

CHELATE LASERS

ANNUAL TECHNICAL SUMMARY REPORT

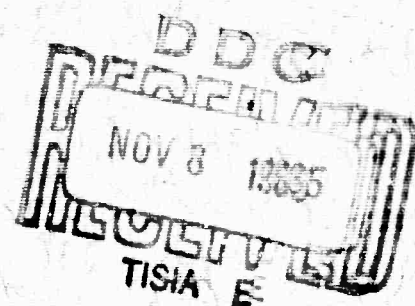
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GENERAL TELEPHONE & ELECTRONICS LABORATORIES

INCORPORATED
BAYSIDE, NEW YORK



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**General Telephone & Electronics Laboratories Inc.
Bayside, New York**

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1. INTRODUCTION

This investigation of chelate lasers, at the General Telephone & Electronics Laboratories, has as its objective the evaluation of the potentialities of liquid lasers and the analysis and improvement of their performance. Toward this end, the work has been designed to proceed along two parallel and complementary lines: an investigation of the chemical properties of the materials, in terms of the requirements for laser action; and an investigation of the physical properties of the chelate laser itself, in terms of the design and improvement of the laser cavity and associated equipment. This report summarizes previous work and describes in detail the progress on these lines in the past year.

2. SUMMARY OF PREVIOUS WORK

The research carried out under this contract has resulted in substantial advances both in the understanding of the chelate materials and in the liquid laser itself. With regard to the latter, the threshold for laser action has been progressively reduced and the temperature of operation increased.^{1,2} In a departure from the original system of europium benzoylacetonate in alcohol, many new chelate laser systems have been produced, and one of these, europium benzoyltrifluoroacetate in acetonitrile, has shown laser action at, or even somewhat above, room temperature. The addition of inorganic cations to the laser solution has been found to alter the emission from the europium chelate solutions in such a way as to shift the laser emission as much as 50 cm^{-1} .³

With regard to the chelate materials themselves, the unique properties of the europium ion have made possible a detailed spectroscopic characterization of the chemical properties of the complexes in solution.^{2,4} The

observation of a splitting in the $^5D_0 - ^7F_0$ transition, between two non-degenerate and unsplittable states, provided conclusive evidence that the four-ligand or tetrakis form of the chelate dissociates to a significant extent into a three-ligand form. Since all chelate lasers thus far reported involve the four-ligand form, this dissociation presented a new and serious chemical problem, which will be considered in more detail later. This spectroscopic study also made it possible to characterize the molecular symmetry and structure of the tetrakis chelates, of considerable importance in the absence of other sources of such information.

Considerable improvement has also been made in the laser apparatus, mostly in refinement of the design of the laser cell. The use of a 1-mm capillary rather than the 4-mm cell first used resulted in more reliable operation of the laser and led to a detailed characterization of the output.⁵ However, thresholds were still much higher than expected.

One of the still puzzling aspects of the chelate laser problem is why certain systems do not exhibit laser action. Among such systems are the tetrakis dibenzoylmethide in the alcohol solvent and a variety of tris chelates, all of which exhibit an extremely bright fluorescence. It has been proposed that in the case of the dibenzoylmethide, the cause of this failure is absorption of the ion fluorescence by an excited state of the chelate molecule. Such processes can be studied by the technique of double flash spectroscopy, and the apparatus required for this work has been set up.

The work just mentioned, carried out during the term of this contract, is described in more detail in references 1-5. Most of this is also covered in the Annual Technical Summary Report of 1964 and in the various Quarterly Letter Reports over the past 18 months.

3. PROPERTIES OF THE MATERIAL

3.1 Chemical Characteristics of Chelate Solutions

The chelate chemistry of rare earth ions has been the subject of much research, and this interest has been further stimulated by the

successful application of europium chelates in lasers. Such application has also raised many questions about the quantum efficiency of the fluorescent process and the path and mechanism of the energy migration from its absorption in the ligand singlet band to its ultimate emission from the ion. The answers to these questions, of course, require a detailed understanding of the molecular species actually present in the medium, and as our earlier studies have made clear, this is not a trivial undertaking. The structure of the chelate molecule, and indeed the stability of the chelate species itself, are extremely sensitive to chemical influences. We have therefore pursued the spectroscopic study initiated earlier in order to probe these chemical influences, to characterize the equilibria involved and to obtain some measure of the magnitudes of the equilibrium constants.

For the purposes of such investigation, most of the effort has centered on the three chelates whose properties are best understood: the benzoyl-acetate, dibenzoylmethide, and benzoyltrifluoroacetate of europium. Six solvents were chosen because of certain characteristic chemical and physical properties: alcohol and EPA, both polar but weakly coordinating; DMFA and nitrile, both polar and strongly coordinating; tolbex, aromatic and non-polar; and alcoholic sodium acetate, a polar solution having a high ionic strength. The emission spectra of the chelates in these solvents were studied, with particular attention to the wavelength regions of the $^5D_0 - ^7F_0$ and $^5D_0 - ^7F_2$ transitions. From the former emission it is possible to identify the species present and to obtain a measure of their relative concentrations, while the latter emission makes it possible to characterize the symmetry and structure of these species.

The spectra reveal that dissociation of the tetrakis form is a phenomenon common to all chelates studied. Furthermore, this dissociation does not necessarily stop at the three-ligand or tris form, but may proceed through the bis and monokis forms all the way down to the bare (solvated) europium ion itself. The equilibrium constants for the various steps in this dissociation process were obtained for the europium benzoylacetonate in alcohol, and these are given in Table IV of Appendix I. Although the constants were evaluated numerically for this system alone, their magnitudes are typical of all systems studied.

Certain patterns of chemical stability have emerged from this study. In the polar but weakly coordinating solvents, alcohol and EPA, the benzoylacetate is the most stable of the three tetrakis chelates, while the benzoyltrifluoroacetate is so unstable that no trace of it can be found. As the coordinating tendency of the solvent increases (the DMFA and nitrile solvents), the order of stability reverses, the tetrakis benzoyltrifluoroacetate becoming progressively more stable, and the benzoylacetate progressively less so. In the non-polar tolbex solvent the same situation is observed, but here the coordination cannot be attributed to the solvent but rather to an ion-pair between the anionic tetrakis form and its attendant cation.

The chemical properties of the solvent affect the molecular structure of the tetrakis form in a similar manner. Here we are concerned with the transformation between two geometrical arrangements of the bonded oxygens, dodecahedral or antiprismatic. Any solvent having a strong tendency to coordinate a ninth group to the tetrakis molecule, whether by direct bonding of a solvent molecule as in DMFA or nitrile, or by ion pairing as in tolbex, tends to favor the antiprism in some form of adduct. By contrast, weakly coordinating polar solvents tend to favor the dodecahedral structure; however, even in the latter solvents the presence of a high concentration of inorganic cations will tend to shift the structure back to the antiprism.

The foregoing discussion presents but a brief resume of the results of the spectroscopic investigation of the chelate intervals. A more detailed account is being submitted in an article to the Journal of Chemical Physics, and is included as Appendix I of this report.

3.2 Sensitization of Chelate Fluorescence

The characteristic of europium chelates which makes possible their intense emission is their ability to absorb excitation in the organic ligand and to transfer it efficiently to the emitting ion. Indeed, this facility is essential for all liquid lasers thus far reported. However, for laser purposes, the molecular absorption of the diketone chelates is far too intense. The result is that at the required concentration, most of the pump energy is absorbed only by those chelate molecules lying within about 100 microns

of the surface, and relatively little can penetrate into the bulk of the medium. One way to circumvent this difficulty is to provide another molecule in the solution which would have an optimum absorption constant in a wavelength region where the chelate is transparent, and which could transfer the energy absorbed by it to the stable chelate species. The chelate would then emit as before. Such a sensitization process could greatly increase the power output of liquid lasers, and an investigation of this possibility has now been undertaken.

Experimentally, it must be determined whether intermolecular transfer does occur, to which chelate species it occurs, and what the efficiency of this process is under a range of conditions of temperature and concentration.

The experimental technique by which investigation of sensitization is carried out is unusually critical because the interpretation of the results depends very markedly on the manner in which the experiment is done. We have chosen to employ straight-through optics as illustrated schematically in Fig. 1.

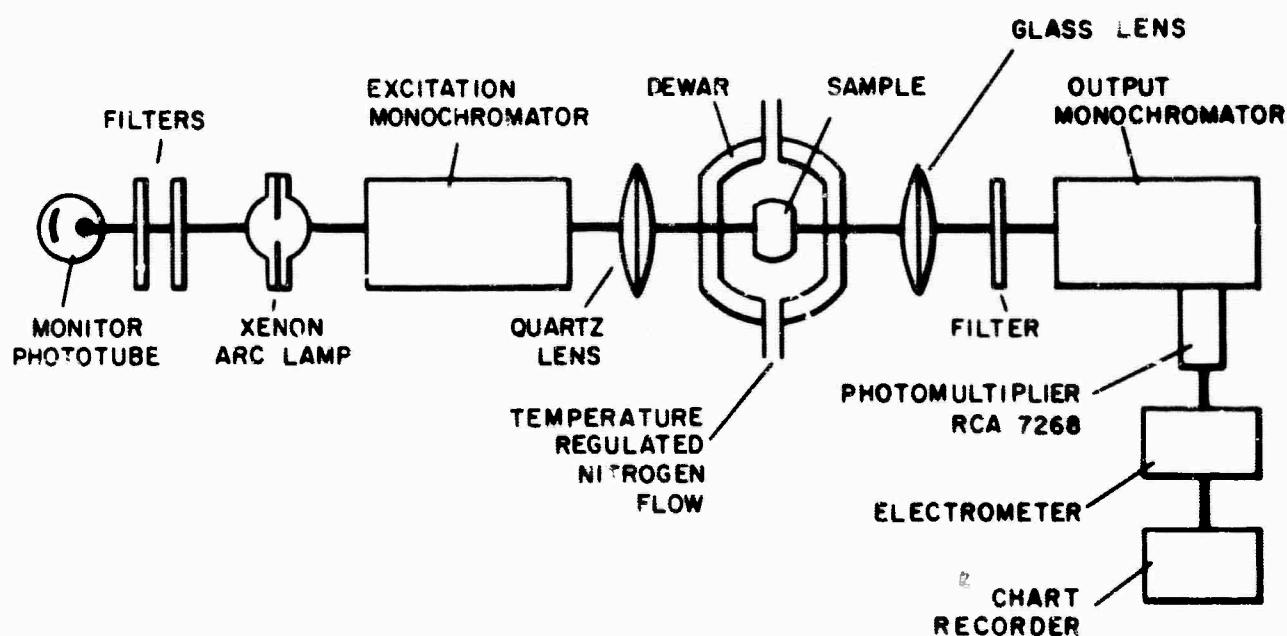


Fig. 1. Schematic of the spectroscopic apparatus for investigation of sensitization.

The excitation monochromator selects the excitation wavelength and puts out a beam with a flux density P_0 photons per cm^2 per sec at this wavelength. A straightforward analysis of the experiment leads to the result that R_s , the ratio of the fluorescence intensity in the presence of sensitizer to the intensity when the chelate alone is present, is given by

$$R_s = \frac{\alpha + f\beta}{\alpha + \beta} \left[\frac{1 - e^{-(\alpha+\beta)l}}{1 - e^{-\alpha l}} \right], \quad (1)$$

where

- f is the fraction of photons absorbed by the sensitizer that ultimately result in fluorescence,
- α is the absorption constant of the chelate at the excitation wavelength,
- β is the absorption constant of the sensitizer at the excitation wavelength, and
- l is the thickness of the sample.

Solution of this equation for f yields

$$f = R_s \left(\frac{1 + e^{-\alpha l}}{1 - e^{-(\alpha+\beta)l}} \right) \frac{\alpha + \beta}{\beta} - \frac{\alpha}{\beta}. \quad (2)$$

In equation (2) all the quantities on the right-hand side are determined from experiment. There are two conditions that appreciably simplify the analysis of the experimental results: (a) α and β are of the same order of magnitude and both are large; then,

$$f = R_s + (R_s - 1) \frac{\alpha}{\beta}; \quad (3)$$

(b) α and β are very small. Then,

$$f = (R_s - 1) \frac{\alpha}{\beta}. \quad (4)$$

The case defined by condition (a) and equation (3) is the most desirable since the fluorescence signal is strongest and the optics of the experiment most favorable.

Aside from the experimental problems, the nature of the sensitization itself makes it a far more difficult process to investigate than energy transfer within a pure chelate. Sensitization necessarily depends on the proximity between the sensitizing molecule and the chelate acceptor. At the higher temperatures, where the medium is highly fluid, the sensitization would therefore necessarily be a diffusion-controlled process, and would be affected by temperature and the viscosity of the medium. At the lower temperatures, where the viscosity of the medium is extremely high, the process would depend mainly on the relative concentration; that is, the statistical probability that a sensitizer and acceptor are located in the rigid medium at a sufficiently close distance to enable transfer of energy.

A third possibility, and one which requires further consideration, is that the sensitizer may actually form a chemical bond between itself and the chelate, resulting in a stable nine-fold coordinated molecular species. Such a species would resemble those complexes already observed in highly coordinating solvents containing strong Lewis bases (e.g., the DMFA and nitrile solvents), and indeed most good sensitizing agents are also strong Lewis bases. Thus, the presence of the sensitizing agent may well disturb the chemical equilibrium between the tetrakis and tris species in solution, in much the same manner as do the Lewis bases, and extreme care must be exercised to separate these effects.

