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Liquid Lasers Based on Lanthanide Complexes

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The review deals with the chemical problems concerning the use of neodymium, europium, gadolinium, and terbium complexes in liquid lasers. The equilibria arising in solutions are briefly examined. The principal liquid laser systems have been analysed. The systems can be divided into two types: chelate systems with transfer of absorbed energy from the ligand molecule to the lanthanide ion (these include europium, gadolinium, and terbium complexes) and systems based on neodymium complexes in inorganic solvents. The latter are distinguished by enhanced stability to the action of light and are at present the most promising for the preparation of liquid lasers.
The effect of solvents and structure of the complexes on the laser properties of the systems is also discussed. The bibliography includes 109 references.

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I. INTRODUCTION

The lanthanide elements have been used successfully to make lasers comparatively long ago. So far the laser effect produced by crystals and glasses has been obtained for the following lanthanides: praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, and ytterbium[1-5]. During the last ten years, several multicomponent liquid systems with laser properties were obtained on the basis of lanthanide complexes.

The formation of lasers based on liquid systems constitutes a major and complicated problem in the development of which the work of both physicists and chemists is combined. Advances in studies in this field depend entirely on their joint efforts. Some of the problems can be solved by physicists and others by chemists.

The first class of problems, which are in principle solved by physicists and therefore may be arbitrarily called "physical", may be said to include problems such as the methods for the design of lasers under different operating conditions, a number of experimental and theoretical problems concerning the development and formation of active media based on organic and inorganic materials, and the choice of resonators, optical pumping systems, and optical shutters.

Usually physicists investigate the fundamental characteristics of lasers: the pumping rate, emission intensity, efficiency, and also the spectroscopic and time characteristics of laser emission. The study of the angular divergence of the emission plays a significant role. Some of these problems have been formulated and examined by a number of workers[6-17]. Certain other information concerning technical applications of solid lasers may be found in the monograph of Mikaelyan et al[18].

All the physicochemical processes associated with the study of the structure of complex multicomponent systems employed as liquid lasers may be included in the second class of problems which we have arbitrarily called "chemical". These are problems solved by methods of classical physical chemistry: the thermodynamics of the formation of the complexes and also the study of the rates of chemical reactions.

The range of problems associated with the study of the structures of the complexes formed and their spectroscopic properties over a wide range of the electromagnetic vibration spectrum is no less important. Finally, it is also possible to formulate a further series of problems connected with the investigation of the interaction between radiation and matter.

In view of the large number of problems which must be solved in the making of liquid lasers, we shall consider only some of them. For example, the choice of solvents and their chemical purification, the choice of complex-forming ligands and aprotic acids which improve the properties of the laser systems, and the preparation and selection of compounds in the form of which lanthanides may be introduced into the solvent can be classified as chemical problems.

The requirements which must be met by complex liquid laser systems are dictated by their own properties, i.e. a sufficiently high concentration of active molecules, optical homogeneity of the system, and its stability with respect to light are required. These "physical" requirements themselves have a profound physicochemical basis and need the most far reaching and thorough physicochemical study.

For example, the problem of solubility is one of the most complex. The point is that in multicomponent systems in which the number of components is greater than 4-5 the introduction of each new component improving the optical properties of the system is extremely difficult. This applies in particular to inorganic systems which at this stage appear to be more promising for the formation of liquid lasers.

For example, the inorganic systems include those containing various oxide halides and a wide variety of aprotic acids. The absence of a single quantitative theory of solubility precludes a reliable theoretical prediction of the solubilities of specific lanthanide compounds in various solvents. In the preparation of liquid lasers with fairly high lanthanide concentrations, experimental

data must be employed in each individual case. Very rigorous requirements must be met by the optical homogeneity and transparency of the laser systems, particularly at the emission wavelength, which in turn entails a need for very careful purification of the components.

However, even the most thorough initial purification of the compounds used to prepare the laser liquids does not always yield satisfactory results, since the occurrence of reactions and the formation of side products are possible in the course of the preparation. The side products greatly influence the optical properties of the laser liquid prepared. Therefore the multicomponent liquid systems obtained must be often additionally purified without impairing the laser properties of the system.

The stability of lasers to the action of light also constitutes a very important problem, which concerns the interaction between radiation and matter, involving the stability of solvates and complex species.

The principal components of liquid laser systems are lanthanides, complex-forming ligands, and solvents. We shall attempt to estimate the effect of the system components on the properties of liquid lasers.

II. PRINCIPAL LANTHANIDE ELEMENTS ON WHICH LIQUID LASERS ARE BASED

So far a laser effect in solutions has been obtained for four lanthanides: europium, neodymium, terbium, and gadolinium. The laser systems based on these lanthanides must be immediately subdivided according to the type of "operation" of the lasers. Whereas the systems based on europium, gadolinium, and terbium operate according to the so called "six level" mechanism with transfer of absorbed pumping energy from the ligand to the lanthanide ion, the system based on neodymium gives rise to a laser effect based on a four-level mechanism. In this connection the role played by each component of the laser system as well as the requirements which must be met by the system components will be different.

