Reviews

Photochemistry of f-element ions

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Published data on photochemical reactions of f-element compounds, namely, uranyl ion and lanthanide and actinide ions, are surveyed and analyzed. The types of reactions of photoexcited ions, reaction mechanisms, and analytical applications of the photochemical methods for the separation, isolation, and determination of f-elements are considered.

Key words: uranyl ion, lanthanides, actinides, europium, cerium, samarium, dysprosium, terbium, neptunium, plutonium, americium, curium, photochemistry, photoreaction, redox reaction.

1. Introduction

1.1. Main types of photochemical reactions in solutions. Photochemistry took shape as an independent branch of science in the 1950s. During this period, intense systematic research into photochemical reactions in the liquid and gas phases began. The majority of researchers concentrated their effort on organic compounds, many of which have relatively long-lived excited states and, depending on the conditions, can either emit light (luminesce) or enter into photochemical reactions. By now, the main features of the photochemistry of organic compounds have been established, the excited states and the types of photochemical reactions have been characterized, and theories permitting prediction of the photoreactivity of organic compounds have been developed. The foundations of the photochemistry of organic compounds were outlined in several monographs (see, for example, Refs. 1, 2).

Yet another important object of photochemical studies is represented by coordination compounds of d-elements. Their electron transitions are noted by great diversity, which gives rise to rather intricate optical spectra. The photochemical activity of transition metal complexes can be due to excited states of several types. Electron transitions between molecular orbitals located mainly on the central atom (these are d—d transitions for d-elements and f—f transitions for f-elements) give rise to ligand-field (LF) excited states. Transitions between the internal states of the ligand result in ligand excitation. Upon transitions between the molecular orbitals of the central atom and the ligand, charge transfer (CT) excited states are generated.[3—5] Apart from inner-sphere CT, outer-sphere CT processes are also possible, for example, charge transfer from the complex as a whole on the solvent or charge transfer within an ion pair formed by a d-element complex and the counter-ion or another complex. Yet another type of transitions is encountered in complexes containing ions of different metals, namely, metal—metal CT (intervalent CT). Depending on the excitation wavelength, it is often possible to activate either the ligand alone, or the central atom

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alone (its redox properties can change), or the complex as a whole, which changes the capability of ligand substitution. In view of the multitude of transition metals, it becomes clear that the photochemistry of their coordination compounds is highly diversified. The main achievements in the photochemistry of coordination compounds have been surveyed in the publications mentioned above[3—5] and in several reviews.[6—10] In addition to the proper photochemical transformations of transition metal coordination compounds, photocatalytic reactions involving these compounds have also found wide use.[11]

One more group of species having rather long-lived excited states and capable of entering into photochemical reactions comprises f-element ions. The most vivid example is the uranyl ion, whose photochemical properties have been known for more than 15 decades. Uranyl photochemistry is the subject of a monograph[12] and several reviews.[13—15] In the last several decades, photochemistry of compounds of other f-elements, lanthanides and actinides, has also been studied. The advances made in this field are not yet as significant as those in the photochemistry of organic molecules or coordination compounds of d-elements or uranyl ion. The theory of photoreactive excited states of f-elements (except for the uranyl ion) is little developed. Data on the photochemical reactions of actinides have been only briefly summarized in a recent review.[16] No publications covering the known data on the photochemical reactions of lanthanides fairly comprehensively are available.

In this work, we attempt to survey the available information on the photochemistry of f-elements including both lanthanides and actinides. The first section of the review covers briefly the photochemistry of uranyl.

1.2. Photochemistry and luminescence. A photochemical reaction is initiated by absorption of a light quantum by a species (molecule, ion, atom, radical, *etc.*), which thus passes into an excited state. Photoexcitation changes substantially the chemical properties of the reactants and allows reactions that would be thermodynamically impossible in the dark. A photochemical reaction consists of two main stages: first, excited states are involved in primary photochemical processes, and second, this is followed by dark reactions of the nonexcited products formed in the first stage and other components of the system.

Some substances that undergo photochemical transformations are capable of luminescence, which is due to transitions from electronic (or vibrational) excited states to states lower in energy, normally, to the ground state. In many cases, both the photochemical reactions and luminescence involve the same excited states. An important characteristic of both phenomena is quantum yield ϕ, defined as follows:

for a photochemical reaction, ϕ is equal to the number of molecules (ions) formed divided by the number of light quanta absorbed;

for luminescence, ϕ is equal to the number of light quanta emitted divided by the number of light quanta absorbed.

In photochemistry, the number of moles is often used in place of the number of molecules, while the number of quanta is replaced by a quantity expressed in "Einsteins" ($6.023 \cdot 10^{23}$ quanta). Photochemical reactions and luminescence can compete with each other and with the nonradiative deactivation of excited states; therefore, the quantum yields of luminescence or a simple photochemical reaction can vary from 0 to 1. The quantum yield of a chain photochemical reaction can reach ~10^6. Detailed accounts of the foundations of photochemistry and luminescence can be found in the literature.[1,3,5,17,18]

2. Photochemistry of uranyl ions

2.1. General remarks. The photochemical properties of the uranyl ion UO_2^{2+} have been studied much more extensively than those of other f-elements. A distinctive feature of uranyl is that it displays bright green luminescence, the same excited state being responsible for luminescence and for photochemical reactions. In view of the enormous body of relevant literature, when discussing the general aspects and features of the photochemistry of the uranyl ion, we will largely rely on the monograph[12] and reviews[13—15] mentioned above rather than on original publications. Some problems not reflected in overview publications but significant for the understanding of subsequent sections will be considered in more detail. The photochemical properties of uranyl have found practical use in nuclear technology,[19] for determination of uranium, and for the synthesis of new uranium compounds; therefore, considerable attention will be paid to the problems of analytical application of the photochemical reactions of uranyl.

2.2. The excited state of the uranyl ion and the pathways for its deactivation. The absorption spectrum of the uranyl ion in the region of 400—500 nm is due to the transitions from the lower (ground) electronic state to vibrational sublevels of the first electronically excited state, more precisely, to transitions from the higher bonding molecular orbital $3\sigma_u$ located mainly on the oxygen atoms to the uranium 5f orbitals.[20,21] The pure electronic transition, *i.e.*, transition to the zero vibrational sublevel of the first electronically excited state is responsible for an absorption band at ~490 nm (~20400 cm^{-1}). The multiplicity of the excited state, of the uranyl ion is still debated.[15] In the majority of studies, this state is considered to be triplet, which is supported by many facts. One of the main arguments is the very long lifetime of the excited uranyl ion. This hypothesis is indirectly confirmed by drawing an analogy between some photochemical reactions of the uranyl ion (which proceed at the O atoms, see below) and the reactions of triplet states of ketones.[15]

The lifetime of the electronically excited state of uranyl ions in solutions can reach hundreds of microseconds. If the uranyl ion is excited to upper vibrational sublevels of the first electronically excited level or to higher electronically excited states, excess energy is rapidly transformed to heat as a result of internal conversion to the lower electronically excited state. There are three possible pathways for further conversion of the electron excitation energy. The first one is dissipation of energy to heat through various physical quenching processes. The second one is luminescence, whose shortest wavelength band (without consideration of the possible appearance of anti-Stokes bands) is also displayed at ~20400 cm^{-1}. The third possibility includes protochemical reactions.

2.3. Classification of photochemical reactions of the uranyl ion. Uranium(V) is formed much more readily in reactions of the photoexcited ion $(UO_2^{2+})^*$ than in the reactions of the nonexcited UO_2^{2+} ion. Upon excitation of the uranyl ion, an electron passes from a molecular orbital to an uranium orbital, *i.e.*, uranium(VI) is "partly reduced." In the ground state, the uranyl ion has only slight electron-acceptor capacity ($E° = 0.06$ V),[22] while on excitation, it becomes a strong oxidant. Its standard redox potential $E°$ is estimated[13,15] to be 2.6—2.7 V. The excited $(UO_2^{2+})^*$ ion oxidizes organic acids, alcohols, amines, amides, phenols, cellulose, and many other organic and inorganic compounds.[12—14] Of the four main types of photochemical reactions peculiar to metal complexes (substitution, isomerization, redox reactions, and photocatalysis or photosensitization),[5,19] the uranyl ion tends to enter into reactions of the third and fourth types. To understand the regularities of photochemical transformations of the uranyl ion, it is necessary to know their mechanisms. Information on the mechanisms of reactions of the uranyl ion is usually obtained from investigation of the structures of the primary products, *i.e.*, radicals, the composition of the final products, isotope effects arising upon replacement of hydrogen by deuterium in the substrate, regularities of quenching of the luminescence of the uranyl ion, *etc.* However, the use of these methods does not always provide unambiguous answers to questions concerning the reaction mechanisms. Relying on published reviews,[13—15] classification of photoreactions of the uranyl ion according to their mechanisms can be now proposed.

The occurrence of the following processes has been confirmed quite reliably:

(1) intramolecular reactions proceeding by an electron transfer mechanism;

(2) intermolecular reactions whose primary step is abstraction of a hydrogen atom from the substrate;

(3) intermolecular electron transfer reactions;

(4) sensitization reactions, which start from the transfer of energy from an excited uranyl ion to the acceptor.

Three more mechanisms have been suggested in some instances but not confirmed reliably:

(5) transfer of an oxygen atom from the uranyl ion to the substrate;

(6) two-electron transfer reactions;

(7) reactions including the formation of a complex of the excited uranyl ion with a nonexcited species (exciplex or excimer).

Examples of various mechanisms are presented below. It is noteworthy that a change in the reaction conditions is often accompanied by a change in the reaction mechanism.

Intramolecular (intracomplex) electron transfer takes place in the decomposition of uranyl oxalate. The reaction ends with evolution of CO_2:

$$UO_2C_2O_4 + 2\,H^+ + h\nu \rightarrow$$
$$\rightarrow UO_2^{2+} + CO_2 + CO + H_2O \qquad (pH\ 0), \qquad (1)$$

$$UO_2C_2O_4 + H_2O + h\nu \rightarrow$$
$$\rightarrow UO_2^{2+} + HCOO^- + CO_2 + OH^- \qquad (pH\ 7). \qquad (2)$$

Decomposition of uranyl oxalate may[23] be accompanied by parallel reduction of the uranyl ion to U^{IV}. Decarboxylation of benzoic, lactic, and acetic acids and other mono- and dicarboxylic acids on treatment with uranyl follows the same mechanism. In this case, the product composition can also depend on the pH and U^{4+} can be formed in the overall process, for example,

$$UO_2^{2+} + h\nu \rightarrow (UO_2^{2+})^*, \qquad (3)$$

$$(UO_2^{2+})^* + MeCH(OH)COOH + 2\,H^+ \rightarrow$$
$$\rightarrow U^{4+} + MeCHO + CO_2 + 2\,H_2O\ (pH > 3.5). \qquad (4)$$

Thus, reactions of this group can belong to the type of either decomposition of organic molecules sensitized by the uranyl ion or redox reactions of the uranyl ion. It has now been found[15] that reactions of the excited uranyl ion can either proceed in the equatorial plane of the linear UO_2^{2+} ion, *i.e.*, involve directly the U atom or occur at the O atoms. The reactions of intracomplex transfer of an electron from the ligands to the uranyl ion proceed in the equatorial plane.

The second group of reactions includes intermolecular abstraction of a hydrogen atom from the substrate. In the general case, these processes are written in the following way:

$$(UO_2^{2+})^* + SH_2 \rightarrow UO_2H^{2+} + SH^{\bullet}, \qquad (5)$$

$$UO_2H^{2+} \rightarrow UO_2^{+} + H^{+}_{solv}, \qquad (6)$$

where SH_2 is the substrate. As a rule, intermolecular hydrogen transfer involves the O atoms. This mechanism is observed in the reactions of the uranyl ion with alcohols, in which the attack is directed at the C atom in the α-position:

$$(UO_2^{2+})^* + RCH_2OH \rightarrow UO_2H^{2+} + {}^{\bullet}RCHOH. \qquad (7)$$

Photoreactions with alcohols are always accompanied by the reduction of the uranyl ion. The mechanisms of these reactions have been studied in detail.[24—26] The quantum yields of photoreduction of the uranyl ion with alcohols are rather high,[27—29] normally ranging from 0.3 to 0.7. The attack by the uranyl ion is directed on the carbon—hydrogen bond of the hydroxylated carbon. The polarity of the substituent R is more important for the rate of this reaction than the steric effects associated with the size of R.

A change in the mode of coordination of the uranyl ion results in a change in the reaction mechanism. The reaction of the uranyl ion with methanol, which gives either the $^{\bullet}CH_2OH$ radical (in aqueous methanol) or the $CH_3O^{\bullet}$ radical (in anhydrous methanol) as the primary product, can be cited as an example.[13,15] One more example is the reaction (4) of the uranyl ion with lactic acid. As the pH decreases, the proportion of the uranyl complex with the lactate ion diminishes, and the reaction starts to proceed by an intermolecular mechanism to give pyruvic acid MeC(O)COOH, instead of acetic aldehyde. The products and the mechanisms of photoreactions of the uranyl ion with organic acids also depend on the concentration of the latter. In neat acids (as well as in aqueous solutions at low pH), abstraction of the H atom from the C_α atom appears to be the primary step, whereas in aqueous solutions, electron transfer followed by decarboxylation predominates.[13] The change in the mechanism of photoreactions of the uranyl ion depending on conditions, *i.e.*, the nature of the solvent, pH, and temperature (in particular, on freezing), is indicative of the presence of competing intermediate steps controlled by both electron donor—acceptor and acid—base interactions.

Quenching of the luminescence of uranyl ions by aromatic hydrocarbons and variable-valence metal ions in the lowest oxidation state is accomplished by reversible electron transfer (the third group of reactions). The occurrence of electron transfer between metal ions and excited uranyl ions is indicated by correlation between the metal redox potentials and the rate constants of quenching.[30—33] The use of pulse photolysis made it possible to obtain direct evidence for electron transfer in the reactions of $(UO_2^{2+})^*$ with Mn^{2+},[31] $Ru(bpy)_3^{2+}$ (bpy is 2,2′-bipyridyl),[34] and Ce^{III}.[35] It was shown that, after a light pulse, the increase in the concentration of the $Ru(bpy)_3^{3+}$ ion in 2 *M* H_3PO_4 is exactly correlated with the rate of deactivation of the excited uranyl. The lifetimes of the reaction products, Mn^{3+}, $Ru(bpy)_3^{3+}$, and Ce^{IV}, reach milliseconds. Evidently, the back reaction between UO_2^+ and the generated oxidizing ions is not an intra-cage reaction in this case.* However, formation of U^{IV} as the final reaction product was not detected (in Section 3.5, we give an example of irreversible oxidation of cerium(III) by excited uranyl ion). Apparently, the reaction of $(UO_2^{2+})^*$ with plutonium(III) proceeds in a similar way. The presence of Pu^{IV} can be detected in an electrochemical experiment carried out simultaneously with photoirradiation.[36] The following overall reaction is supposed to take place:

$$(UO_2^{2+})^* + 2\ Pu^{III} + 4\ H^+ \rightarrow U^{4+} + 2\ Pu^{4+} + 2\ H_2O. \quad (8)$$

No evidence for the formation of U^{4+} is given. It is more likely that Pu^{IV} oxidizes the primary product of the photoreaction (UO_2^+) in a back process. After irradiation has been terminated, dark reaction results in the regeneration of the initial species. Note that Pu^{IV} can also be formed without the uranyl ion as a result of oxidation of the photoexcited plutonium(III) by water; photoreactions of plutonium are considered in Section 4.2.

The fourth group of reactions comprises[13] energy transfer from the excited uranyl ion on the acceptor, which is followed by a photochemical reaction involving an excited energy acceptor (like some reactions of the first group, this is a sensitization reaction). Photopolymerization of vinylic monomers in the presence of uranyl salts seems to correspond to this group.

Transfer of an oxygen atom from uranyl to the substrate is assumed[37] to take place in the photooxidation of dimethyl sulfoxide by the uranyl ion. This conclusion is based on the composition of the final product, dimethyl sulfone. A similar mechanism is assumed for the reactions of the uranyl ion with dialkyl sulfides and triphenylphosphine and some other reactions[15] as well as for the reactions of $(UO_2^{2+})^*$ with SO_2 and O_3 because electron transfer to the uranyl ion is impossible in this case[38] due to the very high ionization potentials of SO_2 and O_3 molecules. This viewpoint is disputed in a publication[39] in which evidence for the reaction of $(UO_2^{2+})^*$ with SO_2 (more precisely, with the SO_3^{2-} ion) by the electron transfer mechanism is given. In our opinion, the transfer of an oxygen atom from the uranyl ion is unlikely because its bond with uranium is very strong.

The hypothetical formation of exciplexes or excimers of the uranyl ion in its photoreduction by water is considered in Section 2.4.

Mention should be made of the photocatalytic reactions of uranyl ions, *viz.*, oxidation of hydrocarbons with oxygen or with hydrogen peroxide.[40—42] The primary step normally follows either the first or second mechanism and gives U^V and an organic radical. Then both the radical and U^V are oxidized with oxygen or hydrogen peroxide. This yields an oxygen-containing organic compound, while the uranyl ion ultimately remains unchanged, *i.e.*, it acts as a photocatalyst.