At present, the most suitable europium chelate for investigation of sensitization appears to be the trifluoroacetylacetonate. This material can be prepared in both the tetrakis and tris forms, both of which are sufficiently stable in both weakly coordinating and strongly coordinating solvents. The peak of the absorption band is at approximately $2930 \text{ \AA}$, and the chelate is almost completely transparent from $3400 \text{ \AA}$ up. Finally, the tetrakis form of this chelate has already displayed laser action without sensitizers present in the solution, so that any sensitization effects on the laser properties could be directly observed. Preliminary experiments into the problems of sensitization are already underway.

3.3 Excited-State Absorption Spectroscopy

Any absorption at the lasing frequency leads to a loss. Normally in materials with four-level schemes this absorption is small because the population of the terminal state is negligible. If, however, absorption can occur from the excited state (to some still higher state) the absorption may be very high when the population is inverted. It was suggested that such excited state absorption may be responsible for the peculiar shape of the fluorescence decay of europium dibenzoylmethide in alcohol solutions. Since absorption from the lowest triplet state to higher triplet states is a fairly common phenomenon in organic molecules, it was decided to check to what extent excited state absorption is present in the chelates of europium.

A schematic of the experimental apparatus is shown in Fig. 2. The liquid sample is contained in a quartz tube and sealed in by two floating pistons, resulting in a liquid cylinder 0.9 cm in diameter and about 10 cm long, depending on temperature. The sample is excited through a filter by ultra-violet light from two xenon flash lamps which are actuated by a pulse-forming network. The lamps and network are electrically matched so that the lamps produce a square pulse of light 300 μ sec long with a decay time of 25 μ sec. The amount of energy included in this pulse is controlled by varying the voltage on the network capacitors.

A second xenon flash lamp, powered by a smaller network, produces a 5-joule pulse whose base width is 20 μ sec. This is the probe beam which is sent through the sample during or after excitation and recorded by a Bausch & Lomb Grating Spectrograph.

A delay line is used to trigger each of the lamps, and it in turn is controlled by a signal from the flying shutter after the manual start is actuated. The function of the shutter is to prevent light from the excitation flash from entering the spectrograph. The excitation pulse followed by the probing pulse after a variable interval is shown in Fig. 3.

The sample cylinder is contained in a dewar through which temperature-controlled nitrogen gas flows. A thermocouple touching the sample measures its temperature, which can be held to $\pm 1^\circ\text{C}$ from -160°C to $+50^\circ\text{C}$.

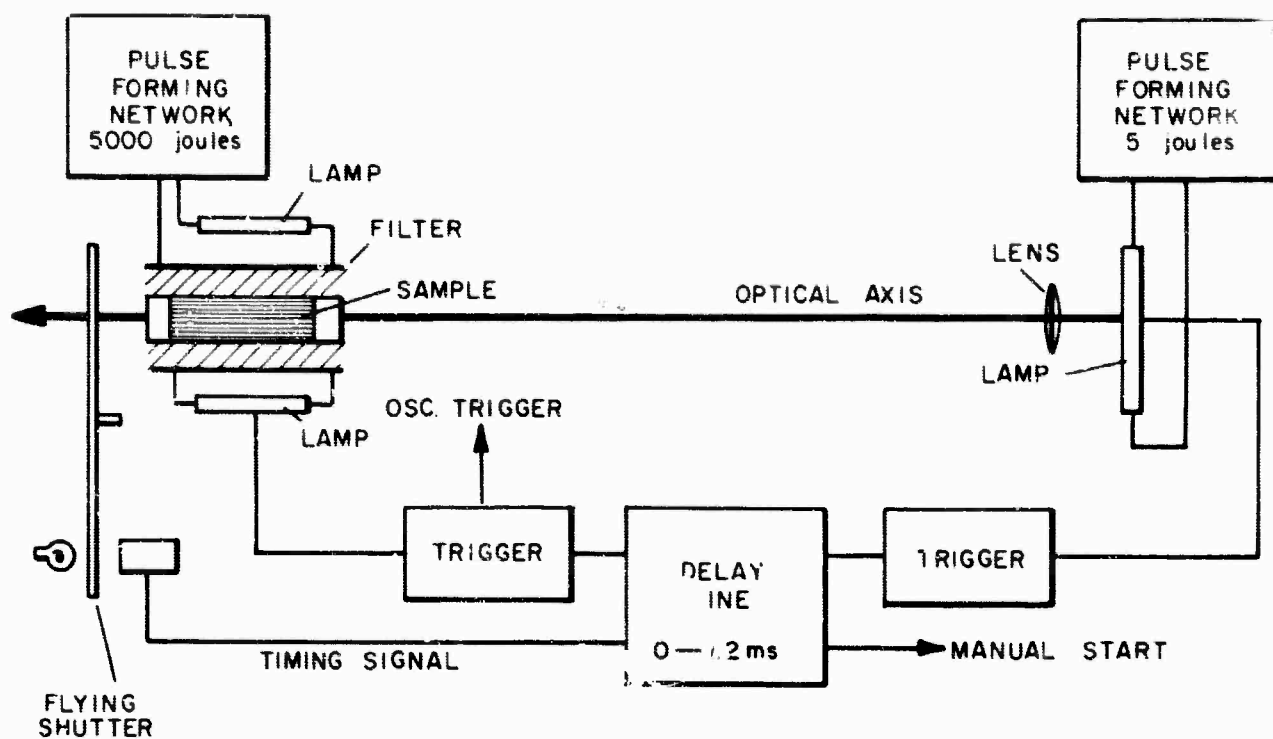


Fig. 2. Schematic of the apparatus for double flash spectroscopy.

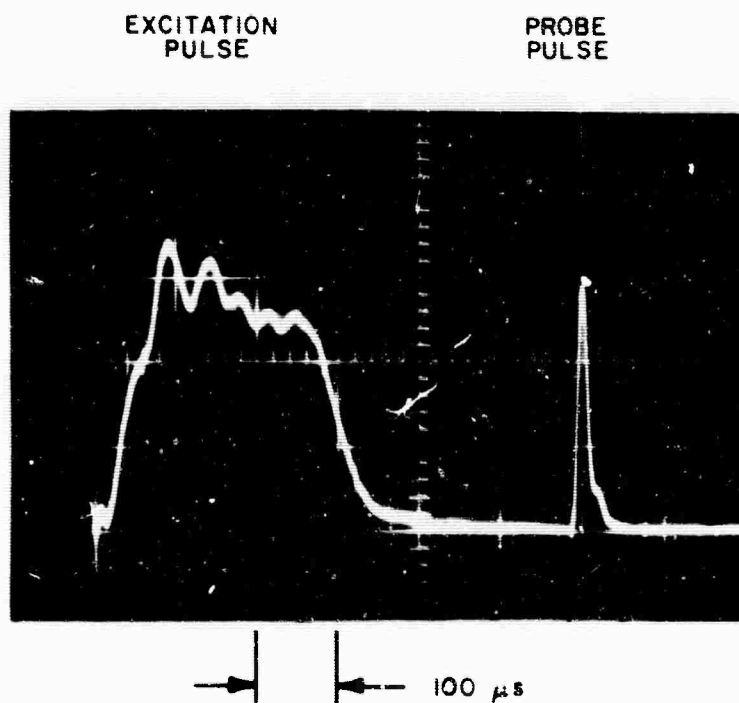


Fig. 3. Oscilloscope trace of the double pulse.

Most of the absorption runs were made at the low temperature because the resultant increased lifetimes and sharpening of the absorption bands aid in the detection.

The system was tested using phenanthrene and chrysene in both ethylene glycol and (1:3 ratio) methanol:ethanol solutions at a concentration of 10^{-3} molar. The absorption from the excited triplet states of each were easily observed at a solution temperature of -150°C with excitation inputs as low as 150 joules. The same results were obtained at room temperature with ethylene glycol solutions of phenanthrene (10^{-3}M) but with 300-joule excitation. Phenanthrene performed best, possibly because the sample used was highly purified by zone refining.

As pointed out by Ross⁶, an experimental arrangement with axial geometry requires that the concentration of the sample solution be optimized to obtain clearly detectable absorption spectra. It was found that the best results were obtained by adjusting the concentration until a 1-cm thickness gave 50 percent absorption at the peak of the first singlet-singlet band. Higher concentration would leave the central region of the liquid cylinder with a low concentration of excited species because of the high absorption of exciting radiation in the outer shell of the sample.

The temperature of the cylindrical sample must be kept constant because variations of index of refraction in the sample can reduce the probe beam intensity markedly. At least 30 seconds between consecutive excitation pulses were required to allow the system to return to thermal equilibrium. Samples of dibenzoylmethane, and the Na, La, and Gd dibenzoylmethides in alcohol solution at concentrations of $1 \times 10^{-4}\text{M}$ were probed at -150°C and showed no excited state absorption. The spectral region from $3000\text{ \AA}$ to $6400\text{ \AA}$ was surveyed, with emphasis on the $6100\text{ \AA}$ region. The usual singlet absorption in the ultraviolet region was noted, but no evidence conclusively indicating absorption by excited states was found. Thus, the results obtained so far indicate that the peculiar behavior of the fluorescence of europium dibenzoylmethide cannot be explained simply by the presence of an excited state absorption such as the familiar triplet-triplet absorption in phenanthrene.

Since it is possible that the excited-state absorption of the dibenzoylmethide fell at wavelengths beyond $6100 \text{ \AA}$ where the photographic plates lose their sensitivity, it was decided to look at the trifluoroacetylacetonate (TFA). In this chelate the singlet-singlet absorption is shifted toward shorter wavelengths, and one may expect the same to be true of other bands. This work is still in progress and no definite results can be reported at this time.

4. LASER APPARATUS

Two aspects in the design of an improved laser apparatus are dictated by the properties of the europium benzoyltrifluoroacetate laser itself. First, room-temperature operation eliminates the problem of liquid contraction. Thus, the variable volume resonator cells that had to be used with solutions operating at -150°C can in principle be replaced by fixed volume cells. Secondly, since the absorption of the benzoyltrifluoroacetate is very high, as in all other lasing chelates, the bores of the cells have to be quite narrow ($\sim 1\text{-mm}$). The use of unfocused excitation sources (spiral flash lamps or arrays of linear lamps) is very inefficient in these cases since the volume occupied by the active medium is small compared with the volume filled with pump radiation. Hence, focused systems are likely greatly to reduce the threshold energy. We shall discuss each of these aspects in turn.

4.1 Fixed-Volume Cells

Two types of fixed-volume cells still in the process of development are shown in Fig. 4 (a) and (b). In each case, part of the outer surface of the cylinder is accurately machined to be coaxial with the bore of the cell. This surface can then be used to align the cell on the focal axis of an elliptical enclosure (sec 6.2). One cell, shown in Fig. 4 (b), has a jacket around the chelate-containing capillary tube; this jacket can be filled with a liquid filter (flowing or stationary) to remove unwanted radiation from the pump. The main problem encountered in the construction of these cells is the alignment of the end plates which have the dielectric mirrors on their inner surface. With a pulsed laser, unlike a cw laser, one cannot merely adjust the mirrors by trial and error until the laser begins to operate; consequently

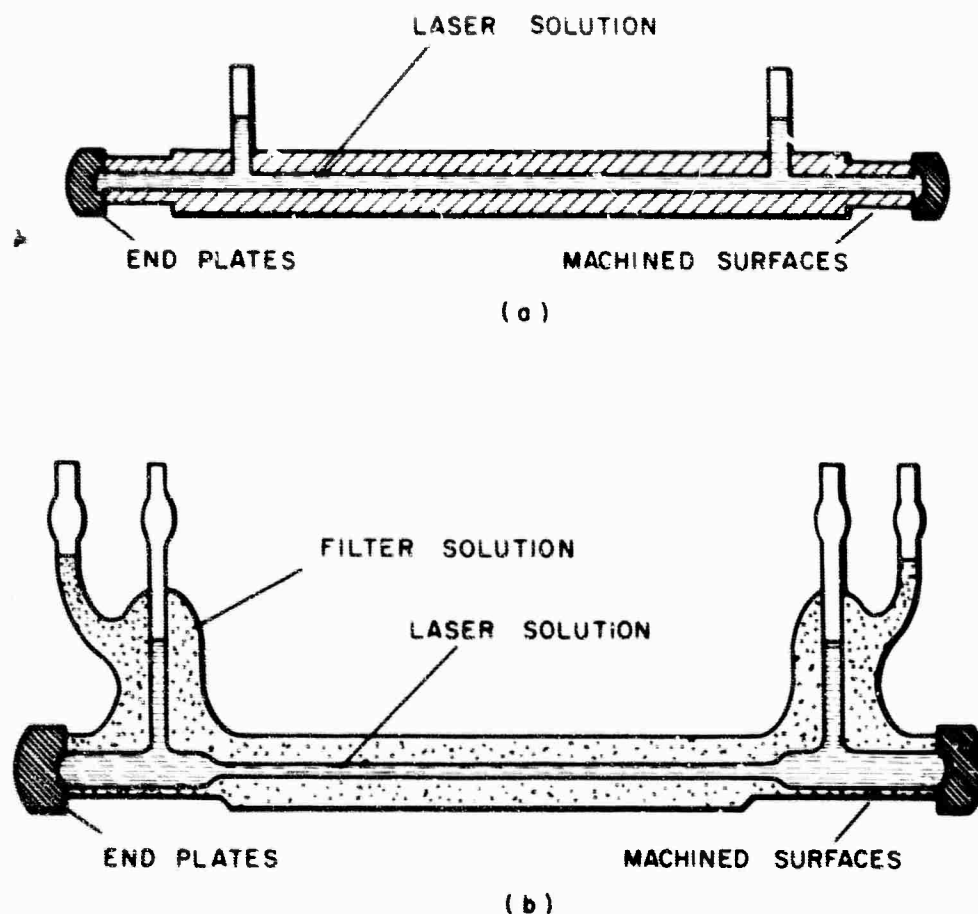


Fig. 4. Fixed volume cells.

the alignment must be directly built into the structure. The techniques presently under study are designed to eliminate the use of any bonding materials for the attachment of the end plates. Only in the absence of any bonding layer can one rely on the accuracy of the individual parts being preserved in the assembled structure. Optical contacting at elevated temperature to achieve fusion is presently being investigated. Final tests on the alignment of the cells is made by filling them with He-Ne mixture and looking for laser oscillation with this gas mixture.