III. THE NATURE OF THE EQUILIBRIA IN LASER SYSTEMS

In order to prepare new liquid laser systems, detailed studies of their thermodynamic properties are required—these include the types of equilibria occurring in the solutions and the changes in the equilibria when the temperature is altered during the pumping process. The temperature range can be varied within wide limits. We may note that the equilibria arising in such systems can be divided into three types:

1. Solvation equilibria which characterise the interaction of neodymium, europium, gadolinium, and terbium with solvent molecules.
2. Equilibria involved in the formation of complexes by lanthanide ions with various organic and inorganic ligands present in the laser systems.
3. Processes where both types of equilibria can be involved in complex formation.

Lanthanide ions interact in solution with both solvent molecules and with the ligands. In these processes, involving competition between solvation and complex formation, the chemical processes can follow largely one of three pathways, depending on the stability of the complexes formed.

In the formation of a laser system an attempt should be made to ensure that the solvent molecules are displaced from the inner sphere of the complex, since the solvent molecules usually include CH_2 and OH groups, which have a high vibration frequency promoting the leakage of energy in radiationless transitions. A complex of this kind should have a stable inner sphere and the solvent molecules should be in the outer sphere.

The distribution of ligands in the inner sphere obeys the coordination laws but the distribution of molecules in the outer sphere may not in fact be subject to these laws and may be determined statistically. The most complete information about the stability of the solvate complexes of lanthanides formed in different solvents may be provided by the thermodynamic functions for the solvation processes, but few data are available for such functions in non-aqueous solvents[19,20].

Another no less important aspect of the study of laser effects is the coordination number of the lanthanides and the structure and symmetry type of the complexes formed. At the present time much attention is being devoted to them[21].

IV. THE COORDINATION NUMBER OF LANTHANIDES AND THE SYMMETRY TYPE OF SOME OF THEIR COMPLEXES

In the study of the competitive complex formation account must be taken of the variable coordination numbers of lanthanides. In certain early investigations, a coordination number of six was attributed to lanthanides[22-24]. Later studies showed that the coordination number of lanthanides is variable. At the beginning of the lanthanide series the coordination number is 9, but, starting with erbium, it decreases to six[26,27]. Table 1 gives a compilation of studies in which various investigators demonstrated particular coordination numbers of lanthanides using different methods. It is noteworthy that the coordination numbers attributed to a particular lanthanide in solutions should strictly speaking be determined in these solutions. However, many investigators refer to the coordination number determined by the X-ray diffraction analysis of solid lanthanide[26,27]. Such assignment of the lanthanide coordination number to solutions is risky and invalid although in some cases the method is justified.

The coordination number, symmetry, and point group determined by X-ray structure analysis of the crystals sometimes help in the elucidation of the structure of the solvate–ligand complexes formed in the solutions. Table 1 therefore includes, together with the coordination numbers of lanthanides obtained in solutions, certain incomplete data concerning the determination of the coordination numbers in solid salts. Probably solutions with a high salt concentration, close to saturation, bear a marked analogy to the structure of the crystalline compounds. In dilute strong electrolyte solutions, the coordination number and symmetry type of the solvate complex depends mainly on the structure of the solvent surrounding the metal ion. The ligands in the outer coordination sphere have a weaker effect on the solvate complex. A change of solvent leads to a change in the coordination number and the symmetry of the solvate complex[31,33,38]. With increase of ligand concentration and its incorporation into the inner sphere of the lanthanide ion, the coordination number and the symmetry of the solvate structure also change.

In this respect the work of Lugina and Davidenko[34,35] is most instructive and correct. They compared the absorption spectra of the aqueous solutions and the solid hydrates of lanthanide chlorides, bromides, perchlorates, and bromates in order to obtain data on the structure of the lanthanides (neodymium, erbium, and europium) aquo-ions. In particular, it was shown that, together with the dominant form of the $Nd(H_2O)_9^{3+}$ aquo-ion with D_{3h} symmetry, aquo-ions having different structures are also present in the solution.

It has been shown[35] that at higher KSCN and LiCl concentrations, reaching respectively 10 and 14 M, structures with a coordination number of 9 and D_{3h} symmetry, structures with a coordination number of 8, and several structures with equivalent and non-equivalent positions of the ligands coexist.

The spectroscopic method proved extremely fruitful for the comparison of the structures of neodymium complexes with β-diketones in crystals and solutions[36].

Table 1. Coordination numbers of lanthanides determined in various systems.

