzuki, J. Chem. Phys. 39, 1442 (1963).
3. M. L. Bhaumik and M. A. El-Sayed, J. Phys. Chem. 69, 275 (1965).
4. R. E. Ballard and J. W. Edwards, Spectrochim. Acta 21, 1353 (1965).
5. D. B. Luten, Jr., Phys. Rev. 45, 161 (1934).
6. Due to the relatively large change of refractive index with temperature in organic liquids, temperature inhomogeneities can cause serious light scattering effects under typical laser pumping conditions (E. P. Riedel, Appl. Phys. Lett. 5, 162 (1964)).
7. T. Moeller, F. A. J. Moss and R. H. Marshall, J. Am. Chem. Soc. 77, 3182 (1955).
8. W. N. White, R. Schlitt and D. Gwynn, J. Org. Chem. 26, 3613 (1961).
9. W. H. Melhuish, J. Opt. Soc. Am. 52, 1256 (1962).
10. T. Moeller, D. F. Martin, L. C. Thompson, R. Ferrus, G. R. Feistel, and W. J. Randall, Chem. Rev. 65, 1 (1965).
11. G. H. Dieke and E. M. Crosswhite, Appl. Opt. 2, No. 7, 675 (1963).
12. The amplifier gains used to record the spectra of the weak fluorescence of EuCl_3 and EuEDTA^- (Figs. 3a and 3b) were much higher than that required to record 3c. Relative peak heights are significant only within individual spectra.
13. C. Brecher, H. Samelson and A. Leppicki, J. Chem. Phys. 42, 1081 (1965).
14. P. K. Gallagher, J. Chem. Phys. 41, 3061 (1964).
15. J. L. Kropp and M. W. Windsor, J. Chem. Phys. 22, 2769 (1963); 42, 1599 (1965).

References and Footnotes (Continued)

16. The bonded europium can also be excited directly in the $(\text{EuEDTA}^-)-(p\text{-BB}^-)$ mixture, but the weak superimposed excitation bands are not evident at the amplifier gain required to obtain Fig. 4c.
17. Numbers in parentheses are relative fluorescence intensities compared with the brightly fluorescent solid piperidine adduct of europium dibenzoylmethide. The intensity of the latter compound is taken as unity (R. C. Ohlmann and R. G. Charles, J. Chem. Phys. 40, 3131 (1964); R. G. Charles and R. C. Ohlmann, J. Inorg. Nucl. Chem. 27, 119 (1965)).

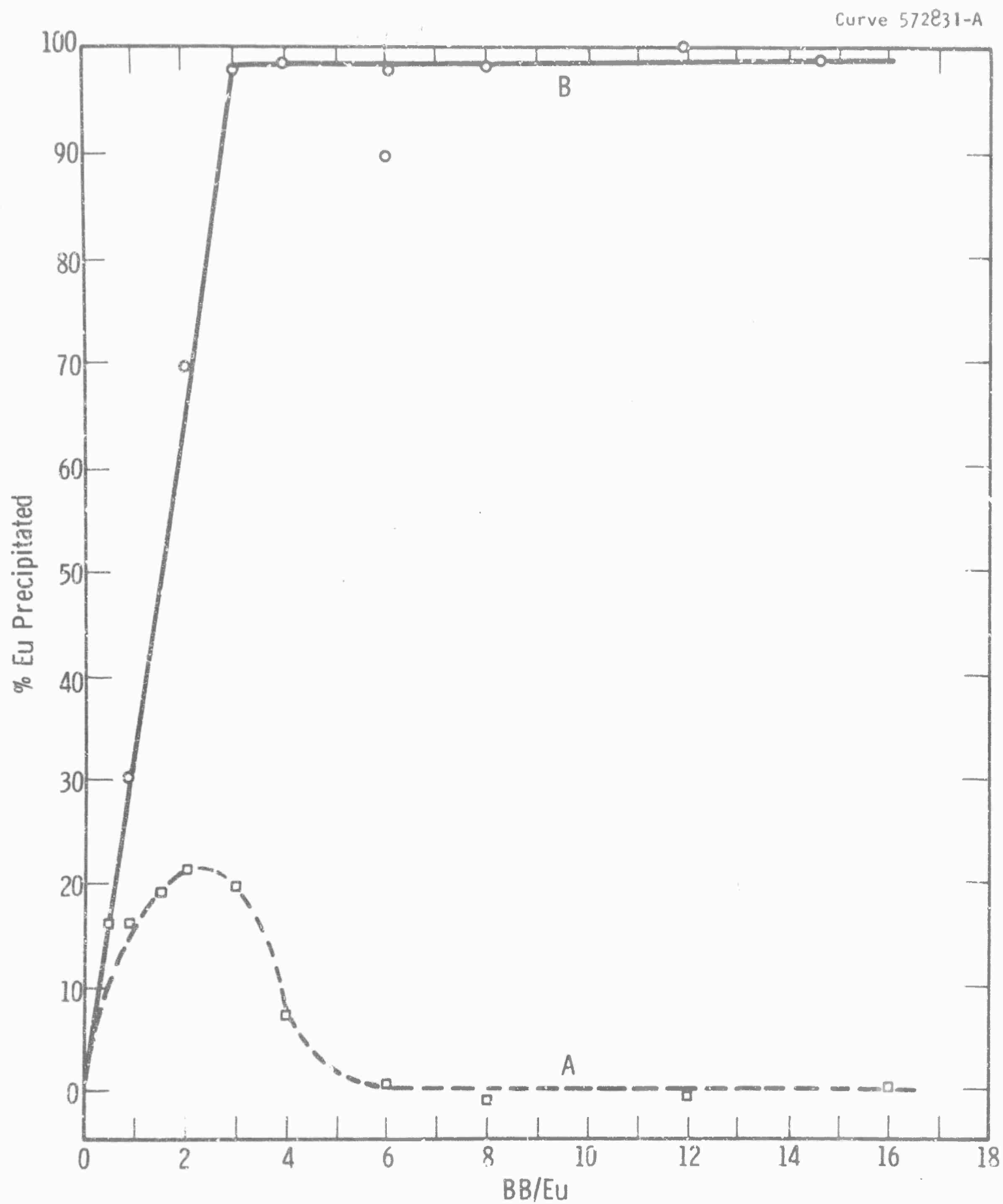


Fig. 1. Fraction of total europium precipitated by sodium p-benzoylbenzoate from solutions containing (A) NaEuEDTA or (B) EuCl_3 .

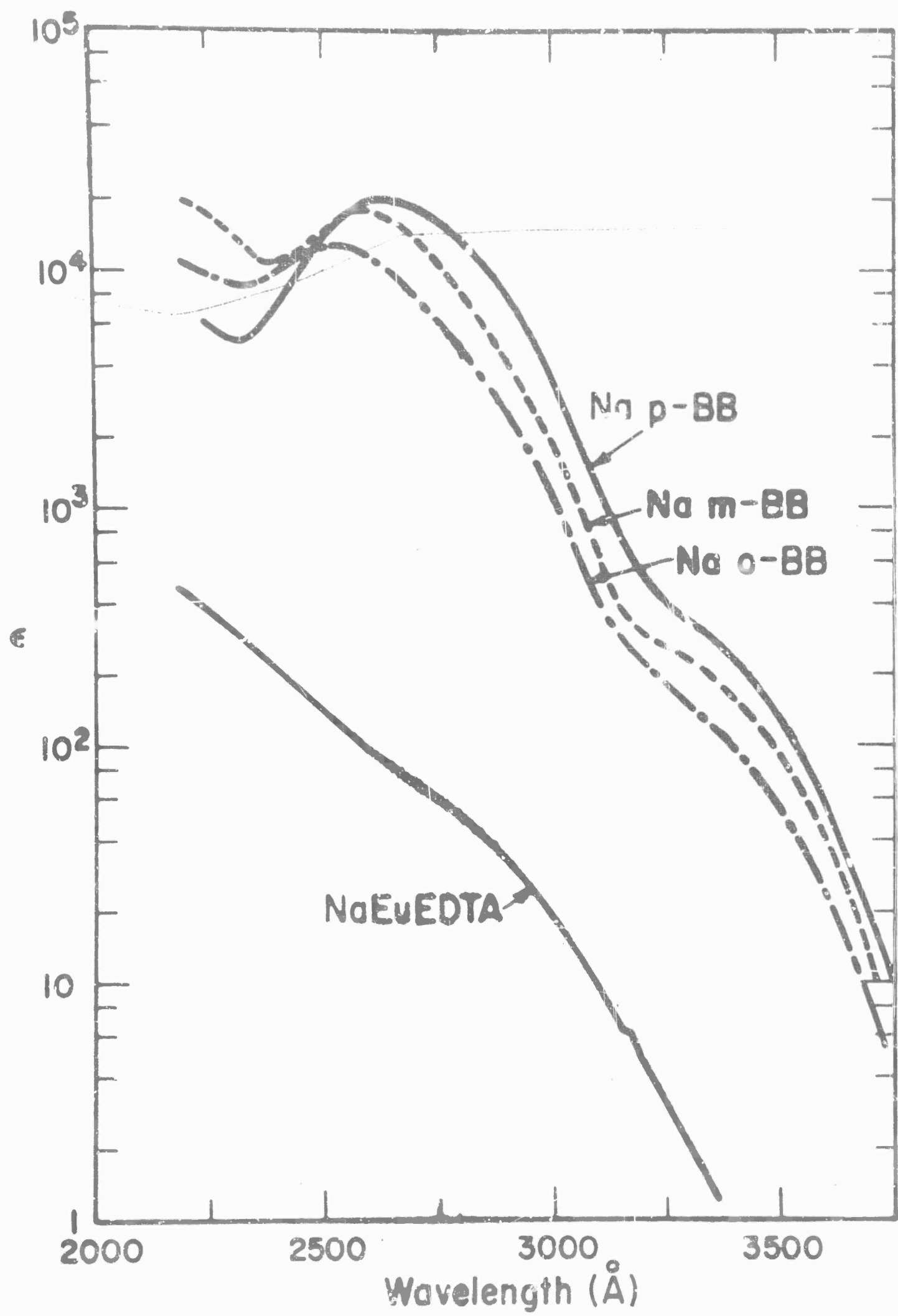


Fig. 2. Absorption spectra in Water.

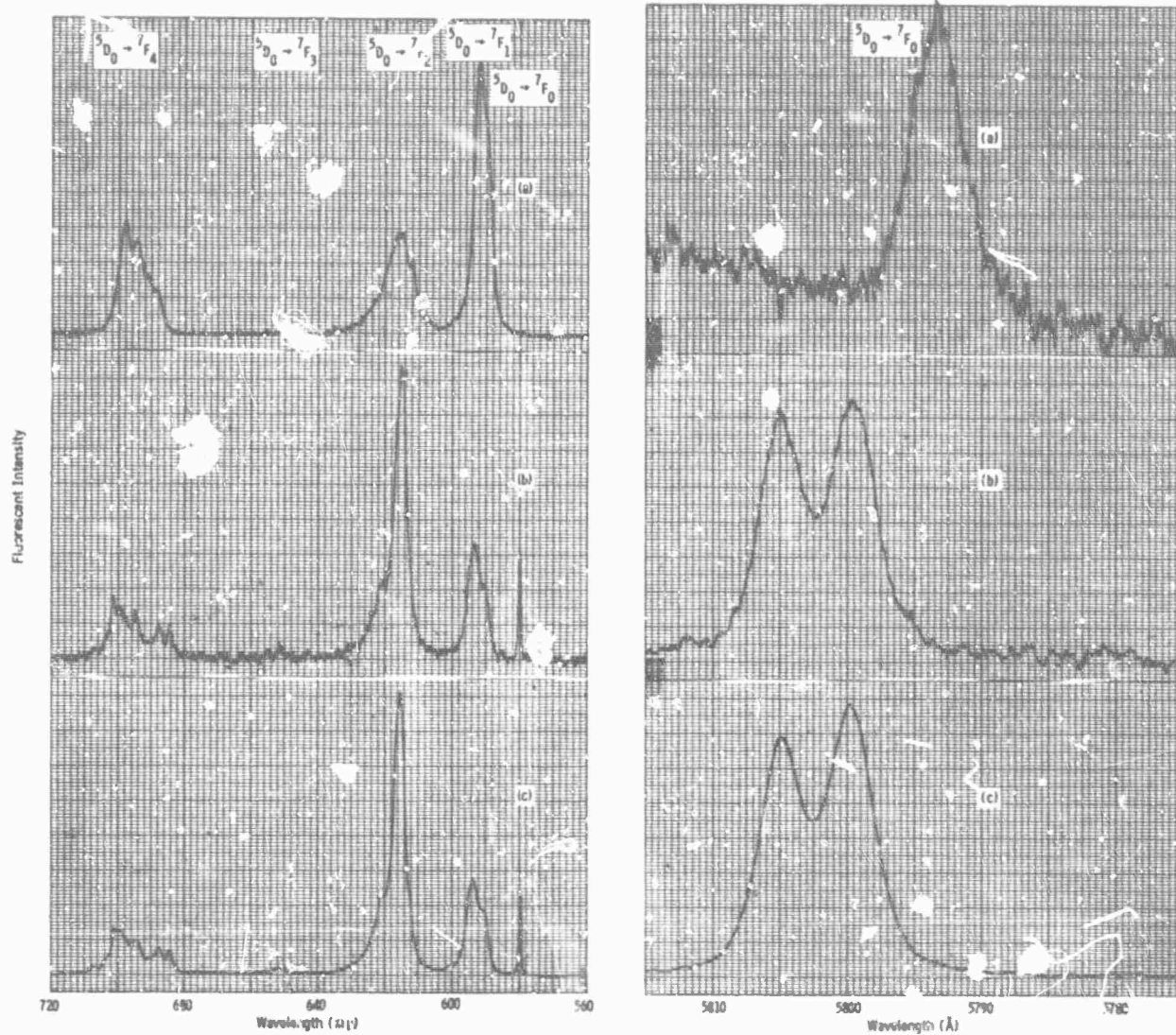


Fig. 3—Room temperature fluorescence spectra in D₂O
 (a) 1.0M EuCl₃
 (b) 0.01M NaEu EDTA
 (c) NaEu EDTA, 0.01M; Na p-Benzoylbenzoate, 0.2M
 (4 Å Resolution Left Three, 1.5 Å Right Three;
 Excitation: 3600 - 4000 Å)

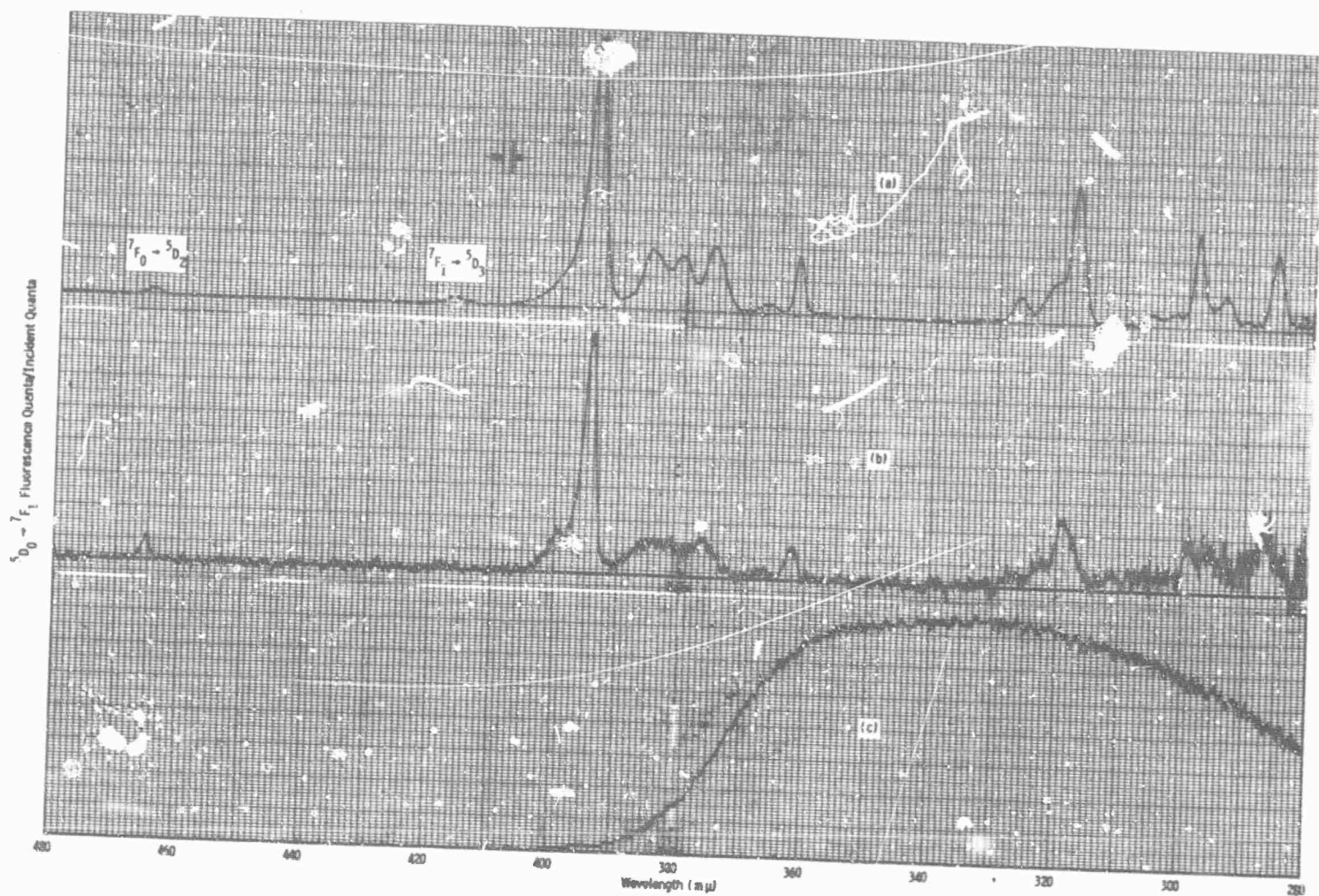


Fig. 4—Room temperature excitation spectra in D_2O
 (a) 1.0M $EuCl_3$
 (b) 0.01M $NaEu$ EDTA
 (c) $NaEu$ EDTA, 0.01M; Na p -Benzoylbenzoate, 0.2M