4.2 Excitation Enclosures

All previous work on chelate lasers carried out in this laboratory had utilized either spiral flash lamps or arrays of linear lamps placed around the cavity. The threshold input energies required with this type of arrangement were of the order of 1000 joules. An improvement is obtained when

a linear flash tube (such as FX-45) is used in an elliptical enclosure, reducing the threshold to around 300 joules. Even in this case, however, the benefits of focusing are small since the volume of the liquid in the cell is only about one percent of the volume of the arc. In principle, therefore, utilization of a flash tube with a bore size comparable to the bore of the cell should make it possible to reduce the threshold to a few joules. This, of course, places stringent requirements on the alignment of both cell and flash tube on the focal axes.

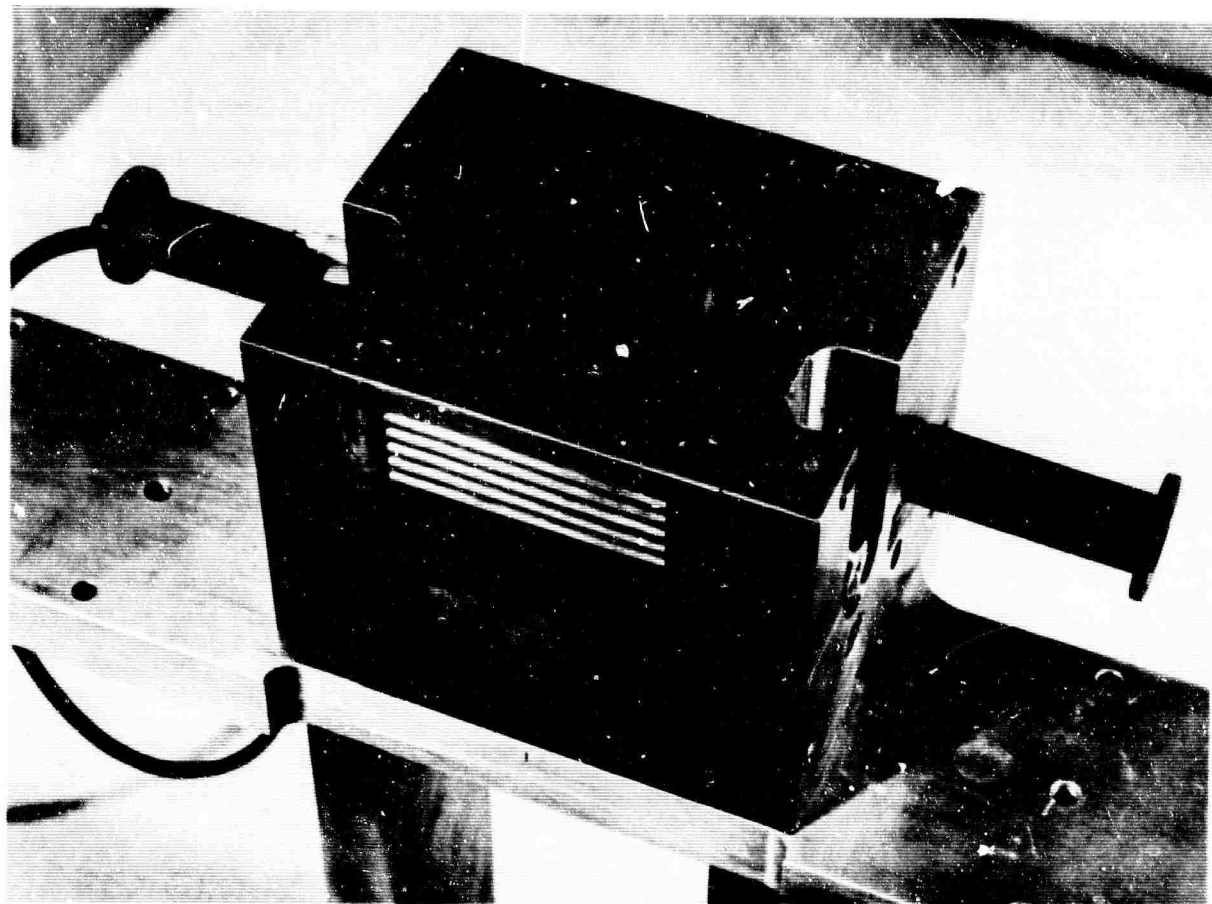
A precision ellipse, which can be split into two halves (Fig. 5), was built, with end plates designed to support the cell and lamp in the proper configuration. Using a PEK XE-14-A-3 flash lamp in a cobalt glass filter tube, a threshold of 48 joules was obtained. Since the bore diameter of the lamp is 3 mm rather than the optimum value of 1 mm, this represents approximately the expected reduction of threshold and indicates the probability of achieving even lower ones.

Another type of efficient excitation housing is shown in Fig. 6. A hollow sphere 8 1/2 inches in diameter was made (in two halves) by casting "castelite" on a bowling ball and aluminizing the inside surface. The radius of curvature is constant to better than 0.001 in.

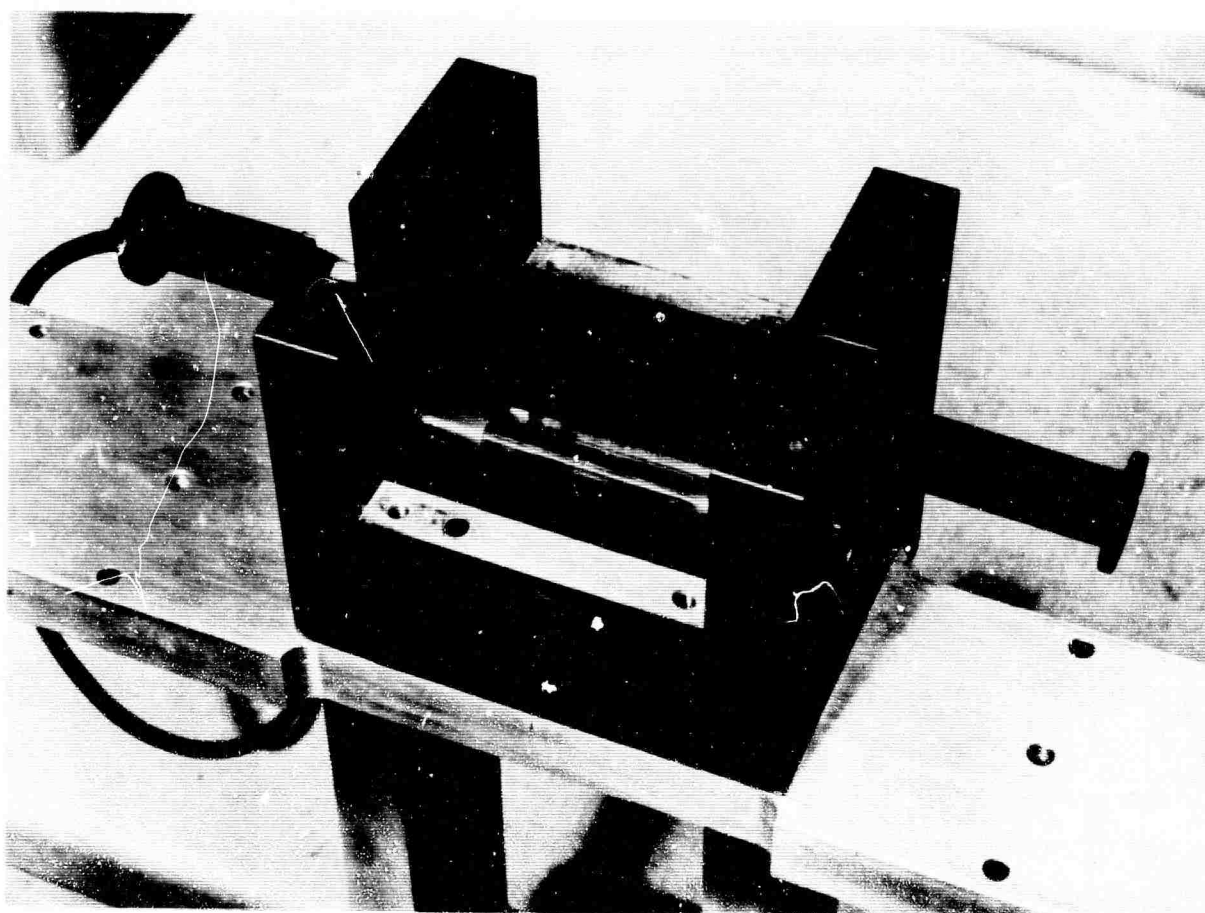
The property of a spherical reflector to form a three-dimensional image can be utilized by placing the flash tube and cell on the equatorial plane, symmetrically with respect to the diameter. A superposition of the flash-tube image with the cell can readily be observed with the top half of the sphere removed. With flash tubes of the same bore, the precision ellipse and the sphere gave the same threshold energies.

5. CONCLUSIONS

At this stage of the investigation, considerable progress has already been made in the understanding and improvement of chelate laser systems. The chemical properties of these materials are now reasonably well understood. Various molecular structures have been ascertained and the equilibria between them characterized. The limitations of particular chelate-solvent systems can be anticipated and the effects of chemical changes on the functioning of the laser can be taken into account.



(a)

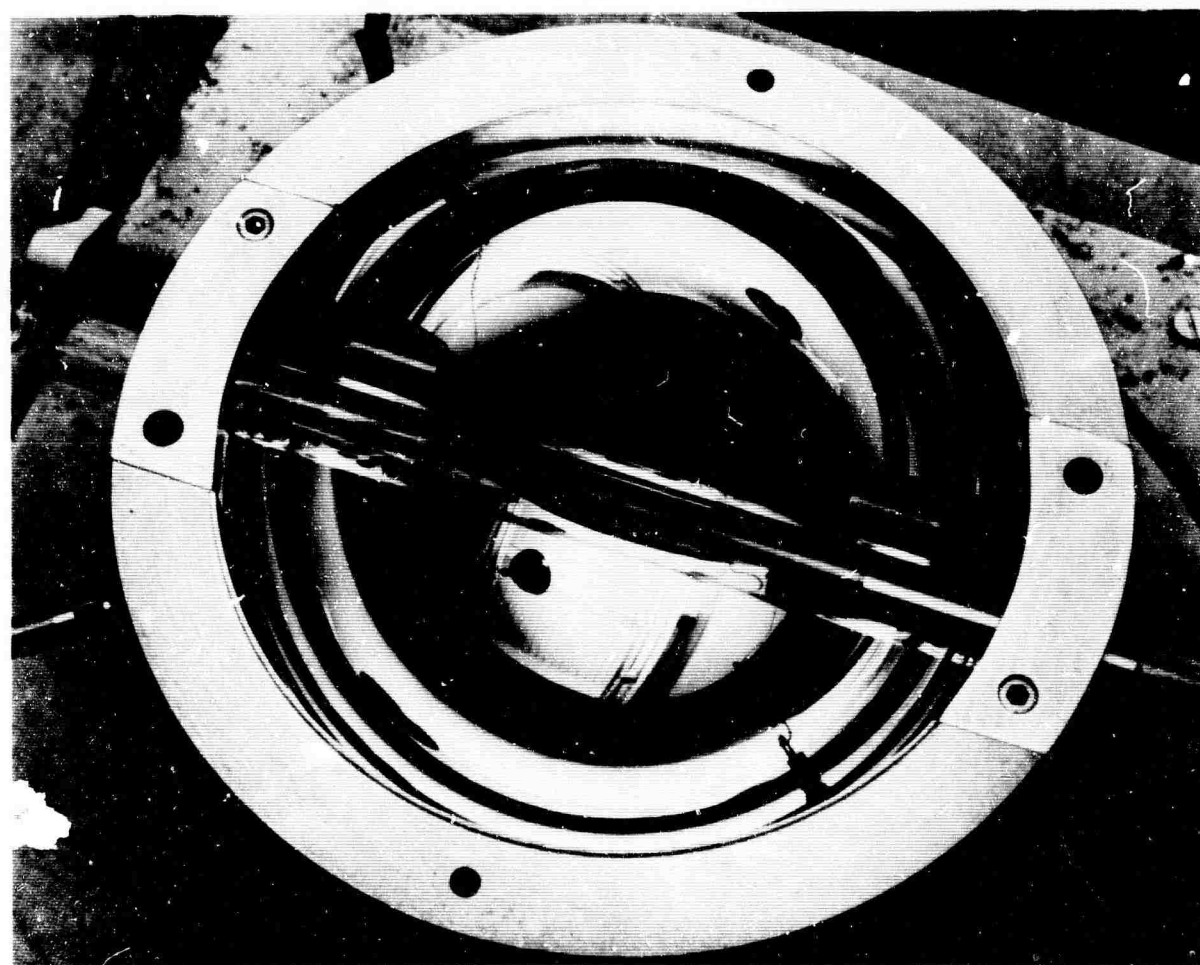


(b)

Fig. 5. Elliptical excitation enclosure. (a) closed; (b) open.