System	Method	Coordination number	Symmetry type and point group	References
$[Ln(H_2O)_9](C_2H_5SO_4)_3$ Ln = La, Ce, Pr, Nd, Sm, Gd, Dy, Y	X-Ray diffraction structure analysis of crystals	9	Trigonal-bipyramidal symmetry of crystal field, C_{3h}	25
$Ln(ClO_4)_3$—H_2O	NMR	Variable, between 9 at the beginning of lanthanide series and 6 at the end, starting with Pr. 9 or 8 for Gd		26, 27
Ln-*N*-hydroxylene-diaminetetra-acetic acid-H_2O	Potentiometric	Assumed to be 8 between La and Ho		28
$Ln(NO_3)_3$—H_2O Ln=Pr, Nd, Sm, Eu, Gd, Er, Yb, Y. Variable $Ln(NO_3)_3$ concn., between 0.140 and 0.325 mole/1000 g	Derivative plots	6 ± 0.6 for all lanthanides		29
Ce^{3+}-diethylenetriamine-penta-acetic acid-H_2O	Potentiometric	Assumed to be 8		30
$PrCl_3$—H_2O $[Pr(H_2O)_9]^{3+}$	Spectrophotometric	9	D_{3h}	31
$PrCl_3$—CH_3OH	»	9	Solution contains two or more solvated species. $PrCl_2.7CH_2OH^+$ species with C_{2v} symmetry predominate	31
$PrCl_3$—C_2H_5OH	»	9	D_{3h}	31
$PrCl_3$—n-C_3H_7OH	»	Apparently 8	Symmetry lower than D_{3h}	31
$[Nd(H_2O)_9](BrO_3)_3$	X-Ray structure analysis of crystals	9	D_{3h}	32
$NdCl_3$—H_2O	Spectrophotometric	8	D_{2h}	33
$NdCl_3$—CH_3OH	Ditto	8	Lower than D_{2h}	33
$NdCl_3$—C_2H_5OH	»	8	Ditto	33
$[Nd(H_2O)_9]X_3$ X=Cl^-, Br^-, Br, O_3^-, ClO_4^-	Spectrographic. Comparison of crystals and solutions	9	D_{3h}; the existence in solutions of aquo-ions with a different structure together with the dominant form is postulated	34
$c \sim 0.1$ M				
$Nd(ClO_4)_3$-H_2O-LiCl or KSCN c_{LiCl} = 10-14 M c_{KSCN} = 3-10 M	Ditto	9 or 8	D_{3h}; several structures present in solution	35

Table 1 (cont'd.).

System	Method	Coordination number	Symmetry type and point group	References
$Nd(A)_n^*$ and $Nd(B)_n^*$ in CH_3OH; CH_3OH-H_2O	Spectrophotometric. Comparison of crystals in solution	8	$Nd(AA)_3$ and $Nd(BA)_3$ complexes exist in solution with two solvent molecules in inner sphere	36
$EuCl_3$—H_2O	Spectrophotometric and luminescence	7—8	D_{2h}	34, 37, 38
$EuCl_3$—CH_3OH	Ditto	7—8	C_{2v}	38
$EuCl_3$—C_2H_5OH		7—8	C_{2v}	38
Eu(TTA)$_3$·2ТБФ*	Extraction	8	—	39
$[Gd(H_2O)_6Cl_2]Cl$	X-Ray diffraction structure analysis of crystals	8	$P2_1/n$	40
$GdCl_3$—H_2O	Spectrophotometric		D_{2h}	33
$GdCl_3$—CH_3OH	Ditto		C_{2h}	33
$GdCl_3$—C_2H_5OH			C_{2h}	33
$[Gd(H_2O)_9](ClO_4)_3$	NMR	9	—	41
$[Er(H_2O)_6]Cl_2^+$ $[Er(H_2O)_6]I_2^+$	X-Ray diffraction structure analysis of solutions	6	D_{2h}; octahedral environment comprising six water molecules. Two chloride ions occupy opposite the corners of octahedron in second layer	42
$ErCl_3$—H_2O	Spectrophotometric		D_{2h}	33
$ErCl_3$—CH_3OH	Ditto		C_{2h}	33
$ErCl_3$—C_2H_5OH			C_{2h}	33

* Note: A = acetylacetone residue; B = benzoylacetone residue; TTA = thenoyltrifluoroacetone residue; TBP = tri-s-butyl phosphate.

Comparison of the reflection spectra of crystalline neodymium acetylacetonates and benzoylacetonates and the absorption spectra of methanol and aqueous methanol solutions of neodymium complexes with acetylacetone and benzoylacetone with different stoichiometric compositions showed that the $Nd(AA)_3$ and $Nd(BA)_3$ complexes exist in solution with two solvent molecules in the inner coordination sphere.

As data accumulate on the crystal structures of the lanthanide complexes with various organic ligands, they may be employed to investigate the structures of the solutions by spectroscopic methods[44-47].

NMR and X-ray diffraction structure analyses of the solutions are also used to establish the structures of the solvate-ligand complexes[37,41-43]. Nowadays X-ray diffraction structure analysis of liquids is being employed with increasing success for the elucidation of the structural characteristics of the immediate environment of cations in aqueous solutions[48,49].

The data in Table 1 permit certain preliminary conclusions. The coordination number of lanthanum, cerium, praseodymium, neodymium, and gadolinium is 9 or 8, while coordination numbers of 8 and 7 are characteristic of europium. Starting with erbium, the coordination number of lanthanides decreases to 6.

The coordination numbers of lanthanides and the symmetry type of their solvate-ligand complexes are influenced primarily both by the structure of the solvent molecules and that of the ligand molecules coordinated in the inner sphere. In the determination of the composition of the inner-sphere lanthanide complexes, one should bear

in mind the variable coordination numbers listed in Table 1. We may note that a study has also been made where a lanthanide coordination number of six was demonstrated by a derivative plot method[29].