So far, we have mainly considered reactions with organic compounds. Meanwhile, mechanisms of reactions of uranyl ions with inorganic compounds can also be classified into one of the above-indicated types. For example, oxidation of the iodide ion[12,13,43,44] and Br^- and NCS^- ions[13,43,44] proceeds *via* intramolecular electron transfer. In the case of N_2H_4, the reaction is assumed[45] to involve reversible formation of a hydrazine exciplex (*i.e.*, a complex existing only in the excited state

* In the liquid phase, solvent molecules form a "cage" around reacting species and thus prevent them from moving apart immediately after the reaction; this sharply increases the probability of back reaction.

and decomposing after the excitation has been removed) with $(UO_2^{2+})^*$, in which transfer of an electron to the uranyl ion takes place. Photodecomposition of hydrogen peroxide is accelerated in the presence of uranyl ions; this is assumed to proceed *via* the intermediate complex $UO_2(H_2O_2)^{2+}$, although its existence has not been proven.[14]

The pathways of transformation of the primary, usually, radical, products of reactions of the excited uranyl ion are fairly diverse. Regarding the UO_2^{2+} ion itself, it is reduced to the uranoyl ion UO_2^+, which retains the initial composition and structure. Therefore, there is a high probability of back electron transfer to give the uranyl ion. If this process does not take place, the uranoyl ion is consumed in the following reactions.

1. Disproportionation

$$UO_2^+ + UO_2^+ + 4\ H^+ \rightarrow UO_2^{2+} + U^{4+} + 2\ H_2O. \quad (9)$$

The standard potential for the UO_2^+/U^{4+} pair is equal to 0.38 V.[22] This is much higher than the potential of the UO_2^{2+}/UO_2^+ pair (0.06 V), *i.e.*, one UO_2^+ ion can oxidize another UO_2^+ ion. Disproportionation is accelerated as the pH decreases.

2. Reaction with the initial SH_2 (see reaction (5)) or with primary ($SH^\bullet$ radicals) or secondary products of its decomposition. The reaction with the $SH^\bullet$ radical, which is often intra-cage, proceeds especially rapidly.

3. Exchange of uranium or oxygen atoms occurring in parallel; these reactions can be detected by isotope labeling, for example,[46]

$$U^{18}O_2^+ + H_3{}^{16}O^+ \rightleftharpoons U^{16}O_2H^{2+} + H_2{}^{18}O, \quad (10)$$

$$U^{18}O_2H^{2+} + H_3{}^{6}O^+ \rightleftharpoons U^{16}O_2H_2^{3+} + H_2{}^{18}O \quad (11)$$

or (see Ref. 47)

$$^{235}UO_2^{2+} + {}^{238}U^{4+} \rightleftharpoons {}^{238}UO_2^{2+} + {}^{235}U^{4+}. \quad (12)$$

Some of these transformations are accompanied by destruction of the uranyl ion. Ultimately, the products of primary and secondary reactions react with U^{4+} and UO_2^{2+}. Thus, the final products can be quite diverse.

The photochemistry of the uranyl ion has been mainly studied in acidic solutions but studies in carbonate media have also been reported.[48,49] In this media, photoreduction of uranyl ions by alcohol or by formate ions gives U^V, which is stabilized as a complex whose composition is supposed to be $[(UO_2)_4(OH)_6(H_2O)_9]^{2-}$.[49] Photolysis of chelates of the uranyl ion with β-diketones gives rise to a precipitate of a uranium(IV) complex.[50] Valuable information on the mechanism of photochemical transformations of the uranyl ion was obtained[51] in investigations of solutions frozen down to 77 K. The radical products formed in the first step of the reactions of the uranyl ion with organic compounds were detected by ESR spectroscopy. The range of products differed from that obtained at room temperature. In some cases, rupture of C—C bonds was observed, which is absolutely uncharacteristic of reactions in liquid solutions. Studies of the cage effects in photoreactions of the uranyl ion, including those in molecular organized systems such as micelles,[52] are in progress.[53] The purpose of these studies is to establish the role of spin dynamics in the reactions of radical pairs (RP). It is assumed that the spin state of the excited uranyl ion is transferred to the primary RP, *i.e.*, the RP formed in the triplet state, which implies spin selectivity in the subsequent processes. The presence of spin selectivity can be confirmed by chemical nuclear polarization in the reaction products. For example, photooxidation of benzilic acid or benzhydrol by uranyl nitrate gives RP consisting of the uranoyl ion and a ketyl radical. The radical is oxidized in the cage to benzophenone, which is found to be polarized.[54] Other effects related to the spin selectivity of uranyl photoreactions are the influence of a magnetic field and the magnetic isotope effect. The latter phenomenon has been described in detail in a review.[15] Other examples of photochemical reactions of the uranyl ion could also be cited but it is beyond the scope of this communication. We will dwell on the reaction of the excited uranyl ion with water.

2.4. Redox reaction of the excited uranyl ion with water. This reaction occupies a special position. Water is a solvent for the majority of systems in which photochemical reactions of uranyl ions and other f-element ions are carried out. In addition, the reaction of the photoexcited uranyl ion with water is interesting regarding the problem of water photodecomposition for the storage of solar energy.[55]

On passing from solutions in H_2O to solutions in D_2O, the duration of luminescence of simple uranyl salts approximately doubles.[56] It has long been suggested[13] that this is largely due to the retardation of the luminescence quenching *via* hydrogen atom transfer:

$$(UO_2^{2+})^* + H_2O \rightarrow UO_2H^{2+} + OH^\bullet. \quad (13)$$

The high redox potential of the excited uranyl ion allows the transfer of hydrogen, although the resulting $OH^\bullet$ radical is also a very strong oxidant ($E^\circ = 2.73$ V at pH 0 and $E^\circ = 2.32$ V at pH 7).[57] Reaction (13) should be expected to be subject to an isotope effect. Theoretical calculation of the rate constant for the abstraction of a hydrogen atom by an excited $(UO_2^{2+})^*$ ion demonstrated good agreement with the experimental value[58] and provided a quantitative interpretation of the isotope effect.

There is also an opinion[59] that quenching of luminescence of the uranyl ion by water follows the route

$$(UO_2^{2+})^* + H_2O \rightarrow UO_2^+ + OH^\bullet + H^+, \quad (14)$$

i.e., it involves transfer of an electron rather than of a hydrogen atom. Although the estimate of the rate of this process in terms of the Marcus theory deviates from the experimental result by several orders of magnitude, this discrepancy is attributed to specific steric difficulties.[59] This approach has not gained acceptance in the literature. In particular, it is at variance with the presence of the isotope effect. Analysis of the temperature dependences of the quenching of luminescence of the uranyl ion in solutions in H_2O and D_2O confirmed[60] that in liquid solutions, quenching occurs by the hydrogen transfer mechanism (13); in frozen solutions at $T < 180$ K, slight quenching of the uranyl ion luminescence occurs only by a physical mechanism as a result of transfer of the electron energy to higher vibrational levels of the O—H bonds. Although quenching of luminescence of the uranyl ion in aqueous solutions can be described quite adequately under certain conditions, the general picture remains obscure. For example, in a study of the effect of the H^+ concentration on the lifetime of uranyl luminescence, the following mechanisms were taken into account[61]: Stern—Volmer luminescence quenching by OH^- ions; hydrolysis of the uranyl ion followed by hydrogen atom intramolecular transfer; formation of an exciplex; transfer of an electron from the H_2O molecule to the uranyl ion; dissipation of the excitation energy to the vibrational quanta of water molecules located in the first coordination sphere of the uranyl ion (similar to the quenching of luminescence of lanthanide ions, see Section 4.8); and transfer of energy to water molecules. None of these mechanisms adequately explains quenching over a broad range of H^+ concentrations. A modified scheme of hydrolysis taking into account ion association and complexation was proposed. However, the question of whether chemical or physical quenching plays the predominant role remains open.[61]

It would be possible to establish the nature of the primary processes if the $OH^{\bullet}$ radical was detected in the reaction of $(UO_2^{2+})^*$ with H_2O. No direct evidence for this process has been found so far,[62] although some data could be interpreted as being indicative of the occurrence of reaction (13). Spin adducts of the $OH^{\bullet}$ radical were detected by ESR upon the photolysis of uranyl ions in molybdate solutions in the presence of a spin trap[63]; however, no adducts of this type were found in the absence of molybdate ions. Pulse photolysis of aqueous solutions of uranyl ions results in a short-term increase of the ionic conductivity of the solution,[64] which was attributed to the increase in the concentration of the H_3O^+ ions after reaction (14).

The $NO_3^{\bullet}$ radical, having a somewhat smaller redox potential than $OH^{\bullet}$, was detected by pulse photolysis in a nitric acid solution.[65] The $NO_3^{\bullet}$ radical is supposed[65] to result from oxidation of the NO_3^- ion directly by the excited uranyl ion rather than by the $OH^{\bullet}$ radical.

Reaction (14) has been discussed in a number of studies (without considering its mechanism) as the first step of various processes. This underlies the theory of photostimulated oxygen exchange in the uranyl ion,[39,46,66–68] which correctly explains numerous experimental facts. An important point of the theory is the formation of the uranoyl ion and its participation in the chain mechanism of the exchange.

There exists an opinion[69–71] that some features of the luminescence of the uranyl ion cannot be explained in terms of mechanism (13) alone. Some facts presented in the literature point to the occurrence of processes that involve a more complex compound, namely, an exciplex. This exciplex, $(U_2O_4H^{4+})^*$, consists conventionally of U^V and U^{VI} and results from the reactions

$$(UO_2^{2+})^* + H_2O \rightarrow (UO_2H^{2+})^* + OH^{\bullet}, \quad (15)$$

$$(UO_2H^{2+})^* \rightarrow UO_2^+ + H^+, \quad (16)$$

$$(UO_2H^{2+})^* + H_2O \rightleftharpoons (UO_2^+)^* + H_3O^+, \quad (17)$$

$$(UO_2H^{2+})^* + UO_2^{2+} \rightleftharpoons (U_2O_4H^{4+})^*. \quad (18)$$

One argument[72] supporting the existence of the exciplex incorporating two uranium atoms is the fact that the luminescence spectrum of the uranyl ion depends on its concentration at low pH values, when the possibility of appearance of "normal" hydrolyzed dimeric species is ruled out; the quantum energy $h\nu_1$ in the equation

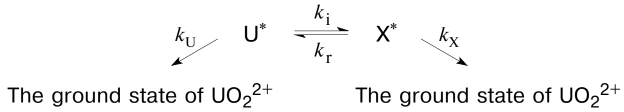
$$(UO_2^{2+})^* \rightarrow UO_2^{2+} + h\nu_1 \quad (19)$$

is greater than $h\nu_2$ in the equation

$$(U_2O_4H^{4+})^* \rightarrow UO_2^{2+} + UO_2^+ + H^+ + h\nu_2. \quad (20)$$

Hence, apart from the uranyl ion, luminescence is emitted by at least one type of particles, which might be an exciplex.[69,72] Other reasons in favor of exciplexes based on pulse photolysis data have also been reported.[73] In the opinion of some researchers,[74] there is no need to invoke the notion of exciplexes. Biexponential decay, the presence of a second-type luminescence with a spectrum shifted to longer wavelength, and other peculiar features of emission by uranyl ions can be rationalized[75,76] in terms of the hypothesis of reversible transition between two radiative levels of the $(UO_2^{2+})^*$ monomeric ion. The set of photophysical processes in the uranyl ion can be expressed by Scheme 1 (retaining the author's notation),[74–76] in which k_U and k_X are the rate constants for deactivation of the U* and X* states, and k_i and k_r are the rate constants for the reversible transition between the U* and X* states. The $U^* \rightleftharpoons X^*$ reversible transition can be induced by the exchange of molecules in the solvation shell of the uranyl ion. The designation U* corresponds to the excited state $\pi_u^3\phi_u^1$, which is higher in energy, while X* implies a lower state, $\pi_u^3\delta_u^1$.

Scheme 1



Although an electronic structure of the exciplex has been proposed based on the theory of valence bonds,[77] the debate can hardly be regarded as concluded. In our opinion, the existence of the $(U_2O_4H^{4+})^*$ exciplex is doubtful for energy reasons. Indeed, the redox potentials of the excited uranyl ion and the $OH^•$ radical are approximately equal, and the energy of $(UO_2{}^{2+})^*$ in water oxidation should be entirely consumed for the formation of the $OH^•$ radical. The excess energy in the $(UO_2H^{2+})^*$ species appears to be insignificant (Eq. (15)). However, the existence of other exciplexes of uranyl ions, *i.e.*, with fluoride ions,[78] thallium(I) ions,[79,80] and other variable-valence metal ions,[81] seems quite probable and accounts for the peculiar features of the luminescence of uranyl ions in solutions containing various additives.

No chemical changes are usually observed upon photoirradiation of aqueous solutions of uranyl salts containing no reducing agents. It has been noted[69] that U^{IV} is formed upon the photolysis of phosphoric acid solutions of uranyl salts. Water photooxidation by the uranyl ion in sulfuric acid solutions has been studied by chemiluminescence.[82,83] The formation of H_2O_2 and uranium(IV) was detected. Apparently, both products exist in solution being exposed to light in a steady-state concentration, which is too low to be detected by conventional chemical methods. Almost quantitative photoreduction of the uranyl ion by water was attained[84] by introducing unsaturated heteropolytungstate anions (HPTA), $P_2W_{17}O_{61}{}^{10-}$ or $SiW_{11}O_{39}{}^{8-}$, into the solution under irradiation. These anions form very strong complexes with U^{IV} and with other tetravalent actinides even in acid media[85]; this sharply increases the stability of this valence state of uranium against oxidation. Under these conditions in 0.01—4.0 *M* H_2SO_4, $HClO_4$ or 0.1—1.0 *M* Na_2SO_4, $NaClO_4$, the uranyl ion is reduced to U^{IV} on exposure to visible or UV light. Simultaneously, hydrogen peroxide appears in the solution. Oxygen seems to be the final product of water oxidation. Upon irradiation for many days at pH ~4 (the region of thermodynamic stability of HPTA), $UO_2{}^{2+}$ passes into U^{IV} (10^{-3} mol L^{-1}) almost quantitatively. The quantum yield of the reaction (λ = 337.1 nm) increases with an increase in the concentration of acids or salts; it is close to $2 \cdot 10^{-3}$ in 1 *M* H_2SO_4 or $HClO_4$.

The question of the mechanism of photoreduction of the uranyl ion by water still remains open. Apparently, HPTA do not participate in the photochemical steps of the process but only stabilize uranium(IV).[84] As noted above, the $OH^•$ radical as a product of reaction (13) or (14) has not been reliably detected yet. We carried out kinetic calculations relying on the known rate constants for the reactions of the $OH^•$ radical with various compounds. Without acceptors of $OH^•$ radicals, U^{IV} should not be formed by this mechanism because the rate of the back reaction between $OH^•$ and U^V exceeds substantially both the rate of $OH^•$ radical recombination to give H_2O_2 and the rate of disproportionation of U^V. (The rate constant for the interaction of $OH^•$ radicals with U^V was estimated to be about 10^{10} L mol^{-1} s^{-1}.) We performed tentative experiments on the photoreduction of uranyl ions in the presence of HPTA and benzene additives; benzene is chemically inert with respect to the excited uranyl ion but efficiently traps $OH^•$ radicals. We expected that trapping of the $OH^•$ radicals by benzene and subsequent reactions would result in accumulation of phenol and the formation of H_2O_2 would be suppressed. Neither was observed in reality. Perhaps, reaction (13) is insignificant in the photoreduction of uranyl ions (although quenching of luminescence of uranyl ions can occur by this mechanism followed by recombination of $OH^•$ and UO_2H^{2+}). A mechanism involving the formation of a dimer can be proposed. The existence of $^*U^{VI}—U^V$ exciplexes seems doubtful but the formation of the $^*U^{VI}—U^{VI}$ excimer cannot be ruled out; this species loses an H_2O_2 molecule rather than an $OH^•$ radical giving rise to two U^V ions. The back oxidation of uranium(V) with hydrogen peroxide proceeds much more slowly than that by $OH^•$ radicals; therefore, there is a probability of disproportionation of U^V:

$$2\ U^V \rightarrow UO_2{}^{2+} + U^{IV}. \quad (21)$$

In a solution devoid of HPTA, U^{IV} is vigorously oxidized by hydrogen peroxide. In the presence of HPTA, U^{IV} forms complexes with it and is thus stabilized. This is followed by the reactions[84]

$$(UO_2{}^{2+})^* + H_2O_2 \rightarrow UO_2{}^+ + H^+ + HO_2{}^•, \quad (22)$$

$$UO_2{}^+ + H_2O_2 + H^+ \rightarrow UO_2{}^{2+} + \text{products}, \quad (23)$$

$$U^{IV} + H_2O_2 \rightarrow UO_2{}^{2+} + 2\ H^+, \quad (24)$$

$$HO_2{}^• + HO_2{}^• \rightarrow H_2O_2 + O_2, \quad (25)$$

$$UO_2{}^{2+} + HO_2{}^• + h\nu \rightleftharpoons UO_2(HO_2{}^•)^{2+}. \quad (26)$$

In addition, $HO_2{}^•$ radicals and their complexes with uranyl, $UO_2(HO_2)^{2+}$, react with each other to give H_2O_2 and oxygen, for example,

$$2\ UO_2(HO_2)^{2+} \rightarrow 2\ UO_2{}^{2+} + H_2O_2 + O_2. \quad (27)$$

The accumulation of U^{IV} in the first minutes of irradiation, when U^V, U^{IV}, and H_2O_2 appear, is markedly retarded. Then quasi-steady-state concentrations of U^V and H_2O_2 are attained; the reaction rate is also stabilized. Since H_2O_2 is consumed not only in the oxidation of U^{IV} and U^V but also in the photoreduction of the uranyl ion, the last-mentioned reaction can occur quantitatively.