(a)



(b)

Fig. 6. Spherical excitation enclosure. (a) closed; (b) open.

Considerable improvement has also been made in the liquid laser apparatus. This has resulted in an increase in pumping efficiency and a concomitant decrease in the threshold energy. Continuous operation at room temperature now appears quite feasible, but success in this area depends on overcoming the difficult problems of fabricating and assembling the precision optical components.

Another aspect of chelate laser systems now being studied is absorption from excited states of the molecule. This process had been proposed as a loss mechanism limiting the behavior of many chelates, but now appears less serious than previously. This conclusion is still tentative, and further experimentation is required.

Finally, a study of the process of sensitization of europium chelate emission through energy transfer from other molecular species has been undertaken. Such a process offers the possibility of greatly increasing the power output of liquid lasers. Preliminary indications are encouraging, and this work is being actively pursued.

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APPENDIX I

SPECTROSCOPY AND COORDINATION CHEMISTRY OF EUROPIUM CHELATE SOLUTIONS: CONCENTRATION AND SOLVENT EFFECTS*

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ABSTRACT

The emission spectra of three β -diketone chelates of europium were studied in five different solvents over a wide range of concentrations. The number of bidentate ligands coordinated to the europium can vary from one to four, and the constants for the various equilibria established between these species in solution are determined spectroscopically for one chelate-solvent system. These equilibria are strongly dependent both on the concentration and on the chemical properties of the solvent. The molecular geometry of the chelate and its effects on the europium emission are similarly solvent dependent. Some laser implications of these results are also discussed.

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INTRODUCTION

The use of rare earth chelates in liquid lasers has served as a stimulus to the study of their coordination chemistry. Considerable research interest has been exhibited in these materials, and the complexity of their coordination chemistry is now becoming more fully appreciated.¹ Unlike the trivalent d-type transition metals with their characteristic six-fold coordination, the rare earths readily bond with eight or even nine complexing groups. This higher coordination can be satisfied in a number of different ways, as evidenced by the preparation and isolation of β -diketone chelates in two distinct chemical forms: a tetrakis species containing four equivalent bidentate ligands and a tris form containing only three such ligands and (usually) two molecules of water.²⁻⁶ In an earlier paper⁷ it was ascertained from the emission spectroscopy of these species that an equilibrium is established between them in solution, and from this work a rather detailed picture of the molecular structure and chemical behavior of the tetrakis chelate has emerged.

The intense fluorescence emission from many such europium chelates, which is the basis for their laser application, has raised a number of questions about the path, mechanism, and overall quantum efficiency of the energy transfer process.⁸⁻¹³ However, direct investigation of these luminescent processes has been hampered by the fact that the spectroscopic properties observed do not arise from one species, but rather from a mixture produced by the dissociation equilibrium. It is, therefore, the purpose of this investigation to characterize these equilibria and their variation as functions of the ligand and the solvent medium. The products of the dissociation will be identified, particularly with regard to steps beyond the tris species, and the spectra of these species will be categorized. Finally, a spectroscopic method for obtaining a quantitative evaluation of the equilibrium constants of the dissociation steps will be described and this method applied to a particular chelate-solvent system. Such detailed information is necessary if a valid picture of the energy transfer processes in these compounds is to be obtained.

EXPERIMENTAL

Materials

The europium chelates used in this investigation were of three generic types: the benzoylacetate (B), the dibenzoylmethide (D), and the benzoyltrifluoroacetate (BTF). Both the tris and tetrakis forms of these chelates were studied, and their preparation has been described in an earlier paper.⁷ Each chelate, in turn, was studied in five distinct solvents: a mixed alcohol solvent, consisting of a 3:1 mixture of ethanol and methanol; DMFA, a 4:1 mixture of the alcohol solvent and dimethylformamide; EPA, a 5:5:2 mixture of ether, isopentane and alcohol; a nitrile solvent, a 1:1:1 mixture of propio-, butyro- and isobutyro-nitrile; and tolhex. and 8:1:1 mixture of toluene, benzene, and xylene. Using these solvents, solutions of the tris and tetrakis chelates were prepared at concentrations ranging from 10^{-2} to 10^{-6} M. In all cases the solvents were distilled and dried before mixing.

For the benzoylacetate in alcohol, a series of solutions with constant 0.01 M europium concentration but varying ligand concentration was also prepared. This was done by using appropriate volumes of solutions of europium tetrakis benzoylacetate and anhydrous europium chloride, both in the mixed alcohol solvent. Equivalent spectra were obtained if the solutions were prepared by mixing appropriate amounts of piperidinium benzoylacetate and europium chloride only, but the former method was somewhat more convenient. The anhydrous solution of EuCl_3 in ethanol was prepared by dissolving the hydrated chloride in alcohol, adding benzene and distilling until all the water was removed, then adding absolute ethanol and distilling until all the benzene was removed. Absolute methanol was then added until the solvent reached the standard 3:1 proportion. The solution was analyzed for europium to establish the concentration, and the anhydrous nature was confirmed spectroscopically.

Measurements

Spectroscopic measurements were made in an apparatus especially designed to maximize their precision and reproducibility. The samples were maintained in a clear glassy condition at a temperature of $93 \pm 0.2^\circ\text{K}$.

Excitation was accomplished by using an AH 6 capillary-type Hg arc lamp, which effectively minimized the problem of arc wander. To prevent mineral deposition on the lamp, cooling was achieved by recirculating deionized water through a heat exchanger containing a bed of ion exchange resin. Finally, to correct for any temporal variations in lamp intensity, the output in the wavelength region of the chelate absorption was monitored, and this value used to normalize all measurements to a constant level of excitation.

The exciting arc was focused on the front surface of the sample solution, and the fluorescence spectrum measured directly through the sample with source, sample and monochromator entrance slit in a straight line. Such "straight through" optics are particularly suited to these experiments since the intense absorption of the ligands results in a sharp fluorescent image of the exciting arc; this image can then be focused on the entrance slit with a minimum of geometrical uncertainties. Except for the very dilute solutions, where the considerable penetration of the exciting radiation produces a more diffuse fluorescent image, geometrical effects were minimal, and even in the latter cases appropriate corrections could be made. The basic apparatus (shown in Fig. 1) is similar to that described in a previous paper, and the spectra were recorded as detailed therein.⁷

Observations

To fulfill the stated purpose of this investigation, three chemically related chelates and five distinct solvents were chosen for study. The chelates, the europium benzoylacetate, dibenzoylmethide, and benzoyltrifluoroacetate, have a number of similar characteristics which make comparison between them more readily interpretable. Their excitation bands are quite similar, and the absorption constant for Hg 3660 Å light is high enough to assure essentially total absorption at all but the lowest concentrations. Moreover, all three chelates have displayed laser action in one or more of the solvents studied. The solvents, in turn, were chosen for certain characteristic properties. Alcohol and DMFA, which have served as laser media

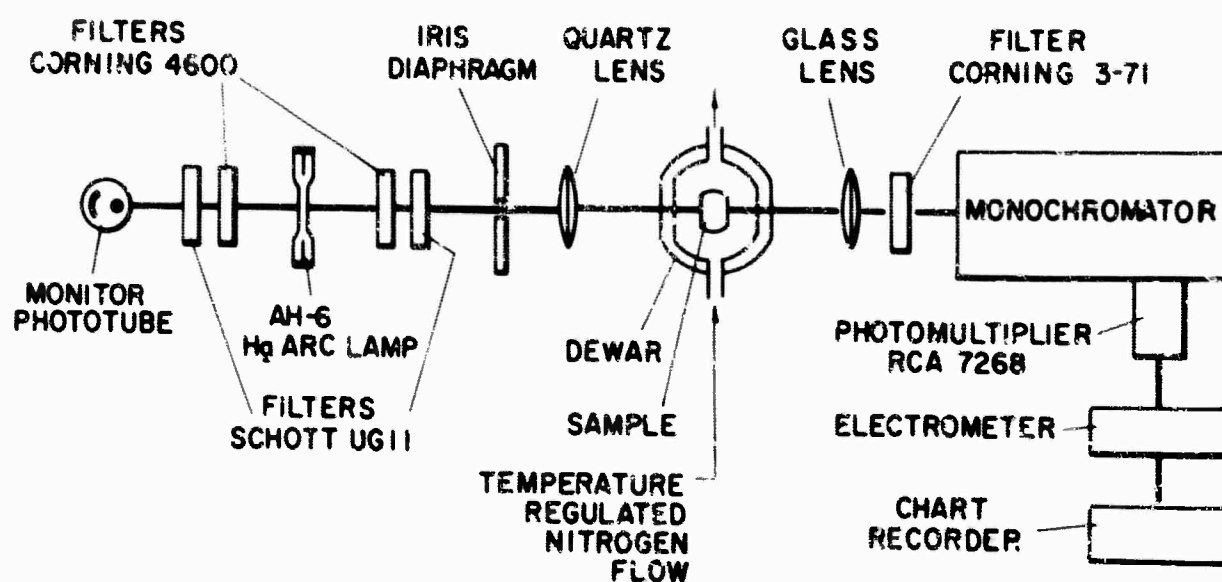


Fig. 1. Diagram of the apparatus used for measurement of the fluorescence emission spectra.

at low temperature, are polar solvents differing mainly in the much higher coordinating tendencies of the latter. The nitrile solvent, also polar and coordinating, has served as a laser medium at room temperature and, unlike acetonitrile, can be cooled to -180°C without crystallizing or cracking. The EPA solvent, although not a laser medium (for reasons which will become apparent later), has extremely good physical properties and is widely used in studies of fluorescence and quantum efficiency. Finally, the tolhex solvent is one of the few non-polar (aromatic) media in which the chelates are readily soluble and which still retains a clear glassy quality at low temperatures.

The emission spectra were measured in two particular wavelength regions: between 5760 and 5820 Å, characteristic of the $^5\text{D}_0 - ^7\text{F}_0$ transition; and between 6060 and 6300 Å, characteristic of the $^5\text{D}_0 - ^7\text{F}_2$ transition. The region between these two, characteristic of the $^5\text{D}_0 - ^7\text{F}_1$ transition, was examined from time to time but, as borne out in an earlier paper,⁷ contained no pertinent information that could not be obtained from the other transitions.

The $^5\text{D}_0 - ^7\text{F}_0$ and $^5\text{D}_0 - ^7\text{F}_2$ transitions complement each other admirably. The former, although at least an order of magnitude less intense, produces quite sharp emission lines at the lower temperatures. There is little overlap between the lines, so that even if they are separated by as little as 4 Å their intensities can be measured with a high degree of precision. Since this $^5\text{D}_0 - ^7\text{F}_0$ transition cannot be split by electrostatic field interactions, multiple lines in this region yield definitive evidence for multiple species, and their intensities can be used quantitatively to determine the individual concentrations.

The $^5\text{D}_0 - ^7\text{F}_2$ transition, much more intense than the former, is readily split by electrostatic fields, and hence is quite sensitive to the ion environment. This gives rise to a more complicated emission whose spectrum is characteristic of the symmetries of the individual species. Although the breadth and overlap of the lines in this region vitiates their use in a quantitative manner, they can nevertheless be used to identify the structure of a given species.

The fluorescent emission of the three chelates in both their tetrakis and tris forms were measured in the five solvents over a concentration range from 10^{-2} M to 10^{-5} or 10^{-6} M. The spectra obtained in these dilution experiments are shown in Figs. 2-6 and the wavelengths of the dominant emissions are given in Tables I and II. In general, the various chelate-solvent systems show quite disparate behavior, but certain common features stand out. One is that at the highest concentration, the spectrum of the tetrakis species is invariably simpler, sharper, and more intense than that of the tris. The structural details of the tetrakis spectrum are thus much more tractable for group theoretical analysis of the molecular structure; this is discussed in some detail subsequently. A second feature is the fact that in virtually all cases, tetrakis and tris alike, the dominant transitions present at the higher concentrations gradually vanish as the concentration is lowered, to be replaced by new ones. This behavior is evidence that dissociation takes place not only in the tetrakis species, but in the tris species as well.

To characterize such dissociation in a more quantitative manner, one particular system, the europium benzoylacetonate in alcohol, has been studied intensively. The emission spectra were measured in a large number of solutions having a constant 0.01 M europium concentration but many different concentrations of ligand. Some of these spectra are given in Fig. 7. These show that as the ligand-to-europium ratio is lowered, the spectra change in exactly the same manner as that seen previously upon dilution of the tetrakis chelate alone. In this case, however, the total concentration of chelate, of all species, remains constant, and the absorption remains sufficiently high to minimize geometrical factors in the optics and enable quantitative treatment of the data. One can identify the observed emissions with the species from which they arise, and determine the concentration of these various species present in solution. Thus it becomes possible to evaluate the actual equilibrium constants for each step in the dissociation process by purely spectroscopic means.