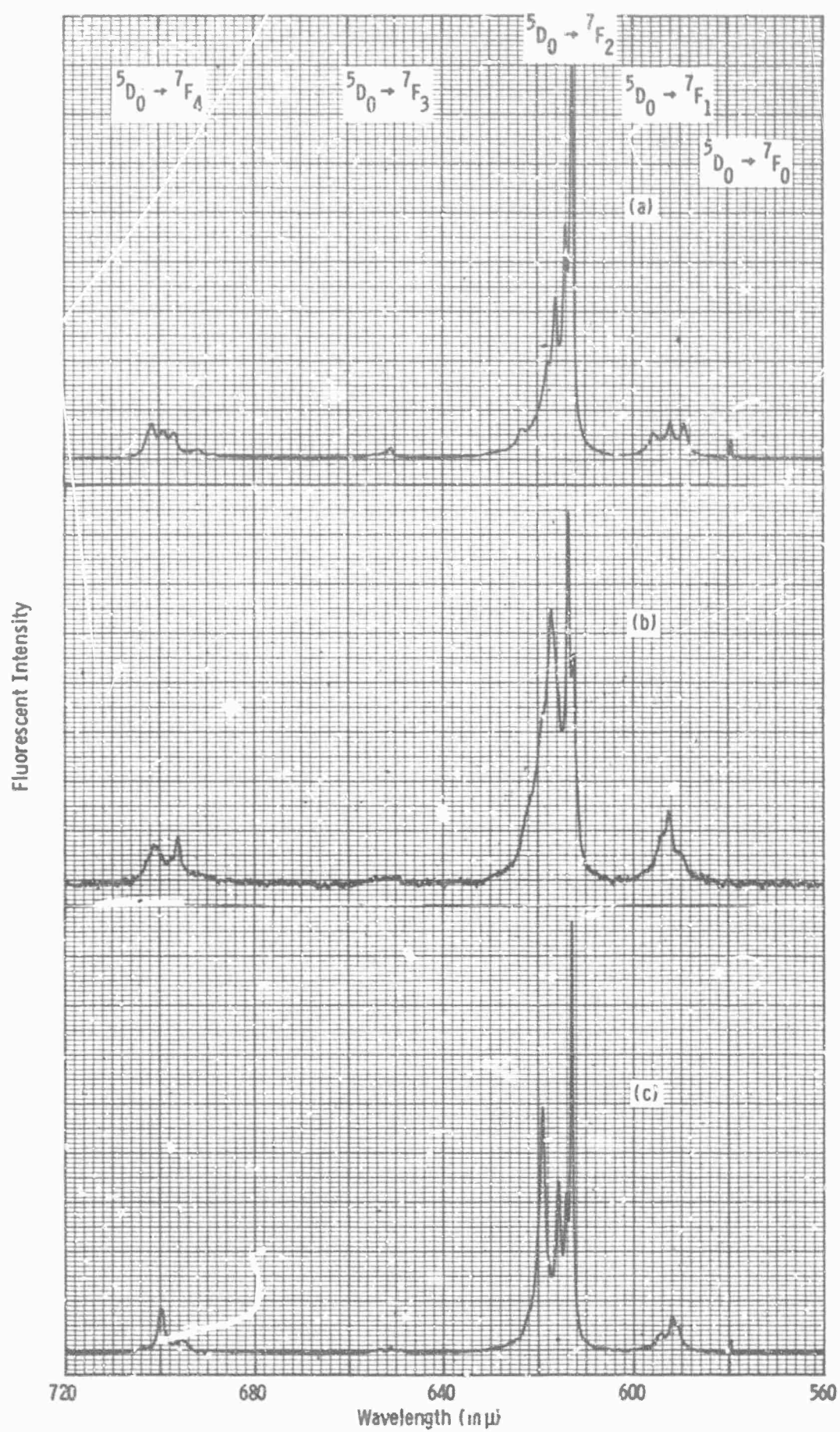


Fig. 5--Room temperature fluorescence spectra of solid:
 (a) Europium o-Benzoylbenzoate
 (b) Europium m-Benzoylbenzoate
 (c) Europium p-Benzoylbenzoate
 (Excitation at 3600 Å, 4 Å Resolution)

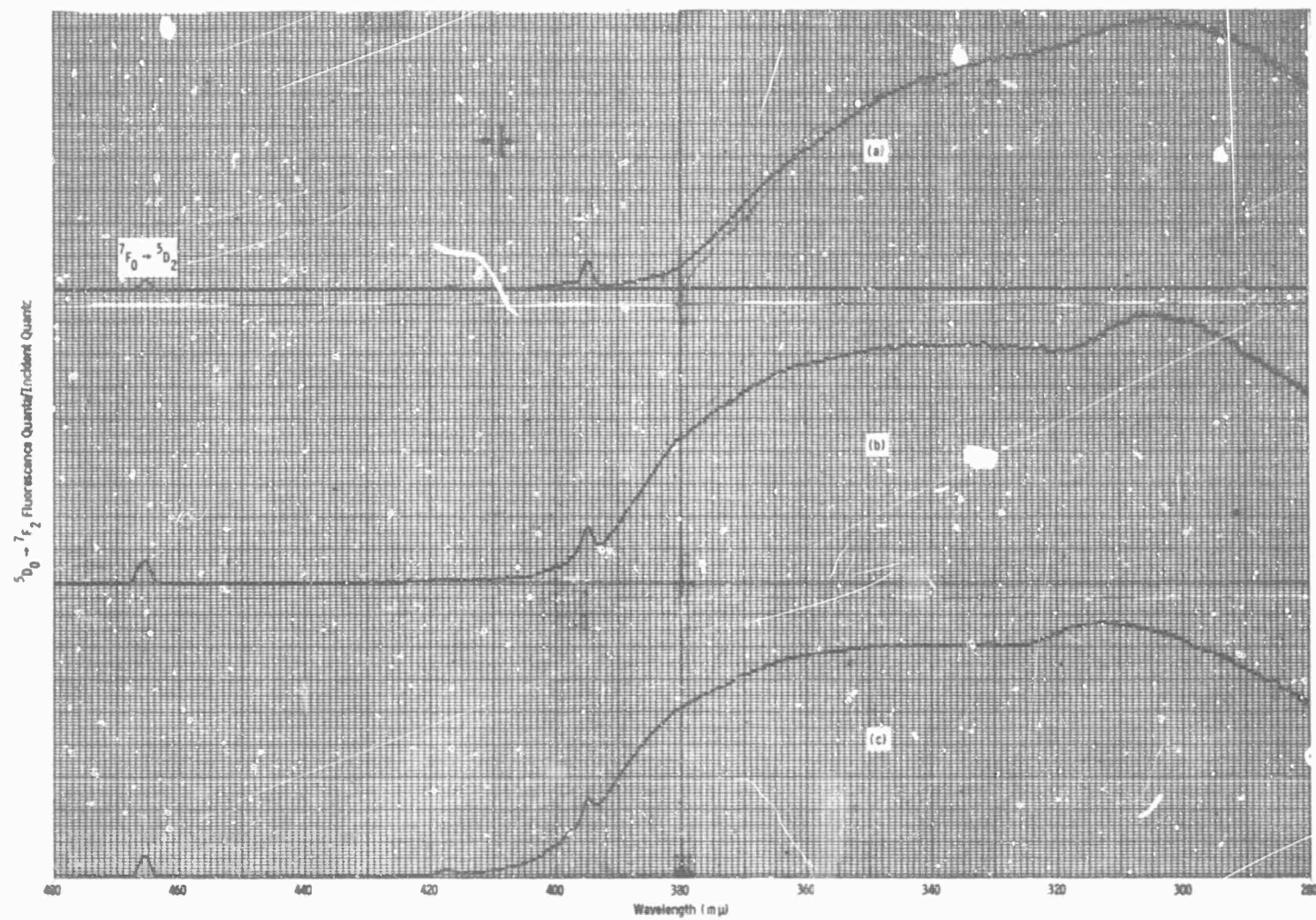


Fig. 6—Room temperature excitation spectra of solids:
 (a) Europium o-Benzoylbenzoylbenzoate
 (b) Europium m-Benzoylbenzoylbenzoate
 (c) Europium p-Benzoylbenzoylbenzoate

APPENDIX B

A Fluorescent Terbium Chelate System in Water Solution

August 20, 1965

A FLUORESCENT TERBIUM CHELATE SYSTEM IN WATER SOLUTION

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Abstract

The terbium ethylenediaminetetraacetate anion forms a 1:1 mixed ligand complex with the trivalent anion derived from 5-sulfosalicylic acid. Ultraviolet radiation absorbed by the organic portion of the mixed complex is efficiently converted to the green fluorescence characteristic of Tb^{3+} . Quantum efficiency for conversion is greater in D_2O than in H_2O solution and is essentially unity in the former solvent at room temperature. The corresponding mixed complex derived from europium ethylenediaminetetraacetate does not fluoresce.

August 20, 1965

- 2 -

A FLUORESCENT TERBIUM CHELATE SYSTEM IN WATER SOLUTION

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There is much interest in solutions of rare-earth chelates for use in laser (optical maser) systems⁽¹⁻⁴⁾. Almost all such work has involved the use of organic solvents. Water (and also D₂O) has potential advantages as a low-viscosity solvent for laser use, notably the small variation of refractive index with temperature near the freezing point⁽⁵⁾, a property which minimizes scattering due to temperature inhomogeneties during optical pumping.

In general, solubility considerations require that chelates other than those which have been investigated for use in organic solvents be used in water. The best known class of rare earth chelates which have both high water solubility and high resistance to dissociation in solution consists of complexes derived from aminopolycarboxylic acids⁽⁶⁾. However, dilute solutions of such chelates do not, in general, have sufficient light absorption in the ultraviolet to be effectively pumped as laser materials. We have therefore been led to consider mixed ligand complexes containing a second complexing agent having more desirable light absorption characteristics. Previous investigations⁽⁷⁾ have established that mixed ligand complexes involving aminopolycarboxylic acids do occur.

We describe here results obtained with water solutions containing the terbium ethylenediaminetetraacetate anion (TbEDTA^-) and the trivalent anion (SSA^{3-}) derived from 5-sulfosalicylic acid (H_3SSA).

Results and Discussion

Complex Formation

Titration of 5-sulfosalicylic acid with NaOH results in curve A of Fig. 1. The hydrogen ions from the sulfonic acid and carboxylic acid groups titrate at relatively low pH values after which the phenolic hydrogen titrates separately at much higher pH. When a mixture of H_3SSA and NaTbEDTA is titrated (curve B) the buffer region characteristic of the phenolic group is shifted to lower pH values. This pH lowering can be attributed to hydrogen ion released by the reaction (1).



Additional evidence for complex formation is provided by the absorption spectra of Fig. 2. The spectrum of a mixture of NaTbEDTA and Na_3SSA differs significantly from those of its components. On the other hand, the spectrum of a 1:1 mixture of Na_2HSSA and NaTbEDTA was identical to that of Na_2HSSA alone, indicating that the mixed ligand complex $\text{Tb(EDTA)(HSSA)}^{3-}$ does not form under our conditions.

To establish the stoichiometry of the reaction at the higher pH values, continuous variation studies based both on ultraviolet absorption

and visible fluorescence (vide infra) were carried out. The curves obtained (Fig. 3) give maxima at mole fraction $\text{SSA}^{3-} = 0.5$, indicative of a 1:1 complex between TbEDTA^- and SSA^{3-} (equation 2).

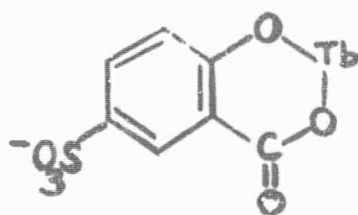
The equilibrium formation constant K for reaction (2) can be evaluated⁽⁷⁾ from



$$K = \frac{[\text{Tb(EDTA)(SSA)}^{4-}]}{[\text{TbEDTA}^-][\text{SSA}^{3-}]}$$

the titration data of Fig. 1. Table 1 summarizes the results obtained. Constancy of the value of $\log K$ (Table I) over the pH range 9 to 10 is further evidence that only the 1:1 complex $\text{Tb(EDTA)(SSA)}^{4-}$ is formed under the conditions used.

The structure of the $\text{Tb(EDTA)(SSA)}^{4-}$ ion cannot be determined without additional evidence. It is possible, however, that the SSA^{3-} ion forms an additional chelate ring with the terbium as shown:



This does not necessarily require the displacement of the six bonded groups from the EDTA^{4-} ion since abundant evidence exists^(1,7) that a coordinated

rare earth ion can have a coordination number higher than six. In particular, a recent X-ray diffraction investigation⁽⁸⁾ shows that the coordination number of La in the solid compound $\text{KLaEDTA} \cdot 8\text{H}_2\text{O}$ is nine; and evidence was presented that a similar situation applied to the hydrated EDTA complexes of other rare earth cations. In the present instance, however, the tendency of the four EDTA carboxylate groups and the bonded SSA^{3-} ion to impose a negative charge on the terbium atom may favor the displacement of one or more carboxylate groups, followed by completion of the terbium coordination sphere by water molecules.

Fluorescence Properties

Water solutions containing $\text{Tb}(\text{EDTA})(\text{SSA})^{4-}$ give a bright green fluorescence when irradiated with ultraviolet light. Fig. 4 shows the variation of fluorescence intensity as a mixture of H_3SSA and NaTbEDTA is titrated with NaOH . Appreciable fluorescence occurs only after the phenolic hydrogen begins to titrate to give SSA^{3-} and the mixed complex $\text{Tb}(\text{EDTA})(\text{SSA})^{4-}$. Maximum fluorescence occurs somewhat beyond the volume of NaOH required by equation (1) due to partial dissociation of $\text{Tb}(\text{EDTA})(\text{SSA})^{4-}$. From the value of K (Table I), approximately 9% of the terbium is calculated to be present as $\text{Tb}(\text{EDTA})^-$ when the stoichiometric amount of NaOH has been added. The $\text{Tb}(\text{EDTA})^-$ ion itself shows negligible fluorescence at these concentrations principally because of low ultraviolet absorption (Fig. 1).^{*} The ultraviolet absorption of $\text{Tb}(\text{EDTA})(\text{SSA})^{4-}$ is very much higher than that of $\text{Tb}(\text{EDTA})^-$ at all wavelengths. Resemblance of the spectrum of $\text{Tb}(\text{EDTA})(\text{SSA})^{4-}$ to that of SSA^{3-} indicates that absorption

^{*} Such ultraviolet radiation as is absorbed by $\text{Tb}(\text{EDTA})^-$ may not be transferred efficiently to the bonded metal atom, as has been shown to be the case for $\text{Eu}(\text{EDTA})^-$, (P. H. Gallagher, J. Chem. Phys. 41, 3061 (1964)).

in the mixed complex is primarily through the bonded SSA^{3-} .

In the presence of large excesses of NaOH (Fig. 4, Curve B) the fluorescence decreases markedly, presumably due to the competition of additional (and less fluorescent) complexes which involve bonded hydroxyl ions. At the highest excesses of NaOH employed, a precipitate of undetermined composition separates (Fig. 4).

Fig. 5 gives the room-temperature fluorescence spectrum of a solution prepared from equimolar quantities of Na_3SSA and NaTbEDTA and having an overall terbium concentration of 0.02M (primarily as $\text{Tb(EDTA)(SSA)}^{4-}$). The observed spectrum arises entirely from transitions within the $4f^8$ shell of the bonded Tb^{3+} . Comparison of Fig. 5 with published^(9,10) fluorescence spectra for Tb^{3+} indicates that the four emission groups in Fig. 5 represent transitions from the $^5\text{D}_4$ level to the $^7\text{F}_6$, $^7\text{F}_5$, $^7\text{F}_4$, and $^7\text{F}_3$ levels at 480-510, 530-565, 575-605 and 610-640 mμ respectively.

The fluorescence of $\text{Tb(EDTA)(SSA)}^{4-}$ was also investigated using heavy water (D_2O) as solvent. D_2O has been shown⁽¹¹⁾ to give enhanced fluorescence intensity for solutions of certain rare earth compounds when compared with the values obtained in water. A solution containing $\text{Tb(EDTA)(SSA)}^{4-}$ in D_2O (0.02M in Tb) gave a fluorescence spectrum identical to that in water (Fig. 5) except for greater overall intensity of fluorescence in D_2O . The ultraviolet absorption spectrum was also identical to that obtained in water. The absolute quantum efficiency of a D_2O solution (0.02M in Tb) was found to be 0.9 ± 0.1 .

This value is insensitive to temperature over the range 5 to 25°C. Since $\text{Tb}(\text{EDTA})(\text{SSA})^{4-}$ is dissociated to the extent of a few percent at this concentration* the quantum efficiency characteristic of the mixed ligand complex in D_2O is essentially unity. To our knowledge this is the highest quantum efficiency which has been achieved for terbium in liquid solution⁽¹²⁾. The quantum efficiency of an identical solution in water at room temperature was determined by comparison with the D_2O solution and found to be 0.7 ± 0.1 .

The decay of the Tb^{3+} fluorescence in D_2O (0.02M Tb) is exponential with a decay time of 2.4 milliseconds between 5°C and 25°C.

The ultraviolet absorption characteristics, the high quantum efficiency and favorable decay time of the present system suggest it as a likely candidate to display laser action. In a number of tests with heavy water solutions, however, no evidence for stimulated emission has been obtained. Some photodecomposition occurs under the intense illumination of the xenon flash tube pump; and this may be a factor in vitiating laser action. There was no indication of photodecomposition with the relatively low levels of ultraviolet illumination used in the fluorescence studies above.

*The precise degree of dissociation cannot be evaluated without a knowledge of the value of the formation constant K in D_2O . The constant should differ to some degree from that characteristic of H_2O solutions.

Comparisons with Related Systems

Exploratory experiments were carried out to determine whether the analogous EuEDTA^- ion formed a fluorescent mixed ligand complex with SSA^{3-} . Europium is of particular interest since all successful liquid laser systems, to date, have employed trivalent europium chelates. Titration data show that $\text{Eu}(\text{EDTA})(\text{SSA})^{4-}$ forms, and is of very similar stability to $\text{Tb}(\text{EDTA})(\text{SSA})^{4-}$. Solutions containing $\text{Eu}(\text{EDTA})(\text{SSA})^{4-}$ in either H_2O or D_2O , did not, however, give the visible red fluorescence characteristic of Eu^{3+} when irradiated with either 2537 or 3660 Å radiation. Attempts to measure the room temperature quantum efficiency at 612 mμ (2537 Å excitation) of a D_2O solution 0.02M in NaEuEDTA and 0.02M in Na_2SSA gave a value of < 1%.