It can be seen from the above data that there are important unsolved problems in uranyl photochemistry, in particular

(1) the relative roles of the electron and hydrogen atom transfer reactions and acid—base processes;

(2) the possibility of multielectron transfer and abstraction of an oxygen atom;

(3) the possibility and mechanism of water oxidation by the excited uranyl ion to give $OH^{\bullet}$ radicals; the role of exciplexes as the products of reactions between the excited uranyl ion and water;

(4) the mechanism of accumulation of U^{IV} in the solution as a result of photoreduction of uranyl ions by water.

All these aspects are also important for the photochemistry of other f-element ions whose reactions are performed in aqueous media.

2.5. Analytical applications of photochemical reactions of uranyl ions. An advantage of the photochemical methods for the separation of elements is the possibility of selective action on one of the components. If only one element in the mixture is photochemically active, a broad spectrum of radiation can be used; in the case of uranyl ions even sunlight is suitable. If several photochemically active components are present, a more monochromatic source acting selectively on one component is needed.

Two types of separation processes making use of the photochemical properties of uranyl ions are documented: (1) direct photochemical separation of uranium by photoreduction of the uranyl ion, which is accompanied by precipitation of an insoluble U^{IV} compound; (2) the use of the product of photoreduction of the uranyl ion, uranium(IV), for the reduction of Pu^{IV} to Pu^{III} in the reprocessing of irradiated nuclear fuel, mainly in the purex process* (see also Section 4.3).

A process for precipitation of U^{IV} on exposure to sunlight of solutions of uranyl salts containing reducing agents and ions able to precipitate uranium(IV) was proposed back in the late 1950s. The photochemical method made it possible to synthesize a number of new poorly soluble uranium(IV) compounds. They incorporated fluoride,[86] formate,[87] carbonate,[88] succinate,[89] tartrate,[89] and some other ions. It is of interest that most compounds contained a UO^{2+} group. If ions of other, photochemically inactive metals were present together with uranyl ions, they remained in solution after precipitation of uranium. For example, uranium occurring as uranyl salts in solutions in sulfuric acid[90] can be quantitatively separated from aluminum and vanadium:

$$(UO_2^{2+})^* + EtOH + SO_4^{2-} \rightarrow \rightarrow UOSO_4\downarrow + MeCHO + H_2O. \quad (28)$$

Similar results (purification of uranium from Fe and V) can be attained by precipitating uranium(IV) from a nitrate solution by fluoride as $NH_4F \cdot UF_4 \cdot H_2O$; in this case, ethanol is also used as the reducing agent.[91] Precipitation of $UOSO_4$ [90] or $NH_4F \cdot UF_4 \cdot H_2O$ [92] provides solution for a more complicated problem, namely, separation of uranium from other f-elements, for example, La^{III}, Ce^{III}, Th (as well as Al, Zr, and Mn). The yield and purity of U^{IV} compounds exceed 90% and, in some cases, 99%.

In order to isolate uranium from an industrial diuranate (commercial name, "yellow cake"), it was dissolved in sulfuric acid, the uranyl ion was reduced by a mixture of ethanol and hydrazine in sunlight, and hydrated uranium(IV) oxide was precipitated at pH 5 or 9. This provided a high degree of purification of uranium from a number of elements.[93]

Poorly soluble U^{IV} hypophosphite might also be suitable for this type of isolation of uranium. This compound crystallizes upon UV irradiation of an acidic solution containing uranyl nitrate and sodium hypophosphite.[94] The hypophosphite itself serves as the reducing agent for uranium. The degree of precipitation reaches 95%.

The efficiency of the purex process is largely determined by the degree of reduction of Pu^{IV} to Pu^{III} at the stage of plutonium re-extraction from tributyl phosphate (TBP) containing also uranyl nitrate. The possibility of using photochemistry for the improvement of the purex process has been considered since the 1960s.[95] This idea is based on the ability of uranium(IV) to reduce Pu^{IV} to Pu^{III}. Uranium(IV) can be easily prepared by photochemical reduction of the uranyl ion, in particular, using many salt-free reducing agents, which decompose upon the reaction to give gaseous or liquid products. For example, compounds such as hydrazine, hydroxylamine, ethanol, oxalic, acetic, and formic acids and other compounds can be perfectly used in the purex process.[96,97] In the mid-1970s, numerous publications dealing with this topic appeared (see, for example, Refs. 96—98). A modified scheme of the purex process with the use of photochemical reactions of uranyl has been proposed,[96,97,99] and the possible technological problems were discussed: equipment, gas evolution, heating of solutions, *etc*. The cost of the process was estimated and the advantages of the photochemical scheme were analyzed.[96,97,99] The use of hydrazine for this purpose was patented in the USA[100]; later, detailed studies using butanol, hydrazine, and hydroxylamine[101] have been carried out. In another patent,[102] photochemical reduction of the uranyl ion to U^{IV} by tributyl phosphite was described. In this process, tributyl phosphite is oxidized to TBP; thus, no foreign compounds appear in the system. An interesting method of photoreduction of the uranyl ion by TBP itself was patented.[103] A series of other publications are also devoted to this topic.[104—108] It was found[109] that the primary step of UO_2^{2+} photoreduction on treatment with TBP follows the mechanism of electron transfer in the equatorial plane of the uranyl ion; the resulting TBP radical cation can be detected in the ESR spectrum. Photolysis of a solution of $UO_2(NO_3)_2 \cdot 2TBP$ in 80% TBP in dodecane[109] gives rise to U^V and then to U^{IV}. Interest in the use of this reaction for the separation of uranium and plutonium is

* Purex process is an extraction technique for separation of Pu and U during reprocessing of irradiated nuclear fuel, based on different extractabilities of plutonium(III) and plutonium(IV) by tributyl phosphate in dodecane.

still retained.[110,111] Some studies devoted to this problem will be considered once again in the section dealing with the practical significance of the photochemical reactions of neptunium and plutonium because their phototransformations in real or model solutions are usually related to uranium reactions.

Yet another analytical application of the photochemistry of uranyl ions is determination of uranium after photochemical reduction of the uranyl ion with ethanol.[112,113] For relatively high uranium concentrations, this was carried out by titrating uranium(IV) with ammonium vanadate using *N*-phenylanthranilic acid as the indicator.[112] In the case of microconcentrations of uranium, it was again oxidized by iron(III) after photoreduction, and iron(II) was determined by colorimetry with *o*-phenanthroline.[113]

Note that light sources most convenient for practical purposes in the photochemistry of uranyl ion are conventional mercury lamps with sufficient power. Nevertheless, it is quite natural that publications considering photoreactions of uranyl ion on exposure to laser radiation appeared in recent years.[27—29]

To summarize this section, it should be noted that, apart from uranyl ions, other uranium compounds can also enter into photochemical reactions. For example, the photochemical method was used to accelerate the dissolution of uranium dioxide.[114] There are quite a few data in the literature[115] on photochemical reactions of uranium halides containing uranium in various oxidation states, alkoxides, borohydrides, and some other uranium compounds.

3. Photochemistry of lanthanide compounds

3.1. Characteristics of the excited states of lanthanide ions. Although luminescence and photochemistry are phenomena having a common nature, here we cannot consider the luminescence of lanthanides in detail. First, the literature dealing with this topic is extremely extensive. A number of reviews discussing comprehensively particular aspects of lanthanide photophysics, in particular, in solutions and in complex compounds, have been published.[116—118] Second, unlike uranyl ion, in the case of lanthanides, different excited states are often responsible for luminescence and photochemistry in solutions; we will touch upon the problems of luminescence only to the degree to which it is necessary for understanding the characteristic features of photoreactions.

The light absorption spectra of lanthanide ions are much simpler than the spectra of most d-elements.[119] They contain narrow bands for f—f transitions (LF bands) and much broader charge transfer bands (CTB). The natures of the latter bands are different for ions in reduced and oxidized forms. In oxidized ions (for example, Eu^{III}, Ce^{IV}), CTB arise due to the transfer of an electron from the coordination sphere to the lanthanide. Apparently, as in the case of d-element complexes,[5] the electron transfer can be either partial (displacement of the electron density toward the lanthanide ion) or complete. In the latter case, the excited state is not formed and, at the instant the light quantum is absorbed, a radical ion pair is formed, which rapidly dissociates in a polar solvent. In the case of reduced ions (for example, Ce^{III}, Eu^{II}), bands due to electron transfer from the 4f to 5d shell of the lanthanide can be considered to be CTB. The excited ion thus formed is oxidized much more easily than a nonexcited ion.[119]

In photochemical redox reactions, lanthanides are always excited to the CTB. Meanwhile, luminescence of lanthanide ions can be due both to f—d transitions and to transitions within the f shell. The f—f luminescence cannot usually provide additional information on the photoreaction, while investigation of f←d luminescence of cerium(III) and europium(II) proves useful in some cases.

Data on lanthanide photochemistry have not been systematized as yet, although brief accounts of the photoreactions can be found in some reviews dealing with the photochemistry of uranyl ion[13] and transition metal complexes.[6,7] Meanwhile, the information accumulated to date is rather vast. Three types of photoreactions have been found for lanthanides, namely, redox reactions, photosensitization or photocatalysis,[3] and ligand photosubstitution.[120] Since the main line of research into lanthanide photochemistry is concerned with redox reactions, the range of objects is rather limited.[119] Of ions in oxidation states other than +3, cerium(IV) and europium(II) can be obtained rather easily in aqueous solutions. Ytterbium(II) and samarium(II) are less stable, and terbium(IV), praseodymium(IV), and thulium(II) ions are known only in solutions containing specific ligands. Correspondingly, the photochemistry of cerium and europium ions is the best studied; some information on the photochemical reactions of samarium, ytterbium, and terbium ions is also available.

3.2. Cerium. Reaction of cerium compounds has been studied for at least a hundred years. In 1908 it was found that the gaseous product formed in the photolysis of aqueous solutions of Ce^{IV} perchlorate is oxygen.[121] Photoexcited Ce^{IV} is even a stronger oxidant than $(UO_2^{2+})^*$, the behaviors of Ce^{IV*} and $(UO_2^{2+})^*$ being often similar regarding the reaction mechanisms. Cerium(IV) is capable of oxidizing many organic compounds even in the dark. These reactions are sharply accelerated on exposure to light. For example, benzoic acid is oxidized to fumaric acid in bright sunlight,[122] although it is stable with respect to an aqueous solution of Ce^{IV} in the dark at room temperature.

Study[123] of photo- and thermal reactions of Ce^{IV} carboxylates in undiluted carboxylic acids RCOOH (R = Me, Bu^n, Bu^i, Bu^t) showed that photolysis of deaerated solutions with light with λ = 350 or 254 nm induces reduction of Ce^{IV} and results in the formation of

CO_2 and an alkane (or isobutylene for R = Bu^t) as the major products, for example,

$$Ce(OAc)_4 + H^+ + h\nu \rightarrow$$
$$\rightarrow Ce(OAc)_3 + CH_4 + CO_2 + \text{side products.} \quad (29)$$

Methyl acetate, ethane, and acetoxyacetic and succinic acids were detected as the side products of reaction (29). The quantum yield of CO_2 in some systems approached unity or was even higher than unity. Analysis of the effect of radical acceptors on the products of photoreactions led to the assumption that decomposition of Ce^{IV} carboxylates proceeds in the following way (the authors′ notation is preserved):

$$Ce^{IV}(RCOO^-) + h\nu \rightarrow Ce^{III} + {}^{\bullet}RCOO, \quad (30)$$

$${}^{\bullet}RCOO \rightarrow {}^{\bullet}R + CO_2. \quad (31)$$

The subsequent reactions of the alkyl radicals $^{\bullet}$R (oxidation by cerium(IV), trapping, dimerization, *etc.*) determine the overall stoichiometry.

The primary products of photoreactions of Ce^{IV} and UO_2^{2+} with several organic compounds in liquid solutions were studied in detail[124] by ESR. In order to enhance the stability of organic radicals, the experiments were carried at the minimum possible temperature at which the solution was still liquid; in some cases, this was 150 K. The results confirmed the formation of alkyl radical $^{\bullet}$R in the reactions of Ce^{IV} with carboxylic acids:

$$RCOOH + Ce^{IV} + h\nu \xrightarrow{\lambda > 300\text{ nm}} {}^{\bullet}R + CO_2 + H^+ + Ce^{III}. \quad (32)$$

However, $^{\bullet}$RCOO radicals were not detected. Therefore, it appears likely that the reaction of the Ce^{IV*} ion photoexcited by UV light (a mercury xenon lamp) with carboxylic acid in solutions (150—270 K) starts with the rupture of the C—C bond in the organic molecule. Similarly, in the photoreduction of Ce^{IV} by normal alcohols RCH_2OH (R = Me, Et, Pr), the formation of $^{\bullet}$R radicals was found; formic aldehyde $CH_2=O$ was produced as the second product. Photolysis of uranyl ions in the same media yielded R$^{\bullet}$CHOH radicals. Thus, the difference between the behavior of photoexcited cerium and uranyl ions is that the attack by Ce^{IV*} is normally directed on the C—C bond, while the $(UO_2^{2+})^*$ ion attacks the C—H bond (see also Section 2.3).

Studies in frozen matrices at 77 K were carried out for photoreactions of Ce^{IV} with alcohols,[125] organic acids,[126] aldehydes, ketones, esters, and amides.[127] The reaction of Ce^{IV} with alcohols at 77 K, unlike that in liquid solutions, results in the rupture of the C—H bond to give the R$^{\bullet}$CHOH radical. It is of interest that methanol, which is inert with respect to photoreactions of cerium ion in liquid solutions,[124] is oxidized at 77 K[125] to give $^{\bullet}CH_2OH$. In reactions with carboxylic acids at 77 K, the Ce^{IV*} ion behaves[126] as in liquid solutions. Both C—C and C—H bonds are cleaved when Ce^{IV*} reacts with ketones and esters, whereas aldehydes and formamide give products indicating cleavage of only C—H bonds.[127]

Somewhat different results were obtained in the photolysis of a solution of $(NH_4)_2Ce(NO_3)_6$ in glacial acetic acid[128] (mercury lamp, 450 W). The presence of the nitrate ion influences the form of existence of Ce^{IV} in solution and the mechanism and the products of photolysis. In addition to CO_2, whose yield is even greater than the yield of Ce^{III}, fairly large amounts of HNO_3, $MeNO_2$, and MeOH and smaller amounts of $MeONO_2$, CH_4, and AcOMe are also formed. A relatively simple set of reactions that accounts for all the experimental results on photolysis was proposed; it was noted that this system can act as a chemical actinometer.