V. PRINCIPAL LIQUID LASER SYSTEMS

The principal data on liquid laser systems are compiled in Table 2. Their analysis permits the following conclusions. While the number of lanthanides used in the preparation of liquid lasers is comparatively small, the number of complex-forming ligands employed for this purpose is fairly large.

A considerable proportion of these ligands have similar properties owing to the mechanism of operation of the laser system. Two laser mechanisms may constitute a kind of barrier, which permits the classification and characterisation of the complexes formed in various solvents.

The majority of laser systems are based on complexes with various β-diketones. These systems involve a single common mechanism in which energy is absorbed by the organic components of the molecule with its subsequent transfer to europium or terbium.

The first eight complexes have approximately the same structure in which the central metal atom is surrounded by four ligands occupying eight coordination sites. Thus the inner sphere of such complexes is completely saturated and all the solvent molecules have been displaced to the outer sphere. According to their structure, these are the usual chelate compounds characteristic of β-diketones.

The study of the luminescence spectra of the octacoordinate europium chelates with the general formula $EuL_4.P$ (where P = piperidine and L is one of the following three β-diketones: benzoylacetone, dibenzoylmethane, or benzoyltrifluoroacetone) led to the conclusion that, among the europium chelates, only the octacoordinate chelates exhibit a laser effect[56]. The following mixtures were employed as solvents: (1) the standard alcoholic solvent (SAS)—a 3 : 1 ethanol–methanol mixture; (2) the dimethylformamide solvent—a 4 : 1 mixture of the standard alcoholic solvent and dimethylformamide (DMF); (3) the nitrile solvent—a 1 : 1 : 1 mixture of acetonitrile, propionitrile, and butyronitrile.

It has been established that chelates with D_4, C_4, and D_2 symmetries are the most effective for the preparation of lasers. The chelates investigated are quite stable with respect to high-intensity radiation pulses. Their chemical stability is determined by the ligand, the solvent, and the concentration of the solution. The chemical structure of the coordinated β-diketones also plays a considerable role.

It is extremely instructive that, out of nine halogeno-substituted derivatives of benzoyltrifluoroacetone (*ortho*-, *meta*-, and *para*-fluoro-, -chloro-, and -bromo-derivatives), only the *ortho*-substituted derivatives can give rise to laser effects in the form of the compounds EuL_4. .DMA. The *ortho*-chloro-compound has the lowest pumping threshold[58].

The ninth and tenth complex (Table 2) are distinguished by the fact that the metal atom in them is coordination-unsaturated. One or two free sites, available to the solvent (acetonitrile or dioxan) molecules, remain in the inner sphere. In the eleventh complex, that of neodymium with pentafluoropropionic acid and *o*-phenanthroline, the variable coordination number of neodymium (which is eight or nine) suggests that the solvent molecules (dimethyl sulphoxide) coordinated to the metal are present in the inner sphere.

The twelfth system, based on neodymium oxide dissolved in selenyl chloride with added aprotic acids, differs somewhat in its physicochemical properties from the systems enumerated above. It is one of the first systems consisting entirely of inorganic components and exhibiting enhanced light stability. Its laser properties are comparable to those of the best specimens of solid systems based on $Nd^{3+}:CaWO_4$ crystals and glasses[63,64].

Analysis of the luminescent properties of this system shows that its structure is closer to that of neodymium crystals in calcium tungstate than to the glasses.

We shall now attempt to describe the chemical reactions occurring when Nd_2O_3 and $NdCl_3$ are dissolved in the $SeOCl_2-SnCl_4$ solvent using the results of certain studies on this problem[65-68]. The reactions occurring in the solvent itself can be described by the following stepwise equilibria:

$$SnCl_4 + 2SeOCl_2 = SnCl_6^{2-} + 2SeOCl^+, \quad (1)$$

$$SbCl_5 + SeOCl_2 = SbCl_6^- + SeOCl^+, \quad (2)$$

$$Nd_2O_3 + 6SeOCl^+ = 2Nd^{3+}_{(solvate)} + 3SeOCl_2 + 3SeO_2. \quad (3)$$

The overall reaction involving the dissolution of neodymium oxide in the $SeOCl_2-SnCl_4$ binary solvent, quoted by Brecher and French[69], can be represented as follows:

$$Nd_2O_3 + 3SnCl_4 + 3SeOCl_2 = 2Nd^{3+}_{(solvate)} + 3SnCl_6^{2-} + 3SeO_2. \quad (4)$$

In these equations the $Nd^{3+}_{(solvate)}$ ion is equivalent to the solvated ion with several selenyl chloride molecules, which are coordinated in the inner sphere with formation of $Nd(SeOCl_2)_n^{3+}$; the $SnCl_6^{2-}$ anions or those of other aprotic acids are coordinated in the outer sphere. The independence of the electronic absorption spectra of neodymium in the visible region of the chemical structure of the aprotic acid may be regarded as indirect evidence that the aprotic acids are combined only in the outer sphere of the solvated neodymium ion. The most intense neodymium absorption bands at 0.53, 0.74, 0.80, and 0.86 nm, corresponding to the $^4G_{5/2}$, $^2G_{7/2}$, $^4S_{3/2}$, $^4F_{1/2}$, $^2H_{9/2}$, $^4F_{5/2}$, and $^4F_{3/2}$ transitions, remain unchanged. Consequently in solution the electrically neutral neodymium complex should have the structure $[Nd(SeOCl_2)_n]_2(SnCl_6)_3$. A detailed elucidation of the complex formation processes and the structures of the compounds formed in solution requires further investigation.