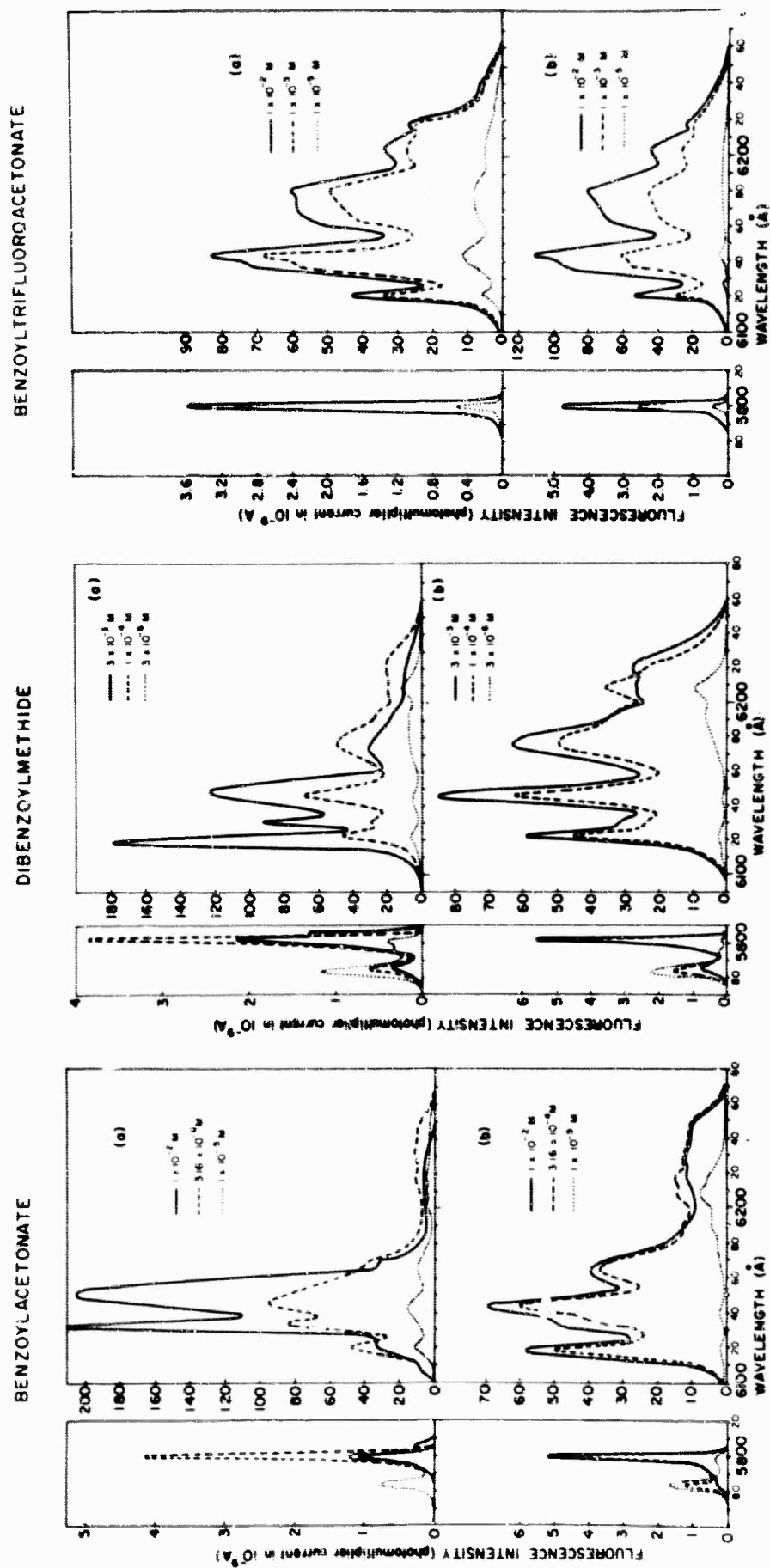


Fig. 2. Emission spectra of the europium chelates in mixed alcohol solvent at various concentrations, at -180°C : (a) tetrakis chelate; (b) tris chelate.

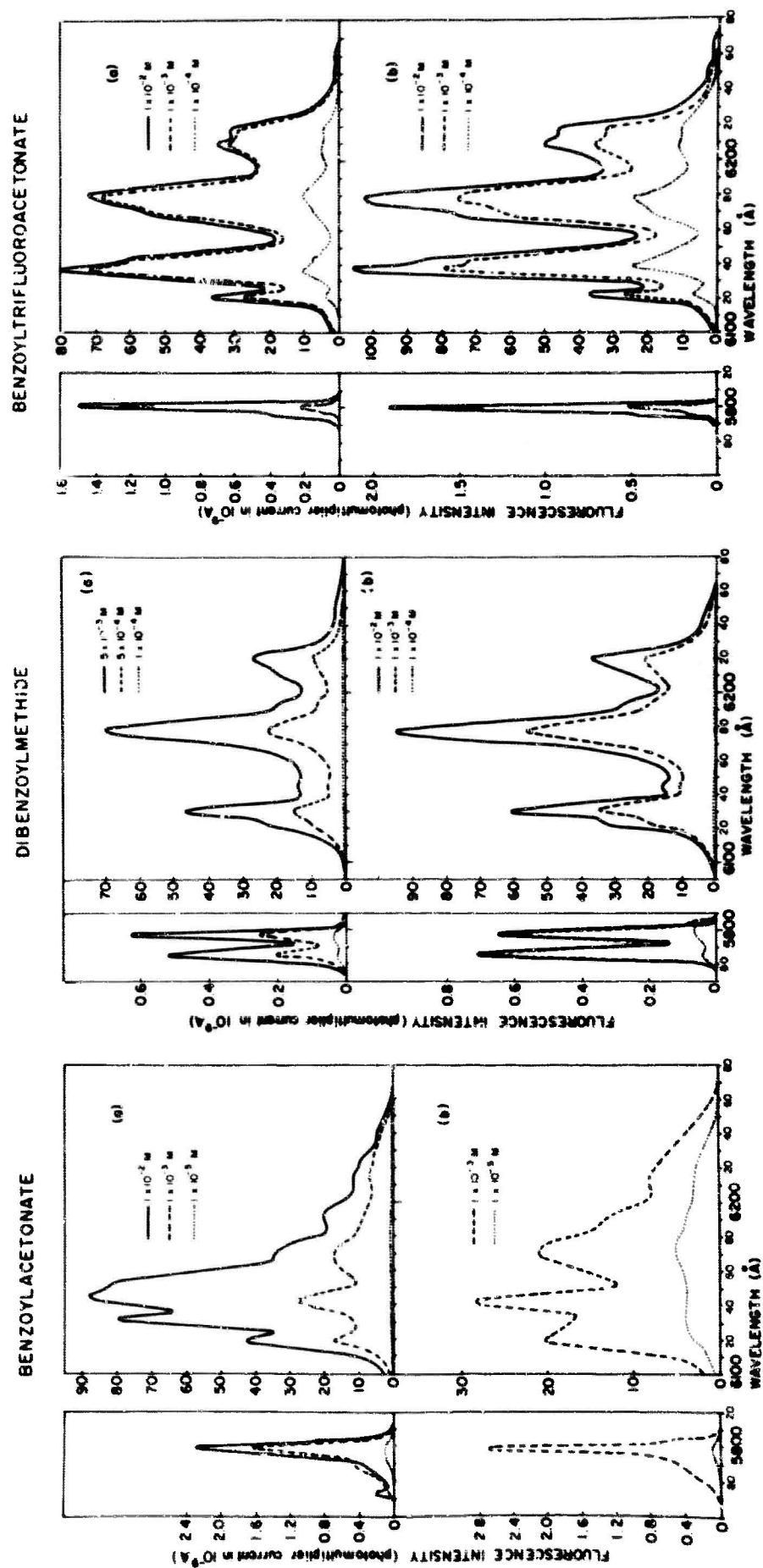


Fig. 3. Emission spectra of the europium chelates in EPA solvent at various concentrations, at -180°C : (a) tetrakis chelate; (b) tris chelate.

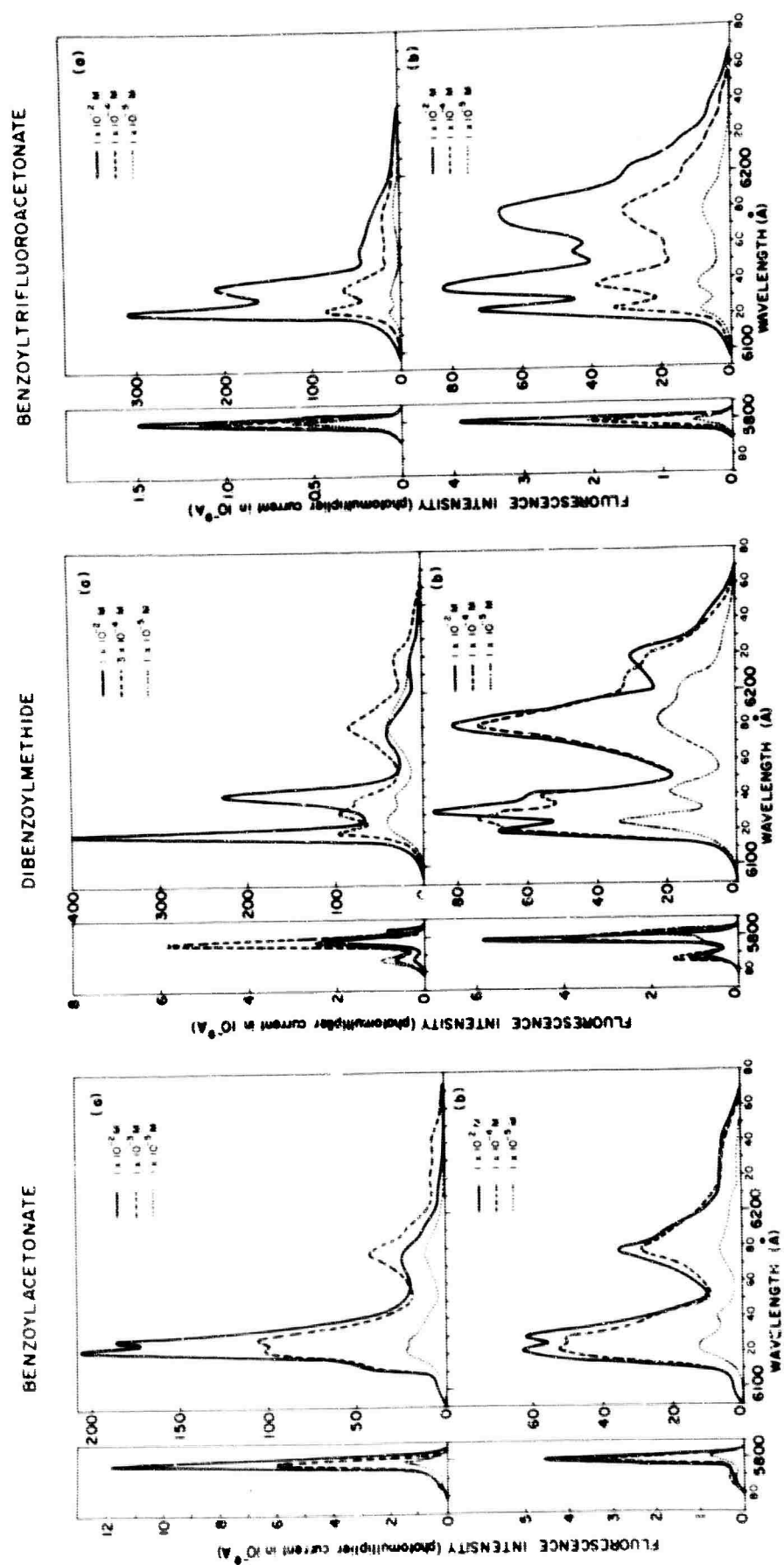


Fig. 4. Emission spectra of the europium chelates in DMFA solvent at various concentrations, at -180°C : (a) tetrakis chelate; (b) tris chelate.