It is generally recognized⁽¹³⁾ that efficient intramolecular energy transfer in rare earth chelates requires that the lowest triplet level of the organic portion of the species lie above that of the resonance energy level of the bonded rare earth ion. Further, one would expect most efficient energy transfer when the two levels have nearly the same energy⁽¹³⁾. The high quantum efficiency observed for the $\text{Tb}(\text{EDTA})(\text{SSA})^{4-}$ ion suggests that the triplet level lies close to (but above) the $^5\text{D}_4$ level of Tb^{3+} . The $^5\text{D}_0$ and $^5\text{D}_1$ resonance levels of Eu^{3+} occur at lower energies. The very low fluorescence characteristic of $\text{Eu}(\text{EDTA})(\text{SSA})^{4-}$ can then be attributed to the mismatch between the energies of the organic triplet level and the europium resonance levels, and to the resulting greater probability for dissipation of energy by nonradiative means.*

* The referee has pointed out that other factors, in addition to the relative positions of organic triplet and rare-earth energy levels, are important in determining europium ion fluorescence intensity. In comparing the ions $\text{Eu}(\text{EDTA})(\text{SSA})^{4-}$ and $\text{Tb}(\text{EDTA})(\text{SSA})^{4-}$, however, one would expect that such factors as gross structure, symmetry about the metal atom, nature and strength of bonding, and the energies of the triplet levels would be nearly the same for the two complexes. The most obvious explanation for the observed difference in fluorescence behavior would seem, therefore, to involve in some manner the difference between europium and terbium resonant energy levels.

A few experiments have also been carried out with mixtures of the trivalent anion of 1-hydroxy-4-sulfo-2-naphthoic acid with TbEDTA^- or EuEDTA^- . These systems in water do not give the fluorescence characteristic of the rare earth ion, although pH titration data indicate that mixed ligand complex formation occurs. Substitution of the naphthalene nucleus apparently lowers the organic triplet level below the $^5\text{D}_4$ level of Tb without improving the energy match with the resonance levels of Eu.

Experimental

Sodium Terbium Ethylenediaminetetraacetate

Twenty ml of 0.50M aqueous TbCl_3 (from Lindsay 99.9% TbCl_3 , hydrate) was converted to the hydroxide by mixing with 200 ml water and adding 40 ml 1M NH_4OH . The gelatinous precipitate was filtered off, air-dried and added to a mixture of 200 ml water and 3.0 g solid ethylenediaminetetraacetic acid. The mixture was heated until all solid had dissolved. After cooling, the liquid was filtered and 600 ml acetone was added to the filtrate. The mixture was cooled overnight in the refrigerator. The solid was filtered off, washed with acetone and air-dried at room temperature. Recrystallization from 150 ml water by the addition of 400 ml acetone gave 5.8 g air-dried product. Calcd. for $\text{C}_{10}\text{H}_{12}\text{O}_8\text{NaTb} \cdot 8\text{H}_2\text{O}$: C, 19.6; H, 4.59; N, 4.56. Found: C, 20.1; H, 4.42; N, 4.59%.

Disodium Sulfosalicylate

Sodium hydroxide (8.0 grams, 0.2 mole) in 20 ml water was added to 25.4 g (0.1 mole) Fisher reagent grade 5-sulfosalicylic acid dissolved in 50 ml water. Acetone (150 ml) was added and the mixture cooled in the refrigerator. The solid was filtered off, washed with acetone and air-dried at room temperature. Yield 23 g. The compound was recrystallized by precipitating from 100 ml water with 250 ml acetone. Yield 16.5 g. Calcd. for $C_7H_4O_6SNa_2 \cdot 3H_2O$: Na, 14.6; H_2O , 17.1. Found: Na, 14.6; H_2O , 16.5% (by thermogravimetry to 200°C in an argon atmosphere).

pH Titrations

Twenty-five ml water containing 4×10^{-4} moles sodium terbium ethylenediaminetetraacetate 8-hydrate and 4×10^{-4} moles of Fisher reagent grade 5-sulfosalicylic acid was titrated with carbonate-free standard 1M NaOH from a micrometer syringe. Readings of pH were made with a Thomas No. 4858-45 combination glass-reference electrode used with a Leeds and Northrup Model 7664 pH meter. A stream of argon was bubbled continuously through the solution to exclude CO_2 . Measurements were carried out at room temperature (ca 25°C).

It was established by a separate titration that NaTbEDTA alone did not titrate in the pH region employed to calculate formation constants.

The formation constant K was calculated from the titration data as described by Thompson and Lorass⁽⁷⁾. The value of pK_g for the dissociation of the phenolic hydrogen of 5-sulfosalicylic acid was taken as 11.74⁽¹⁴⁾.

Fluorescence Titrations

Solutions of the same composition as used for the pH titrations (vide supra) were titrated with standard 1M or 10M NaOH. After each addition of titrant a sample of solution was removed to a 2 mm thick quartz spectrophotometer cell, by means of a hypodermic syringe, and a fluorescence intensity reading was taken from the front surface of the cell (the surface exposed to the exciting ultraviolet radiation).

The fluorescence titration apparatus was constructed in this laboratory. It consisted of a short wavelength (predominately 2537 Å) Mineralight ultraviolet source and a Clairex Type 505L CdS photoconductive cell as the sensor. A Corning CS 3-72 filter was used in front of the photocell to filter out ultraviolet radiation. The ultraviolet source and photocell were oriented at 90° with respect to each other. The photocell was used in series with two mercury cells (total of 2.8 V) and an R.C.A. Ultra-Sensitive microammeter. Meter readings were related to light intensity by means of a series of calibration experiments which employed a fluorescing $\text{Tb}(\text{EDTA})(\text{SSA})^{4-}$ solution and neutral density filters of known transmission.

Since the ultraviolet intensity tended to change significantly during the course of a titration, it was monitored by means of a second CdS photocell which was separated from the U.V. source by means of a piece of fluorescent uranium glass. The voltage to the U.V. lamp was adjusted during the titration to keep the reference reading constant.

Fluorescence Spectra

Solutions with an overall terbium concentration of 0.02M were made up by combining equimolar quantities of NaTbEDTA and Na₃SSA. The Na₃SSA was prepared by adding the calculated volume of standard NaOH solution to a solution of Na₂HSSA in water. Solutions in D₂O were prepared first in H₂O. The mixture was then evaporated to dryness at room temperature with a stream of H₂ and the residue brought up to volume with Volk 99.8% D₂O.

The fluorescence spectra were obtained with a 1 meter Jarrell Ash Spectrometer with a dispersion at the exit plane of 16 Å per millimeter. A photo-multiplier with an S-20 characteristic response was used to detect the signal at the exit plane. The spectrum shown in Fig. 5 has been corrected for sensitivity change with recorded wavelength.

Absorption Spectra

Absorption spectra were measured with a Cary Model 14 spectrophotometer. Solutions of rather high concentration (0.01 or 0.02M) were employed to more accurately approximate the concentrations required for laser testing. Path lengths of the quartz cells were chosen to give optimum absorbance values. For the more absorbing solutions this required quite short path lengths, 0.05 mm or 0.2 mm. These were achieved by means of 1 cm cells with quartz inserts. For the low-absorbing NaTbEDTA, path lengths up

to 10 cm were employed. The spectrum of Na_3SSA was obtained in 0.1 M NaOH, rather than in water, to suppress hydrolysis. Results are expressed in Fig. 2 in terms of the molar extinction coefficient $\epsilon = A/cl$, where A is the absorbance, c is the molar concentration, and l is the cell path length in cm.

Continuous Variations Studies (Method of Job)⁽¹⁵⁾

Separate water solutions 0.04M in NaTbEDTA and 0.04M in Na_3SSA (from Na_2HSSA and NaOH) were prepared. Measured volumes of the two solutions were combined. Optical absorbance was measured at 257 and 310 m μ , employing 0.05 mm path length cells. The ordinate in Fig. 3a is the difference between the observed absorbance and that calculated from the absorbance of a 0.04M solution of Na_3SSA , assuming Beers Law to be obeyed.

In a separate series of runs (Fig. 3b) fluorescence intensity, rather than U.V. absorbance, was measured.

Quantum Efficiency

The absolute quantum efficiency of the 1:1 mixture of NaTbEDTA and Na_3SSA in heavy water was measured using the arrangement shown in Fig. 6. The Hg lamp was a General Electric AH-4, the output of which was found to be constant during the course of the experiment. The liquid samples were contained in a thin walled rectangular quartz cell having inside cavity dimensions of 1 x 3 x 0.1 cm. The thickness of the solution exposed to the exciting radiation was one millimeter and the area that defined by a

7 mm diameter circle cut in a thin blackened wall placed in contact with the 1 x 3 cm face of the cell. The distance between the cell and the photomultiplier was 1/2 meter.

An 8×10^{-4} M solution of fluorescein in 0.1M NaOH used as a standard⁽¹⁶⁾⁽¹⁷⁾. The concentration of the unknown solution was 2×10^{-2} M. At these concentrations essentially all of the exciting radiation was absorbed within the 1 mm thickness for the standard as well as for the unknown solutions. Then since the amount and geometrical distribution of exciting radiation is the same for all solutions,

$$Q_u(\lambda_p) = (R_s/R_u)(A_u/A_s)(S_u/S_s) \left(\frac{\int_0^\infty F(\lambda) dA_s}{\int_0^\infty F(\lambda) dA_u} \right) Q_s(\lambda_p) \quad (3)$$

where subscripts s and u refer to standard (fluorescein) and unknown respectively and where

$Q(\lambda_p)$ = quantum efficiency of solution for exciting radiation of wavelength λ_p .

R = photomultiplier sensitivity at the wavelength of maximum fluorescent light intensity reaching the photo-multiplier.

A = area of the fluorescence spectrum after spectrum has been corrected for nonuniform response of detecting system with recorded wavelength (fluorescein spectrum taken with dilute sample in order to minimize spectrum distortion due to absorption of part of the initial fluorescence).

S = Keithley signal

$F(\lambda)$ = transmission of Corning filters CS-4-64 and CS-3-69 at wavelength λ .

This equation neglects errors from two sources. First, the index of refraction of the standard and unknown solutions may differ. The ray path geometry is then not the same between the standard and unknown. In the present case, this source of error is negligible since all solutions had nearly the same index of refraction. The second source of error arises from absorption of part of the fluorescein fluorescence followed by re-emission⁽¹⁶⁾. A correction for this effect similar to that described in reference 16 has been applied to the result given by equation 3 and is included in the stated quantum efficiencies.

Acknowledgments

The writers are grateful to Dr. R. C. Ohlmann for his contributions to the early phases of this work, and to Miss P. Haverlack and Mr. R. Williams for help in the experimental portion of the program.

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Table I

Formation Constant for the Reaction



4×10^{-4} moles NaTbEDTA, 4×10^{-4} moles H_3SSA ,
initial volume = 25 ml

<u>ml 1M NaOH</u>	<u>pH</u>	<u>log K</u>
0.90	9.00	4.14
0.92	9.20	4.11
0.94	9.35	4.04
0.96	9.49	4.04
0.98	9.60	4.06
1.00	9.71	4.09
1.05	10.00	<u>4.13</u>
	av.	4.09

References

1. C. Brecher, H. Samelson and A. Lempicki, J. Chem. Phys. 42, 1081 (1965).
2. R. C. Ohlmann, E. P. Riedel, R. C. Charles and J. M. Feldman, in
"Quantum Electronics III", P. Grivet and N. Bloembergen, Editors,
Columbia University Press, New York (1964), p. 779.
3. M. L. Bhaumik, P. C. Fletcher, L. J. Nugent, S. M. Lee, S. Figa,
C. L. Telk and M. Weinberg, J. Phys. Chem. 68, 1490 (1964).
4. E. J. Schimitschek, R. B. Nehrich and J. A. Trias, J. Chem. Phys. 42,
788 (1965).
5. D. B. Luten, Jr., Phys. Rev. 45, 161 (1934).
6. T. Moeller, D. F. Martin, L. C. Thompson, R. Ferrus, G. R. Feistel
and W. J. Randall, Chem. Rev. 65, 1 (1965).
7. L. C. Thompson and J. A. Lorass, Inorg. Chem. 2, 89 (1963).
8. J. L. Hoard, B. Lee and M. D. Lind, J. Am. Chem. Soc. 87, 1611,
1612 (1965).
9. K. S. Thomas, S. Singh and G. H. Dieke, J. Chem. Phys. 38, 2180 (1963).
10. A. Heller and E. Wasserman, J. Chem. Phys. 42, 949 (1965).
11. J. L. Kropp and M. W. Windsor, J. Chem. Phys. 39, 2769 (1963);
42, 1599 (1965).
12. M. L. Bhaumik and C. L. Telk, J. Opt. Soc. 54, 1211 (1964).

References (Continued)

13. N. Filipescu, W. F. Sager and F. A. Serafin, J. Phys. Chem. 68, 3324 (1964).
14. S. Chaberck and A. E. Martell, "Organic Sequestering Agents", Wiley, New York (1959), p. 515.
15. Ref. 14, p. 78.
16. W. H. Melhuish, J. Phys. Chem. 65, 229 (1961).
17. W. H. Melhuish, J. Opt. Soc. Am. 52, No. 11, 1256 (1962).

Curve 573587-8

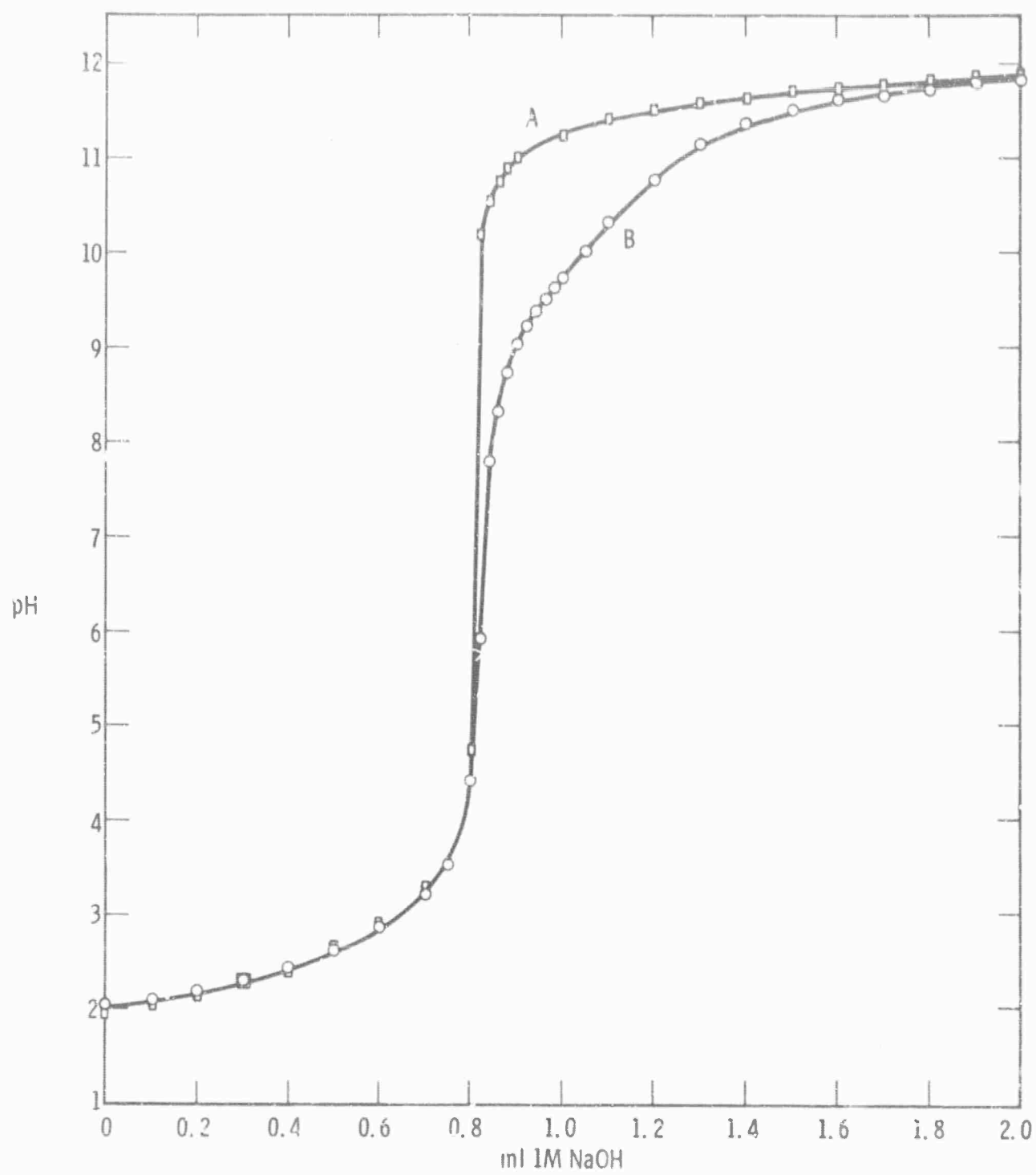


Fig. 1—Titration curves: A, 4×10^{-4} moles H_3SSA . B, 4×10^{-4} moles $H_3SSA + 4 \times 10^{-4}$ moles $NaTbEDTA$.
Initial volume 25 ml