Selenium dioxide formed on dissolution of neodymium oxide must be carefully filtered off, since its presence can constitute a serious obstacle to the occurrence of a laser effect[65].

It is noteworthy that, when neodymium chloride is dissolved, the solutions do not contain selenium dioxide particles. The solubility of $NdCl_3$ in pure selenium oxide chloride is limited, but in the $SeOCl_2-SnCl_4$ two-component solvent neodymium chloride dissolves fairly readily. In this case too the final compounds in the oxide chloride solution are probably the solvate–ligand neodymium complexes of the type $Nd(SeOCl_2)_x(SnCl_6)_y^{(3-2y)-}$.

Heller[68] employed lanthanide chlorides obtained by vacuum drying in hydrogen chloride vapour. These compounds usually contain 1–2.5% of water. Traces of water have a marked effect on the luminescence lifetime of the inorganic system, reducing it to 20–30 μs. It is impossible to achieve a laser effect in such systems[65]. Therefore, in order to obtain anhydrous lanthanide chlorides, it is necessary to employ more effective drying conditions[70] or an attempt must be made to separate water and hydrogen chloride vapours during the preparation of the laser system.

Table 2. Properties of the laser solutions.

No.	Complexes	Solvent	Concentration	Laser transition	Laser emission wave-length, Å	Width of laser emission, Å	Life-time, μs	Laser threshold, J	Temp., °K	References
	1	2	3	4	5	6	7	8	9	10
1	EuB_3HB* Thermogravimetric analysis shows that EuB_3 is weakly bound to one molecule of benzoyl acetone	3:1 C_2H_5:CH_3OH (Standard alcoholic solvent)	$2.5\cdot10^{-2}$ *M*	$^5D_0 - {}^7F_2$	6114	—	445 (150° K)		298° K	50, 51, 52
2	$Eu(BTFA)_4P$	CH_3CN Acetonitrile	0.01 *M*	$^5D_0 \rightarrow {}^7F_2$	6119	—	5200	1700	298° K	53
3	$Eu(TTA)_4$.DMA m.p. = 194-195°C	Ditto	$5\cdot10^{-3}$ *M*	$^5D_0 \rightarrow {}^7F_2$	6115	—	—	800	268° K	54, 55
4	$Eu(TFA)_4.HNR_3$ m.p. 194-195°C	»	10^{-2} *M*	$^5D_0 - {}^7F_2$	6119	—	—	800	268° K	54, 55
5	$Eu(BTFA)_4$.I m.p. 194-195°C	»	$7.5\cdot10^{-3}$ *M*	$^5D_0 - {}^7F_2$	6118	—	—	800	268° K	54, 55
6	$Eu(BFTA)_4$.Pyrr m.p.212-213°C	»	Variable, 10^{-2}-10^{-3} M, minimum concn for laser effect 1.5×10^{-3} M	$^5D_0 - {}^7F_2$	6118	40	—	Depends on concn. of complex (850-500)	233÷303°K	54, 55, 56
7	$Eu(O\text{-}Cl\text{-}BTFA_4)$.DMA m.p. 194-195°C	»	$7.5\cdot10^{-3}$ *M*	$^5D_0 - {}^7F_2$	6117.5±1	25	670±20	140—150	294	57, 58
8	$Eu(B)_4Na$	2:5.6:0.8 dimethyl formamide-ethanol-propanol	10^{-2} *M*	$^5D_0 - {}^7F_2$	6111	19 cm^{-1}	—	—	293	59
9	$Tb(TFA)_3$ m.p. 135-137°C	Acetonitrile or 1,4-dioxan	$2.5\cdot10^{-3}$ *M*	$D_4 - {}^7F_5$	5470	—	200	1700	298° K	60
10	$Gd(TTA)_3.B$	Acetonitrile	$2.5\cdot10^{-3}$ *M*	Unresolved		—	—	—	Room	61
11	$Nd(PFA).C_{12}H_8N_2$	Dimethyl sulphoxide	0.2 *M*	$^4F_{3/2} - {}^4I_{11/2}$	10 570	—	50	314—315	298° K	63—68
12	Nd_2O_3—$SeOCl_2$—$SnCl_4$ $NdCl_3$—$SeOCl_2$—$SnCl_4$ Nd_2O_3—$SeOCl_2$—$SbCl_5$ $NdCl_3$—$SeOCl_2$—$SbCl_5$	$SeOCl_2$	0.02-0.75 *N* Nd^{3+}, optimum concn. 0.5 *N*, 500 g litre^{-1} $SnCl_4$	$^4F_{3/2} - {}^4I_{11/2}$	10 566	160	110÷260	6÷40	298° K	62
13	Nd_2O_3—$POCl_3$—$SnCl_4$ $POCl_3 : SnCl_4 = 5:1$	$POCl_3$	Threshold concn. of Nd 3.2×10^{-4} M	$^4F_{3/2} - {}^4I_{11/2}$	10 530	28	170÷200	3300	Room	73,74
14	$Nd(ClO_4)_3$—$POCl_3$—$TiCl_4$	ditto	0.1 *M*	$^4F_{3/2} - {}^4I_{11/2}$	10 530	4	—	30	ditto	75
15	Nd^{3+}—$POCl_3$—$SnCl_4$ Nd^{3+}—$POCl_3$—$TiCl_4$	»	3%	$^4F_{3/2} - {}^4I_{11/2}$	10 522 10 540	4	120—180 140	28 32	300° K	76
16	Nd_2O_3—$POCl_3\cdot SnCl_4$ $\theta = 4,41\cdot10^{-3}$ *pad*	»	0.1—0.2 *M*	$^4F_{3/2} - {}^4I_{11/2}$	10 600		240	375	Room	77—79
17	Nd^{3+}—$POCl_3$—$SnCl_4$	»	C_{Nd} = 2—10%	$^4F_{3/2} - {}^4I_{11/2}$	10 525±5	10 in planar resonator	260—280			80—82
18	Nd^{3+}—$POCl_3$—$TiCl_4$	»	ditto	$^4F_{3/2} - {}^4I_{11/2}$	10 525±5		210—230			80—82
19	Nd^{3+}—$POCl_3$—$TaCl_5$	»	»	$^4F_{3/2} - {}^4I_{11/2}$	10 525±5	Fabry-Perot	150—180			80—82
20	Nd^{3+}—$POCl_3$—$HfCl_4$	»	»	$^4F_{3/2} - {}^4I_{11/2}$	10 525±5	3 in spherical resonator	150—180			80—82