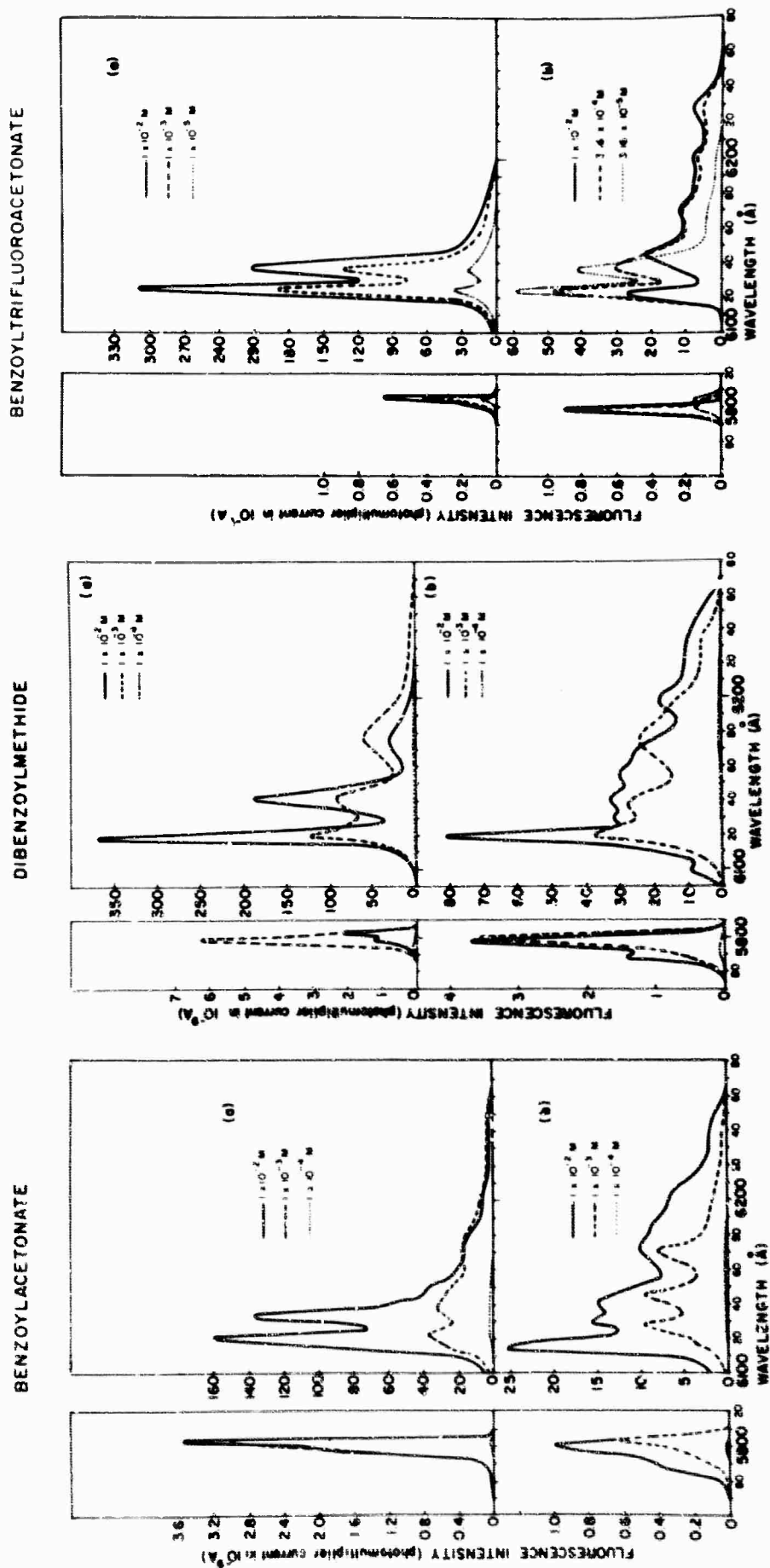


Fig. 5. Emission spectra of the europium chelates in nitrile solvent at various concentrations, at -180°C: (a) tetrakis chelate; (b) tris chelate.

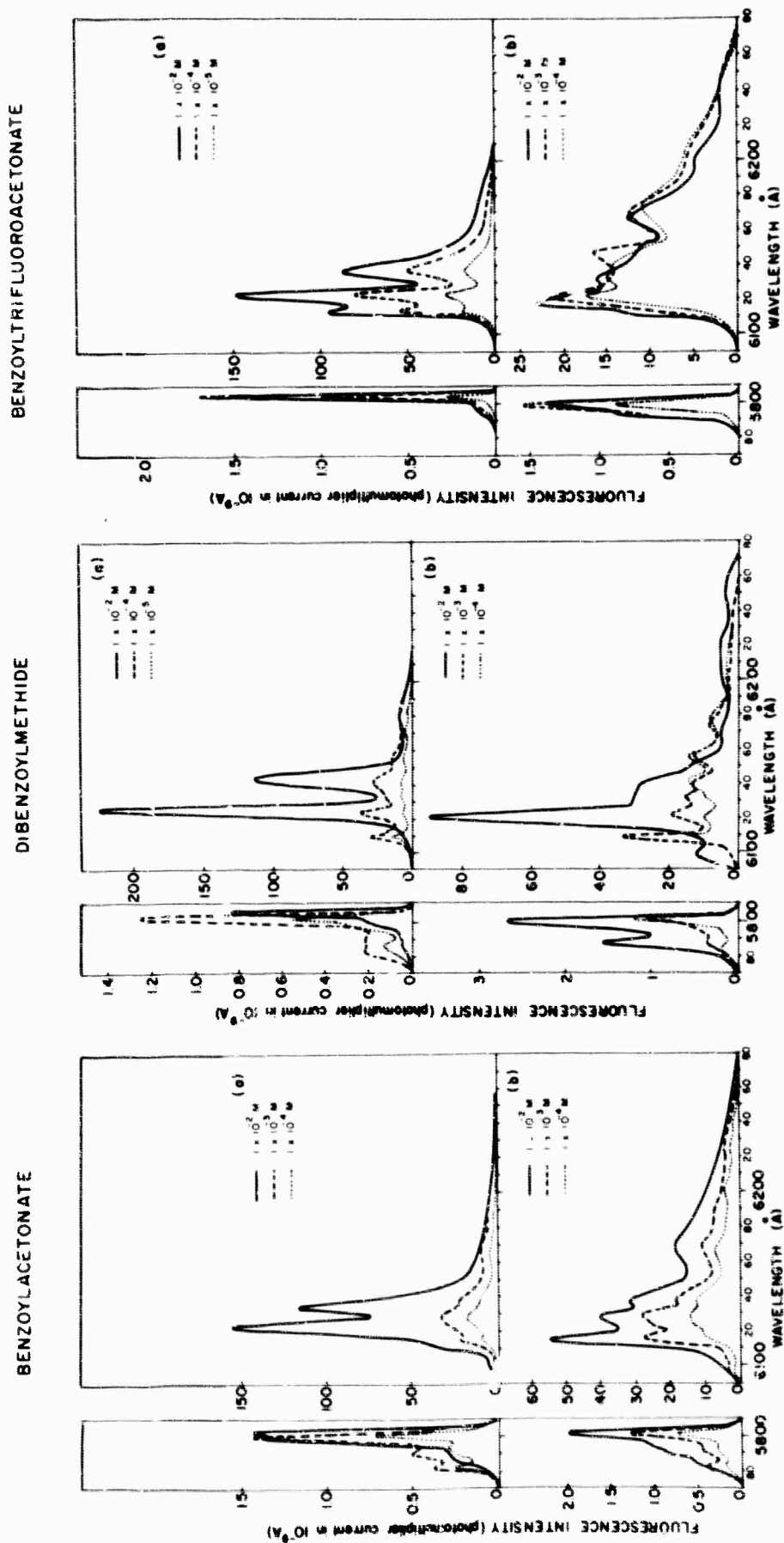


Fig. 6. Emission spectra of the europium chelates in toluene solvent at various concentrations, at -180°C : (a) tetrakis chelate; (b) tris chelate.

TABLE I
Dominant Emissions From the $^5D_0-^7F_2$ Transition of the Europium
Chelates in Various Solvents

Wavelengths (Å)						
Chelate	Alcohol	EPA	DMFA	Nitrile	Tolbex*	
Benzoylacetone	6131 6149 6118 6133 6143 6162	6131 6148 6119 6142 6167	6124 6129 6121 6128 6177	6120 6132 6114 6135 6171	6124 6136 6117 6128 6137	6169
Tetrakis						
Tris						
Bis	6105 6195 6207 6215	6136 6172 6215	6123 6140 6179 6206	6127 6145 6168		
Monokis	6116 6176 6202					
Dibenzoylmethide	6118 6130 6147	6120 6142	6119 6142	6123 6142		
Tetrakis						
Tris	6121 6129 6145 6175	6122 6129 6177 6218	6121 6132 6140 6181 6218	6119 6138 6175	6107 6121 6141 6153 6174	6098 6121 6130 6138
Bis	6121 6184 6194 6208	6126 6142 6183 6200	6121 6138 6171 6200			
Benzoyltrifluoroacetone						
Tetrakis						
Tris	6121 6143 6168 6180	6122 6137 6178 6210	6122 6145 6170 6230	6122 6145 6170 6230	6121 6146 6170 6166	6111 6117 6131 6148

* For the tolbox solvents, the first column refers to anhydrous chelate, the second to hydrated chelate.

TABLE II
Emissions From the $^5D_0-^7F_0$ Transition of the
Europium Chelates in Various Solvents

Chelate	Wavelengths (Å)				
	Alcohol	EPA	DMFA	Nitrile	Tolbex*
Benzoylacetate					
Tetrakis	5805	5804	5803(?)	5802	5803
Tris	5798	5798	5799	5798	5800
Bis	5783	5783	5786		
Monokis	5793	5792(?)	5794(?)		
Dibenzoylmethide					
Tetrakis	5805		5805	5804	5804
Tris	5801	5798	5798	5799	5788
Bis	5784	5786	5787	5795	
Benzoyltrifluoroacetate					
Tetrakis			5804	5804	5805
Tris	5800	5801	5801	5798	5794

* For the tolhex solvent, the first column refers to anhydrous chelate, the second to hydrated chelate.

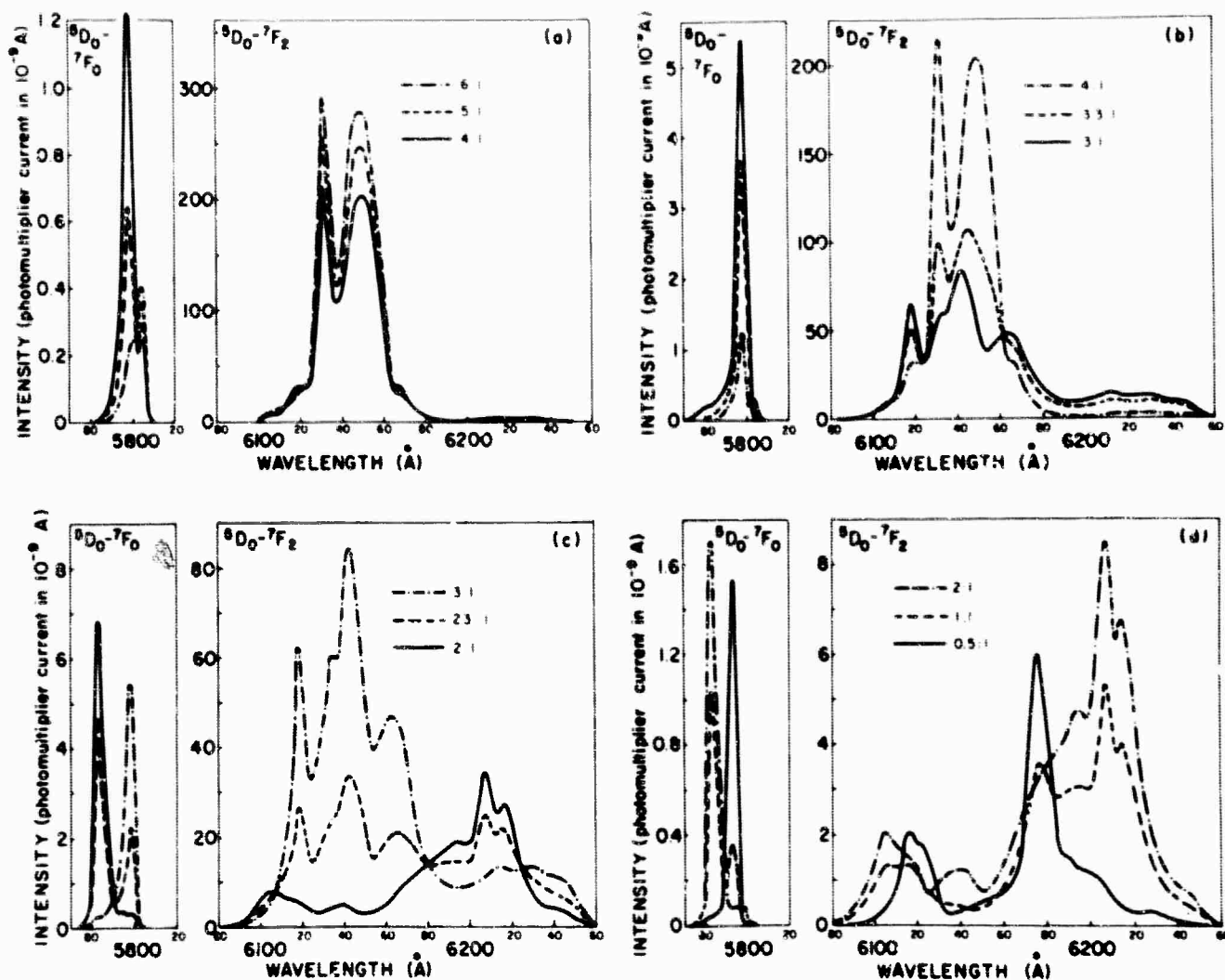


Fig. 7. Emission spectra of europium benzoylacetonate in alcohol, at -180°C with constant 0.01 M europium concentration but varying ligand-europium ratios: (a) greater than tetrakis; (b) tetrakis to tris; (c) tris to bis; (d) bis to less than monokis. In (a) the intensities have been corrected for absorption by the excess (non-chelated) ligand, while in (d) the 2:1 curve has been reduced by a factor of four and the 0.5:1 curve increased by a factor of four, to simplify comparison of the spectroscopic features.

DISCUSSION

Characterization of the dissociation equilibria

The determination of the equilibrium constants of the benzoylacetone-alcohol system depends on a detailed interpretation of its spectroscopic properties. Two basic assumptions are involved in the analytical treatment of the spectral data, one involving the excitation, the other the emission. The first assumption asserts that the only significant excitation takes place through the singlet absorption of the benzoylacetone, that this is indeed the only absorbing species of consequence and that its absorption is essentially the same whether it is free or bonded in any chelate species.¹⁴ Secondly, it is assumed that the europium emissions from the various chelate species are additive, i.e., that each species emits independently of the presence of other species in the same solution. These assumptions have been found to be consistent with experimental observations over the range of compositions studied.