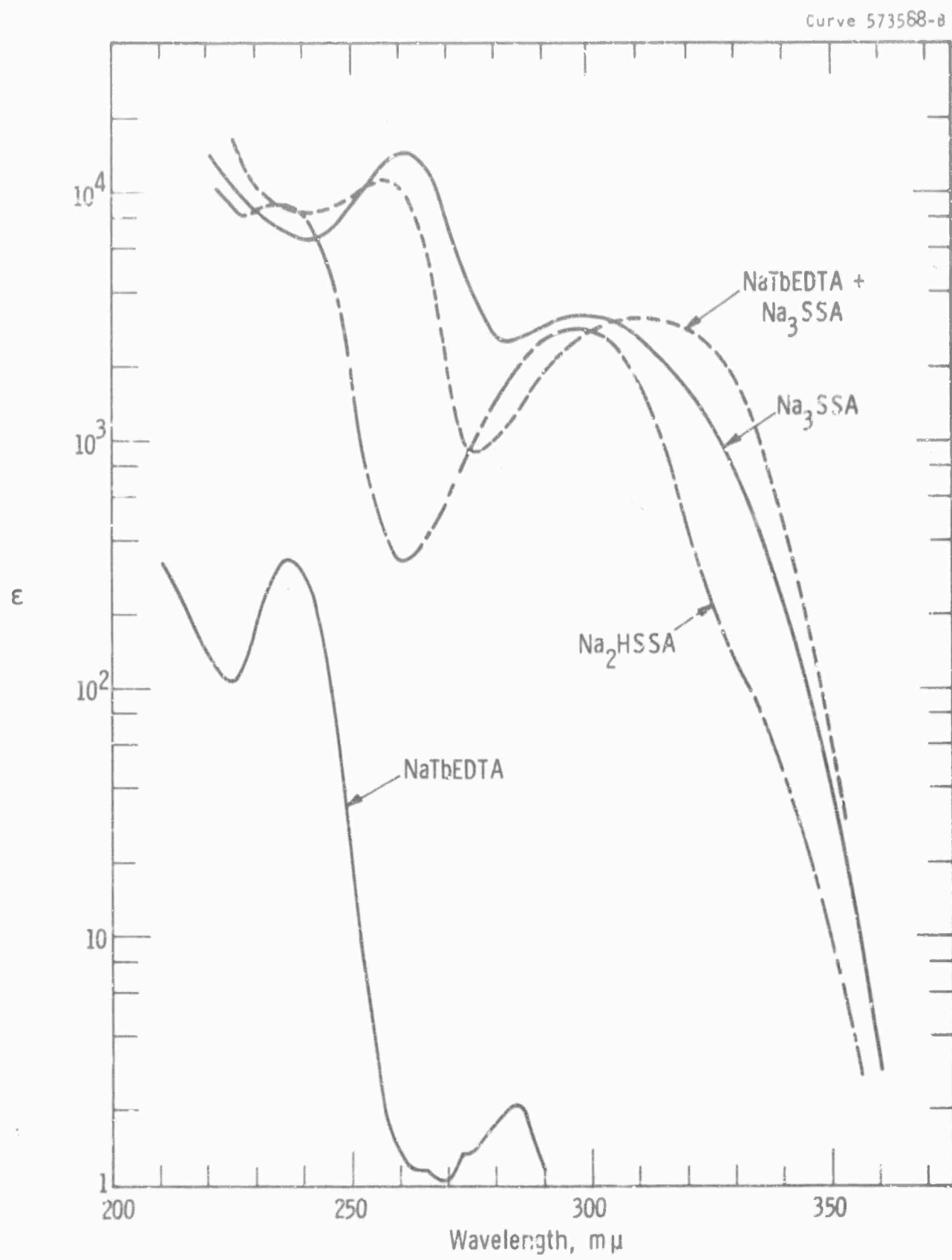


Fig. 2—Ultraviolet absorption spectra in water

Curve 573589-8

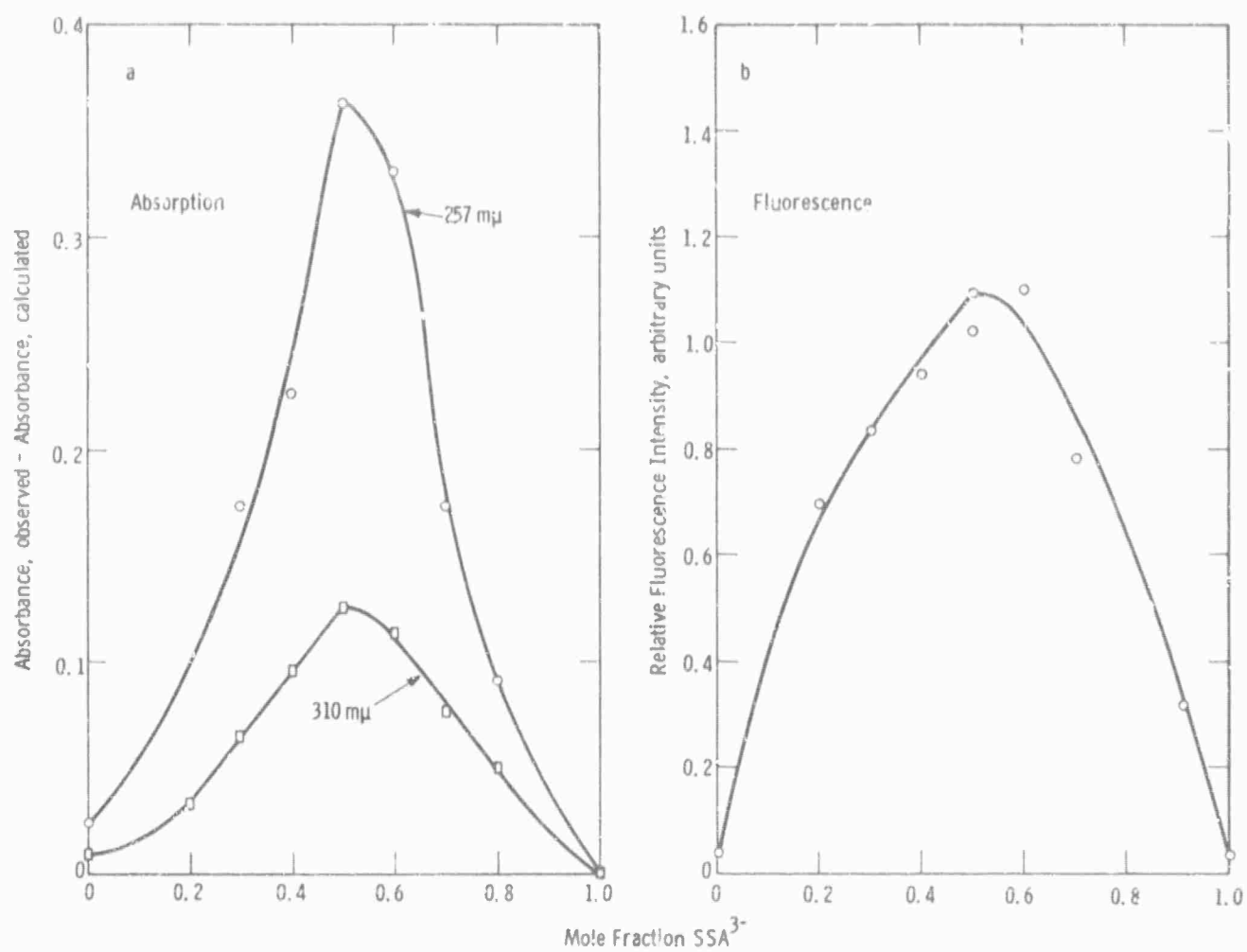


Fig. 3—Continuous variations studies for mixtures of sodium terbium ethylenediaminetetraacetate and trisodium sulfosalicylate in water solution ($\text{NaTbEDTA} + \text{Na}_3\text{SSA} = 0.04 \text{ M}$)

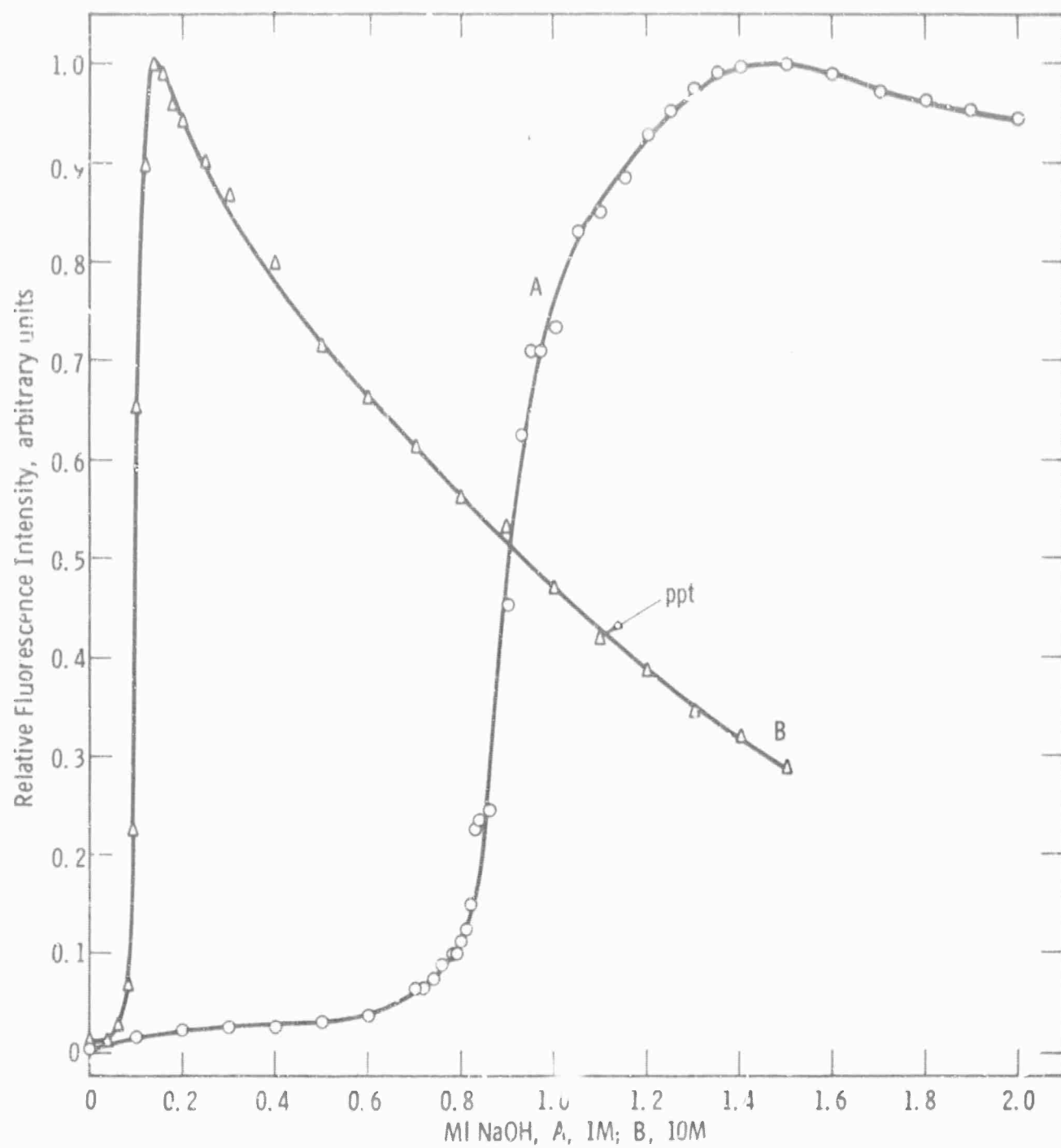


Fig. 4—Titration of a water solution 0.02M in H_3SSA and 0.02M in $NaTbEDTA$ with $NaOH$

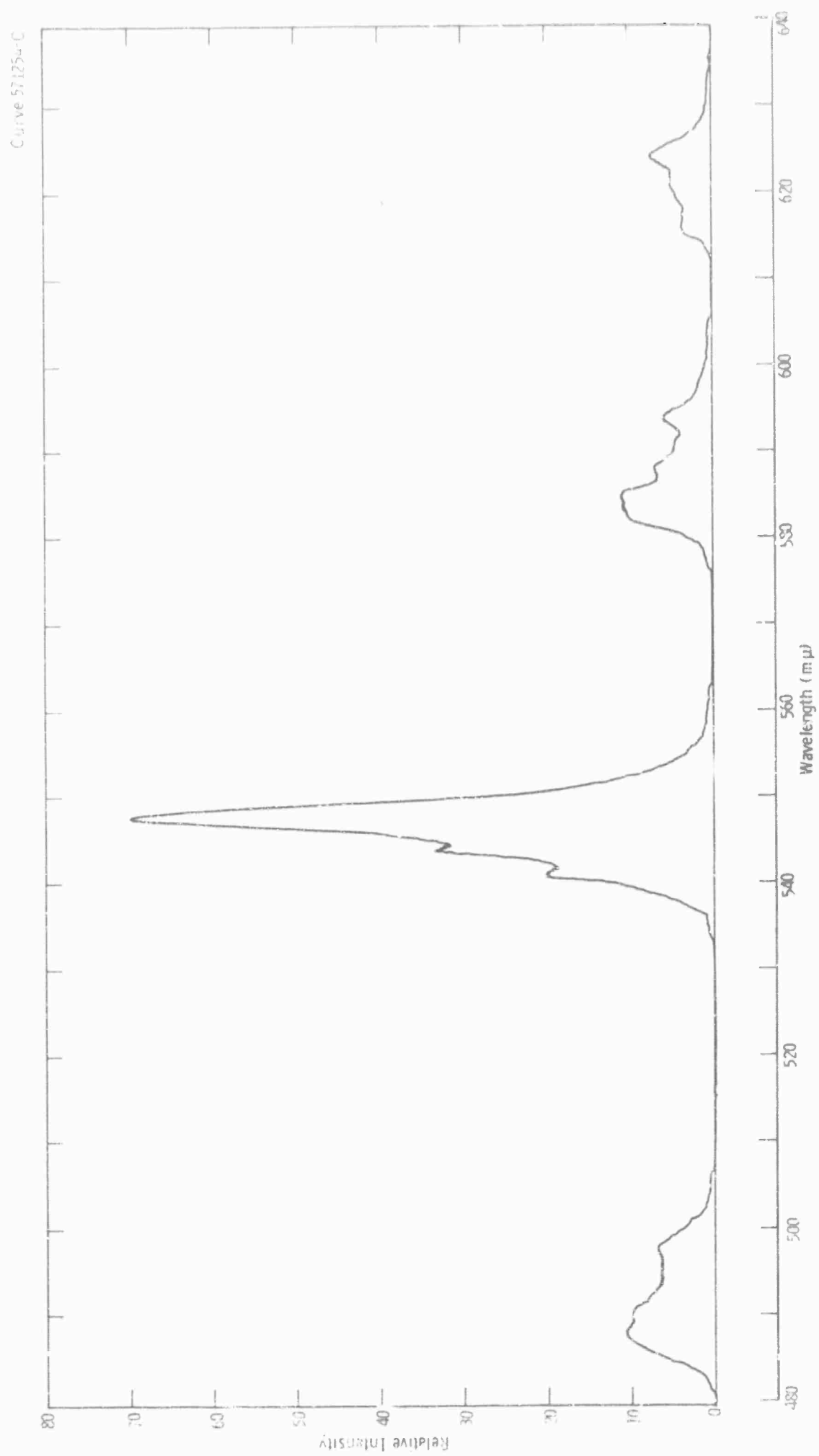


Fig. 5—Fluorescence spectrum of 0.02M $[Tb(SSA)(EDTA)]^{4-}$ at 300°K with near UV excitation and 4 Å resolution

Dwg. 745A896

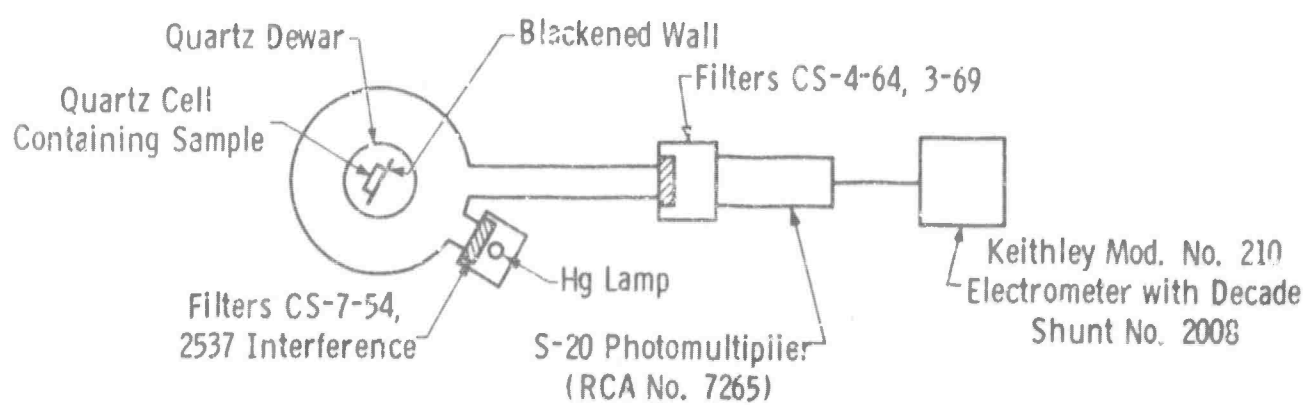


Fig. 6—Arrangement used for measuring quantum efficiency

APPENDIX C

The Effect of Organic Cations on the Laser Threshold of
Solutions of Europium Tetraakis Benzoyltrifluoroacetate

May 21, 1965

THE EFFECT OF ORGANIC CATIONS ON THE LASER THRESHOLD OF
SOLUTIONS OF EUROPIUM TETRAKIS BENZOYLTRIFLUOROACETONATE¹

by

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Recently, Samelson *et al*² and Schimitschek *et al*³ reported laser action at room temperature for the piperidinium (P) and pyrrolidinium salts, respectively, of the tetrakis form of europium benzoyltrifluoroacetate ($\text{Eu}(\text{BTF})_4^-$) dissolved in acetonitrile.

We have investigated 15 organic salts of $\text{Eu}(\text{BTF})_4^-$ in acetonitrile and have obtained laser action for 14 of them. The stored electrical energy required to reach threshold oscillations in these solutions is, however, dependent to a surprising degree on the nature of the organic cation, as shown in Table 1. In addition to the results of Table 1, we have also observed room temperature laser action with a threshold of 660 J, using a 0.05 M concentration of the piperidinium salt, but operation at this temperature (24°C) is erratic. The laser threshold values listed in Table 1 are, however, reproducible to ± 20 percent at 0°C and at -30°C.