Note. B = benzoylacetone (HB) residue; BTFA = benzoyltrifluoroacetone residue; P = piperidine; TTA = thenoyltrifluoroacetone residue; DMA = dimethylamine; TFA = trifluoroacetylacetone residue; I = imidazole; Pyrr = pyrrolidine; PFA = pentafluoropropionic acid; B = bipyridyl.

The principal equations of the preparative method for the making of laser solutions were described by Heller[67]. Usually the mixture obtained is coloured brown owing to the the presence of selenium monochloride (Se_2Cl_2):

$$2SeOCl_2 = SeO_2 + SeCl_4, \quad (5)$$

$$2SeCl_4 = Se_2Cl_2 + 3Cl_2, \quad (6)$$

$$Se_2Cl_2 = 2Se + Cl_2. \quad (7)$$

The presence of selenium monochloride may be avoided by oxidation with $KClO_3$.

The chlorine and chlorine dioxide vapours are removed by vacuum treatment. The role of $SbCl_5$ as an aprotic acid improving the solubility of neodymium oxide is analogous to that of $SnCl_4$.

Information about the laser effect of neodymium in a binary phosphorus oxide chloride–aprotic acid system was published almost simultaneously in several papers [72-80]. The principal data for these systems are presented in the Tables and are numbered 12–20. We may note that $BeCl_2$, $ZnBr_2$, $CdCl_2$, $HgCl_2$, BCl_3, BBr_3, $AlBr_3$, $AlCl_3$, $GaCl_3$, $GaBr_3$, $LnCl_3$, $SnBr_4$, $TiBr_4$, $ZrCl_4$, $ZrBr_4$, $AsCl_3$, $NbCl_5$, and $SbCl_5$ as well as the solvents $SOCl_2$ and CCl_4 have also been used in these systems.

Systematic studies by a group of investigators [80-83] suggest that liquid lasers based on phosphorus oxide chloride are more effective than systems based on selenium chloride. There exists also another view, namely that the systems are equivalent in their effectiveness [69].

The dissolution of neodymium oxides and chlorides in a phosphorus oxide chloride–aprotic acid binary solvent resembles in some of its features the dissolution in $SeOCl_2$. The chemical reaction between the binary solvent and neodymium oxide can be represented schematically as follows [69,84,85].

$$Nd_2O_3+3SnCl_4+6POCl_3 = 2Na^{3+}Nd^{3+}_{(solvate)}+3SnCl_6^{2-}+3P_2O_3Cl_4\,. \qquad (8)$$

Here $Nd_{(solvate)}$ is the solvated neodymium ion surrounded by several $POCl_3$ molecules. The study of the structure of this solvate complex and also of its thermodynamic equilibrium with the surrounding medium is of direct theoretical and practical interest for the improvement of the properties of liquid luminescent systems.

Various neodymium compounds have been employed [84,85] to prepare liquid luminescent systems. Most reproducible results were obtained for the $Nd_2O_3-SnCl_4-POCl_3$ system.

The absorption and luminescence spectra of neodymium led to the conclusion that the similarity of the spectra of solutions obtained under different conditions is due to the presence of the same type of immediate environment of the activator in the solution. In the neodymium solvate complex the first coordination sphere consists of $POCl_3$ molecules coordinated to neodymium via oxygen [86]. It is sufficiently stable to form identical luminescence centres in several versions of the solution which the present author investigated, this being reflected in a similarity of the spectra. The existence of a fairly stable solvate shell has been confirmed by Antipenko et al. [85], who showed the occurrence of energy transfer between lanthanide ions in the $POCl_3-SnCl_4$ system.