The problem of photoreaction of Ce^{IV} with water is significant for the photochemistry of cerium ions. Aqueous solutions of Ce^{IV} are responsible for a broad absorption band with charge transfer to the metal, which occurs in the UV region and partly extends to the visible region. The absorption of light in this band sharply enhances the oxidizing properties of cerium(IV). For example, an aqueous solution of Ce^{IV} in hydrochloric acid, although thermodynamically unstable, still can be stored in the dark for several months without substantial changes. When it is irradiated by UV light, water oxidation takes place. Whereas photoreduction of the uranyl ion gives unstable U^V, which tends to be oxidized again, the reduction of Ce^{IV} yields a relatively stable product, Ce^{III}. Therefore, photolysis of Ce^{IV} in water proceeds much more efficiently, giving rise to Ce^{III} and oxygen[121,129] according to the overall reaction

$$4\,Ce^{IV} + 2\,H_2O + h\nu \rightarrow 4\,Ce^{III} + 4\,H^+ + O_2. \quad (33)$$

Apparently, the primary step of the reaction[129] is transfer of an electron from a water molecule to the metal atom to give $OH^{\bullet}$ radicals. Detailed investigation of the photoreaction of Ce^{IV} with water showed[130] that the quantum yield of Ce^{IV} photolysis in $HClO_4$ solutions using light with $\lambda = 254$ nm increases with an increase in the Ce^{IV} concentration and decreases upon an increase in the Ce^{III} concentration. It does not depend on light intensity and is 0.145 at the most. Based on the regularities found, it was concluded that the species participating in the photochemical reactions is a hydrolyzed Ce^{IV} dimer, while Ce^{III} serves to deactivate the excited dimer.[130] This conclusion was criticized by other researchers,[131] who favored the mechanism of electron transfer to the monomeric Ce^{IV} ion to give the $OH^{\bullet}$ radical:

$$CeOH^{3+} + h\nu \rightarrow Ce^{3+} + OH^{\bullet}. \quad (34)$$

The concentration effects of Ce^{IV} and Ce^{III} are attributed to the reactions

$$CeOH^{3+} + OH^{\bullet} \rightarrow Ce^{3+} + H_2O_2, \quad (35)$$

$$Ce^{III} + OH^{\bullet} \rightarrow Ce^{IV} + OH^-, \quad (36)$$

$$H_2O_2 + 2\,Ce^{IV} \rightarrow 2\,Ce^{III} + 2\,H^+ + O_2 \text{ (fast).} \quad (37)$$

Generally, this scheme can account for experimental data[130]; however, it should be noted[131] that the $OH^•$ radical acts in reaction (35) as the reducing agent; to the best of our knowledge, a similar approach cannot be found in any other publication. Later ESR studies[132] of irradiated frozen aqueous solutions of $HClO_4$ containing Ce^{IV} perchlorate point to the formation of trapped $H_2O^{•+}$ radical ions, apparently, due to electron transfer from the hydration sphere to the Ce^{IV} ion. In the liquid phase, $H_2O^{•+}$ radical ions rapidly dissociate to $OH^•$ and H^+. Thus, the overall reaction can be written as

$$Ce^{4+} + H_2O + h\nu \rightarrow Ce^{3+} + OH^• + H^+. \quad (38)$$

In 0.4 *M* aqueous H_2SO_4, in which Ce^{IV} does not form dimers and exists as a mixture of sulfate complexes, it also undergoes photoreduction.[133—135] The quantum yield of Ce^{III} upon photolysis with light with $\lambda = 254$ nm increases in the presence of Br^-, Cl^-, HCOOH, and Tl^I. Kinetic calculations suggest[134,135] that photooxidation of water may occur according to reaction (38). The above-listed reagents trap the $OH^•$ radicals, thus preventing the back reaction of these radicals with Ce^{III}. An effect similar to the effect of HCOOH or Tl^I on the photoreduction of Ce^{IV} is also exerted[136] by Hg^I. It was noted that the photochemical step involves the Ce^{4+} ion rather than its dimers. In our opinion, arguments given by the authors of these publications are not indisputable, and this aspect requires further studies.

The $OH^•$ radicals, resulting from the photoreaction of Ce^{IV} with water in solutions in sulfuric acid, oxidize the anions of the medium to give $SO_4^{•-}$ or $HSO_4^•$. This process has been taken into account in the discussion[133—135] of the photolysis of sulfuric acid solutions of Ce^{IV}. The $HSO_4^•$ radicals formed in the pulse photolysis of sulfate solutions of Ce^{IV} were detected directly[137] based on the short-lived absorption at 455 nm. In nitric acid, the reaction of $OH^•$ with NO_3^- gives rise to $NO_3^•$ radicals. They were detected upon pulse photolysis by UV light of a solution of $(NH_4)_2Ce(NO_3)_6$ in 6 *M* HNO_3[138,139] or $K_2Ce(NO_3)_6$ in 0.1—6 *M* HNO_3. The formation of the $NO_3^•$ radicals is attributed to both oxidation of nitrate ions by the $OH^•$ radical[137] and direct electron transfer from NO_3^- to Ce^{IV}.[138,139] The question of the origin of the $NO_3^•$ radical has not yet been answered unambiguously. Studies of the photolysis of frozen solutions of $(NH_4)_2Ce(NO_3)_6$ in an HNO_3—$HClO_4$ aqueous mixture (88 K) appear to attest[140] to the formation of $NO_3^•$ radicals without reaction between NO_3^- and $OH^•$. Recall that a similar pathway was preferred in the photolysis of uranyl ions (Section 2.4).[65] The photolysis of $(NH_4)_2Ce(NO_3)_6$ is a simple and convenient method for the generation of $NO_3^•$ radicals in aqueous solutions at a controlled rate.[138,139]

Photolysis of Ce^{IV} in frozen hydrochloric acid matrices at 77 K results in the inner-sphere transfer of an electron from the chloride ligand to Ce^{IV} to give $Cl^•$. This is then converted into a $Cl_2^{•-}$ radical ion, which was detected by ESR and spectrophotometry.[141]

In general, in investigations of the photolysis of aqueous solutions of Ce^{IV}, reactions like (38) are assumed to proceed in the majority of cases. Experiments on the photo-evolution of oxygen from water on treatment with cerium(IV) were interpreted in the same way.[142] The rate of the process sharply (by about an order of magnitude) increased when quartz pieces had been placed in the reaction cell. This is regarded as being indicative of the fact that the $OH^•$ radicals arising upon photolysis are sorbed on the quartz surface where they recombine to give O_2. Despite these results, in our opinion, the question of the mechanism of water photooxidation by cerium(IV), like that by the uranyl ion, remains open. Indeed, when solutions are irradiated by mercury lamps, the steady-state concentration of $OH^•$ radicals is very low; calculations based on known rate constants for the transformations of $OH^•$ radicals indicate that the efficiency of recombination of these radicals is very low. The vast majority of the $OH^•$ radicals should be consumed in the back reaction with Ce^{III} ions even when the concentration of the latter is $\sim 10^{-6}$ mol L^{-1}, *i.e.*, Ce^{III} is not accumulated under these conditions.

The photochemical activity is peculiar not only to Ce^{IV} but to Ce^{III}. Photooxidation of Ce^{III} in aqueous $HClO_4$ has been detected[130] in the photolysis of Ce^{IV} with light with $\lambda = 254$ nm. The reaction is accompanied by hydrogen evolution:

$$2\ Ce^{III} + 2\ H^+ + h\nu \rightarrow 2\ Ce^{IV} + H_2. \quad (39)$$

Presumably, when $\varepsilon_3\varphi_3[Ce^{III}] = \varepsilon_4\varphi_4[Ce^{IV}]$ (ε_3 and ε_4 are the molar extinction coefficients at the irradiation wavelength and φ_3 and φ_4 are the quantum yields of Ce^{III} and Ce^{IV}, respectively), the concentrations of Ce^{III} and Ce^{IV} would remain invariable, although water would decompose to H_2 and O_2:

$$2\ H_2O + h\nu \xrightarrow{Ce^{IV}/Ce^{III}} 2\ H_2 + O_2. \quad (40)$$

Photoreactions (39) and (40) have been studied in detail[143,144] in 0.114—1.05 *M* $HClO_4$. Photooxidation of Ce^{III} proceeds virtually identically in the presence and in the absence of dissolved air. The quantum yield of Ce^{IV} increases with an increase in the Ce^{III} or $HClO_4$ concentration and, under optimal conditions, it is equal to 0.0014. Based on the regularities found, a mechanism of Ce^{III} photooxidation was proposed[143,144]; according to this mechanism, the crucial role is played by the formation of a cerium complex with the H_2^+ ion:

$$CeH_2O^{3+} + h\nu \rightarrow Ce^*H_2O^{3+}, \quad (41)$$

$$Ce^*H_2O^{3+} + H_3O^+ \rightarrow [Ce\text{—}OH^-\text{—}H_2^+]^{4+} + H_2O, \quad (42)$$

$$[Ce\text{—}OH^-\text{—}H_2^+]^{4+} + CeH_2O^{3+} \rightarrow \rightarrow 2\ CeOH^{3+} + H_2 + H^+. \quad (43)$$

The symbols CeH_2O^{3+} and $[Ce—OH^-—H_2^+]^{4+}$ designate the $(H_2O)_5Ce^{3+} \cdot H_2O$ and $(H_2O)_5Ce^{4+}OH^-—H_2^+$ hydrated ions, respectively. According to the current views, the first hydration sphere of the Ce^{III} ion contains nine rather than six H_2O molecules. The potential of the H_2^+/H_2 pair was calculated[144] to be 2.3 V, which stipulates the possibility of reaction (43). Another possible reaction mechanism is the formation of H atoms in the primary step. This is indicated by the fact that cerium(III) initiates photopolymerization of vinylic monomers; this would be impossible without participation of H atoms.[145] The characteristic features of quenching of Ce^{III} luminescence also indicate[145] that transformations of Ce^{III*} in acid media yield H atoms. These results were obtained for solutions in sulfuric acid.

Critical analysis of the data on the mechanisms of cerium photoreactions in acid media has been reported.[146] It was noted that the estimated potential for the H_2^+/H_2 pair presented above is markedly overestimated. It was established reliably that the H_2^+ ion serves as the oxidant only when contacting with a partner whose redox potential does not exceed 1 V. For example, H atoms (perhaps, *via* the formation of H_2^+) oxidize Fe^{2+} ions[147] as well as Np^{III} and U^{IV} ions in aqueous solutions of $HClO_4$ or H_2SO_4. However, they are inert with respect to Np^V and reduce U^{VI}, Pu^{VI}, Pu^{IV}, and Np^{VI} in aqueous $HClO_4$ [148] and Ce^{IV} in aqueous H_2SO_4.[147] The standard potentials of the Fe^{III}/Fe^{II}, U^{VI}/U^V, Np^{IV}/Np^{III}, Pu^{IV}/Pu^{III}, Pu^{VI}/Pu^V, and Np^{VI}/Np^V pairs are equal to 0.771,[149] 0.17, 0.15, 1.01, 1.02, and 1.24 V, respectively,[150] while that of Ce^{IV}/Ce^{III} is 1.7 V.[144] Thus, reaction (43) is hardly possible.

In a neutral aqueous solution of Ce^{III} perchlorate, photolysis results[151] in the precipitation of CeO_2 (more precisely, apparently, $CeO_2 \cdot xH_2O$).

Unlike in solutions in hydrochloric acid, in an aerated solution of K_2CO_3 without redox additives, Ce^{III} is quantitatively oxidized to Ce^{IV}.[152] In solutions of sodium or potassium bicarbonates, the oxidation rate is lower, and in $(NH_4)_2CO_3$, the reaction does not occur at all.[152] In solutions saturated with argon, this reaction did not take place; hence, it was concluded that photooxidation of cerium is accomplished by dissolved oxygen rather than by water. The proposed mechanism includes the dark formation and photochemical decomposition of peroxide—carbonate complexes, giving rise to Ce^{IV}. More recent studies[153] showed that cerium(III) photooxidation occurs equally effectively both in aerated and deaerated carbonate solutions; in both cases, water molecules serve as the oxidizing species. The degree of photooxidation of Ce^{III} under optimal conditions reaches 85%. Photoirradiation of the initial Ce^{IV} induces its slight (to several percent) photoreduction.

Photolysis of Ce^{III} in 4 *M* H_2SO_4 in the presence of an oxidant, persulfate ions, results in the formation of Ce^{IV}, irrespective of the presence of dissolved oxygen.[154] Simultaneous measurements of Ce^{III} f←d-luminescence led to the conclusion that luminescence quenching by the persulfate ion is due to irreversible electron transfer by the reaction

$$Ce^{III*} + S_2O_8^{2-} \rightarrow Ce^{IV} + SO_4^{2-} + SO_4^{\bullet -}. \quad (44)$$

As opposed to the above data,[145] no noticeable formation of H atoms as a product of Ce^{III*} quenching by H^+ ions was detected, although this might be due to the fast reaction of $H^\bullet$ with $SO_4^{\bullet -}$.

3.3. Europium and other lanthanides. Whereas most studies of photoreactions of cerium ions are devoted to the reduction of Ce^{IV}, in the case of europium ions, greater attention was devoted to photooxidation of Eu^{II}. In both cases, the most stable valence state of the lanthanide is generated and the photoreaction occurs in a high yield.

The Eu^{2+} ion is quite stable in acidic solutions in the absence of oxygen.[155] The absorption spectrum of this ion contains two broad bands with maxima at ~250 and ~320 nm,[156] corresponding to 4f→5d electron transitions.[157] The tail of the long-wave band extends to ~400 nm. Light excitation to these absorption bands results in a sharp acceleration of Eu^{2+} oxidation accompanied by hydrogen evolution. For example, in a solution of HCl virtually devoid of oxygen, Eu^{2+} ($2.5 \cdot 10^{-3}$ mol L^{-1}) was oxidized[158] to 50% over a period of ~40 min; the same percentage of europium oxidation was induced by UV irradiation ($8 \cdot 10^{15}$ quanta s^{-1}) for ~1 min. According to the first estimate,[159] the quantum yield of Eu^{2+} photooxidation in 0.5 *M* HCl using light with λ = 360 nm was ~0.15—0.20. The reaction affords Eu^{3+} and H_2. Subsequently, the quantum yield of this reaction was measured repeatedly[156,158,160] under different conditions and, generally, it can be stated that the yield varies from several hundredths to unity and increases with an increase in the HCl concentration and with a decrease in the excitation wavelength.

The scheme of the process includes activated phototransfer of an electron from the europium atom to a water molecule[158]:

$$(Eu^{2+}{}_{aq})^* + H_3O^+ \rightarrow Eu^{3+}{}_{aq} + H + H_2O. \quad (45)$$

Then the formation of H_2^+, able to react with both Eu^{2+} and Eu^{3+}, is assumed[160]:

$$H + H^+ \rightarrow H_2^+, \quad (46)$$

$$H_2^+ + Eu^{3+} \rightarrow Eu^{2+} + 2\,H^+, \quad (47)$$

$$H_2^+ + Eu^{2+} \rightarrow Eu^{3+} + H_2. \quad (48)$$

Ultimately, Eu^{2+} is oxidized with hydrogen evolution and Eu^{3+} inhibits the reaction. Instead of reactions (46)—(48), the intermediate complex (Eu^{2+}...H) might be formed; it reacts with H^+ to give[156] Eu^{3+} and H_2. In this case, the mechanism of Eu^{II} photooxidation is similar to the photooxidation of Fe^{II}.[5,156] Reaction (45) is followed by the transformations

$$H + Eu^{2+} \rightarrow (Eu^{2+}...H) + H^+ \rightarrow Eu^{3+} + H_2, \quad (49)$$

$$H + H \rightarrow H_2, \quad (50)$$

$$H + Eu^{3+} \rightarrow Eu^{2+} + H^+. \quad (51)$$

The reaction can take place not only from the lower excited state (λ_{excit} = 365 nm) but from a higher state (λ_{excit} = 250 nm),[156] the quantum yield being 0.22 higher in the latter case.

Large amounts of Eu^{3+} (more than 10^{-2} mol L^{-1}) decrease the quantum yield of the reaction.[156] However, the influence of Eu^{3+} becomes less pronounced with an increase in the HCl concentration and disappears when [HCl] = 6 mol L^{-1}.[156,160] Apparently, the back reduction of Eu^{3+} by reaction (51) is insignificant. Reaction (47) is also relatively unlikely because reaction (48) would rather be expected in view of the ratio of the redox potentials of the Eu^{3+}/Eu^{2+} and H_2^+/H_2 pairs (see Section 3.2).

In frozen (77 K) solutions of Eu^{2+} in aqueous HCl or HBr, the primary step gives rise to the excited $(Eu^{2+})^*$ ion, from which electron transfer to the H_3O^+ ion occurs; only after that, are H atoms formed.[161,162] The efficiency of photochemical processes at 77 K, as at room temperature, increases with an increase in $[H^+]$ but still remains much lower than that in liquid solutions. As opposed to liquid solutions, at 77 K, bright f←d luminescence of Eu^{2+} is observed, *i.e.*, at lower temperatures, the yield of electron phototransfer decreases and, correspondingly, the yield of photoluminescence increases.[158,162] These results confirm the activated character of electron phototransfer, in which the formation of the excited Eu^{2+} ion is followed by a thermal stage.

In the presence of europium(III), photolysis of europium(II) in a hydrogen chloride matrix follows a different pathway.[163] The first step may be fast electron transfer from the excited $(Eu^{2+}{}_{aq})^*$ aqua complex to the Eu^{III} chloride complex:

$$(Eu^{2+}{}_{aq})^* + Eu^{3+}...Cl^- \rightarrow Eu^{3+}{}_{aq} + Eu^{2+}...Cl^-, \quad (52)$$

which is followed by photooxidation of europium(II) chloride complexes:

$$Eu^{2+}...Cl^- + H_3O^+ + h\nu \rightarrow Eu^{3+}...Cl^- + H + H_2O. \quad (53)$$

Apparently, the europium(II) chloride complex $Eu^{2+}...Cl^-$, formed upon reaction (52), occurs in a nonequilibrium reactive state.[163] A similar formation of nonrelaxed forms of halide complexes has also been observed[5] for Fe^{II} and Cu^I ions.

It was proposed to use photoirradiation of Eu^{2+} in frozen solutions of HCl for controlled generation of H atoms and subsequent investigation of their behavior.[164] Unlike the radiation method, which gives rise to lots of diverse radical products, the photochemical method provides more selective treatment.