At 0°C, we found the threshold of the solutions containing the piperidinium salt to decrease as the concentration was lowered below 0.05 M to a value of 260 J at 7.5×10^{-3} M. The three salts in Table 1 which did not lase at 0.05 M concentration were, therefore, tested again at

0.01 M. The results are included in parentheses in Table 1. Only the quinolinium salt did not lase under any condition.

The cell used to contain the liquid solution was a 1 mm inside diameter quartz capillary cell which will be described in detail along with some laser emission characteristics at a later date.

The tetrakis chelates were prepared by combining, in ethanol-water solution, EuCl_3 with benzoyltrifluoroacetone and the organic amine or tetraalkylammonium hydroxide in the molar ratios 1:4.5:4.5. The precipitated solid was air-dried at room temperature. Elemental analyses were in each case in satisfactory agreement with the composition $\text{BEu}(\text{BTF})_4$. The use of triethanol amine in this preparation gave the hydrated tris chelate $\text{Eu}(\text{BTF})_3 \cdot 2\text{H}_2\text{O}$, rather than the expected tetrakis compound.

The magnitude of the variation in threshold energy requirements with organic cation (Table 1) was not expected since electrical conductivity measurements indicate that each of the salts in acetonitrile is dissociated to a large degree to the free cation and $\text{Eu}(\text{BTF})_4^-$. In order to obtain additional information pertaining to this question, the piperidinium and quinolinium salts, which represent the extremes in threshold of those listed in Table 1, were investigated in detail.

The ultraviolet absorption spectra of 0.05 M solutions of these two salts in acetonitrile are essentially identical. At 0.05 M concentration, most effective laser pumping occurs in a 1 mm capillary cell near $3900\text{\AA}$. At this wavelength, the absorptions of both cations are negligible compared to the anion. Therefore, "blocking" of laser pump light by the cations does not take place to any important extent.

The absolute quantum efficiency of the piperidinium salt (0.05 M in acetonitrile, irradiated with 3150Å light) has been measured by comparison with rhodamine B as a standard^{4,5} and found to be $0.75 \pm .15$. The ratio of the quantum efficiency of the quinolinium to the piperidinium salt solution is, however, only 0.65. At room temperature about 95 percent of the total fluorescence from both solutions occurs near 6120Å in the $^5D_0 \rightarrow ^7F_2$ transition characteristic of Eu^{+3} .

One possible reason for the lower quantum efficiency of the quinolinium salt solution involves quenching of the anion emission by interaction with the quinolinium ion. If such a process is operative, one would expect the quantum efficiency to decrease as the concentration of the chelate salt in solution is increased. However, while the quantum efficiency of the piperidinium salt remained constant on increasing the concentration from 5×10^{-3} to 1×10^{-1} M, that of the quinolinium salt increased about 18 percent. This result indicates that such a quenching process is not taking place.

An alternate explanation for the lower quantum efficiency of the quinolinium salt, which is consistent with the observed results, can be given in terms of the dissociation of the chelate anion, reaction 1.



The quantum efficiency of the electrically neutral tris chelate $\text{Eu}(\text{BTF})_3$ in acetonitrile is only about 1/10 that of $\text{PEu}(\text{BTF})_4$ solutions. Any dissociation according to (1) will, therefore, result in lower overall quantum efficiencies.

Since the $^5D_0 \rightarrow ^7F_2$ emission band for $\text{Eu}(\text{BTF})_3$ occurs at nearly the same wavelength as for $\text{PEu}(\text{BTF})_4$, the presence in solution

of $\text{Eu}(\text{BTF})_3$ is more easily detected by means of the much weaker $^5\text{D}_0 \rightarrow ^7\text{F}_0$ emissions. Fig. 1 shows this portion of the fluorescence spectrum for solutions made up from $\text{PEu}(\text{BTF})_4$, $\text{Eu}(\text{BTF})_3$, and $\text{QEu}(\text{BTF})_4$, where Q is the quinolinium ion. From the nearly symmetrical shape of the main peak of curve (a) and the relative intensities of curves (a) and (b), the amount of $\text{Eu}(\text{BTF})_3$ in the solution prepared from $\text{PEu}(\text{BTF})_4$ is found to be less than 10 percent of the total europium present. Curve (c), however, shows an asymmetry which we attribute to the presence of appreciable $\text{Eu}(\text{BTF})_3$.

If f represents the fractional dissociation of tetrakis molecules in the quinolinium solution and r the ratio of the intensity of the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ emission from tris molecules in the quinolinium solution (c) to that from the pure tris solution (b), we have⁶

$$r = 3f/4. \quad (2)$$

Constructing curve (c) from the sum of two appropriate curves of shape (a) and (b), we find f to be equal to 0.40.

The greater amount of $\text{Eu}(\text{BTF})_3$ observed in solutions prepared from $\text{QEu}(\text{BTF})_4$ suggests that the quinolinium ion facilitates the dissociation of $\text{Eu}(\text{BTF})_4^-$. We postulate, as one possible mechanism, that this is the result of ion pairing according to reaction (3). To the



extent that (3) occurs, BTF^- is removed from solution and equilibrium (1) is shifted to the right.

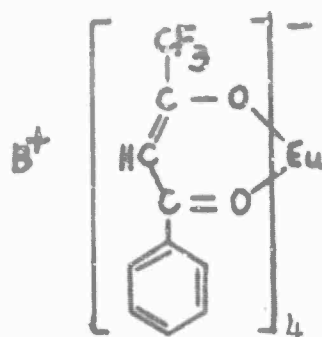
In summary, the results presented here show that the cation in the salt $\text{BEu}(\text{BTF})_4$ can be important in determining the laser capabilities of solutions containing the salt without interacting directly with the lasing species $\text{Eu}(\text{BTF})_4^-$ to change its spectral properties.

References

1. This work was partially supported by Project DEFENDER under joint sponsorship of ARPA, ONR and DOD under Contract Number Nonr-4573(00).
2. H. Samelson, A. Lempicki, C. Brecher, and V. Brophy, Appl. Phys. Lett. 5, No. 9, 173 (1964).
3. E. J. Schimitschek, J. A. Trias and R. B. Nehrlich, Jr., J. Appl. Phys. 36, No. 3, 667 (1965).
4. G. Weber and F. W. J. Teals, Trans. Faraday Soc. 53, 646 (1957).
5. W. H. Melhuish, J. Phys. Chem. 65, 229 (1961).
6. C. Brecher, H. Samelson, and A. Lempicki, J. Chem. Phys. 42, 1081 (1965).

Table 1*

Measured Threshold Energy for
Various β -diketone Chelates of Structure:



Threshold Energy in Joules
(Concentration: $5 \times 10^{-2} \text{M}$ in Acetonitrile)

B	0°C	-30°C
piperidinium	600	No Test
tetra-n-butylammonium	>1800 (300)	1800 (No Test)
diethylammonium	800	No Test
triethylammonium	1100	No Test
n-butylammonium	800	No Test
pyridinium	900	No Test
isoquinolinium	1400	No Test
2-hydroxyethylammonium	1300	No Test
tetramethyl guanidinium	800	No Test
tetramethylammonium	700	No Test
benzylammonium	900	No Test
quinolinium	>1800 (>1600)	>1800 (>1600)
dibenzylammonium	>1800 (1600)	>1800 (No Test)
tetraethylammonium	1800	No Test
tetra-n-propylammonium	>1800	1800

*The symbol > signifies that laser action was not observed up to the indicated energy and that tests at higher energies at that temperature were not conducted.

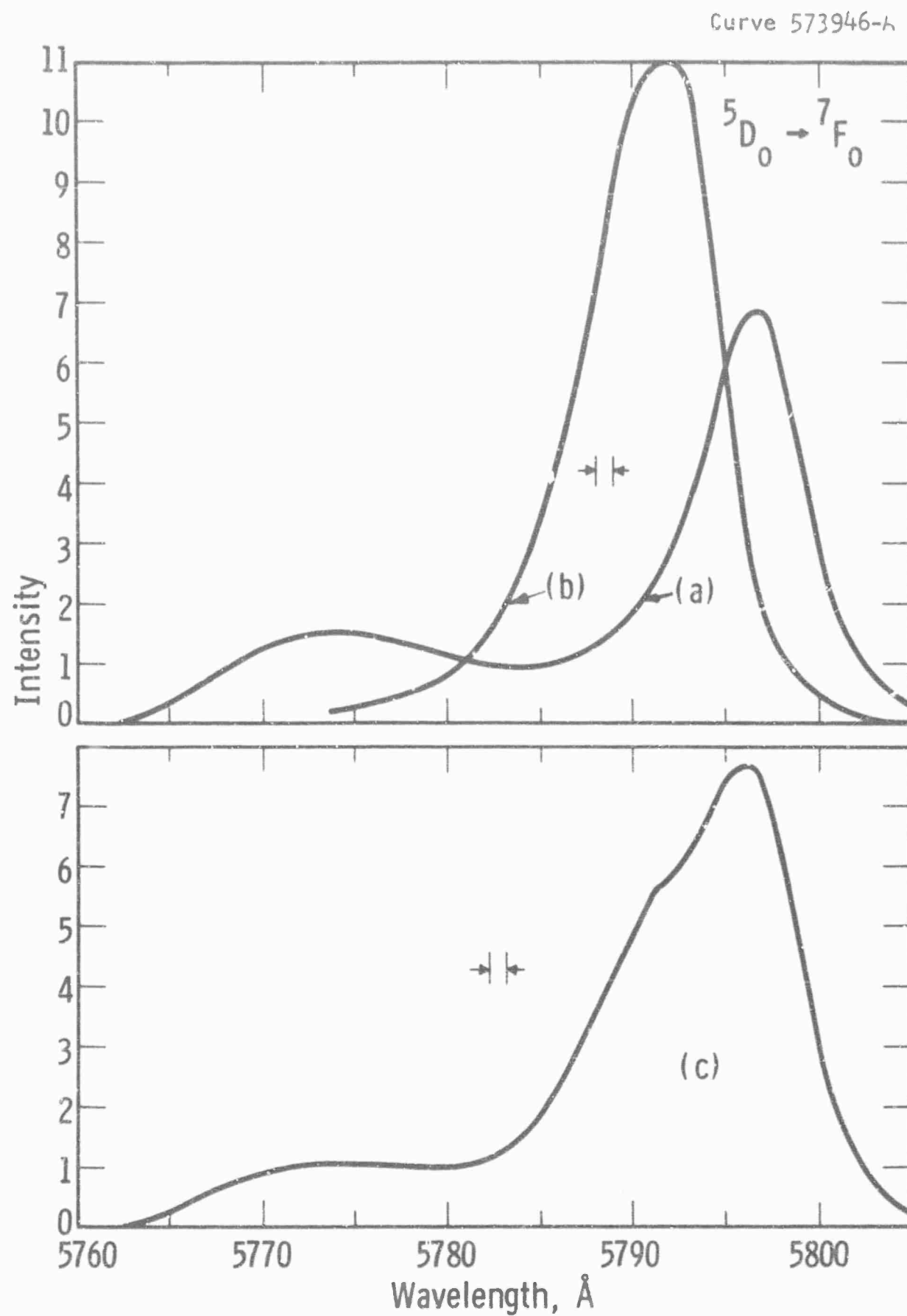


Fig. 1—Room temperature $^5D_0 \rightarrow ^7F_0$ fluorescence of 0.05 M solution of (a) P $\text{Eu}(\text{BTF})_4$, (b) $\text{Eu}(\text{BTF})_3$ and (c) Q $\text{Eu}(\text{BTF})_4$ in acetonitrile. (Intensity scale is the same for all three curves)

APPENDIX D

Spectroscopic and Laser Properties of Europium
 α -Naphthoyltrifluoroacetate in Solution

Spectroscopic and Laser Properties of Europium
 α -Naphthoyltrifluoroacetate in Solution*

by

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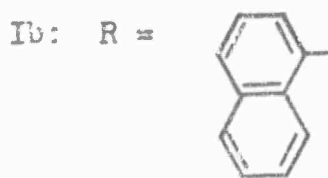
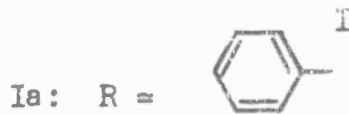
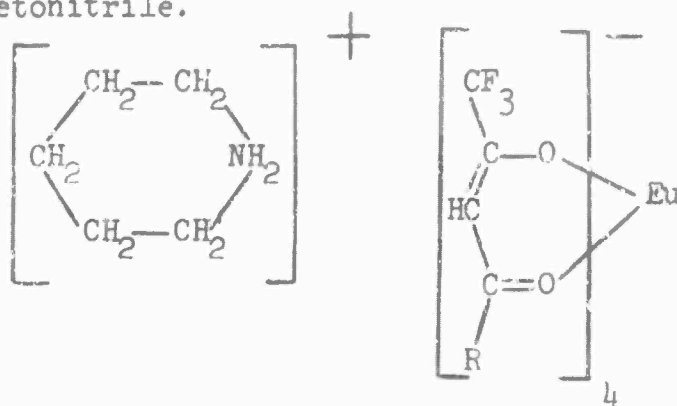
* This work was partially supported by Project DEFENDER under joint sponsorship of ARPA, ONR and DOD under Contract Number Nonr 5033(00).

ABSTRACT

Ultraviolet radiation absorbed by the organic ligands surrounding the europium ion in europium α -naphthoyltrifluoroacetate $\text{Eu}(\alpha\text{-NTF})_4^-$ is efficiently converted via intramolecular energy transfer to fluorescence characteristic of Eu^{+3} . The quantum efficiency for this process is shown to be a constant from 2600 to 3900Å in acetonitrile solution. Laser operation has been observed at temperatures up to -10°C . The effect of the relatively high scattering losses on both the threshold and the radiance of the laser are discussed.

INTRODUCTION

During the past few years a considerable amount of information has been obtained on the chemical, spectroscopic, and laser characteristics of rare-earth chelates⁽¹⁻¹⁰⁾. Much of this work stems from the early demonstration by Weissmann⁽¹¹⁾ of intramolecular energy transfer in these materials and their more recently demonstrated suitability for use as the active material in liquid lasers⁽¹²⁻¹⁶⁾. The interesting spectroscopic and laser properties^(17,13) of the europium tetrakis benzoyltrifluoroacetate anion ($\text{Eu}(\text{BTF})_4^-$, Ia) have led us to investigate the consequences of altering the structure of the anion while maintaining the basic tetrakis form. One of the compounds we have considered in this study is the piperidinium salt of europium tetrakis α -naphthoyltrifluoroacetate, $\text{PEu}(\alpha\text{-NTF})_4$, Ib. This paper describes some of the spectroscopic, chemical, and laser properties of this material dissolved in acetonitrile.



EXPERIMENTAL

Materials

The previously unreported β -diketone, α -naphthoyltrifluoroacetone, was synthesized by the condensation of ethyl trifluoroacetone with methyl- α -naphthyl ketone in the presence of sodium methoxide. The procedure was similar to that of Reid and Calvin⁽¹⁸⁾. The compound was conveniently isolated as the crystalline piperidinium salt, formed from the crude β -diketone and a small excess of piperidine in ethanol. Overall yield 70%. Calculated for $(C_5H_{12}N)^+(C_{14}H_8F_3O_2)^-$: C, 65.0; H, 5.7; N, 4.0%. Found: C, 65.0; H, 5.8; N, 3.9%.

The europium chelate $PEu(\alpha-NTF)_4$ was prepared as follows. The piperidinium salt above (6.32 grams, 0.018 moles) was dissolved in 60 ml 95% ethanol by warming. $EuCl_3$ (0.004 moles) dissolved in 20 ml water was added to the warm solution. The chelate separated as a semisolid which crystallized on standing at room temperature. The solid was washed with 1:1 (V/V) ethanol-water and air-dried at room temperature. Yield 96%, based on the $EuCl_3$. Calcd. for $(C_5H_{12}N)^+[(C_{14}H_8F_3O_2)_4Eu]^-$: C, 56.4; H, 3.4; N, 1.1%. Found: C, 56.3; H, 3.5; N, 1.5%.

Solutions in acetonitrile were prepared from Fisher reagent grade solvent.

Spectroscopy

Absorption spectra of solutions of $PEu(\alpha-NTF)_4$ in acetonitrile were obtained on a Cary Model 14 spectrophotometer. The wavelength range below 3850 Å where the absorption cross section is high was obtained using a concentration of $2.5 \times 10^{-3} M$ and 0.05 mm quartz cells (1 cm cells with quartz inserts).

For wavelengths longer than $3850\text{\AA}$, a concentration of 0.01M was used and 1.0 mm quartz cells.

Fluorescence spectra were obtained with a 1/2 meter Jarrell Ash spectrometer with a dispersion of $32\text{\AA}$ per millimeter. A photomultiplier with an S-20 characteristic response was used to detect the signal. A Corning CS3-69 filter was placed between the sample and the entrance slit in order to remove scattered lamp light below $510\text{ m}\mu$. The fluorescence spectra are presented corrected for system sensitivity as a function of wavelength. The samples were contained in quartz cells. By passing the light from an Osram (XBO-900) xenon arc lamp through a second 1/2 meter Jarrell Ash spectrometer, the samples were illuminated in a band between 380 and $350\text{ m}\mu$. A Corning CS7-37 filter was placed between the exit plane and the sample in order to eliminate scattered light above $390\text{ m}\mu$.

The excitation spectrum was obtained by scanning with the spectrometer used in illumination of the sample and setting the other spectrometer at the desired wavelength of the fluorescent spectrum to be monitored. The spectrum is presented reduced to constant quanta per unit wavelength interval of the exciting beam. This was achieved by detecting with a photomultiplier the fluorescence of a rhodamine B quantum counter⁽¹⁹⁾ which was excited by a portion of the beam used to excite the sample. This signal was then ratioed with the signal from the sample fluorescence.

Laser Apparatus

The laser cell used in these experiments is somewhat different than those used by other investigators⁽²⁰⁾. The cell shown in Fig. 1 is a 0.1 centimeter inside diameter quartz capillary tube with an active pump length of 6.7 centimeters and a mirror spacing of 9.3 centimeters. The ends of the tube were first polished flat to $\lambda/10$ and parallel to better than ten seconds of arc. Quartz disks flat to $\lambda/10$ and parallel to about two seconds of arc were wrung on to the ends of the tube. Each disk was then attached to the tube with epoxy cement. Multilayer films having approximately 99 percent reflectivity at $6120\text{\AA}$ were deposited on the outside surface of each disk and are, therefore, not in contact with the liquid material within the capillary. Three EG & G linear flash lamps (FX-42) are connected in series and placed at 120° intervals around the cell as shown in Fig. 2 with Corning CS7-59 filters inserted between the lamps and the cell. A heavy aluminum foil is then wrapped around the outside of the three lamps. The cell assembly is held in an insulated chamber so that the temperature may be both stabilized and controlled by a flow of precooled and dry nitrogen.