The probability of exciting a chelate species is directly proportional to the number of ligands in that species. Under conditions where all the exciting radiation is absorbed, the number of photons absorbed per cm² per sec by a species having n ligands per molecule is given by

$$P_n = P_o \frac{nC_n}{C_l} \quad (1)$$

where P_o is the incident flux density, C_n is the concentration of the species with n ligands and C_l is the total concentration of ligand, free and combined. The intensity, I_n , of the emission from the species with concentration C_n is proportional to P_n :

$$I_n = A_n P_n = A_n P_o \frac{nC_n}{C_l} \quad (2)$$

If I_n^o is defined as the intensity obtained when $nC_n = C_l$, then

$$I_n = I_n^o \frac{nC_n}{C_l} \quad (3)$$

If the values for I_n^0 are known and I_n measured, then C_n can be determined. The I_n^0 values are the intensities characteristic of the pure species, with no dissociation and no other species present. This situation is, in general, experimentally unattainable, so that the I_n^0 quantities can be evaluated only by an iterative procedure. Five of the solutions having various ligand-to-europium ratios were chosen for this calculation. The spectra of these particular solutions are shown in Fig. 8, and their compositions and the intensities of their $^5D_0 - ^7F_0$ transitions are listed in Table III. Assuming spectrum b to arise entirely from the tris species, the measured intensity of the $^5D_0 - ^7F_0$ transition is taken as a tentative value for I_3^0 . Inserting this value into Eq. (3) and considering the material balance requirements, one can calculate the concentration of tris species in solutions a and c, and thus, by difference, obtain a tentative measure of the concentrations of the tetrakis and bis species in the respective solutions. The values of I_2^0 and I_4^0 thereby obtained can be used to compute the concentration of these species in solution b, from which one can get a corrected value of I_3^0 and then repeat the process. By such an iteration procedure, one can rapidly converge on a consistent set of values for I_4^0 , I_3^0 , I_2^0 . Similarly, using I_2^0 and the spectra d and e, one can then find I_1^0 . These values are listed in Table IV. The I_n^0 values depend, of course, on the particular experimental arrangement employed, but their ratios are characteristic of this chelate-solvent system itself.

The equilibrium constant for each step in the dissociation is defined in terms of the concentrations of the relevant species:

$$K_n = \frac{C_{n-1}C_B}{C_n} \quad (4)$$

where C_n and C_{n-1} follow from previous definitions, and C_B is the concentration of free benzoylacetate anion. Using the concentration values from Table III, the equilibrium constants given in Table IV can be readily evaluated.

The spectroscopic technique is complementary to other methods for determining equilibrium constants. Within the limits imposed by the system

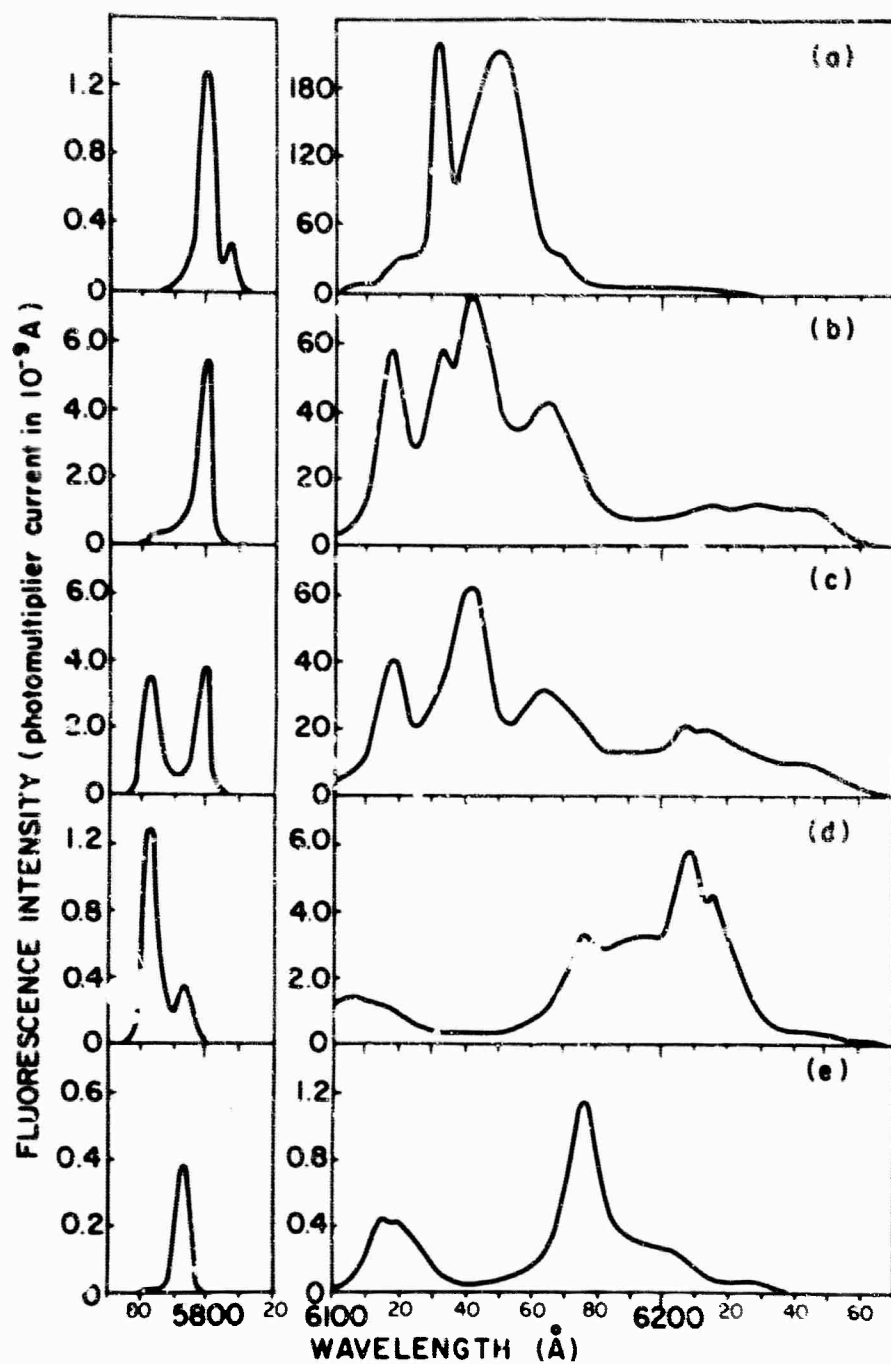


Fig. 8. Emission spectra of the solutions of europium benzoylacetonate in alcohol, at -180°C , used for calculation of the equilibrium constants of the system. Benzoylacetonate concentration: (a) 0.04 M; (b) 0.03 M; (c) 0.025 M; (d) 0.01 M; (e) 0.005 M. Europium concentration: 0.01 M throughout.

TABLE III
Solutions of Europium Benzoylacetate in Alcohol Used for
Calculation of Equilibrium Constants

Solutions [Eu ⁺³] = 0.01 M	Ligand-europium ratio (Ke ⁻¹ :Eu ⁺³)	Intensity of the ⁵ D ₀ - ⁷ F ₀ line (I _n)				Actual proportion of chelate species (%)			
		Tetrakis	Tris	Bis	Monokis	Tetrakis	Tris	Bis	Monokis
a	4 : 1	0.32	1.26			71	29		
b	3 : 1	0.02	5.43	0.21		3.1	94	3.1	
c	2.5 : 1		3.77	3.51		0.07	54	46	
d	1 : 1		0.002	1.18	0.36		0.01	5.2	88
e	0.5 : 1			0.01	0.40			0.3	>99

TABLE IV
Species Intensities and Equilibrium Constants for
Europium Benzoylacetate in Alcohol

Number of ligands (n)	True intensity of the $^5D_0 - ^7F_0$ line (I_n^0)	Equilibrium constants $K_n = \frac{C_{n-1} C_B}{C_n}$
4	0.45	1.2×10^{-3}
3	5.80	1.3×10^{-6}
2	9.60	2.9×10^{-8}
1	0.41	1.5×10^{-10}

parameters, this approach is generally applicable and will provide information not obtainable by any other means.

Effects of Dilution and Solvent

Although quantitatively correct for only one specific chelate-solvent system, the dissociation constants just derived are typical of the entire class. With such values, the chelate species present in solution will necessarily be dependent on the concentration even when they are as high as those used in laser experiments. Furthermore, the equilibria will also depend on the solvent itself and will shift as the solvent is altered. To study these effects, three chelates of europium, the benzoylacetate, the dibenzoylmethide, and the benzoyltrifluoroacetate, were selected because of interest in their laser application. The solvents were chosen because of the prevalence of their use either in fluorescence studies or as a laser host medium.

Mixed Alcohol Solvent - The behavior of the tris and tetrakis europium chelates in the mixed alcohol solvent at concentrations of from 10^{-2} to 10^{-5} M is shown in Fig. 2. With the benzoylacetate the spectroscopic features change in the same manner on dilution as they do when the ligand-to-europium ratio is decreased at constant europium concentration. This behavior is what would be expected on the basis of the equilibrium constants already determined. In each case there is a gradual increase in dissociation, so that at the lower concentration the solute consists not of the starting compound, but of lower species having one or two fewer β -diketone ligands.

The behavior of the dibenzoylmethide is quite similar to that of the benzoylacetate. For both the tris and tetrakis forms, the dominant species present in solution at high concentrations is, as expected, the initial or parent compound. In both cases, however, evidence of at least one or two of the other coordination species can be found. By 10^{-6} M almost none of the parent compound remains and dominant species in the solution is the bis.

The tris and tetrakis benzoyltrifluoroacetates exhibit a different sort of behavior in this solvent. For this ligand the tetrakis compound is completely

dissociated into the tris even at the highest concentration, since the spectra obtained from both compounds are identical except for intensity. The spectrum of the tris compound is about 1/3 more intense than that of the tetrakis because the dissociated ligand absorbs energy but does not lead to fluorescence. Dilution decreases the intensity but does not alter the spectrum. For the benzoyltrifluoroacetate, therefore, only the tris form of the chelate is stable in alcohol; the dissociation constants for the other forms must be extremely high.

EPA Solvent - EPA is a solvent commonly used for fluorescence experiments, and the results of dilution experiments in this solvent are shown in Fig. 3. In the case of both the tris and tetrakis benzoylacetates at least four species are present in solution even at concentrations as high as 10^{-2} M. As the concentration is decreased, the relative amounts of the lower coordination components increase until at 10^{-4} M it is difficult if not impossible to identify the chelate components with any degree of confidence. In this solvent the chelates are less stable than in the mixed alcohols, and the dissociation proceeds more rapidly in terms of concentration. Furthermore, interpretation is hampered by the fact that EPA contains two coordinating components, alcohol and ether, which may produce species with different spectroscopic properties.

The behavior of tris and tetrakis dibenzoylmethide is similar to the benzoylacetate but more extreme. Even at 10^{-2} M the dominant species is the tris chelate with varying amounts of the bis. By 10^{-4} M the chelate has deteriorated to such an extent that it yields only a weak and extremely diffuse emission which defies interpretation.

With the benzoyltrifluoroacetate, both the tetrakis and tris compounds produce solutions that consist mostly of the tris species. The spectra of these solutions remain unchanged on dilution from 10^{-2} M to 10^{-5} M.

DMFA Solvent - The behavior of the three chelates in the DMFA solvent is illustrated in Fig. 4. Of the tetrakis forms, the benzoylacetate is the

least stable and the benzoyltrifluoroacetate the most stable, but in all three cases the tetrakis form readily dissociates into the tris form upon dilution. It should be noted that in this solvent the order of stability is opposite to that in alcohol and the spectrum of the tetrakis species of the benzoyltrifluoroacetate is now readily observed. The tris species of all these chelates are much more stable than the tetrakis on dilution, and only at concentrations of 10^{-5} M or lower can appreciable amounts of the bis species be detected.

Nitrile Solvent - The spectra of the tris and tetrakis forms of the three chelates in the nitrile solvent are shown in Fig. 5. These reveal that the stability trend first seen in the DMFA solvent is carried further. The tris and tetrakis benzoylacetonates and the corresponding dibenzoylmethides are less stable here than in alcohol, and by 10^{-4} M the chelates have dissociated nearly completely into free ligand and free Eu^{+3} ion. The benzoylacetonate dissociates more rapidly on dilution than does the dibenzoylmethide. In both cases all the transitions become diffuse and relatively structureless, the increased breadth of the $^5\text{D}_0 - ^7\text{F}_0$ transition giving a clear indication of the poorly defined environment of the ion.

The tetrakis benzoyltrifluoroacetate, by contrast, is far more stable in this solvent than either of the other two tetrakis chelates, and dilution does not alter the spectrum in any way except for a diminution of intensity. The spectrum of the corresponding tris chelate, however, does change, becoming more rather than less intense upon dilution and gradually assuming the much simpler structure of the tetrakis spectrum. Thus the tetrakis benzoyltrifluoroacetate is so much more stable than the lower forms that the tris compound does not simply dissociate upon dilution, but actually disproportionates to form the tetrakis compound and some free (solvated) europium ion.

Tolbex Solvent - The spectra of the chelates in the tolbex solvent are given in Fig. 6. With regard to dilution, the benzoyltrifluoroacetate is the most stable of the three tetrakis chelates, and shows no evidence of any significant

dissociation even at the lowest concentration. The other two tetrakis chelates do dissociate into the tris form upon dilution, the dibenzoylmethide being the more stable. Further dilution, however, yields no spectroscopic evidence of any further dissociation of the tris into lower chelate species.