Photolysis of Eu^{2+} ions in perchloric acid solutions at room temperature[157] is similar to the photolysis of solutions in hydrochloric acid. The quantum yield of H_2 is proportional to $[H^+]^{1/2}$ and increases upon decrease in the light wavelength. An assumed mechanism implies the reaction of $(Eu^{2+})^*$ with H^+ as the primary step, giving rise to the $(Eu^{3+}...H^\bullet)$ radical pair. The radical pair reacts with H^+, which prevents recombination and creates conditions for the oxidation of another europium(II) ion with H_2^+. In frozen solutions of Eu^{2+} with 9 mol L^{-1} of $HClO_4$ at 77 K, the formation of the $^\bullet ClO_2$ radical was detected[165] in addition to the above-described photoreactions. Evidence was obtained indicating that these radicals result from photoreduction of $HClO_4$ by $(Eu^{2+})^*$ ions rather than from secondary reactions. The ESR spectrum of the irradiated matrix showed the presence of other chlorine-containing radicals, $^\bullet ClO_2$ and $^\bullet ClO$. For $[HClO_4]$ = 0.2 mol L^{-1}, the formation of $^\bullet ClO_2$ radicals was not observed.

The photoreduction of europium(III) upon excitation with light to the CTB from a water molecule to the Eu^{3+} atom (250—330 nm) was first detected[166] in an $HClO_4$ solution. The photoreactions of europium(III) were accompanied by luminescence of unknown nature in the region of 320—460 nm consisting of two components. It was shown that the primary step is the formation of a CT state $(Eu^{2+}—H_2O^+)$, which can decompose to give either the initial fragments, $(Eu^{3+})^*$ and H_2O, or $(Eu^{2+})^*$, $OH^\bullet$, and H^+; the latter pathway is possible only for a relatively high quantum energy, $\lambda < 270$ nm. One component of the luminescence corresponds to the $(Eu^{3+})^*$ ion formed, while the other one is due to $(Eu^{2+})^*$. It is of interest that the photoexcited Eu^{2+} ion virtually does not luminesce due to quenching by water or H_3O^+ (see above). Thus, the excited state of europium(II) in this process[166] differs from the typical europium(II) photoexcited state, although some $(Eu^{2+})^*$ still reacts with H_3O^+:

$$(Eu^{2+})^* + H_3O^+ \rightarrow Eu^{3+} + H + H_2O. \quad (54)$$

The subsequent transformations of H atoms may give rise to H_2 molecules; however, in the overall reaction, no evolution of H_2 was observed. This occurs only in the presence of acceptors of H atoms such as EtOH,[155,166] Pr^iOH, HCOOH, and HCOONa.[155] Upon irradiation of a solution of Eu^{3+} containing the above-listed substances, a steady-state Eu^{2+} concentration is attained, which can be 5% of $[Eu^{3+}]$. Hydrogen evolution is due to the photolysis of the europium(II) formed. The reactions of the acceptors with H atoms result in the generation of $CH_3{}^\bullet CHOH$, $^\bullet COOH$, and other radicals, which are capable of additional reduction of Eu^{3+} to Eu^{2+}. The evolution of hydrogen was also detected[155] in the photolysis of ions of trivalent Sm and Yb, which are also capable of being transformed into the oxidation state 2+.

These results confirmed the mechanism proposed for the photolysis of Eu^{3+}. The formation of Eu^{2+} as an intermediate product in the photolysis of Eu^{3+} has also been noted by other researchers.[167,168] The highest quantum yield of hydrogen in the photolysis of a solution of Eu^{3+} in the presence of formate ions was observed at pH 1—2, and the highest steady-state concentration $[Eu^{2+}]_{st}$ was found at pH 3—5.3.[168] Owing to the extensive absorption of light by Eu^{2+} ions in the UV region, even small amounts of these ions, formed in the photolysis of Eu^{3+}, start participating efficiently in photochemical reactions with water. This is why photolysis of Eu^{3+} is accompanied by hydrogen evolution.

Thus, the final outcome of the photolysis of Eu^{3+} in the presence of acceptors of H atoms is the same as that of the photolysis of Eu^{2+}, *i.e*,. evolution of molecular hydrogen, except that in this case, the acceptor rather than Eu^{2+} is consumed. This interesting finding stimulated attempts to use photolysis of europium(III) for chemical accumulation of solar energy.[169] In irradiation of solutions of Eu^{3+}, even rather long-wave light with wavelengths of up to 400 nm is photoactive and the quantum yield of H_2 at λ = 365 nm is 5%.[170] Nevertheless, the use of photoreactions of Eu^{3+} [169] or Eu^{2+} [160] for this purpose can hardly be expected to give rise to a practically useful process[171] due to the low efficiency of the photolysis of europium by visible and mild UV light. The yield of hydrogen under conditions of this irradiation can be appreciably increased by using sensitizers, for example, benzophenone,[172] although in this case, europium ions do not participate in primary reactions. The reaction occurs on exposure to light with λ = 365 nm; benzophenone is not consumed in the process. The first step is excitation of the benzophenone molecule, which reacts with alcohol. The resulting radicals reduce Eu^{3+}, benzophenone being thus regenerated.

The photo-evolution of hydrogen from solutions of alcohols in the presence of Eu^{3+} and Sm^{3+} ions is markedly accelerated by colloidal platinum.[173] As in the processes discussed above, the photochemical formation of M^{2+} occurs initially (M = Eu, Sm). Presumably, after that, $(M^{2+})^*$ directly reduces the alcohol rather than reacts with water (reaction (54)). However, in anhydrous alcohols or in neutral media, no hydrogen evolution takes place, *i.e.*, the presence of H^+ ions is required. These processes occur only on exposure to light with a wavelength of <250 nm.

The quantum yield of Eu^{3+} photoreduction by alcohols increases as the light wavelength decreases within one absorption band.[174] Presumably, the primary species formed in the reaction is the intra-cage pair $(Eu^{2+}RHOH^+)^*$, which can either emit a light quantum or recombine, or dissociate to Eu^{2+} and $RHOH^+$. An increase in the excitation energy increases the probability of the last-mentioned process. If we compare CTB of various natures in methanolic solutions of $EuCl_3$, the highest quantum yield of europium photoreduction ($\phi \approx 1$) is observed in the $Cl^- \rightarrow Eu^{3+}$ CTB (272 nm).[175] A less efficient reaction takes place on excitation of the MeOH $\rightarrow Eu^{3+}$ CTB (228 nm). Thus, the $Cl^{\bullet}$ radicals virtually do not recombine with the Eu^{2+} ions but react effectively with the surrounding alcohol molecules.

When pressed KBr pellets containing $EuCl_3 \cdot 6H_2O$ are exposed to the radiation of an XeCl laser (λ = 308 nm),[176] transfer of an electron from the matrix to the Eu^{III} ion takes place. The Eu^{II} ion thus formed was detected by the short-lived absorption at 410 nm and by f←d luminescence with a maximum at ~420 nm.

Photolysis of Eu^{III} complexes with macromolecular ligands based on acrylic acid results in the destruction of the macroligand. Interestingly, this is accompanied[177—179] by an increase in the intensity of europium(III) photoluminescence. The photolysis was performed by the full light of a high-pressure mercury lamp. Neither the mechanism of photolysis nor the nature of the photoactive sites were elucidated.

The photoreduction can also be carried out for other lanthanides, for example, Sm^{III} and Dy^{III}. This occurs on irradiation of Sm and Dy trichlorides in anhydrous methanol with the light of a Kr—F excimer laser.[180] The lifetimes of both divalent ions are several hours; they markedly increase in the presence of macrocyclic ethers. This might be a multiquantum process because irradiation with a mercury lamp does not give products.

A study dealing with photooxidation of Tb^{3+} in an alkaline solution of KIO_4 under the action of light with λ = 366 nm was published.[181] The absorption by the photolysis products at 420 nm was attributed to an unstable Tb^{IV} complex. The formation of Tb^{IV} was observed[182] in the photolysis of Tb^{III} complexes with the heteropolytungstate anion $P_2W_{17}O_{61}{}^{10-}$ in the presence of $S_2O_8{}^{2-}$ ions. In this case, oxidation of terbium(III) is not related to its excitation but is performed by $SO_4{}^{\bullet -}$ radical ions, arising upon photodecomposition of the persulfate ion.

3.4. Photochemistry of lanthanide ions with photoexcitation to the f—f transition bands. The photochemical reactions of lanthanide ions considered above are induced by excitation to the CTB or to f—d transition bands. This type of excitation changes the redox properties of the lanthanide ion. As for d-elements, photolysis to the ligand field bands (these are f—f transitions for lanthanides) can change the ability of the metal ion to replace the ligand. In view of the fact that lanthanide complexes are much more labile than coordination compounds of d-elements, it can be concluded that the influence of irradiation does not manifest itself so clearly. Nevertheless, photo-substitution of the ligand was accomplished after excitation of the Pr^{3+}, Eu^{3+}, or Ho^{3+} ion complexed with a β-diketone (2,2,6,6-tetramethylheptane-3,5-dione).[120] Irradiation of solutions of complexes of the three elements in coordinating solvents (pyridine, ethanol, acetone) in the presence of dissolved oxygen with a frequency-controlled argon laser gives rise to a new absorption band. This indicates photo-

Table 1. Stability constants (*K*) and thermodynamic parameters of adduct formation by $Eu(fod)_3$ in the ground (*A*) and excited (*B*) states with ketones[183] in benzene solutions at 300 K

Ketone	$K/L\ mol^{-1}$		$\Delta H/kJ\ mol^{-1}$		$\Delta S/kJ\ mol^{-1}\ K^{-1}$		$\Delta G/kJ\ mol^{-1}$	
	A	*B*	*A*	*B*	*A*	*B*	*A*	*B*
Acetophenone	134	1090	−10.9	−17.2	1.2	0.4	−12.2	−17.6
Benzophenone	104	2700	−27.2	−21.4	−12.7	−1.2	−11.7	−19.7
Adamantanone	122	157	−21.0	28.1	−7.2	33	−11.7	−13.4
Acetone	109	750	−22.2	24.3	−8.5	32	−11.7	−16.3
Acetone-d_6	120	360	−10.5	0	1.2	12	−12.2	−14.7

substitution of a solvent molecule for the β-diketone molecule. The latter reacts with O_2 to give a peroxide, which decomposes to give triketone (the product of photolysis).

In a series of studies,[183—187] the influence of f—f excitation of lanthanides on the stability of complexes has been studied. Thus the stability constants of the adducts of the $[Eu(fod)_3]^*$ (fod is heptafluorodimethyloctanedione) chelate excited to the f—f transition band with aliphatic and aromatic ketones were measured. Table 1 contains thermodynamic parameters for the adduct formation of $Eu(fod)_3$ with ketones.

In the excited state, adducts with aromatic ketones (acetophenone, benzophenone) are much more stable than in the ground state. For aliphatic ketones, excitation of $Eu(fod)_3$ changes the thermodynamics of adduct formation; this is an exothermic process in the ground state and an endothermic process in the excited state.

Dissociation of the complex of excited $^*Eu^{3+}$ with 2-thenoyltrifluoroacetone (TTA) was considered as one of the mechanisms of quenching of europium luminescence.[188] Thermodynamic characteristics for the dissociation of $[(EuTTA)^{2+}]^*$ were calculated. In this case, no difference between the dissociation ability of excited and nonexcited complexes was noticed. The data on the activation energy of ligand substitution in the first coordination sphere of the Tb^{3+} ion provided the conclusion that the stability of the Tb^{3+} complex with 2,2′-diadamantane 2,2′-dioxide in acetonitrile decreases upon excitation and the equilibrium shifts toward the $^*Tb^{3+}$ solvate with acetonitrile.[189]

In aqueous solutions of $EuBr_3$, the $^*Eu(H_2O)_n{}^{3+}$ ion (n = 8, 9) photoexcited to the $^5D_1$ level can form[190] the $[^*Eu(H_2O)_7Br]^{2+}$ exciplex, in which relaxation to the lower excited state $^5D_0$ occurs. The thermodynamic parameters of the formation of the exciplex were determined. The hydrated $Gd(H_2O)_8{}^{3+}$ ion abstracts upon excitation[191] two water molecules and is thus transformed into $^*Gd(H_2O)_6{}^{3+}$. The changes are attributed to different degrees of compression of the sphere of 4f-electrons in the ground and excited states.

No data on redox transformations of lanthanides induced by excitation to the f—f transition bands are available to date, although quenching of the luminescence of variable-valence lanthanide ions by an electron transition mechanism will be considered in Section 4.8. The bands of f—f transitions can be used for multiquantum excitation in which the state with CT is ultimately populated. Thus in KBr pellets containing $EuCl_3 \cdot 6H_2O$, the electron transfer from the matrix to the Eu^{III} ion is induced not only by light with λ = 308 nm[176] but also by a focused laser beam with λ = 455—475 nm.[192] This points to a two-photon mechanism of the last-mentioned process. In the case of one-photon absorption, only f—f luminescence of europium(III) arises.[192] The use of the second harmonics of the titanium-sapphire laser (λ = 394 nm, pulse duration 2 ps) made it possible to perform photochemical reduction of Eu^{3+} by alcohol through multiphoton absorption in the f—f transition excitation band.[193,194] The efficiency of pumping of the europium ion to a CT state drops sharply on passing to nanosecond pulses with the same frequency.

3.5. The use of photochemistry for separation and isolation of lanthanides. Photochemical reactions provide the possibility of separating lanthanides.[119] This is done either by selective oxidation of Ce^{3+} to Ce^{4+},[195,196] or by selective reduction of Eu^{3+} to Eu^{2+}.[197,198] The reaction product is removed from the reaction mixture as a precipitate. To precipitate Ce^{4+}, iodate ions are used. The quantum yield of Ce^{III} photooxidation in the presence of $IO_3{}^-$ using light with λ = 250 nm reaches[195] 0.1. Presumably, intra-complex electron transfer from Ce^{III} to the iodate ion is the primary photochemical step in this reaction. A disadvantage of the method is that it cannot be realized using light with wavelengths of >300 nm. This restricts the range of suitable media; for example, photo-evolution of cerium is impossible in solutions in nitric acid, which markedly absorb the short-wave light. This limitation can be overcome[196] by oxidizing cerium by the photoexcited uranyl ion. As a result, photo-evolution of cerium from solutions in nitric acid was performed even by visible light. Europium(II) is precipitated by sulfate ions. In aqueous alcohols, separation is much more efficient than in aqueous solutions.[198,199] The potential and prospects of laser photochemical methods for purification of rare earth elements in the liquid phase have been surveyed in reviews.[119,200]

Photochemical precipitation of europium was used[201] to process an industrial concentrate containing Sm, Eu, and Gd. Photoreductive precipitation of europium can be combined with extraction methods for separation of other rare earth elements (REE).[202] For example, $EuSO_4$ is selectively precipitated from a solution of alkyl dihydrogen phosphate in xylene containing Sm, Eu, and Gd. For photochemical isolation of $EuSO_4$, the presence of Ce^{III} or Fe^{II} in the solution is undesirable. Both ions can be photochemically oxidized and then Ce^{4+} or Fe^{3+} oxidize Eu^{2+}, thus decreasing its yield and increasing the induction period of the reaction.[203] A substantial increase in the efficiency and in the degree of reduction of europium(III) by isopropyl alcohol can be attained by adding acetone to the sulfuric acid solution.[204] Apparently, acetone prevents back photooxidation of europium(II) by water or protons.

Photoreduction in the presence of sulfate ions was used[205] to precipitate not only Eu but also Nd and Sm. Isopropyl formate served as the acceptor of $OH^{\bullet}$ radicals (or directly as the reducing agent); irradiation was performed by a mercury lamp in a nitric acid solution. No precipitation of Gd was observed. Thus, Nd was separated almost completely from Gd in 0.5 *M* HNO_3 in the presence of $(NH_4)_2SO_4$. In 1 *M* HNO_3, no precipitation of Nd was observed. Note that no other information on the photoreduction of Nd^{III} is available from the literature and these results look surprising if one takes into account the exceptional instability of Nd^{II} in aqueous solutions.

The photooxidation of Ce^{III} to Ce^{IV} in carbonate solutions can be used to separate cerium from trivalent lanthanides after they have been co-precipitated with $La(OH)_3$.[152] The optimal concentration of K_2CO_3 is 5%; in this case, the fraction of Ce precipitated from the irradiated solution was 10.3%, whereas 92.6% of Ce precipitated without irradiation.

3.6. Photocatalysis and photosensitization by rare earth metal ions. Chemiluminescence of REE. Photocatalysis and photosensitization are phenomena related rather closely but not identical. Fairly detailed consideration of the types of photocatalytic reactions of metal ions, mainly d-elements, can be found in the literature.[5,11] We will not now focus attention on the problems of terminology but will consider examples of photoreactions in which the REE ions surely do not change their chemical state, but the change of other components of the system would occur much more slowly or not at all without REE ions.

It has been noted above that cerium(III) ions initiate photopolymerization of vinylic monomers. The primary step includes[145] electron transfer and formation of an H atom. Many other REE ions, namely, Pr^{III}, Sm^{III}, $Eu^{II,III}$, Er^{III}, Yb^{III}, Lu^{III}, Y^{III}, and La^{III}, also exhibit photocatalytic activity with respect to this reaction.[3] Most of these ions appear to sensitize polymerization of vinylic monomers by a different mechasnism, *i.e.*, by energy transfer from the REE ion to the acceptor (like the uranyl ion).