The intensity of the light output from the end of the laser capillary and from the pump light from the flash lamps were presented simultaneously, as a function of time, on an oscilloscope screen. The traces were recorded photographically on Polaroid 3000 speed film.

The light output-time recording, the spectral width, the wavelength and the beam divergence of the laser emission may all be obtained simultaneously during one optical pumping cycle. The first three of these are obtained by passing the light from one end of the cell through a 1/2 meter Jarrell Ash

spectrometer and splitting the output, part going to a photomultiplier and part being recorded on film. The spectrometer is used in second order where its dispersion is $10\text{\AA}$ per millimeter. The entrance slit is a Hilger-Watts model F1497 individually adjustable slit. The exit slit is also a Hilger-Watts F1497 slit but modified so that it can open to 5 millimeters. A partially transparent mirror placed two inches beyond the exit plane splits the beam--one part going to a photomultiplier and the remainder to a lens. The lens magnified the spectrum at the exit plane approximately ten times. The magnified image is recorded on Polaroid 3000 speed film. A Wratten #24 red filter is placed in front of the film while a CS2-63 is placed in front of the photomultiplier in order to remove scattered flash lamp light. Calibration of the dispersion of the system at the film plane which is $1.63\text{\AA}$ per millimeter was accomplished by setting the entrance slit at ten microns and the exit slit at four millimeters and allowing two neon reference lines to expose the film at 6096.16 and 6143.06 $\text{\AA}$. The source used was a neon-fill hollow cathode lamp. The laser emission which falls between these two lines⁽²¹⁾ is then used to expose the film a second time. The resolution of this spectrograph at this entrance slit setting was found to be 0.2 $\text{\AA}$ by measuring with the aid of a traveling microscope the width of a line on the film obtained by using the 6328 $\text{\AA}$ emission of a He-Ne gas laser as a narrow line source.

The directionality of the laser output was studied during the same flash tube pulse by photographing the far field pattern of the light output from the other end of the laser cell. A red Wratten #24 filter and appropriate neutral density filters were placed in front of the Polaroid 3000 speed film in order to obtain proper exposures free of flash lamp light.

RESULTS AND DISCUSSION

Structural Considerations

The considerable activity in the field of liquid lasers has resulted in the demonstration of laser action with a number of europium chelates. All such lasing species are tetrakis chelates derived from β -diketones.* Laser action in solution has not, so far, been obtained with chelates derived from other classes of organic chelating agents nor has it been obtained with rare earths other than europium.

Of the europium β -diketone chelates which have been investigated, particular interest attaches to those containing a trifluoromethyl group as part of the organic structure (the anion of formula I, above), since solutions containing these compounds show laser action at relatively high temperatures^(13,15,16). Most effort has been devoted to solutions containing the europium chelate anion of Ia, derived from benzoyltrifluoroacetone. In some instances solutions containing this anion lase near room temperature^(13,15,16). The compound Ic, in which the 2-thienyl group is substituted for phenyl in Ia, also shows laser action⁽²²⁾, although apparently not at as high temperatures as Ia. Further studies of the compounds I, in which R is varied, would be expected to provide additional evidence on the structural parameters which influence laser action. We report here data obtained with the compound Ib, in which the α -naphthyl group is substituted for phenyl.

* Although early liquid laser work was carried out with materials thought to be the tris chelates, current evidence indicates that these also were actually the tetrakis forms.

Substitution at R in I can alter the chelate anion in several different ways which could influence laser action. (1) The nature of R can affect the ultraviolet absorption spectra of solutions containing I, and hence can alter the wavelength range over which effective optical pumping takes place. (2) R, through resonance and inductive interaction with the chelate rings, can influence the electron distribution within these rings and can alter the energy of the lowest organic triplet level relative to the energy of the europium $^5D_0$ resonance level. (3) Bulky groups at R could presumably, through steric hindrance, alter the symmetry of the eight bonded oxygen atoms about the Eu^{3+} and influence the probability of the $^5D_0 \rightarrow ^7F_2$ transition which gives rise to laser action.

Spectroscopy

When an acetonitrile solution of $PEu(\alpha\text{-NTF})_4$ is illuminated with near ultra-violet light, characteristic Eu^{+3} ion fluorescence⁽²³⁾ is observed as shown in Fig. 3. As may be seen from Curve A, the $^5D_0 \rightarrow ^7F_2$ group is by far the most intense, accounting for approximately 90% of the total emission. The main line is centered at $6118\text{\AA}$ with a width at half height of $28\text{\AA}$. Curve B was obtained by increasing the amplifier gain by a factor of 19.2. This shows in more detail the remaining groups which are barely apparent in Curve A. Analysis of the $^5D_0 \rightarrow ^7F_0$ emission has been shown to be of value in determining the number of different europium containing species contributing to the observed fluorescence^(17,16). The $^5D_0 \rightarrow ^7F_0$ emission is shown in greater detail in Fig. 4. The appearance of only one line in this region is consistent with the assumption that only one europium species is responsible for the observed fluorescent spectrum.

The ultraviolet absorption spectrum of $\text{Eu}(\alpha\text{-NTF})_4^-$ in acetonitrile is shown in Fig. 5. The very large values of the molar extinction coefficient are characteristic of $\pi\text{-}\pi^*$ absorption bands associated with the organic ligands of the molecule. As has previously been pointed out⁽¹⁾, such intense absorption bands prevent effective pumping (at the concentrations required for laser operation) along the axis of a laser cell, even when the cell is as small as one millimeter in inside diameter. For this reason, the long-wavelength tail of the absorption band is the most effective pumping region for laser purposes. For example, at a concentration of 0.002M, the penetration depth defined as the reciprocal of the absorption coefficient, for pump radiation is equal to the radius of the laser material at a wavelength of 379 m μ . This wavelength excites the cross-section of the laser material in a 0.1 cm bore diameter cell efficiently and fairly uniformly. At a concentration of 0.01M, the wavelength for a penetration depth of 0.05 cm is shifted to 390 m μ . Wavelengths within this general range will, however, only be effective for laser pumping if the fluorescent quantum efficiency is high for excitation at wavelengths within this range.

A change in the quantum efficiency as a function of excitation wavelength may be ascertained by comparing the absorption spectrum with the excitation spectrum. The excitation spectrum of a solution containing $\text{Eu}(\alpha\text{-NTF})_4^-$ is shown in Fig. 6. For wavelengths longer than 3900 $\text{\AA}$, absorption of the exciting light by the sample decreases very rapidly. However, for shorter wavelengths essentially all of the exciting light is absorbed. The nearly horizontal line below 3900 $\text{\AA}$ indicates therefore a quantum efficiency which is a constant within about $\pm 10\%$ between 3900 and 2600 $\text{\AA}$. At room temperature, the quantum efficiency

of a 0.01M solution in acetonitrile excited by 3150Å radiation is $0.52 \pm .15$. This was obtained by comparing the fluorescent intensity of this solution with a solution of piperidinium europium-benzoyltrifluoroacetate ($\text{PEu}(\text{BTF})_4$) in acetonitrile, the quantum efficiency of which has been measured and found to be $0.75 \pm .15^{(16)}$. The fluorescent decay time of a 0.01M solution of $\text{PEu}(\alpha\text{-NTF})_4$ in acetonitrile at 24°C is 408 microseconds. As the temperature is lowered, both the decay time and the quantum efficiency of $\text{PEu}(\alpha\text{-NTF})_4$ increase reaching $0.9^{+.05}_{-.15}$ and 735 microseconds respectively at -30°C.

Laser Characteristics

We have been able to obtain laser operation at various concentrations of $\text{Eu}(\alpha\text{-NTF})_4$ in acetonitrile at temperatures up to -10°C. As the temperature of the solution is increased above -30°C, the flash lamp energy required to obtain laser oscillations steadily increases. At -10°C this energy is near the maximum allowable energy for our excitation system and therefore this is the highest temperature at which we have observed laser operation with this material. The rise in threshold requirements as the temperature is increased is due, at least in part, to the drop in quantum efficiency with rise in temperature. This drop in quantum efficiency is somewhat more severe than it is for $\text{Eu}(\text{BTF})_4$ in acetonitrile where we and others have been able to obtain laser operation near room temperature^(13,15,16). In order, therefore, to insure consistent results in laser experiments with $\text{Eu}(\alpha\text{-NTF})_4$ we have conducted all experiments discussed in this paper at -20°C.

A photomultiplier recording of the laser emission at approximately 1.2 times threshold input energy to the flash lamps is shown in Fig. 7. For approximately the first 360 microseconds only a small photomultiplier signal due to spontaneous emission is observed. Intermittent laser emission then

occurs for the next 270 microseconds followed by the decay of spontaneous emission.

Figures 8a, 8b, and 8c were all taken simultaneously (see experimental section) at approximately 2.3 times threshold. In Fig. 8a, the laser spikes are again clearly evident. Laser threshold is reached sooner in Fig. 8a than in Fig. 7 as one would expect on the basis of the greater pumping rate. The cause of the somewhat more erratic character of the spiking, i.e., the separation of about 140 μ seconds between the first two groups of spikes is not clear. One possible explanation for this laser suppression is scattering losses⁽²⁴⁾ due to the effects of non-uniform heating of the liquid. This is a reasonable explanation, in view of the fact that these losses are shown in a following section of this paper to be quite large even near threshold pumping conditions. In addition, it has been shown⁽²⁴⁾ that the scattering effects increase rapidly as the pumping energy is increased.

Figure 8b is a one-to-one reproduction of the magnified image of the spectrum at the exit plane of the spectrometer. Fig. 8b is actually a double exposure, the neon reference lines being exposed before the flash lamps are discharged. From the position of the laser line relative to the neon lines, the laser output wavelength is found to be $6113.2\text{\AA}$. From a measurement of the width of the laser line and a knowledge of the dispersion at the film plane ($1.63\text{\AA}/\text{mm}$) the laser emission is found to take place over a wavelength band $0.3 \pm 0.1\text{\AA}$ wide. Since the spontaneous line width at -20°C is $23\text{\AA}$, considerable spectral narrowing is evident during laser operation. The $0.3\text{\AA}$ band width is much larger than the spacing between individual modes of a plane parallel resonator⁽²⁵⁾ with the dimensions used in this experiment. Therefore laser oscillations are evidently taking place in more than one mode during one pumping cycle.

Fig. 8c shows the pattern (1 to 1 reproduction) of the unaltered laser beam at a distance of 250 centimeters from one mirror. When this exposure is repeated just below the flash lamp energy needed for laser threshold, no pattern appears, i.e., the film remains completely dark. The diameter of the pattern in Fig. 8c is approximately 2.4 centimeters. The laser beam divergence is therefore about 0.01 radians. The pattern size associated with laser operation in the longitudinal mode TEM_{00} such as described by Fox and Li⁽²⁶⁾ would, at this distance, be approximately 0.4 centimeters in diameter. Therefore since the film in Fig. 8c is not overexposed, most of the recorded emission, i.e., that outside a central circle about 0.4 centimeters in diameter, cannot be associated directly with the output from resonant modes. The spiking character of the output radiation shown in Fig. 7 and 8a and its narrow spectral width are however consistent with the existence of resonant modes. It seems reasonable to suppose that the pattern shown in Fig. 8c represents a composite of the pattern from more than one resonant mode together with the pattern produced by radiation scattered out of these modes. Scattered rays will, of course, be amplified by stimulated emission while traveling back and forth in the liquid. They will also be repeatedly rescattered and finally lost from the resonator by partial transmission at the mirrors and by "walk off".

In order for the output pattern, shown in Fig. 8c, to consist mostly of scattered radiation, the scattering loss per pass for a resonant mode must be appreciable. An estimate of the scattering losses at threshold can be obtained by using the experimentally determined minimum concentration of ions needed to obtain laser operation. Fig. 9 is a graph of the stored electrical energy required to reach threshold vs. concentration of $PEu(\alpha-NTF)_4$. The minimum concentration needed to reach threshold is approximately .0017M. This corresponds to a concentration of $1.0 \times 10^{18}/cm^3$. Because not every ion is

inverted, this number is strictly an upper limit to the minimum population inversion ΔN required for threshold. We may use it however to estimate the scattering losses at threshold. At threshold a wave traveling back and forth between mirrors with reflection coefficients r_1 and r_2 and separated by a distance L must be amplified just enough in the medium to overcome all losses, i.e.,

$$(1 - d_1)(1 - d_2) r_1 r_2 e^{-2(\alpha + S)L} = 1 \quad (1)$$

where α and S are the absorption coefficient and the scattering coefficient of the material respectively at the wave frequency and d_1 and d_2 are the diffraction loss per bounce at mirror 1 and 2 respectively. Using this relation, taking account of the degeneracies g_i of levels i , the index of refraction μ of the laser material, and assuming a gaussian line shape, the population inversion requirement at threshold⁽²⁷⁾ may be written as

$$\Delta N = N_2 - g_2/g_1 N_1 = 2\pi^{3/2} c \mu^2 \tau \Delta\lambda \left\{ 2LS - \ln[r_1 r_2 (1-d_1)(1-d_2)] \right\} \sqrt{\ln 2} \lambda^4 L \quad (2)$$

where

N_i = number of atoms per unit volume in level i

τ = the lifetime of the upper level 2 due to spontaneous emission of radiation by a transition between levels 2 and 1.

λ = the wavelength in vacuum at the peak of the gaussian spontaneous emission line with a full width at half height of $\Delta\lambda$.

c = speed of light.

Using the dimensions of the optical cavity and the results of Fox and Li⁽²⁶⁾, the values of the diffraction losses d_1 and d_2 for the TEM_{00} mode may be shown to be 0.018. Spectroscopic and other data yield the following values for the

other parameters: $\mu = 1.346$, $\tau = 7.4 \times 10^{-4}$ seconds, $\Delta\lambda = 2.3 \times 10^{-7}$ centimeters, $\lambda = 6.12 \times 10^{-5}$ centimeters, $r_1 = r_2 = 0.99$ and $L = 6.7$ centimeters. Using these values and the minimum concentration of $1.0 \times 10^{18} \text{ cm}^{-3}$ for ΔN in equation (1) yields a scattering loss per pass of 30%. We see therefore that an appreciable scattering loss exists at threshold. If the scattering losses are set equal to zero and the other parameters unchanged in equation (1), the required population inversion ΔN would be only $8 \times 10^{16} \text{ cm}^{-3}$. Thus, a scattering loss of 30% per pass, in the case, raises the required population inversion at threshold by a factor of 12. In addition to raising the threshold for laser oscillations to take place in resonant cavity modes, scattering losses from these modes serve to increase the radiation density in off axis rays. Since these rays are also amplified in the medium and may traverse the medium a number of times before "walk off" occurs, they can contribute a major portion to the total output beam energy. Since these rays are inclined to the axis of the resonator, they serve to increase the beam divergence angle of the laser output above that expected for diffraction limited operation in longitudinal resonant modes. This is an important deleterious effect if high radiance is desired in the emitted laser beam since the radiance of a laser is proportional to the inverse of the square of the output beam divergence angle. In addition to this effect, the loss of energy from the laser when "walk off" of off axis rays occurs may be an important factor in lowering the energy of the output beam of the laser.

There appears to be no satisfactory way to avoid these losses in optically pumped liquid lasers employing organic solvents. This is because all organic solvents for which data are available in the range where their viscosity

is low have the comparatively large value of the change in refracted index with temperature, dn/dT , near $-4 \times 10^{-4}/^{\circ}\text{C}$. It has been suggested^(28,29) that heavy water be used as a solvent for liquid lasers in order to minimize the scattering effects associated with dn/dT . This is because dn/dT for heavy water is zero at approximately 6°C ⁽³⁰⁾, while its freezing point is below this at 3.8°C . It should be noted that the europium tetrakis β -diketone chelates which have been shown to lase in organic solvents are insufficiently soluble for use in water. There is no known reason, however, why suitable water-soluble systems should not be devised. The principal difficulty is that the fundamental knowledge relating laser activity to chemical structure is still not sufficiently developed to predict which of the many possible systems in D_2O are likely to give laser action. In recent work from this laboratory^(29,31) we have investigated two different rare earth systems, each of which has two of the necessary qualifications for laser action in D_2O , i.e. suitable ultraviolet absorption characteristics and high quantum efficiency for conversion of absorbed energy to rare-earth ion fluorescence. The fact that neither system shows laser action, however, illustrates the importance of other parameters, in addition to ultraviolet absorption and fluorescence efficiency, in determining liquid laser action, and emphasizes the need for further studies in these areas.

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REFERENCES

1. R. C. Ohlmann, E. P. Riedel, R. G. Charles and J. M. Feldman in "Quantum Electronics III", P. Grivet and N. Bloembergen, Editors, Columbia University Press, New York, p. 779 (1964).
2. R. E. Whar and G. E. Crosby, J. Mol. Spectroscopy 8, 315 (1962).
3. R. G. Charles and A. Perrotte, J. Inorg. Nucl. Chem. 26, 373 (1964).
4. R. C. Ohlmann and R. G. Charles, J. Chem. Phys. 40, 3131 (1964).
5. R. G. Charles and R. C. Ohlmann, J. Inorg. Nucl. Chem. 27, 119 (1965).
6. R. G. Charles, J. Inorg. Nucl. Chem. 26, 2295 (1964).
7. R. G. Charles, J. Inorg. Nucl. Chem. 26, 2298 (1964).
8. R. G. Charles and R. C. Ohlmann, J. Inorg. Nucl. Chem. 27, 255 (1965).
9. F. Halverson, J. S. Brinen and J. R. Leto, J. Chem. Phys. 40, 2790 (1965).
Ibid 41, 157 (1964).
10. M. L. Bhaumik, J. Chem. Phys. 40, 3711 (1964).
11. S. I. Weissman, J. Chem. Phys. 10, 214 (1942).
12. A. Lempicki and H. Samelson, Phys. Letters 4, 133 (1963).
13. H. Samelson, A. Lempicki, C. Brecher and V. Brophy, Applied Phys. Letters 5, 173 (1964).
14. A. Lempicki, H. Samelson and C. Brecher, J. Chem. Phys. 41, 1214 (1964).
15. E. J. Schimitschek, J. A. Trias and R. B. Nehrich, Jr., J. Appl. Phys. 36, 867 (1965).
16. E. P. Riedel and R. G. Charles, "The Effects of Organic Cations on the Laser Threshold of Solutions of Europium Tetrakis Benzoyltrifluoroacetate", J. Appl. Phys., in press.