Different workers suggest a wide variety of metal halides as aprotic acids [63-83]. Aprotic acids play an important role in the enhancement of the effectiveness of luminescence [quantum yield of luminescence (Ed. of Translation)]. This does not involve merely an improvement of the solubility of neodymium salts; for example, when neodymium perchlorate was employed [75], the metal concentration in solution was fairly high, since the perchlorate is readily soluble in $POCl_3$, but the luminescence intensity of the $POCl_3-Nd(ClO_4)_3$ solution was low. The luminescence of the same solutions increases abruptly by a factor of five when small amounts of aprotic acids are added.

The present author explains the increase of the effectiveness of the luminescence by the association of chloride anions with the aprotic acid. The most effective aprotic acids are $SnCl_4$, $SbCl_5$, $TiCl_4$, $TaCl_5$, and $HfCl_4$. The behaviour of these compounds in $POCl_3$ has already been partially investigated; thus the following equilibrium (equilibrium constant K) has been suggested for the reaction of $SbCl_5$ and $POCl_3$: [87]

$$Cl_5SbOPCl_3 \rightleftarrows SbCl_6^- + POCl_2^+\,, \qquad (9)$$

where $K = 4\times10^{-6}$. For the next reaction stage,

$$SbCl_6^- + POCl_3 \rightleftarrows Cl_5SbOPCl_3 + Cl^-; \qquad (10)$$

K not exceeding 10^{-9}. The mobilities obtained from conductimetric data are more characteristic of non-solvated ions.

VI. SOLVENTS

The principal physicochemical information about the nature of the solvents is presented in Table 3. The number of solvents in which laser effects of lanthanide ions have been observed is small.

All the solvents can be arbitrarily divided into two groups. Proton-containing organic compounds may be included in the first group and aprotic solvents in the second. On introduction of binary solvents such as metal oxide halide–aprotic acid, the number of solvents which can be used to obtain laser systems will increase.

It is noteworthy that three-component solvents of the type $POCl_3-SOCl_2$–aprotic acid have already appeared [81]. The addition of $SOCl_2$, carbon tetrachloride, and certain other components tends to extend the region of the liquid state and to stabilise neodymium solutions while the luminescent and laser characteristics are retained [81].

Thus multicomponent liquid laser systems, the individual components of which will successfully supplement one another in creating the optimum operating characteristics of the system, will probably be employed in the future. The use of a number of components in the test system is reasonable, since none of the solvents usually has the entire set of the necessary properties. All this applies equally to proton-containing organic solvents and to aprotic solvents [89,90].

An attempt has been made [90] to assess the prospects for the application of various solvents in liquid laser systems. Hydrogen-bonded organic solvents have been mainly examined. Analysis of the physicochemical properties of solvents makes it possible to find ways for the selection of the most effective solvents in broad outline only.

VII. THE STRUCTURE OF THE COMPLEXES AND ITS RELATION TO LUMINESCENCE

An excited lanthanide ion, for example a neodymium ion, can lose its energy via two main mechanisms. One may assume that the first mechanism whereby the energy of the excited neodymium ion is dissipated is a direct transfer to the surrounding medium via vibrations. The mechanism of this type of transfer has been studied by different investigators on various models [63,91,92].

In the second case account must be taken of the high neodymium concentration as a result of which self-quenching of neodymium occurs [93] owing to an energy jump between adjacent neodymium atoms [94]. It is suggested that the radiationless energy transfer from neodymium and other lanthanides is analogous to the processes occurring in organic compounds [95-97] and also in inorganic ions [98-102].

Table 3. Solvents.

Name and structural formula	M	Dielectric constant ε	M.p.-b.p., °C	n_D	d, g cm^{-3}	κ, Ω^{-1} cm^{-1}	η, cP	References
CH_3OH	32.04	32.63	−97.47÷64.56	1.3266 at 15°	0.78675	$1.5\cdot10^{-9}$	0.5445	88
C_2H_5OH	46.086	24.3	−117.3÷78.327	1.3594	0.78506	$1.35\cdot10^{-9}$	1.078	88
Standard alcoholic solvent, 3:1 C_2H_5OH-CH_3OH								
Acetonitrile CH_3CN	41.052	37.5 at 20°	−45.72÷81.60	1.34163	0.77683	10^{-8}	0.3448 at 30°	89
Dioxan $C_4H_8O_2$	88.1	2.209	11.7÷108.8	1.42436	1.03375 at 20°	$5\cdot10^{-15}$	1.439	89
Dimethylformamide	73.01	36.71	−61÷153.0	1.4294	0.9443 at 25°	$2\cdot10^{-7}$	0.796	89
Propyl alcohol solvent−2:5.6:0.8 dimethylformamide-ethyl alcohol-propyl alcohol	60.09	19.7 at 25°	−127÷97.2	1.3873	0.80753 at 15°	$5\cdot10^{-8}$	2.18 at 20°	88
Dimethyl sulphoxide $(CH_3)_2SO$	78.13	48.9	18.2÷189		1.100	$3\cdot10^{-3}$	2.473 at 20°	89
Selenyl chloride	165.9	46.2 at 20°	8.5÷168	2.64 at 25°	2.44 at 25°	$2.5\cdot10^{-5}$		87, 88
Phosphorus oxide chloride $POCl_3$	153.33	13.9	1.25÷105.8	1.460	1.648	$2\cdot10^{-8}$	1.018	87

The main conclusions which may be drawn from these studies reduce to the condition that the solution should not contain light atoms with a high bond vibrational energy for example hydrogen atoms or at any rate these atoms should not be linked directly by chemical bonds to atoms coordinated to the lanthanides.