In contrast, solutions of the tris powders do show evidence of dissociation upon dilution. These materials, however, are all hydrates and at the lower concentrations their spectra become essentially identical with those obtained from the dilute tetrakis chelates. Moreover, careful drying of the tris solutions over anhydrous calcium sulfate produced the same spectroscopic effect even at the higher concentrations, and we must conclude that the "dissociation" of the hydrated tris material is nothing more than a dehydration.¹⁵

These dilution studies reveal the profound effect which the solvent can have on the stability of the various chelate forms. Of the solvents studied, it is clear that EPA, despite its attractive physical properties which have led to its wide use in fluorescence investigations, is the least suitable for meaningful interpretation. The dissociation of the chelates is so extensive that one never has present in solution the species that was originally added or indeed a single species of any kind. Furthermore, the presence of more than one class of weakly coordinating solvent molecules results in a poorly defined environment making the interpretation of spectroscopic results even more difficult.

Many of the disadvantages of EPA are absent from the mixed alcohol solvent. There is only one class of solvating molecule present, making the interpretation easier. Furthermore, in two cases, the B and D chelate, it is a more congenial solvent for the tetrakis form and the EuB_4^- ion is more stable here than in any other solvent. The dissociations have magnitudes such that progressive dilution produces a regular stepwise dissociation process. The BTF chelate, in contrast, is almost exclusively tris in this solvent regardless of starting material, and the species present is independent of concentration.

The most striking feature to emerge from this study is the inversion of the relative stabilities of the tetrakis benzoylacetonate and benzoyltrifluoroacetate as the coordination characteristics of the solvent are changed. The relative magnitudes of the dissociation constants are readily altered, and as the nature of the solvent is changed from hydroxylic to carbonyl to nitrile, in the order of increasing coordination tendency, the tetrakis benzoyltrifluoroacetate becomes progressively more stable. The stabilities of the dibenzoylmethide chelates always seem to fall between the other two, and hence its dissociation is less affected by solvent changes.

Because of the aromatic nature of the ligand, all chelates studied, both tris and tetrakis, are also readily soluble in an aromatic solvent like tolbex. Being non-polar, this solvent should provide a compatible environment for the neutral tris species, with minimal dissociation into the lower, charged species and this is borne out in the spectra. This solvent, however, is much less hospitable for the tetrakis species since the latter is anionic in nature even when accompanied by its cation, piperidinium, in an ion-pair. Consequently the tetrakis form dissociates into the tris form on dilution more readily the less aromatic the ligand.

It is clear that comparisons of the fluorescence properties of chemically different europium chelates may not be attempted without a detailed investigation of the interaction between the chelate and the solvent. After this is done, corrections can be applied to the spectroscopic data to insure that the comparison is between molecules of a similar species. Only in this way can meaningful considerations of salient effects be made.

Effects of Coordination Geometry

Tetrakis Chelate - Although the solvent has been considered thus far only with regard to its effect on the stability of the various complexes, its influence is far more deeply felt. This influence extends beyond the number of ligands on the ion to their actual geometrical configuration. This is most readily interpretable in the case of the tetrakis species, where the metal ion

resides in a uniform cage formed by the eight oxygen atoms of the four ligands. Without direct involvement of the f orbitals, nine metal orbitals ($5d$, $6s$, $6p$) are available for bonding. Two geometrically feasible arrangements of the bonded oxygens are the vertices of an Archimedean antiprism or of a dodecahedron, and both of these structures have been observed.⁷ These two structures both arise from the same type of orbital hybridization, d^4sp^3 , and both provide the central ion with very nearly the same volume. Thus the two should be readily interconvertible, and the solvent can play a key role in determining the structure.

The $^5D_0 - ^7F_2$ emission of the europium benzoylacetate in alcohol has already been shown to be consistent with a dodecahedral structure, having a symmetry of D_{2d} . The presence of a high concentration of inorganic cation, such as sodium, causes the structure to shift from the dodecahedral, so that the emission then becomes consistent with the antiprism, having a D_4 symmetry.¹⁶ The presence of highly coordinating species such as dimethylformamide and acetonitrile in the solution causes the same type of shift in structure, but in the latter cases the coordinating solvent molecule can bond directly with the ion through its one remaining vacant orbital, resulting in an overall nine-fold coordinated species.⁷ Formed by a d^5sp^3 hybridization, this structure is derived from the antiprism and has a symmetry of C_4 .

The spectra of all of the tetrakis chelates studied here, in all of the solvents, can be understood in terms of these three structures alone. These are found in Table V. Thus in the dominantly hydroxylic solvents, alcohol and EPA, both the benzoylacetate and dibenzoylmethide assume a dodecahedral structure. The latter compound, presumably because of steric effects between the many phenyl groups, is somewhat distorted, reducing the site symmetry at the central ion to S_4 . These points are entirely consistent with the spectroscopic data.

In the more highly coordinating carbonylic and nitrile solvents, the spectra of all three tetrakis chelates are consistent with the antiprism adduct structure. The behavior in the DMFA and nitrile solvents is nearly identical,

TABLE V
Structures of the Tetrakis Chelates in Various Solvents

Chelate	Solvent	Structure	Symmetry	Electric dipole representations for the $5D_0-7F_2$ transition
Benzoylacetonate	Alcohol	Dodecahedron	D _{2d}	B ₂ , E
	EPA	Dodecahedron	D _{2d}	B ₂ , E
	DMFA	Antiprism adduct	C ₄	A, E
	Nitrile	Antiprism adduct	C ₄	A, E
	Tolbex	Antiprismatic ion pair	C ₄	A, E
Dibenzoylmethide	Alcohol	Dodecahedron	S ₄	B, B, E
	EPA	Not stable		
	DMFA	Antiprism adduct	C ₄	A, E
	Nitrile	Antiprism adduct	C ₄	A, E
	Tolbex	Antiprismatic ion pair	C ₄	A, E
Benzoyltrifluoro- acetate	Alcohol	Not stable		
	EPA	Not stable		
	DMFA	Antiprism adduct	C ₄	A, E
	Nitrile	Antiprism adduct	C ₄	A, E
	Tolbex	Dodecahedron(?)	S ₄ (?)	B, B, E (?)

and it is difficult to distinguish them without careful examination of the spectra.

Tolbex, an aromatic and essentially non-polar solvent, would provide a vastly different environment from that found in the polar solvents. The effect of this should be most serious in the case of the tetrakis chelate, which, being an ionic species, finds itself here in an intrinsically hostile medium. This fact notwithstanding, the emission spectra of the tetrakis chelates in tolhex are quite similar to those obtained in the coordinating DMFA and nitrile solvents. Indeed, in two cases, the benzoylacetonate and the dibenzoylmethide, the emission spectra are virtually identical to those arising from the respective nine-coordinated antiprism adducts with C_4 symmetry, despite the obvious absence of coordinating solvent molecules to form the adducts. This seemingly preverse behavior can, however, be readily explained as the manner by which the tetrakis chelates accommodate to the non-polar medium, assuming the form of a tight ion pair with no net charge. Since the antiprismatic arrangement allows the two ions of the pair to approach each other more closely, this would be the most stable arrangement. Such a structure is really little else than an antiprism adduct, albeit through ionic rather than covalent bonding. The spectra would then necessarily resemble those of other antiprism adducts, as in fact they do. The only disconcerting element in this picture is the benzoyltrifluoroacetate, which displays one more emission line in the $^5D_0 - ^7F_2$ region than can be accounted for by such a structure. Indeed, taking the spectrum at face value, it is most consistent with an S_4 symmetry, which would imply a distorted dodecahedral arrangement for the molecule with the cation too far from the europium to be seen. In view of the non-polar nature of the solvents, such a configuration would seem energetically unfavorable. Alternatively, it should be noted that the benzoyltrifluoroacetate is the only one of the three chelates in which the opposite ends of the ligand have widely different electronegativities, and it is possible that two antiprismatic species exist in solution, differing only in their charge distribution. Such a situation has already been postulated for the crystalline powder,⁷ and would explain the spectrum in the $^5D_0 - ^7F_2$ region. However, the absence of parallel evidence for such isomers in the $^5D_0 - ^7F_0$ region (in solution) casts doubt on this explanation as well. Present information does not enable resolution of the problem.

Ligand-Deficient Chelates - In theory, the spectra of the tris, bis and monokis species could be treated in the same manner as that of the tetrakis. However, unlike the latter compound in which the oxygens of the β -diketones are the only coordinators, the lower forms do not possess a sufficient number of β -diketones to satisfy the coordination appetite of the ion. This fact makes it necessary for solvent molecules to enter into the coordination, producing an abundance of possible low symmetry structures for the chelate molecule.¹⁷ This in turn gives rise to a spectrum far more complicated than that of the tetrakis form, making interpretation on the same high level of confidence extremely difficult in practice.

In spite of these difficulties, certain patterns emerge which can be qualitatively understood in terms of the electrostatic influence of the coordinating groups. The effect of the ligands is most easily seen in the $^5D_0 - ^7F_0$ transition. The energy of this transition for the various species in the solvents used is given in Table II. It is seen that this energy, for a given species, is relatively insensitive to changes in solvent and chelating agent and is, therefore, independent of the geometrical structure. In contrast to this, it is sensitive to the number of β -diketone ligands. The energy is smallest in the tetrakis form and progressively higher for the tris and bis forms. Finally the monokis form reverses the trend, occurring at a lower energy than that of the bis form.

This behavior can be qualitatively understood in terms of the net charge on the europium ion. In the tetrakis form the eight oxygens of the β -diketone ligands all donate electrons into the otherwise empty orbitals of the ion. This, in effect, reduces the charge on the central ion, making it easier to excite an electron. As the number of β -diketone ligands surrounding the central ion is decreased, they are replaced in the coordination by solvent molecules which, being neutral, are less electronegative. This decreases the electrostatic effect of the ligands, increasing the energy of the 5D_0 state. This energy reaches a maximum with the bis compound, but decreases on going to the monokis. Here a second effect sets in, since for the first time the number of ligands is not sufficient to form some sort of protective cage around the ion. Thus the ion can feel the presence not only of the molecules

to which it is directly coordinated, but also of other solvent molecules which can now approach more closely. It is also possible that the single remaining ligand may be bonded more strongly and covalently than was the case with more ligands present.

For the ${}^5D_0 - {}^7F_2$ transition a similar electrostatic effect is observed. The 7F_2 state, however, is split by the ligand field and some of the components of the ${}^5D_0 - {}^7F_2$ transition are not optically active so that the center of gravity of this state cannot be determined with any precision. From the data available, however, it appears that the 7F_2 level shifts in the same manner as the 5D_0 .

Certain features of the ${}^5D_0 - {}^7F_2$ transition are characteristic of the individual chelate species. The tetrakis form invariably has a sharp simple spectrum with two or at most three strong lines in the region of 6110 to 6150 Å. The tris spectrum is always more complicated, with intense emissions extending to 6180 Å and weaker ones as high as 6230 Å. The bis spectrum is concentrated largely in the region of 6180 to 6230 Å, while the monokis emission falls in two regions, weaker components at 6110 to 6130 Å and stronger ones at 6150 to 6190 Å. This behavior is characteristic of the number of ligands and is common to all chelates studied.

The multiplicity of lines obtained from the ligand deficient forms make it difficult to interpret these spectra from a structural point of view with a high degree of confidence. However, assuming that the eight-fold coordination is maintained as the bidentate ligands are progressively replaced by solvent molecules, the highest symmetry attainable by the tris and monokis forms would be C_{2v} while that by the bis form would be D_{2d} . As is seen most clearly in the case of the benzoylacetonate, the dominant feature of the emissions from the various species are not inconsistent with the proposed symmetries. However, the many other possible low symmetry arrangements give rise to complications in the spectrum, making positive identification difficult.

Optical Maser Applications

These studies add only a little to the laser lore of these materials. The inherent advantage of the eight- or nine-fold coordinated chelates, such as fluorescence intensity and spectral sharpness, have already been discussed. In fact, laser action has been observed only in chelates having this structure but not in all of them. Since both tolhex and the nitrile solvent lead to structures in which laser action has been observed, they should be good solvents from this point of view. Indeed, the $\text{Eu}(\text{BTF})_4^-$ chelate exhibits laser action in the nitrile solvent from room temperature to -70°C . However, none of the chelates studied in the tolhex solvent display this phenomenon. This can be understood only in terms of a deterioration of the optical qualities of these solvents as the temperature is decreased. Both these solvents are extremely difficult to dry, and even though they appeared to be clear in fluorescence experiments, it is possible that their optical qualities were inadequate for laser purposes.

CONCLUSION

The interaction between the solvent and the chelate molecule can be adequately described in terms of two parameters: the number of ligands and the geometrical arrangement they assume. With regard to the first, equilibria are established principally between a given chelate species and those having one more and one fewer ligand up to a maximum of four β -diketone ligands. These equilibria are sensitive to changes in both the solvent and the ligand and the equilibrium constants can be determined spectroscopically. In general, the degree of dissociation increases on dilution, and the relative proportions of the various chelate species can be strongly dependent on concentration.

The second effect, seen most clearly in the tetrakis chelates, is primarily concerned with the transformation between two geometrical arrangements, the dodecahedral and the antiprismatic. In moderately polar solvents such as alcohol and EPA the former is dominant. However, any solvent having a strong tendency to coordinate a ninth group to the tetrakis molecule will

favor the antiprismatic structure. This is true whether there is direct coordination as in DMFA or the nitrile solvent or whether it takes the form of ion association as in tolhex. Similar effects are observed in the lower chelates but they cannot be determined with precision.

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APPENDIX I

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