17. C. Brecher, H. Samelson and A. Lampicki, J. Chem. Phys. 42, 1081 (1965).
18. J. C. Reid and M. Calvin, J. Am. Chem. Soc. 72, 2948 (1950).
19. W. H. Melhuish, J. Opt. Soc. Am. 52, 1256 (1962).
20. A. Lampicki and H. Samelson, Proceedings of the Symposium on Optical Masers, Polytechnic Press, Brooklyn, New York, p. 347 (1963).
21. American Institute of Physics Handbook Second Edition, Dwight E. Gray, coordinating editor, McGraw-Hill, New York, p. 7-52 (1963).
22. E. J. Schimitschek, R. B. Nehrlich and J. A. Trias, J. Chem. Phys., 42, 729 (1965).
23. G. H. Dieke and H. M. Crosswhite, Appl. Opt. 2, 675 (1963).
24. E. P. Riedel, App. Phys. Lett. 5, No. 8, 162 (1964).
25. G. D. Boyd and J. P. Gordon, Bell System Tech. J. 25, 489 (1961).
26. A. G. Fox and Tingye Li, Bell System Tech. J., 40, 453 (1961).
27. A. L. Schawlow and C. H. Townes, Phys. Rev. 112, 1940 (1958).
28. E. P. Riedel, paper presented at the National Aerospace Electronics Conference, Dayton, Ohio (May 31, 1963).
29. R. G. Charles, E. P. Riedel and P. G. Haverlack, "Energy Transfer Between p-Benzoylbenzoate and Europium Ethylenediamine tetraacetate in Water Solution", J. Chem. Phys., in press.
30. D. B. Luten, Jr., Phys. Rev. 45, 161 (1934).
31. R. G. Charles and E. P. Riedel, "A Fluorescent Terbium Chelate System in Water Solution", J. Inor. Nucl. Chem., in press.

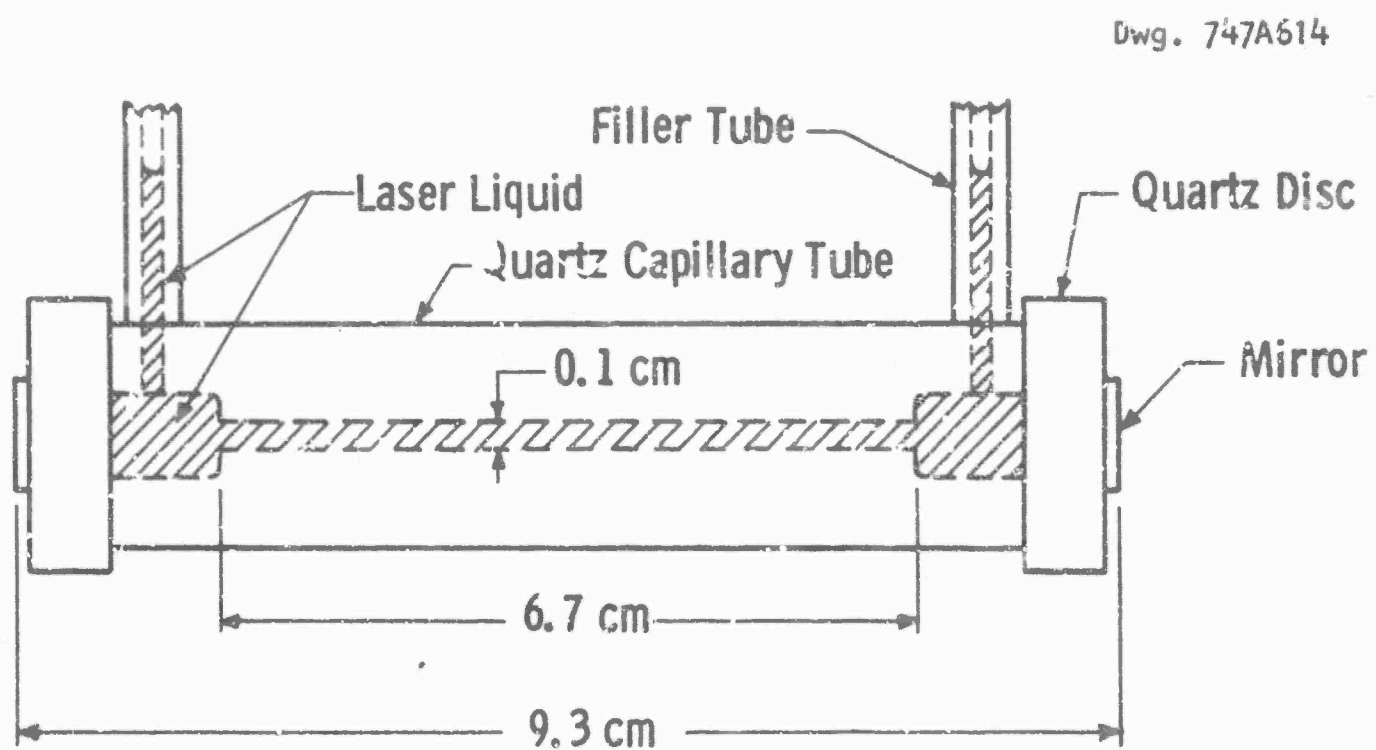


Fig. 1-- Schematic drawing of liquid laser cell (not to scale)

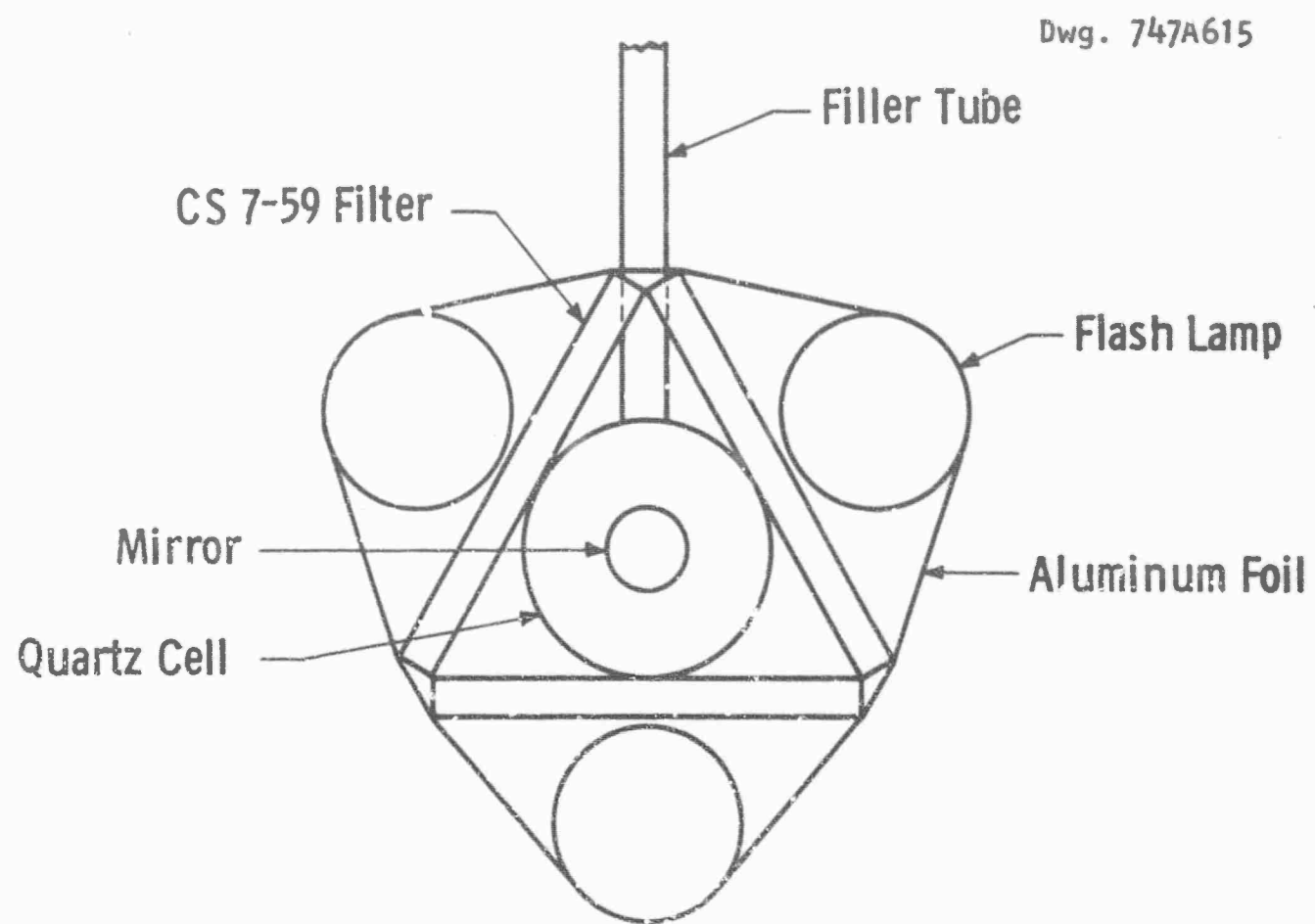


Fig. 2—Schematic Drawing of end view of laser assembly (not to scale)

Curve 576313-A

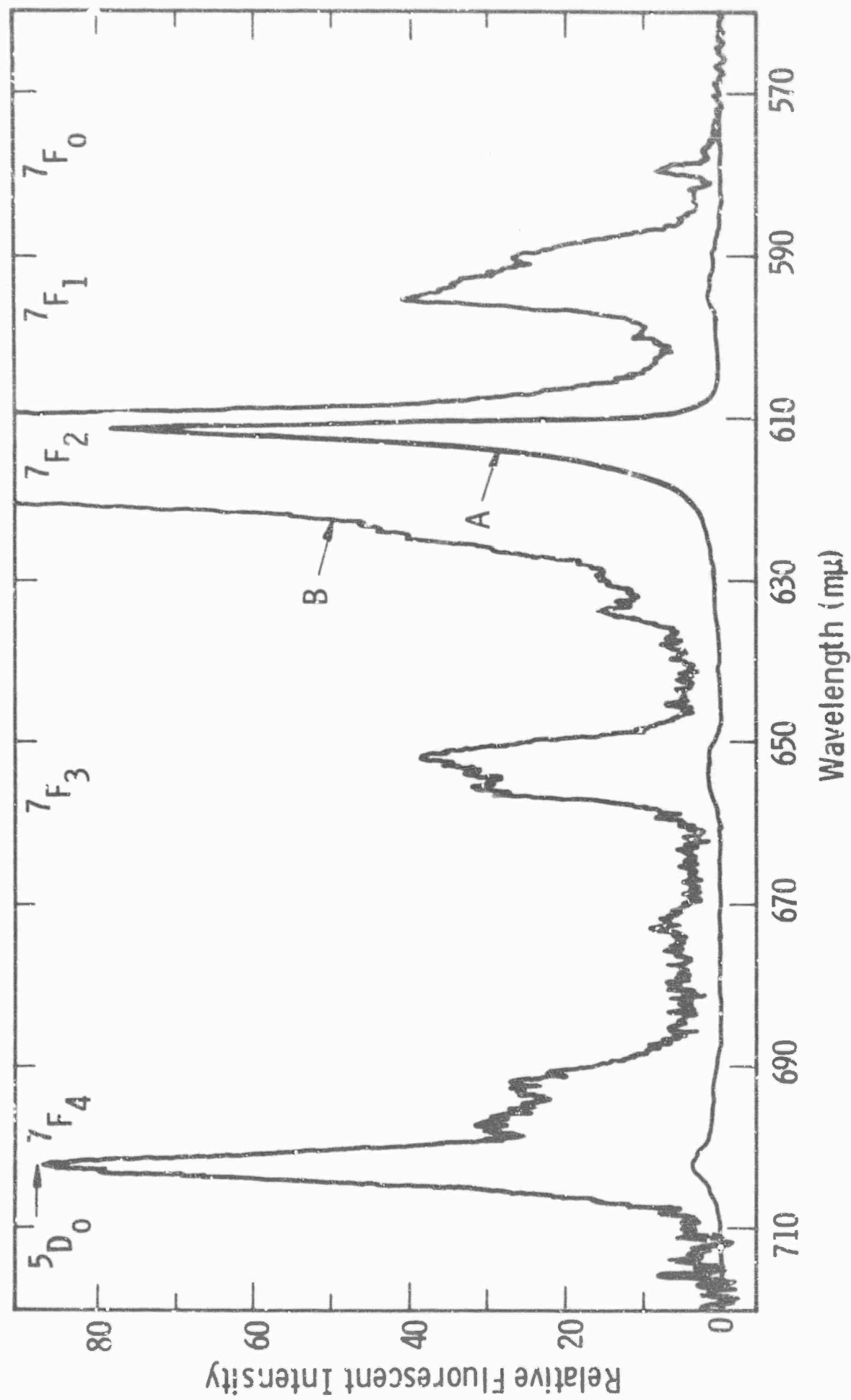


Fig. 3--Room temperature fluorescence spectra of 0.01 M $\text{PEu}(\alpha\text{-NTF})_4$ in acetonitrile.
Gain for Curve B is 19.2 times that for Curve A. Resolution: $5\text{\AA}$

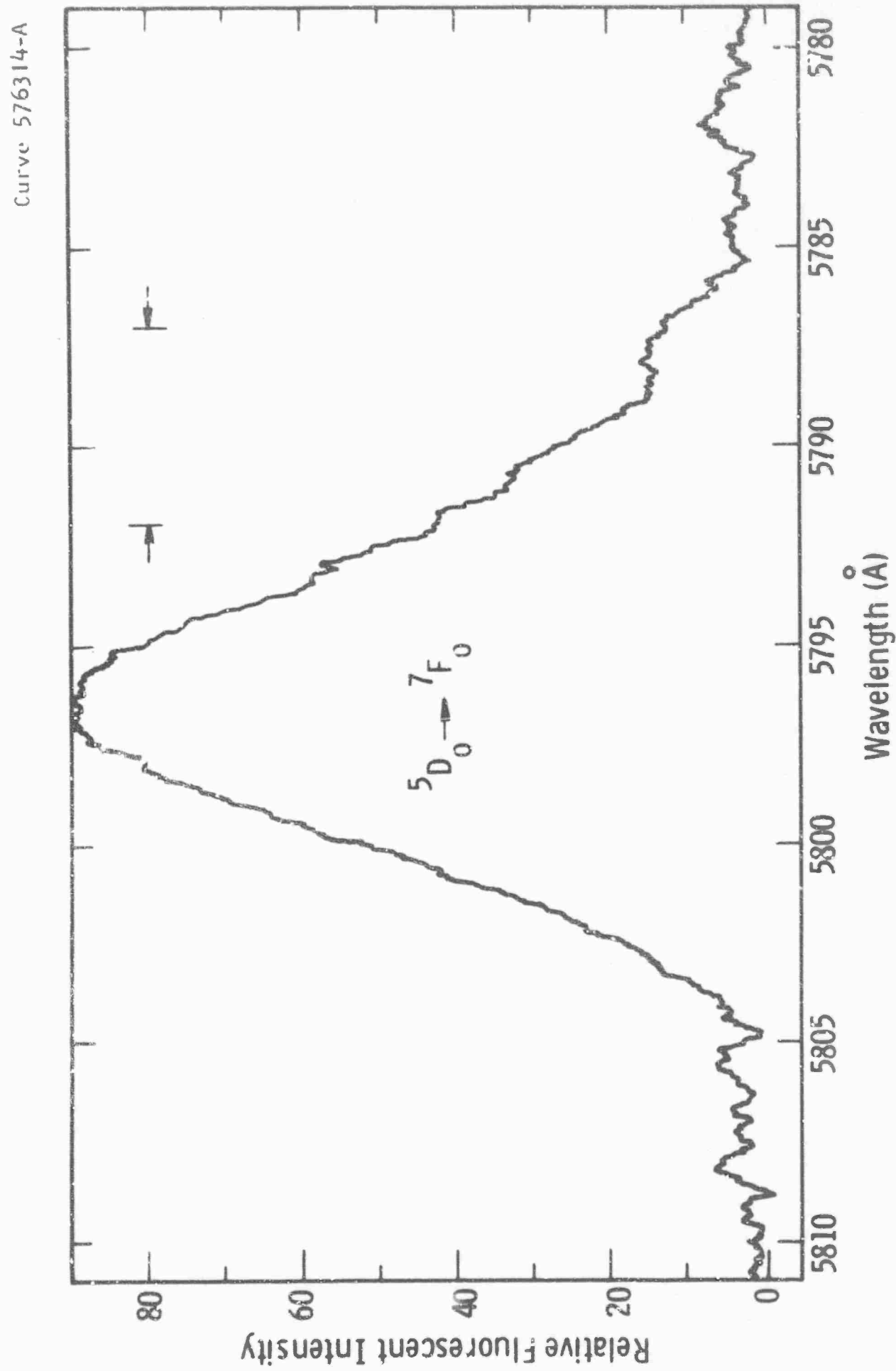


Fig. 4—Room temperature $5D_0 \rightarrow 7F_0$ fluorescence of 0.01 M PEu (α -NTF)₄ in acetonitrile