Another class of photocatalytic reactions of lanthanides is decomposition of dioxetanes.[183,206,207] Thus decomposition of adamantylideneadamantane-1,2-dioxetane is accelerated by 7—10 orders of magnitude in the presence of photoexcited Eu^{III}, Pr^{III}, Tb^{III}, or Ce^{III} compounds. The first three ions are excited to the f—f states, and the mechanism of photocatalysis consists in the transfer of the electron excitation energy to the vibrational levels of dioxetane, which induces its decomposition. The energy evolved upon decomposition of dioxetane is, in turn, consumed for the excitation of lanthanides. This phenomenon was called a quantum-chain process. Unlike trivalent europium, praseodymium, or terbium, cerium(III) is excited in the f—d transition band; this stipulates another mechanism of photocatalysis. The first step is the transfer of an electron to dioxetane, which is followed by back electron transfer from the radical anion to the cerium ion.

Chemiluminescence should be regarded as a phenomenon reverse to photochemical reaction. Indeed, in photochemical reactions, the energy of light induces chemical changes, whereas in the former case, the evolution of chemical energy in the reaction results in excitation of the reaction products or energy acceptors, and this is followed by emission of a light quantum. In some cases, chemiluminescence helps to study fine mechanisms of photochemical reactions. Data on the chemiluminescence of lanthanides and uranyl have been surveyed in monographs,[208,209] dissertations,[183,210] and in a recent review.[211]

4. Photochemistry of compounds of transuranium elements

4.1. Characteristic features of the photochemistry of actinides. The first observations of the photochemistry of neptunium and plutonium compounds. Most of the data on the photochemistry of transuranium elements refer to two elements, neptunium and plutonium. Only in recent years, did publications on the photochemistry of americium appear. The NpO_2^{2+} or PuO_2^{2+} actinide ions differ from uranyl in that they have no equally long-lived "triplet" state. Therefore, the quantum yields in their photochemical reactions are much lower than in the case of uranyl.[212] Generally, the nature of the excited states from which they enter into photochemical reactions has not been reliably established. For example, uranyl-like transitions (*i.e.*, transitions from the highest occupied molecular orbital to quasiatomic orbitals having mainly 5f character) in PuO_2^{2+} and NpO_2^{2+} ions occur at a lower energy than those in UO_2^{2+}, *i.e.*, they are mainly located in the visible region. Their intensity is very low[21] and excitation of PuO_2^{2+} and NpO_2^{2+} with visible light to the corresponding absorption bands does not induce photoreactions of these ions. Photoreactions of NpO_2^{n+} and PuO_2^{n+} might take place only from states with higher energies. Regarding triple- and quadruple-charged actinide ions, their known photochemical reactions take place upon photoexcitation to the bands corresponding to states with higher energies than f—f transitions, *i.e.*, to electron transfer bands, evidently, similar to those considered in Section 3.1 for lanthanide ions.

Light sources with a broad spectrum (mercury lamps) are normally used in the photochemistry of transuranium elements. This is convenient for the photolysis of real systems because, apart from plutonium(IV), this also activates HNO_3 and uranyl ions, which play an important role in further transformations. However, the use of polychromatic light results in simultaneous excitation of various valence forms of Np or Pu and gives rise to numerous photochemical (and dark) reactions. The outcome of photoirradiation depends on many factors, *viz.*, the concentrations of acids and actinides, the intensity and time of irradiation, light wavelength, *etc.* Apparently, this accounts for some discrepancies between experimental data obtained by different researchers. A specific feature of the photochemistry of transuranium elements is the diversity of the valence forms of these elements; therefore, photolysis often gives mixtures containing simultaneously three or even four valence forms of the same element.

Unlike the photochemistry of uranyl ions or lanthanides, the mechanisms of photoreactions of transuranium element ions have not been studied profoundly. No data exist on the composition of primary products or analysis of gaseous substances evolved upon photolysis, *etc.* In addition, luminescence, which is a powerful supplementary tool, cannot be used for Np and Pu. Therefore, discussion of the mechanisms of photoreactions of neptunium and plutonium is always conjectural. This drawback is counterbalanced by the practical value of the studies performed. Presumably, the primary steps in the reactions of actinyl ions are the same as those in the reactions of uranyl ions, while tri- and tetravalent actinides react similarly to lanthanides. Now it is difficult to propose a reliable classification of photochemical reactions of transuranium elements; we will group the photochemistry of Np and Pu in accordance with the solution employed.

The discovery of the effect of light on the distribution coefficient of ${PuO_2}^{2+}$ in the water—hexanone extraction system can be regarded as the beginning of the photochemistry of transuranium elements.[213] This finding was attributed to the photochemical reduction of Pu^{VI} to Pu^{IV}. Later, it was demonstrated[214] that extraction of Pu^{VI} from acid media into a benzene solution of TTA is accompanied by its photoreduction to Pu^{IV}. Here the plutonium(VI) ion is not excited, its reduction being related to photodecomposition of the β-diketone. The reduction of Np^{VI} to Np^{V} should apparently be considered to be the first photoreaction of an excited ion of a transuranium element.[215]

Vigorous investigations into photochemical reactions of neptunium and plutonium are related to the possibility of using them for the processing of irradiated nuclear fuel. Naturally, most of the known data refer to acid solutions, especially those in nitric acid.

4.2. Acidic aqueous solutions containing neptunium and plutonium. As noted above, the greater part of studies on the photochemistry of neptunium and plutonium was carried out using mercury lamps. Therefore, below we will specially note only those cases where another light source was used.

4.2.1. Solutions in nitric acid. Neptunium. For $[HNO_3] < 1$ mol L^{-1}, photoirradiation of neptunium(V) does not result in a change in its oxidation state, while upon irradiation of neptunium(IV),(VI), Np^V is formed quantitatively.[216—220] As the acid concentration increases, the rate of Np^{VI} reduction decreases,[216—220] while the rate of Np^{IV} oxidation passes through a maximum[216] at $[HNO_3] = 0.5$ mol L^{-1}. In more concentrated HNO_3, according to one publication[216] only Np^V is formed, while according to other data[219] a mixture of Np^V and Np^{VI} is produced. The degree of photochemical reduction of Np^{VI} to Np^V in 3.0 *M* HNO_3 exceeds[221] 93%. It follows from these results that photooxidation of Np^{IV} and photoreduction of Np^{VI} take place in HNO_3. Since the photochemical processes in aqueous nitric acid are accompanied by numerous dark reactions, it is clear that the final outcome depends on several factors, *e.g.*, photoradiation intensity, duration, and wavelength, neptunium concentration, *etc.* The influence of the first two factors on the formation of HNO_2 and photoreduction of Np^{VI} was studied[221] in 3.0 *M* HNO_3. Dissolved oxygen also might play a certain role. In any case, bubbling of air through irradiated solutions favors[219] the formation of Np^{VI}.

The quantum yields of photoreactions of neptunium are presented in Table 2. The same reactions take place on exposure to light with $\lambda = 300$ nm but the yields are much lower.[218]

Under the action of irradiation by a xenon lamp, the result of phototransformations of neptunium(V),(VI) in HNO_3 is the same as with a mercury lamp.[222] Irradiation with a Kr—F excimer laser ($\lambda = 249$ nm) induces photochemical transformations of neptunium in solutions of nitric acid, which mainly proceed toward the formation of Np^V, although complete transformation is not achieved.

Table 2. Quantum yields (ϕ) of photoreactions of neptunium in 1.0 *M* (*A*) and 4.0 *M* HNO_3 (*B*) on exposure to light with $\lambda = 254$ nm in the absence of additives and in the presence of 0.5 *M* hydrazine[218]

Process	ϕ	
	A	*B*
	In the absence of additives	
$Np^{VI} \rightarrow Np^V$	0.03	0.003
$Np^{IV} \rightarrow Np^V$	0.053	0.017
$Np^V \rightarrow Np^{VI}$	0.015	0.022
	In the presence of hydrazine	
$Np^V \rightarrow Np^{IV}$	—	0.006
$Np^{IV} \rightarrow Np^V$	0.023	0.01
$Np^V \rightarrow Np^{VI}$	—	0.044

The lower the HNO_3 concentration and the higher the temperature, the fuller the reduction of neptunium(VI) to Np^V. In general, this is in line with the results obtained with polychromatic irradiation. In the case of low neptunium concentrations (no more than 10^{-4} mol L^{-1}), the major role is attributed[222] to the reactions of neptunium with the products of HNO_3 photodecomposition. Irradiation of a solution of Np^{IV} results in a partial transition of neptunium into the pentavalent state. No neptunium(VI) is detected in this case.

There are data on photochemical reactions of neptunium in the presence of uranyl ions.[219,223] In a concentration of ~5 g L^{-1}, the uranyl ion has virtually no influence on photoreactions or dark equilibria of neptunium. An increase in $[UO_2^{2+}]$ to 100 g L^{-1} and more increases[219,223] the final Np^V concentration resulting from photoreduction of Np^{VI}. This effect is ascribed to the sensitizing influence[219] of the uranyl ion on the formation of NO_2^- or to the stabilization of Np^V upon the formation of its radical cation complexes with the uranyl ion.[223] However, the overall rate of formation of Np^V decreases, obviously, due to the internal filter effect of the uranyl ion.[223]

The photochemical method permits quantitative preparation of not only Np^V but also other valence forms of neptunium in nitric acid solutions. The addition of urea, which traps nitrite ions, to 0.1—4.0 *M* solutions of HNO_3 gives Np^{VI}.[216,218,219,222,224] As the concentration of HNO_3 increases, this process is accelerated.

Photochemical preparation of neptunium(IV) proved a fairly complicated task. Photoreactions with reducing agents such as N_2H_4, H_2O_2, and EtOH in nitric acid solutions do not provide quantitative formation of Np^{IV}. The result of the photochemical reaction of neptunium with hydrazine depends on the concentration of nitric acid. At HNO_3 concentrations upward of 1 mol L^{-1}, N_2H_4 only prevents the quantitative photochemical formation of Np^V, and the mixture exposed to radiation contains Np^{IV} (the dark reaction of hydrazine with Np^V under similar conditions occurs exceptionally slowly[225] but Np^{VI} is reduced to Np^V over a period of several minutes[226]). The fraction of Np^{IV} increases with an increase in $[HNO_3]$; however, 100% yield is not attained even in 4 *M* HNO_3. In 0.1 *M* HNO_3, photoirradiation with light with $\lambda = 254$ nm results in almost quantitative formation of Np^V. Under these conditions, hydrazine does not influence[218] the photooxidation of Np^{IV}. In 3.0 *M* HNO_3, neither hydrazine[219] nor a mixture of hydrazine and hydroxylamine (10^{-2} mol L^{-1} each)[224] prevents the formation of neptunium(VI) upon photoirradiation with a relatively powerful light source (λ = 250—600 nm, power 1.5 W cm^{-2}).[224] This is quite explicable because dark reduction of Np^{VI} with hydrazine is markedly retarded upon an increase in HNO_3 concentration,[226] while the efficiency of photooxidation of Np^V increases. It follows from these experiments that the outcome of irradiation is mainly determined by the reactions of neptunium and hydrazine with the products of HNO_3 photolysis, which absorb most of the excitation light. The quantum yields of photoreactions of neptunium in the presence of hydrazine are listed in Table 2.

In the presence of H_2O_2 when $[HNO_3] < 1.0$ mol L^{-1}, Np^{IV} is oxidized to Np^V; this occurs much faster than in the dark reaction. As the acid concentration increases, the oxidation becomes incomplete; in 6 *M* HNO_3, it entirely stops.[216] In 1.0—4.0 *M* HNO_3 in the presence of 3.0 mol L^{-1} of ethanol, the rate and especially the quantum yield of the photochemical reduction of Np^{VI} to Np^V increase.[218]

The quantitative photochemical formation of Np^{IV} upon the photoirradiation of neptunium(V) in nitric acid solutions is possible when hydrazine and uranyl ions are present simultaneously in the solution.[227] The essence of the processes is the photoreduction of uranyl ions by hydrazine to U^{IV}, which then reduces Np^V:

$$U^{4+} + 2\ NpO_2^+ + 4\ H^+ \longrightarrow 2\ Np^{4+} + UO_2^{2+} + 2\ H_2O. \quad (55)$$

As a consequence, the uranyl ion proves to be the catalyst of photoreduction, so that the overall reaction is written as follows:

$$4\ NpO_2^+ + N_2H_5^+ + 11\ H^+ \xrightarrow[UO_2^{2+}]{h\nu} 4\ Np^{4+} + N_2 + 8\ H_2O. \quad (56)$$

In the absence of uranyl ions or hydrazine, Np^{IV} is not formed.[227]

Yet another photochemical pathway to Np^{IV} is the use of semiconductor photocatalysts (PC).[228] Platinated TiO_2 and SiC were used as PC, while ethanol and hydrazine, respectively, served as the reducing agents. A solution of Np^V in 3.0 *M* HNO_3 containing a reducing agent and a PC remained unchanged without irradiation. When a solution of Np^V without PC was exposed to the light of a xenon lamp (the main light flux falls in the range of $\lambda > 300$ nm), no changes were observed either. If the solution contained a solid PC, Np^V was reduced to Np^{IV}; no Np^{VI} or Np^{III} were detected in the experiments. Fast complete reduction of Np^V was performed in the SiC(Pt)—N_2H_4 system. The first step of the reaction is the light-induced formation of a hole h^+ on the SiC surface and an electron e^-. Then e^- reacts with H^+ to give H and the hydrogen atom reduces NpO_2^+:

$$H + NpO_2^+ + 3\ H^+ \rightarrow Np^{4+} + 2\ H_2O. \quad (57)$$

No influence of PC (platinated TiO_2) on the reduction of Np^{VI} to Np^V was detected under similar conditions.[229] In the presence of urea, the PC accelerated the reaction by ~30% and increased the degree of Np^V photooxidation to Np^{VI}.

Plutonium. On exposure to UV light, plutonium in solutions in rather concentrated nitric acid is oxidized to give ultimately Pu^{VI}. In 3.0 *M* HNO_3, Pu^{III} is rapidly oxidized to Pu^{IV} and then, more slowly, to Pu^{VI}.[230] The two reactions occur both in air and in an atmosphere of CO_2. The formation of Pu^{VI} is apparently due to disproportionation of Pu^{IV}, which is the rate-determining step of the process. The rate of oxidation of Pu^{III} to Pu^{IV} was found to be[231] proportional to $[Pu^{3+}]$, $[H^+]$, and $[NO_3^-]$, although according to another publication,[230] $NaNO_3$ does not affect the rate of Pu^{III} oxidation.

When photoreactions of plutonium (mixed with neptunium) are carried out in the presence of a tenfold excess of hydrazine and hydroxylamine,[232,233] Pu^{III} resulting from the photo- and dark reduction of Pu^{IV} with hydrazine is always present in the solution. Upon intense UV irradiation (0.5 W cm^{-2}) of the initial Pu^{III} in 3 *M* HNO_3, its concentration decreases to a level equal to several percent of the initial concentration as soon as in several minutes. The main bulk of plutonium is converted almost completely into Pu^{IV}. Subsequently Pu^{IV} is slowly oxidized to Pu^{VI}. If faint fluxes are employed (0.015 W cm^{-2}), the process stops at the step of formation of Pu^{IV} (in ~95% yield) and Pu^{VI} + Pu^{III} (several percent). In 1 *M* and 0.17 *M* HNO_3, the sum of the steady-state concentrations of Pu^{VI} and Pu^{III} increases to 30—50%. Presumably, the major contribution to the conversions of plutonium is made by its reaction with excited nitrate ions $(NO_3^-)^*$. As for neptunium, the influence of the reactions of excited plutonium ions seems to be insignificant because the greater part of light is absorbed by nitric acid. It is worth noting that HNO_3 is the only acid in which Pu^{VI} is accumulated by a photochemical route. Evidently, this is due to the photoformation of nitrogen compounds capable of oxidizing plutonium to the hexavalent state.

Interestingly, the dark reduction of Pu^{IV} immediately after its photoirradiation in hydrazine-containing solutions of nitric acid occurs faster than that in the normal dark reaction with hydrazine.[234] This is attributed to peroxide complexes of Pu^{IV}, which are reduced faster than free plutonium(IV) ions. The H_2O_2 molecule is formed upon photolysis of HNO_3 in the presence of N_2H_4. The photoreduction of plutonium to Pu^{III} by hydrogen peroxide is much faster than that in the dark reaction.[230]

The quantum yields of the photoreduction of Pu^{VI} to Pu^{IV} and of Pu^{IV} to Pu^{III} by alcohol and hydrazine in 1.0 *M* HNO_3 amount to 0.01 and 0.03, respectively ($\lambda < 350$ nm).[220]

4.2.2. Solutions in perchloric acid. Neptunium. In 0.22—1.0 *M* $HClO_4$, neptunium(VI) undergoes photochemical reduction[215] to Np^V in the quantum yield $\phi = 0.032\pm0.011$. Presumably, the products of water photolysis are the reducing agents. According to other studies,[235,236] the major reactions in relatively concentrated solutions of $HClO_4$ are photooxidation reactions of neptunium in which any valence form of neptunium can be quantitatively converted into Np^{VI}. Since perchloric acid itself does not absorb the light of a mercury lamp, the photooxidation of neptunium(IV),(V) is attributed[220,236] to the excitation of actinide ions and their reactions with ClO_4^- ions giving rise to reduced ClO_n^- species.