The studies of Heller and Lempicki confirm these postulates in broad outline.

Earlier experiments in organic solutions showed that the removal of quenching elements from the intervening spaces between excited ions and vibrating adjacent molecules rapidly increases the luminescence quantum yield[103]. An aqueous neodymium chloride solution may be adopted as a standard solution with the specified minimum quantum yield. The replacement of an aqueous solution by a deuterated solution increases the luminescence factor fivefold. The replacement of water by a solvent such as dimethyl sulphoxide, in which the solvating oxygen atoms are not linked to hydrogen atoms, increases the luminescence intensity by a factor of 10 and the quantum yield rises almost by two powers of 10 compared with aqueous solutions; on the other hand, deuteration increases further the luminescence yield by a factor of three. From this standpoint, organic halogeno-derivatives are the most suitable compounds, since they do not contain atoms lighter than carbon.

Therefore it is also not surprising that the most effective luminescent systems proved to be those in inorganic solvents, of the type $Nd^{3+}-SeOCl_2$−aprotic acid or $Nd^{3+}-POCl_3$−aprotic acid; the quantum yield for the first system is sometimes higher than the luminescence yield in aqueous solutions.

Table 4 presents the principal characteristic vibration frequencies of groups of atoms in the solvent and ligand which in solvation and complex formation processes may be in the immediate vicinity of the central atom with a specified energy store[104-106].

Table 4. Characteristic bond vibration frequencies in various components of laser systems.

Compound	Bond	Absorption region, cm^{-1}	References
Primary alcohols	O−H	3650—3590	104
Primary alcohols	C−H	1050	104
Nitriles	−C≡N	2260—2240	104
Sulphoxides	>S=O	950	106
Selenyl chloride	>Se=O	955	105, 106
Phosphorus oxide chloride	→P=O	486, 1261	106
β-Diketones	−C(=O)−CH$_2$−C(=O)−	1646—1540	104
Primary amines	>N−H	3506—3300	104
Dimethylamines	CH_3>N− CH_3	2825—2810 2775—2765	104
Skeletal vibrations of five-membered heterocycles	Imidazole, pyrrolidine	1598—1510	104
Nitrogen-containing heterocycles	N−H	3440—3400	104
Stretching vibrations of six-membered rings	Piperidine	1640—1555	104
Carboxylic acid salts	O=C−O$^-$	1610—1550	104
Tin tetrachloride	$SnCl_4$	368	106
Antimony pentachloride	$SbCl_5$	356	106
Titanium tetrachloride	$TiCl_4$	388	106
Anion	$SnCl_6^{2-}$	311	106
"	$SbCl_6^-$	337	106
"	$TiCl_6^{2-}$	463	106

The smallest distances between the excited lanthanide levels for Nd^{3+} ($^4F_{3/2}-{}^4I_{15/2}$) Eu^{3+} ($^5D_0 \rightarrow {}^7F_6$), and Tb^{3+} ($^5D_4-{}^5F_5$) are respectively 5500, 12500, and 18300 cm^{-1} [107,108], while the bond vibrational energies in phosphoryl and selenyl groups, tin tetrachloride, and antimony pentafluoride are much lower. The stretching vibrational energies of the O−H and C−H bonds are much closer to the energy differences between the excited levels in lanthanide ions.

The study of lanthanide complexes in aprotic solvents led to the development of new views on their structure and also made it possible to discover a relation between the dissipation of energy from the excited ions to the surrounding medium as a function of the type of bond. These concepts were used initially by a group of investigators for polyphosphoric acids which had been subjected to extensive chlorination and fluorination[86]. Extensive chlorination of polyphosphoric acids leads to the occurrence in solutions of non-bridged structures isolated from the surrounding medium by halogen atoms. Important additional information is provided by studies on the vibrational spectra, which showed that in aprotic solvents lanthanide ions are surrounded by oxygen atoms. These investigations also led to the discovery that unchanged metal halide molecules are absent from the solutions.

The determination of the crystal field parameters and the study of the vibronic spectra made possible a number of conclusions concerning the immediate environment of lanthanide ions in solvents such as H_3PO_4, $SeOCl_2-SnCl_4$, $H_2SeO_3-POCl_3$, and $POCl_3-SnCl_4$. These data show that the ion has C_{4V} symmetry with some distortion. The immediate environment of the ion consists of P–O groups or, less probably, [109].

In conclusion one must emphasise that the discovery of liquid luminescent and laser systems based on inorganic solvents with heavy atoms gives rise to the hope for a rapid development and application of these systems as lasers, which will not be inferior in their properties to solid lasers. One should also bear in mind liquid laser systems based on organic solutions of lanthanide chelates. The studies in this field are still far from completion.

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