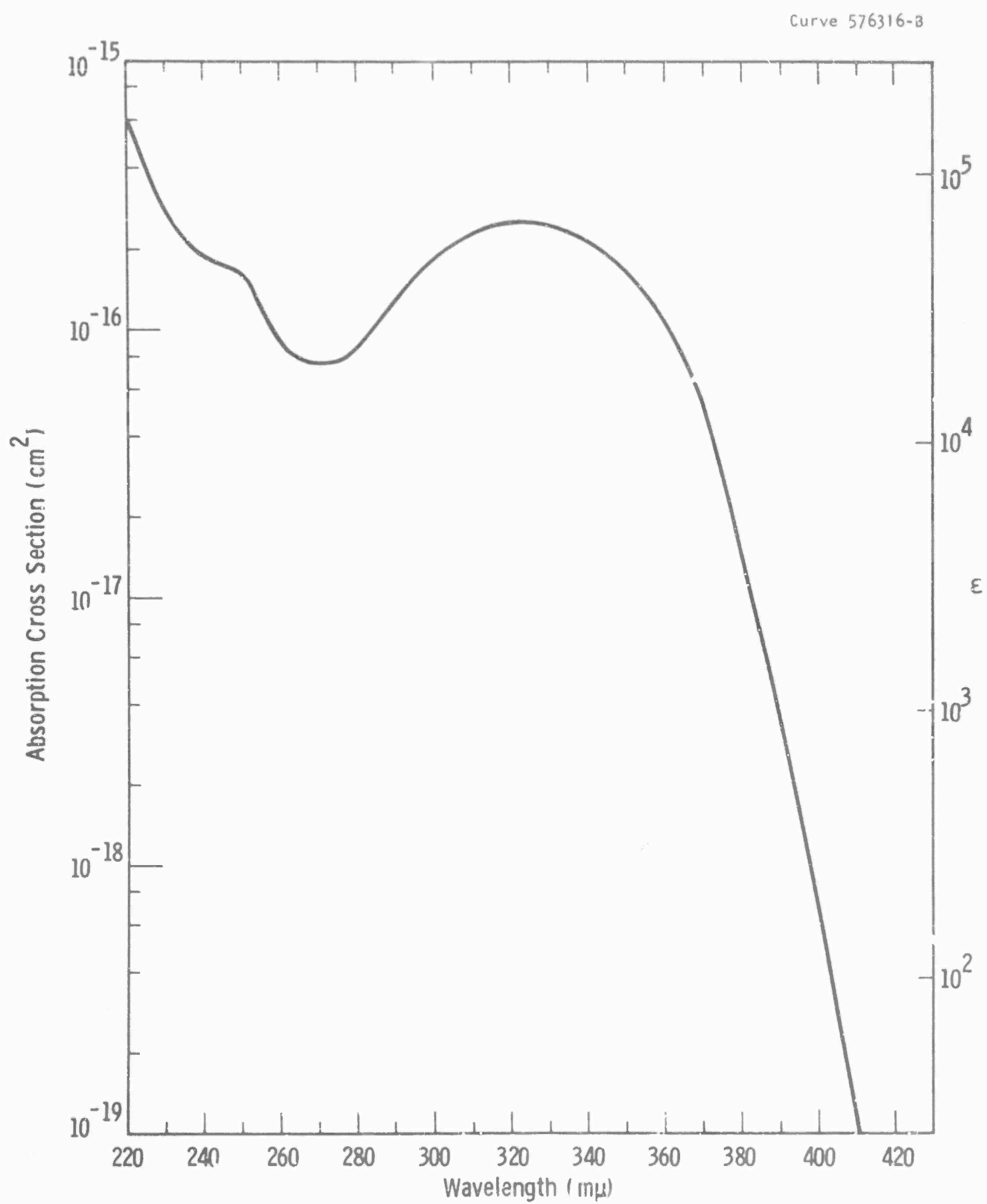


Fig. 5—Room temperature absorption spectrum of $\text{PEu}(\alpha\text{-NTF})_4$ in acetonitrile

Curve 576317-B

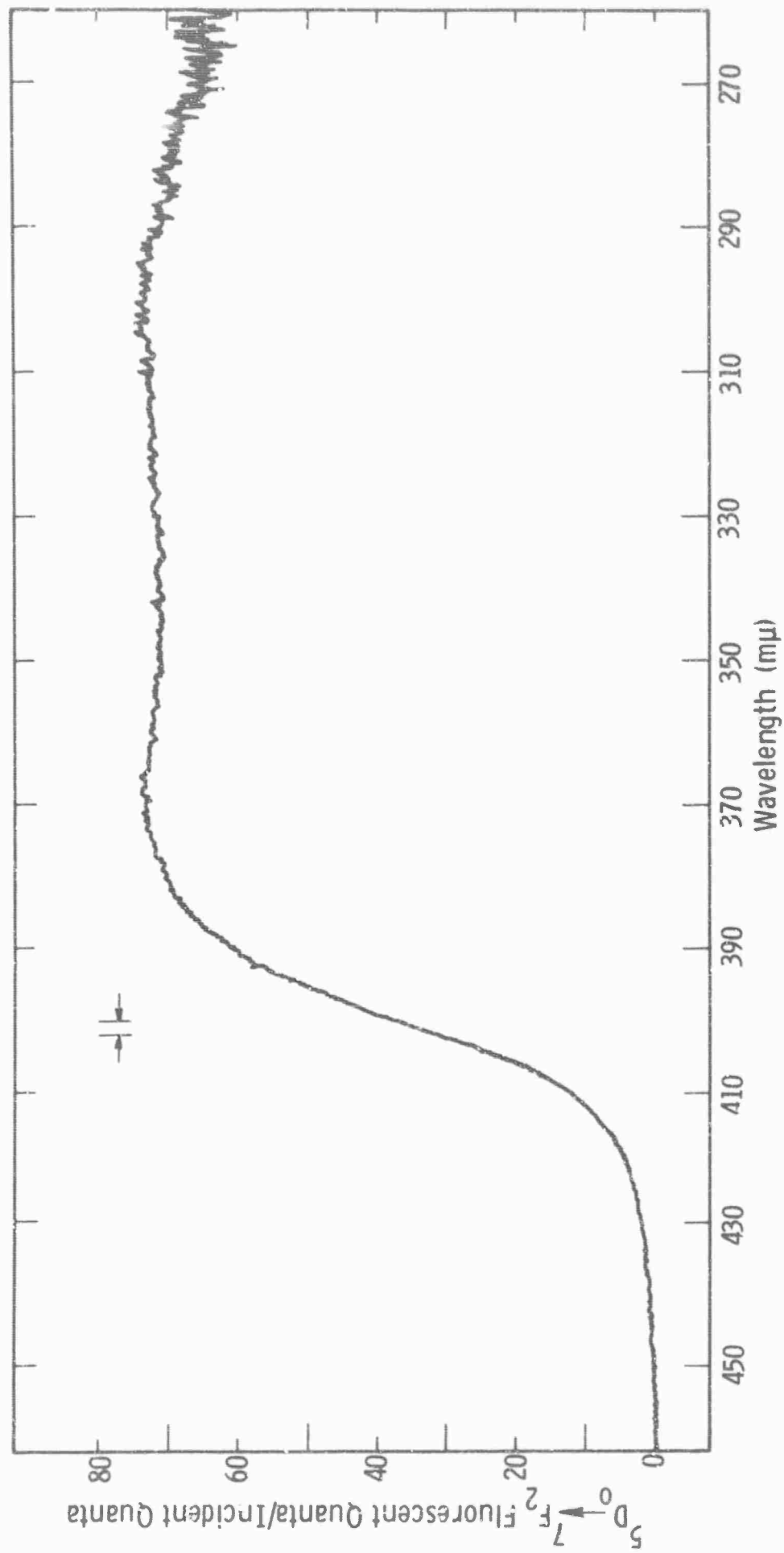


Fig. 6—Room temperature excitation spectrum of $5D_0 \rightarrow 7F_2$ fluorescence of a 0.1M solution of $PEu(\alpha-NTF)_4$ in acetonitrile

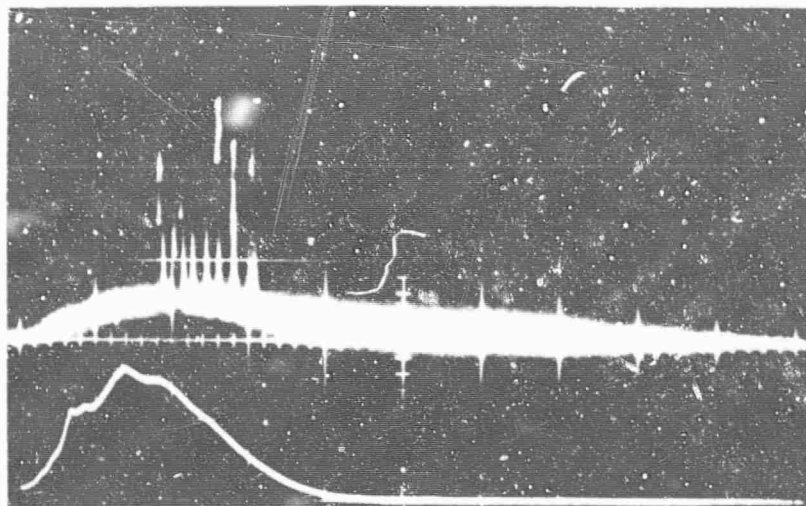
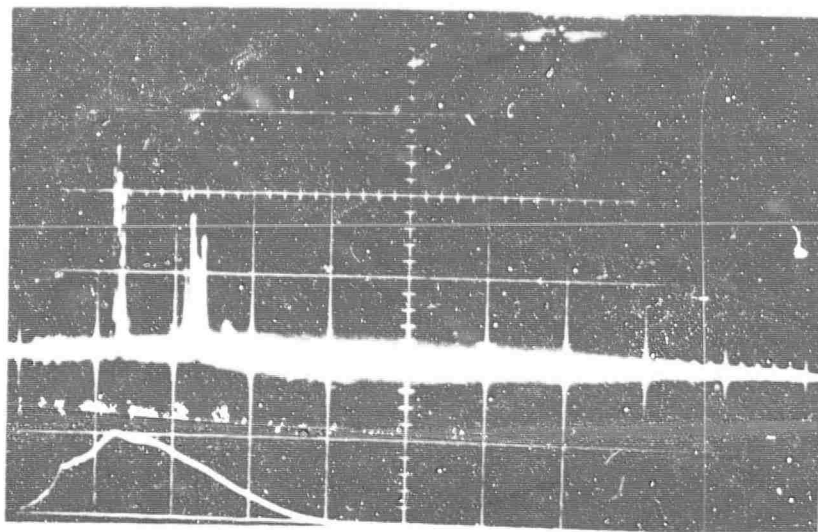
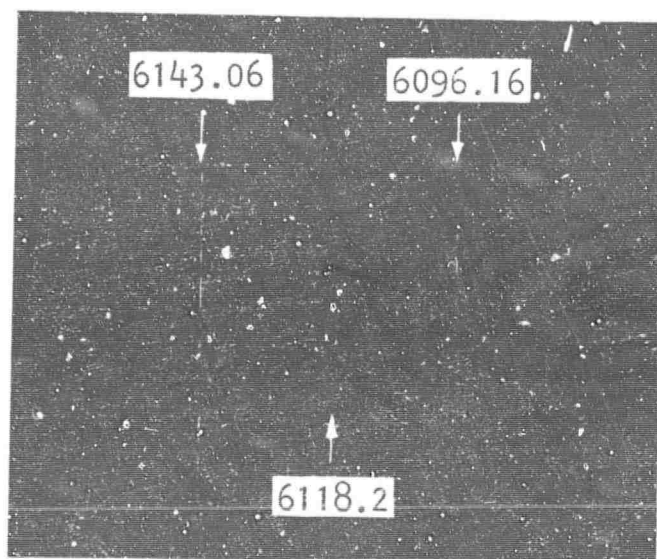


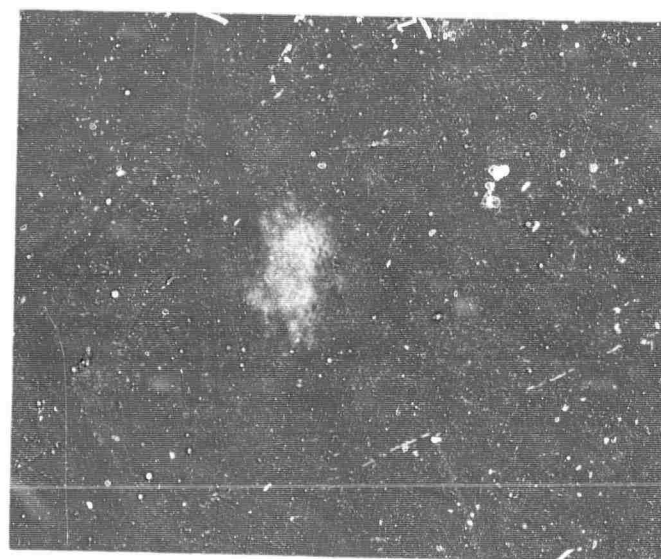
Fig. 7—Top: Photomultiplier recording of light output from 0.01 M PEu (α -NTF)₄ in acetonitrile. Bottom: Recording of flash lamp light. 625J input (1.2 times threshold). Scale: 200 microseconds from left to right



(a)



(b)



(c)

Fig. 8 -(a) Top: Photomultiplier recording of light output from 0.01 M PEu (α -NTF)₄ in acetonitrile. Bottom: Recording of flash lamp light. 1160J input (2.3 times threshold). Scale: 200 microseconds from left to right. (b) One to one reproduction of film image showing neon reference lines and laser emission at 6118.2 Å. (c) One to one reproduction of laser beam pattern at a distance of 250 centimeters from one end of laser cell

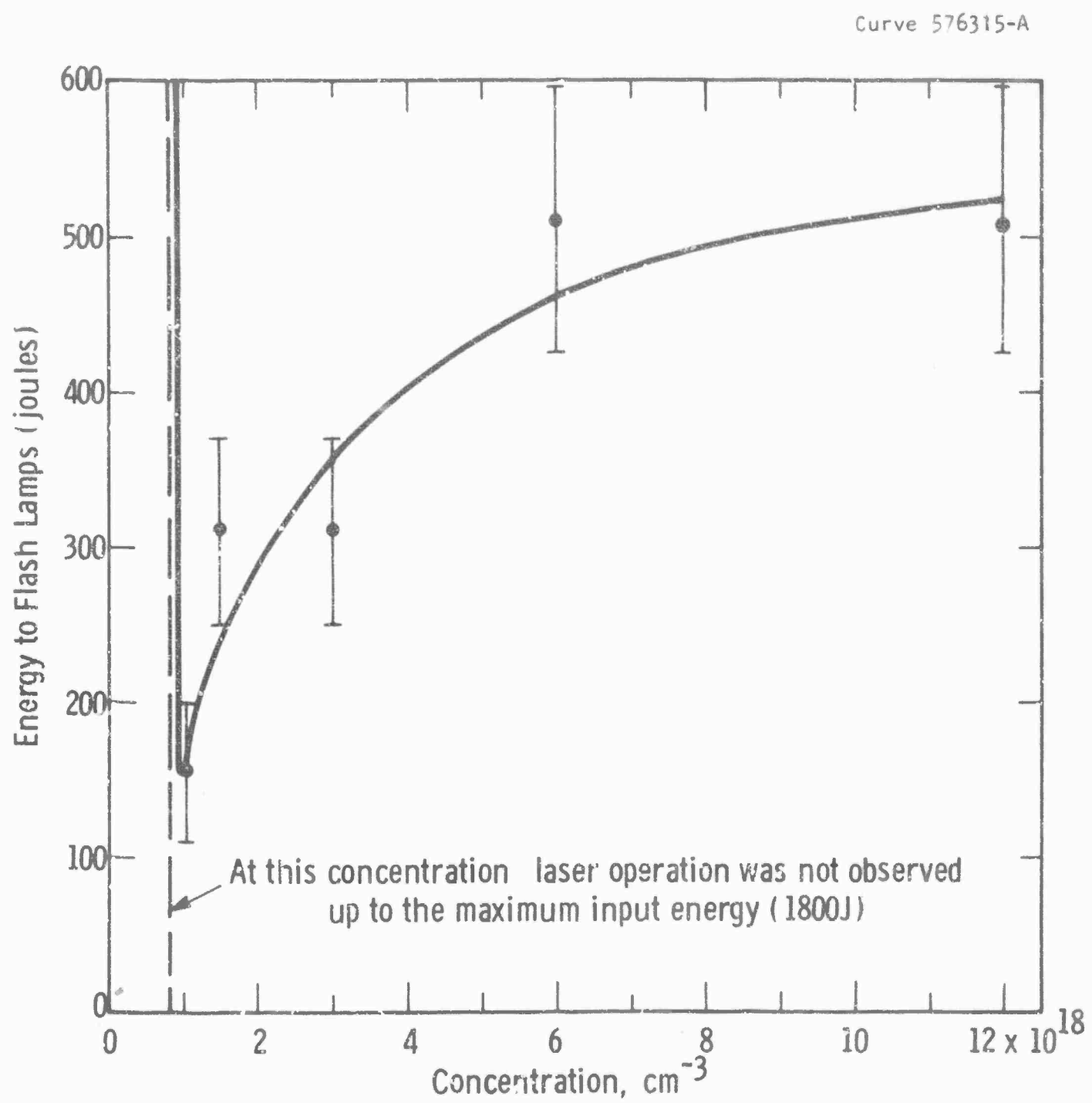


Fig. 9—Energy required to reach threshold vs concentration of PEu ($\alpha\text{-NTF}$)₄

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11. SUPPLEMENTARY NOTES Report on the preparation, spectroscopy and laser phenomena of liquid laser materials.		12. SPONSORING MILITARY ACTIVITY Advanced Research Projects Agency and Office of Naval Research, Washington, D.C.	
13. ABSTRACT Because heavy water should be a superior liquid laser solvent, studies of various systems soluble in heavy water have been emphasized. In order to obtain materials which can be efficiently optically pumped in large volumes of practicable dimensions, two different approaches have been employed. The first is to form mixed ligand complexes in solution. This modifies the absorption band of the chelate directly. Two systems of this type are described. The second approach is that of utilizing intermolecular energy transfer in solution. We have demonstrated, for the first time, intermolecular energy transfer in heavy water solutions. Two systems of this type are described. The use of heavy water as a solvent and the use of intermolecular energy transfer to solve the problem of efficient optical pumping appears to be the most promising approach to the development of a high radiance liquid laser. Studies of systems soluble in organic solvents have aided in the development of systems in heavy water. The organic cation has been shown to have an important effect on the laser threshold of solutions of europium benzoyltrifluoroacetate. A series of new europium chelates have been synthesized and some of their properties studied. Laser operation has been achieved with three of these new europium chelates in acetonitrile. The effects of scattering on laser performance are shown to be large for these systems soluble in organic solvents.			

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Lasers						
Liquids						
Europium						
Terbium						
Water						
Heavy Water						
Homogeneity						
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