In the presence of ethanol, acetaldehyde, and other reducing agents with medium activity, the neptunium(VI),(V) ions in solutions of perchloric acid undergo photochemical reduction.[235,236] Upon prolonged radiation in the presence of EtOH, neptunium entirely passes into Np^{IV}; this can be used for analytical purposes.[235]

The quantum yields of photooxidation of $Np^{IV,V}$ and photoreduction of $Np^{VI,V,IV}$ are listed in Table 3.

Photooxidation of Np^V with xenon trioxide in perchloric acid solutions gives rise[237] to Np^{VI}. The reaction has the zero order with respect to Np^V and is described by the equation

$$d[Np^V]/dt = k_1[XeO_3].$$

The reaction rate is limited by photodecomposition of XeO_3 and does not change upon an increase in the acid concentration from 0.5 to 2.0 mol L^{-1}. The k_1 value depends on the irradiation intensity and the spectral distribution of light. The average experimental value was $6.28 \cdot 10^{-6}$ s^{-1}. In the absence of light, the reaction occurs very slowly and follows apparently a different mechanism because the reaction order with respect to neptunium changes.

Plutonium. Unlike nitric acid solutions, in $HClO_4$, the final outcome of plutonium photoreactions depends on its initial state. In aerated solutions with $[HClO_4] > 0.5$ mol L^{-1}, plutonium(III) is partially converted into Pu^{IV}, while the amount of Pu^{VI} does not change.[230] According to another study,[238] reduction of Pu^{VI} does occur under these conditions, although to a small extent. Upon prolonged photolysis of Pu^{VI} or Pu^V, a quasi-steady state independent of the initial oxidation number of plutonium is established. The quantum yield of Pu^{VI} photoreduction (λ = 337 nm) increases from $5 \cdot 10^{-4}$ to $5 \cdot 10^{-3}$ as the $HClO_4$ concentration decreases from 1.65 to 0.0077 mol L^{-1}. The opposite pattern holds for the photooxidation of Pu^V. Correspondingly, the reaction rates and the Pu^{VI} : Pu^V ratio in the quasi-steady state change. The photoreduction of Pu^{VI} takes

Table 3. Quantum yields (ϕ) of photooxidation of $Np^{IV,V}$ in 0.1 (*A*), 1.0 (*B*), and 4.0 *M* $HClO_4$ (*C*) without redox reagents added and photoreduction of $Np^{VI,V,IV}$ with ethanol on exposure to light with λ = 254 nm [236]

Process	ϕ		
	A	*B*	*C*
	Photooxidation (without additives)		
$Np^{IV} \rightarrow Np^V$	0.02	0.097	0.0049
$Np^V \rightarrow Np^{VI}$	0.004	0.01	>0.01
	Photoreduction by ethanol		
$Np^{VI} \rightarrow Np^V$	0.070	0.068	0.040
$Np^V \rightarrow Np^{IV}$	0.006	0.008	0.011
$Np^{IV} \rightarrow Np^{III}$	~0.03	0.020	0.020

place even in 9.4 *M* $HClO_4$; in this case, the resulting Pu^V rapidly disproportionates and Pu^{IV} is photoreduced. Finally, Pu^{VI} is converted into Pu^{III} by 27—28%. In the photolysis of Pu^{III}, it is photooxidized[238] to Pu^{VI} to 72—73%.

The introduction of reducing agents allows quantitative preparation of plutonium in low oxidation states. Photoirradiation of a plutonium solution in the presence of H_2O_2 results in stabilization[230] of Pu^{III}. Oxalic acid reduces Pu^{VI} to Pu^{IV}, which forms a poorly soluble oxalate.[230] Ethanol in 1.32—1.42 *M* $HClO_4$ reduces Pu^{VI} to Pu^V and Pu^{IV} to Pu^{III}; in the presence of hydrazine, photoreduction of Pu^{IV} to Pu^{III} was observed.[212,220] The quantum yields of photoreduction of plutonium with ethanol and hydrazine amount to[212,220] 0.01—0.03.

Exposure to UV light sharply increases the rate and the degree of disproportionation of Pu^{IV} in perchloric acid solutions.[212,234,239] The quantum yield of disproportionation in 0.47 *M* $HClO_4$ was found to be 0.004. The process is reversible, *i.e.*, after irradiation has been terminated, the system arrives at the dark equilibrium.

Another photochemical effect discovered is a severalfold acceleration of the destruction of colloid polymeric hydrolyzed plutonium(IV) forms to afford hydrated Pu^{4+}_{aq} ions in 0.47 *M* $HClO_4$.[212,234,239] In these experiments, Pu^{IV} hydroxide was dissolved in $HClO_4$ and exposed to UV light. In more dilute $HClO_4$ (0.13—0.16 *M*), dark decomposition of plutonium(IV) polymeric species does not occur at all, only photodestruction being possible. This effect was observed for both freshly prepared and aged solutions.

4.2.3. Hydrochloric acid solutions. Neptunium. In hydrochloric acid solutions, Np^{IV} is oxidized to Np^V and then to Np^{VI}. The higher the acid concentration, the faster both reactions; at [HCl] > 3 mol L^{-1}, Np^{VI} is formed quantitatively.[240] Removal of air from the solutions does not influence the course of the reaction.

In the presence of H_2O_2, both Np^{IV} and Np^{VI} are rapidly converted into Np^V, and the addition of EtOH (2%) results in quantitative photoreduction of Np^{VI} and Np^V to Np^{IV}. Deaeration of the solutions does not change the results.[240]

Plutonium. During UV irradiation of Pu^{III} in 0.5—5.5 *M* solutions of HCl in air, Pu^{IV} is gradually accumulated; in an atmosphere of CO_2, the process occurs somewhat more slowly.[230] No formation of Pu^{VI} was observed under these conditions. A mixture of Pu^{IV} and Pu^{VI} in hydrochloric acid is almost photochemically inert. In the presence of H_2O_2, Pu^{VI} is reduced[230] first to Pu^{IV} and then (partially) to Pu^{III}.

4.2.4. Sulfuric acid solutions. Neptunium. In 1—2 *M* solutions of H_2SO_4, neptunium(IV) is photochemically oxidized[241] to Np^V and then to Np^{VI}. On prolonged irradiation under these conditions, Np^{VI} is formed quantitatively. When $[H_2SO_4]$ > 2 mol L^{-1}, an admixture of Np^{IV} remains in the solution; the higher the acid concentration, the greater its amount. If Np^V is the initial form, then Np^{VI} is produced quantitatively, at least for $[H_2SO_4] \le 3$ mol L^{-1}, and the reaction rate increases with an increase in the acid concentration. On prolonged irradiation of solutions of Np^{VI}, no changes are observed.[241]

In the presence of small additives of EtOH, photooxidation of Np^{IV} and Np^V is suppressed; for [EtOH] = 5% in 0.5—3 *M* H_2SO_4, neptunium(V),(VI) is quantitatively converted[241] into Np^{IV}.

Plutonium. The behavior of plutonium in sulfuric acid solutions is nearly the same as in hydrochloric acid solutions. Plutonium(III) undergoes photochemical oxidation to Pu^{IV}; Pu^{VI} is not formed.[230] It is of interest that Pu^{IV} is formed even on exposure to daylight but not in the dark. This indicates that the crucial role in sulfuric acid is played by reactions of excited plutonium ions rather than by reactions with the excited molecules and ions of the medium. Plutonium(VI) remains unchanged upon photoirradiation. In the presence of EtOH, photoreduction of Pu^{VI} to Pu^{IV} takes place.[230]

4.2.5. Mechanisms of photochemical reactions of transuranium element ions in acid solutions. It is clear from the above data that most of the valence forms of neptunium and plutonium are photochemically active in acid solutions even when no oxidants or reducing agents have been specially added. In a study of the mechanism of the photoreactions of neptunium in nitric acid, it was suggested that the proper excited states of neptunium play a minor role, the UV light being absorbed almost entirely by the medium. Therefore, excited nitrate ions and the products of photolysis of nitric acid, first of all, HNO_2, actively participate in the reactions. Nitrous acid appears to play an important role in the stabilization of Np^V.[216,221] In hydrochloric acid, photolysis of the ions of the medium can also be significant for the oxidation of Np^{IV} and Np^V [240]:

$$Cl^- + h\nu \rightarrow Cl^{\bullet} + e^-_{aq}, \quad (58)$$

$$Np^{4+} + Cl^{\bullet} + 2\,H_2O \rightarrow NpO_2^{+} + 4\,H^+ + Cl^-, \quad (59)$$

$$NpO_2^{+} + Cl^{\bullet} \rightarrow NpO_2^{2+} + Cl^-. \quad (60)$$

Then hydrated electrons react with protons, and the resulting hydrogen atoms recombine with evolution of H_2.

Light absorption of perchloric acid in the range of radiation of a mercury lamp is slight; therefore, in this medium, the reactions start directly with excitation of the actinide ions. It is assumed that[236] Np^{III}, Np^{IV}, and Np^V can subsequently be oxidized by perchlorate ions. Redox photoreactions of plutonium, like those of neptunium, are obviously due to the excitation of plutonium itself. This also applies to depolymerization, which is confirmed by the fact that this reaction is not accelerated on photoirradiation of solutions of Pu^{IV} in HNO_3. In this case, UV light is completely absorbed by nitric acid.[239]

Recently,[242—244] it was found that Np^V photooxidation and Np^{VI} photoreduction in solutions of nitric, hydrochloric, and perchloric acids and transformations of Pu^{V} and Pu^{VI} in perchloric acid[238] in the range of H^+ concentrations from 0.001 to 1 mol L^{-1} obey common regularities: as the acid concentration increases, the rate and the quantum yield of the former reaction increase, while those of the latter reaction decrease. Apparently, apart from the above-mentioned reactions, oxidation of Np^{V*}, Pu^{V*} and reduction of Np^{VI*}, Pu^{VI*} by water molecules also play an important role in all solutions. It is these processes that stipulate the similarity of the photochemical behavior of neptunium in any medium studied. During prolonged photolysis, a steady state is established, in which the concentrations of penta- and hexavalent forms substantially depend on $[H^+]$. Evidently, the condition for the steady state is the same as for Ce^{III}/Ce^{IV} (see Section 3.2). Calculations using the known values of rate constants for the reactions of radical products (H atoms, $OH^{\bullet}$ radicals, and some other) were carried out. It was noted that the formation of products upon recombination of these species is an ineffective process; the vast majority of radicals finally enter into the back reaction. It was suggested that the actinide species participating in the photooxidation—photoreduction are dimers.[242—244]

4.3. Extraction systems containing TBP (purex process). In Section 2.5, we have already discussed the use of photochemical methods for the isolation of U and Pu from irradiated nuclear fuel (see, for example, Refs. 95—102). These studies are concerned with systems containing TBP (purex process); their main idea is transition of plutonium into a non-extractable form, Pu^{III}, by virtue of U^{IV}, which is formed upon the photoreduction of uranyl ions. The photochemical reactions of plutonium itself should also be taken into account.[245,246]

The photochemical method also permits more complete separation of Np/Pu and Np/U pairs and isolation of neptunium in TBP-containing systems.[247] In extraction systems modeling the purex process (3 *M* HNO_3 and a solution of TBP in dodecane), on exposure to the light of a mercury lamp, neptunium is stabilized photochemically as Np^{V}, whereas plutonium is reduced to Pu^{IV}. This is the optimal result as regards the separation of these two elements; the same can be attained by adding hydrazine or hydroxylamine.[232,233,248] Stabilization of Np^{V} is related to the photo-formation of nitrous acid. About 90% of neptunium is separated from uranium in such a system.[221] Laboratory research modeling the purex process has been carried out using an eight-stage mixer-settler. At the second, fourth, and sixth stages, the emulsion was fed to a photochemical reactor. The separation gave uranium containing 10% of the initial neptunium and neptunium with 0.3% of the initial uranium.[249] Optimization of this process might substantially improve these characteristics.

When the light of a xenon lamp is employed, similar reactions take place, namely, in solutions without redox agents added, neptunium(v) is stabilized and can be better separated from U and Pu.[222] It was also proposed to use photoirradiation at the stage of neptunium(vi) extraction with tributyl phosphate. In the presence of urea, photoirradiation increases the extent of oxidation of neptunium to the oxidation state +6 because it counterbalances its partial dark reduction. Correspondingly, the extent of transfer of neptunium to the organic phase increases.[222]

Fairly complete formation of Np^{V} in 0.75—3 *M* HNO_3 was demonstrated in experiments with laser irradiation (Kr—F excimer laser). This is not hampered by excess reducing agent (iron sulfamate) or oxidant (potassium permanganate).[250,251] When a TBP extract of Np^{VI} in dodecane was photoirradiated by a laser, the resulting pentavalent neptunium was re-extracted to an aqueous phase.[252]

Studies of the photochemical methods for the reprocessing of nuclear fuel are still in progress.[253,254] Upon photochemical stabilization of neptunium(v) and plutonium(iv) in aqueous nitric acid with simultaneous or subsequent extraction with 30% TBP in dodecane, 86% of Pu and no more than 1% of Np pass to the organic phase. By varying conditions, one can carry out an equally efficient simultaneous extraction of Np^{VI} and Pu^{VI}.[253]

4.4. Other extraction systems containing neptunium and plutonium. Whereas in TBP-containing systems, photoreduction of plutonium is usually accomplished by special additives or uranium(iv), in other extraction systems, effective photoreduction of plutonium can occur upon the reaction with organic extractants or products of their decomposition. In some cases, this results in substantial differences between the partition coefficients of Pu found for extraction in the dark and those found with conventional room lighting, for example, in a water—hexanone system.[213] Photoreduction of Pu^{VI} to Pu^{IV} also takes place during its extraction by a solution of TTA in benzene,[214,255] toluene, or other hydrocarbon solvents.[255] The rate of reduction depends on the solvent; the presence of TBP decreases photoreduction of $Pu^{VI,V}$. The products of TTA photodecomposition serve as the reducing agents for plutonium; however, their composition was not determined.[255] It was found[256] that, if the extract is equilibrated with the aqueous phase, plutonium photoreduction can proceed further, *i.e.,* to the trivalent state. The reduction takes place in the aqueous phase; its rate increases with an increase in the acid concentration. Neptunium(vi) is also able to be reduced by the products of TTA photolysis in toluene.[255]

To conclude this section about the methods of photochemical separation of U, Np, and Pu, a study proposing a new method for removing impurities from gaseous UF_6 should be mentioned.[257] On exposure to UV light, the hexafluoride dissociates to give UF_5 and an F atom. In the presence of CO (fluorine atom acceptor), NpF_6 and PuF_6 are reduced by uranium pentafluoride to give a solid phase, while UF_6 is regenerated. A 5000-fold purification from plutonium and a 40-fold purification from neptunium were achieved in demonstration experiments.

4.5. Carbonate alkaline solutions of neptunium and plutonium. Neptunium. Irradiation with the light of a mercury lamp of Np^{VI} in a solution containing 0.09 *M* LiOH + 0.28 *M* K_2CO_3 and saturated with N_2O results[258] in the formation of Np^{VII}. In a carbonate solution containing neither LiOH nor N_2O, neptunium(VI) is partly reduced to Np^V upon photoirradiation.[259] In a pure alkali saturated with N_2O, no photo-formation of Np^{VII} is observed either. Photooxidation is described by the following equations:

$$CO_3^{2-} + h\nu \rightarrow {}^{\bullet}CO_3^{-} + e^-_{aq}, \quad (61)$$

$$N_2O + e^-_{aq} \rightarrow N_2 + O^-, \quad (62)$$

$$O^- + H_2O \rightleftharpoons OH^{\bullet} + OH^-, \quad (63)$$

$$OH^{\bullet} + CO_3^{2-} \rightarrow OH^- + CO_3^{\bullet -}, \quad (64)$$

$$Np^{VI} + CO_3^{\bullet -} \rightarrow Np^{VII} + CO_3^{2-}, \quad (65)$$

$$Np^{VI} + OH^{\bullet} \rightarrow Np^{VII} + OH^-. \quad (66)$$

Thus, photoexcited neptunium does not participate in these reactions and Np^{VII} is formed due to photolysis of carbonate ions. These results are consistent with previous data[260] on pulse radiolysis of N_2O-saturated alkaline carbonate solutions of neptunium(VI).

It was not until recently that the transformations of Np^{IV} and Np^V in carbonate and hydrogen carbonate solutions were studied. In the absence of any additives, Np^{IV} is slowly oxidized[259] to Np^V and then to Np^{VI}. The same result is obtained if the initial form is Np^V. However, whereas Np^{IV} entirely vanishes under any conditions studied, the oxidation of Np^V to Np^{VI} is relatively complete (not less than 94—95%) only when the pH is 9 or lower. At higher pH, the system arrives at an equilibrium between Np^V and Np^{VI} after some period of time; the same result is observed when Np^{VI} was taken as the initial form. Thus, an increase in the pH decreases the fraction of Np^{VI} in the equilibrium mixture. This is due to the fact that the rate and the quantum yield of Np^V oxidation decrease, while those for Np^{VI} reduction increase.[259] Photolysis of the carbonate ions giving rise to $CO_3^{\bullet -}$ radicals cannot result in the reduction of Np^{VI}. Most likely, the primary step of this reaction, as in photooxidation of $Np^{IV,V}$, is the reaction of the excited neptunium ion with water molecules.

When a bicarbonate—carbonate solution is saturated with N_2O, neptunium(IV),(V) photooxidation is sharply accelerated[261] and quantitative formation of Np^{VI} can be attained at pH 8.4—12.0. In this case, reactions of excited actinide ions with water are relatively insignificant and neptunium is mainly oxidized by $CO_3^{\bullet -}$ radicals. The photooxidation of Np^{IV} is also substantially accelerated[262] in the presence of Am^{III} ions, *i.e.*, they act as a photocatalyst. This is due to the fact that in the bicarbonate—carbonate medium, Am^{III} is converted fairly efficiently[263] into Am^{IV} (photoreactions of americium are considered below), which acts as the direct oxidant for Np^{IV} because the potential of the Am^{IV}/Am^{III} pair in a bicarbonate—carbonate solution is higher than the potentials of the Np^V/Np^{IV} and Np^{VI}/Np^V pairs.

Plutonium. Pulse photolysis of Pu^{VI} in Na_2CO_3 showed[264] the possibility of oxidation of Pu^{VI} by the $CO_3^{\bullet -}$ radical anion *via* a reaction similar to reaction (65). In the medium in question, Pu^{VII} is very unstable and disappears with a rate constant of $(7.61\pm0.09) \cdot 10^2\ s^{-1}$; this value does not depend on the pH in the range of 10—12.6, on the initial plutonium concentration, or on the content of Na_2CO_3 in the 5—30 mmol L^{-1} range. Selection of appropriate conditions, first of all, creation of a strongly alkaline medium, might allow one to attain photochemical stabilization of Pu^{VII} through oxidation of Pu^{VI} by the $CO_3^{\bullet -}$ radical anion.

The Pu^{IV} ion in carbonate and bicarbonate solutions is stable against UV irradiation; apparently, excited Pu^{IV} ions do not react with water molecules under these conditions. However, upon saturation of a carbonate solution (pH 11—12) with N_2O, the mechanism of photooxidation of Pu^{IV} with the $CO_3^{\bullet -}$ radicals is switched on, and Pu^{VI} can be obtained quantitatively.[261] Photooxidation of Pu^{IV} to Pu^{VI} also takes place[265] in the presence of Am^{III} (pH 10.1—10.9), which is due to the same reasons as in the case of Np^{IV}. The maximum fraction of Pu^{VI} in the experiments performed was 24% but, apparently, higher degrees of transformation of Pu^{IV} into Pu^{VI} can also be achieved by increasing the time of photolysis.[265]

4.6. Photochemical dissolution of plutonium dioxide. Dissolution of plutonium dioxide is known to require highly stringent conditions. Nevertheless, this process was performed at room temperature.[266] The reaction was carried out in 5 *M* HCl on exposure to the radiation of a mercury lamp in the presence of 0.015 *M* of uranyl and 0.2 *M* of hydrazine. Over a period of 5 h, 95.6% of PuO_2 dissolved. As the acid concentration increases, dissolution decreases. Presumably, the action of light results in excitation of the plutonium dioxide surface and in the photochemical generation of U^{IV}:

$$PuO_2^{*}\ (solid) + U^{IV} \rightarrow Pu^{III}_{aq} + U^{VI}, \quad (67)$$

$$PuO_2^{*}\ (solid) + N_2H_4 \rightarrow Pu^{III}_{aq} + N_2. \quad (68)$$

In the photochemical method of dissolution of UO_2 in nitric acid mentioned above (see Section 2.5),[114] the acceleration of the reaction was attributed to the excitation of HNO_3.

4.7. Photochemical reactions of americium ions. Photochemical reactions of americium were unknown before 1992. Analysis of the possibility of photochemical transformations of americium(III) in acid solutions[267] led to the conclusion that several conditions should be observed to obtain the result, in particular, light with $\lambda < 240$ nm and, perhaps, an inert atmosphere should be used. Apparently, the optimal medium is 0.1 *M* $HClO_4$. The last conclusion relies, in particular, on the data of radiation-chemical oxidation of americium(III) in a weakly acidic medium.[268]

Easier photooxidation of americium(III) can be expected in alkaline media or in the presence of strong ligands. Indeed, the first reactions of photoexcited americium(III) and americium(V)[263,269,270] were accomplished in bicarbonate—carbonate solutions. In the absence of redox reagents, americium(III) can be oxidized[263,269] to Am^{IV} on exposure to UV light from a mercury lamp. As opposed to the nearly quantitative photooxidation of Ce^{III},[153] the maximum fraction of Am^{IV} is only ~60% under the optimum conditions (pH 9—10 and $[CO_3^{2-}]$ = 1—2 mol L^{-1}). This might be due to the fact that the redox potential of the Am^{IV}/Am^{III} pair is higher than that of Ce^{IV}/Ce^{III}. The quantum yield of photooxidation of Am^{III} in the initial period of the reaction is close to 0.1. The Am^{IV} ion is partially reduced upon photoirradiation. At pH ≥11, oxidation of Am^{III} does not occur. The Am^V ion in bicarbonate—carbonate solutions partially disproportionates[270] to Am^{IV} and Am^{VI} on exposure to UV light. In addition, traces of Am^{III} also appear, obviously, due to photoreduction of Am^{IV}. Finally, different valence forms of americium exist as a mixture in the solution and undergo both dark and photochemical reactions with one another. The quantum yield of photodisproportionation of Am^V was estimated to be 0.003.

Quantitative formation of Am^{IV} from Am^{III} in bicarbonate—carbonate media (pH 8.5—10.5) is observed in the presence of oxidants (persulfate,[271] bromate,[272] and hypobromite ions[273]); however, in this case, the introduced additives rather than the americium ions themselves act as photoactive substances. The quantum yields of photooxidation at pH ~9.9 are 1.07, 0.20, and 0.56, respectively. The mechanism of americium oxidation includes photolysis of the oxidant as the first step, for example,

$$S_2O_8^{2-} + h\nu \rightarrow 2\ SO_4^{\bullet -} \quad (69)$$

or

$$BrO^- + h\nu \rightarrow Br^\bullet + O^-. \quad (70)$$

This is followed by the reactions

$$Br^\bullet + Br^- \rightarrow Br_2^-, \quad (71)$$

$$Br_2^- + CO_3^{2-} \rightleftharpoons 2\ Br^- + CO_3^{\bullet -}, \quad (72)$$

$$SO_4^{\bullet -} + CO_3^{2-} \rightarrow SO_4^{2-} + CO_3^{\bullet -}. \quad (73)$$

Subsequently the $CO_3^{\bullet -}$ radical ion oxidizes Am^{III}.

Americium(III) is also completely photooxidized in bicarbonate—carbonate solutions containing XeO_3 [274] or saturated with N_2O[275]; in the latter case, carbonate ions are photooxidants for americium. The oxidation starts with reactions (61)—(64); this is followed by reactions of Am^{III} with $OH^\bullet$ or $CO_3^{\bullet -}$ radicals. The method allows preparation of Am^{IV} solutions containing no foreign substances.

As the solution pH increases to 11—12, the outcome of the photoreaction appreciably changes. In the presence of N_2O, photooxidation of Am^{III} does not occur at all. Photooxidation of Am^{III} with xenon trioxide or with $S_2O_8^{2-}$, BrO_3^-, or BrO^- ions does not stop under these conditions when Am^{IV} has been formed; instead it proceeds until americium completely passes into the oxidation state +6. The mechanism of the process includes disproportionation of Am^{IV} followed by photooxidation of Am^V.

Quantitative photooxidation of Am^{III} to Am^{IV} by persulfate ions is also attained[276,277] in solutions of unsaturated HPTA, *viz.*, $PW_{11}O_{39}^{7-}$, $P_2W_{17}O_{61}^{10-}$, and $SiW_{11}O_{39}^{8-}$. The process occurs both in neutral media and in perchloric acid when its concentration does not exceed 0.1 mol L^{-1}. The highest stability of Am^{IV} is observed in solutions containing the $PW_{11}O_{39}^{7-}$ anion. The quantum yield of photooxidation is 0.1.

In ~0.1 *M* HNO_3, photolysis of Am^{III} by the light of a deuterium lamp resulted[278] in a slight formation of Am^{VI}. The concentration of americium in the experiments was about 10^{-9} mol L^{-1}; therefore, this result should be confirmed for solutions with at least microquantities of americium. In the presence of ozone, photooxidation of Am^{III} to Am^{VI} can be rather effective.[278]

4.8. Electron transfer in the processes of quenching of f—f luminescence of Tb^{III}, Pr^{III}, Eu^{III}, Am^{III}, and Cm^{III}. It was noted in Section 2.3 that one of the types of photochemical reactions of uranyl ions is intermolecular reversible electron transfer from variable-valence metal ions or intramolecular reversible electron transfer from the Cl^-, Br^-, and SCN^- ions. This process results in the quenching of luminescence of the uranyl ion but does not give new chemical products. The oxidized forms of metal ions are able to quench[279] d—f luminescence of cerium(III) in the same way. The higher the ability of the cation to be reduced, the higher the rate constant for quenching of the luminescence of Ce^{III} in aqueous sulfate solutions by Fe^{3+}, Cr^{3+}, Tl^{3+}, Eu^{3+}, or Cu^{2+}. In the case of the Cu^{2+} ion, the formation of Ce^{IV} and Cu^I was detected by pulse photolysis; subsequently, reverse electron transfer occurs between these ions.

A similar phenomenon has been found for some lanthanides and actinides excited in the f—f transition bands. Although redox reactions are not typical of ions excited in the ligand field band, in some cases reversible oxidation or reduction still does occur.

Very interesting results were obtained in a study[280—284] of luminescence of europium(III) kryptates. In the presence of cyanide complexes of some transition metals, $Fe(CN)_6^{4-}$, $Ru(CN)_6^{4-}$, $Os(CN)_6^{4-}$, and $Mo(CN)_8^{4-}$, the f—f luminescence of Eu^{3+} is quenched. This is possible under both static and dynamic conditions. In the former case, quenching is due to the formation of nonluminescing ion pairs, $[EuPODAT]^{3+}—M(CN)_6^{4-}$ (PODAT is 4,7,13,16,21-pentaoxo-1,10-diazabicyclo-[8.8.5]tricosane), while in the latter case, this is due to the intermolecular transfer of an electron to $^*Eu^{III}$ to give Eu^{II}:

$$^*[Eu(PODAT)]^{3+} + M(CN)_6^{4-} \rightarrow \rightarrow [Eu(PODAT)]^{2+} + M(CN)_6^{3-}. \quad (74)$$

The bimolecular rate constants for quenching are close to 10^8—10^9 L mol^{-1} s^{-1}. The electron transfer is confirmed by the appearance of a new absorption band in the visible region and also by the absence of a strong quenching effect in the case of Co^{III} and Cr^{III} cyanide complexes. This is due to the fact that the redox potentials of the $Co(CN)_6^{3-}/Co(CN)_6^{4-}$ and $Cr(CN)_6^{3-}/Cr(CN)_6^{4-}$ pairs are too high.[280—282] Similar luminescence quenching was discovered[283,284] for hydrated europium(III) ion. The above-listed reactions are apparently the only example of outer-sphere electron transfer to an f—f excited lanthanide ion.

The inner-sphere electron transfer resulting in quenching of europium f—f luminescence takes place in Eu^{III} thiocyanate complexes.[285] The charge transfer gives rise to the Eu^{II}—$SCN^{\bullet}$ state.

In the case of excited Tb^{III}, Pr^{III}, Am^{III}, and Cm^{III} ions, electron transfer increases the oxidation numbers of these ions. They all exhibit f—f luminescence in aqueous solutions,[116,286,287] the luminescence quantum yields being fairly high for terbium and curium. Quenching of luminescence of these ions in aqueous solutions is usually considered to occur *via* the mechanism of energy dissipation through vibrational modes of water molecules.[116,286] The luminescence of these ions is enhanced in complexes with many inorganic ligands due to the displacement of water molecules from the f-element coordination sphere. Specific properties are displayed by Pr^{III},[288] Tb^{III},[289,290] and Cm^{III} [291—294] complexes with polytungstate ligands, namely, the decatungstates $MW_{10}O_{36}^{9-}$ (M = Pr, Tb, Cm) and complexes with unsaturated HPTA. Luminescence of the above-listed f-element ions in this type of complexes is markedly attenuated and is subject to a substantial temperature dependence. Complexes of Tb^{III} with HPTA luminesce only in the frozen state,[289] and luminescence of Am^{III} is not observed at all. As shown for terbium[290] and curium,[293] this is due to the electron transfer from M^{III} to W^{VI} (M = Cm, Tb) to form a state with the M^{IV}—W^{V} CT. Electron transfer is an activated process; quenching is attenuated at low temperatures. The differences in the quenching efficiency of terbium and curium luminescence are, apparently, due to the difference in the excitation energy of these ions; the complete quenching of Am^{III} luminescence is due to the fact that the potential of the Am^{IV}/Am^{III} pair is much lower than those of the Cm^{IV}/Cm^{III} or Tb^{IV}/Tb^{III} pairs. A similar phenomenon, even more pronounced than that in complexes with HPTA, is observed in Cm^{III} complexes with heteropolymolybdotungstate anions in which no curium luminescence is observed.[295] This is due to the fact that Mo^{VI} is a much stronger oxidant than W^{VI}.

5. Conclusions

Photochemistry of ions and compounds of f-elements underlies many practically valuable methods for the separation, isolation, and utilization of these elements. An indisputable advantage of these methods is the possibility of selective action on one component of a complex mixture. Technological processes in which the purex process is combined with photochemical stages were designed. Practical engineering along this line is still in progress. Increasing attention is devoted to the use of lasers. However, many problems in the photochemistry of uranyl, lanthanides, and, especially, transuranium elements are still to be solved; most of them are related to the mechanisms of the primary steps of photoreactions. Elucidation of the characteristic features of photochemical transformations of ones ions with water requires new detailed investigations including ones making use of modern pulse equipment. The photochemistry of f-elements in the presence of various ligands is an undoubtedly interesting field; original results have been already obtained along this line and further progress should be expected.

References

1. J. G. Calvert and J. N. Pitts, *Photochemistry*, J. Wiley and Sons, New York, 1966.
2. J. A. Barltrop and J. D. Coyle, *Excited States in Organic Chemistry*, J. Wiley and Sons, London, 1975.
3. V. Balzani and V. Carassity, *Photochemistry of Coordination Compounds*, Academic Press, London, 1970, 432 pp.
4. V. Balzani, N. Sabbatini, and F. Scandola, *Chem. Rev.*, 1986, **86**, 319.
5. A. I. Kryukov and S. Ya. Kuchmii, *Osnovy fotokhimii koordinatsionnykh soedinenii* [*Foundations of Photochemistry of Coordination Compounds*], Naukova Dumka, Kiev, 1990, 280 pp.
6. A. W. Adamson, W. L. Waltz, E. Zinato, D. W. Watts, P. D. Fleischauer, and R. D. Lindholm, *Chem. Rev.*, 1968, **68**, 541.
7. P. C. Ford, R. E. Hintze, and J. D. Petersen, in *Concepts of Inorganic Photochemistry*, Eds. A. W. Adamson and P. D. Fleischauer, J. Wiley and Sons, New York, 1975, 203.
8. V. Balzani, F. Bolletta, M. Gandolfi, and M. Maestri, *Topics in Current Chemistry*, 1978, **75**, 1.
9. A. Vogler and H. Kunkley, *Top. Curr. Chem.*, 1990, **158**, 1.
10. V. Balzani, F. Barigeletti, and L. De Cola, *Top. Curr. Chem.*, 1990, **158**, 31.
11. H. Hennig, D. Rehorek, and R. D. Archer, *Coord. Chem. Rev.*, 1985, **61**, 1.
12. E. Rabinovich and R. Belford, *Spectroscopy and Photochemistry of Uranyl Compounds*, Pergamon Press, The Macmillan Company, New York, 1964.
13. H. D. Burrows and T. J. Kemp, *Chem. Soc. Rev.*, 1974, **3**, 139.
14. *Gmelin Handbook of Inorganic Chemistry*, B.: Uranium, Springer Verlag, Berlin, 1983, **A6**, 80.
15. A. L. Buchachenko and I. V. Khudyakov, *Usp. Khim.*, 1991, **60**, 1105 [*Russ. Chem. Rev.*, 1991, **60** (Engl. Transl.)].
16. A. B. Yusov and V. P. Shilov, *Usp. Khim.*, 1995, **64**, 888 [*Russ. Chem. Rev.*, 1995, **64** (Engl. Transl.)].

17. C. A. Parker, *Photoluminescence of Solutions*, Elsevier, Amsterdam, 1968.
18. J. Rabek, *Experimental Methods in Photochemistry and Photophysics*, J. Wiley and Sons, Chichester—New York, 1982.
19. T. Gangwer, *Photochemistry Relevant to Nuclear Waste Separations. A Feasibility Study*, Report BNL50715, Brookhaven National Laboratory, New York, 1977, 138 pp.
20. J. H. Wood, M. Boring, and S. B. Woodruff, *J. Chem. Phys.*, 1981, **74**, 5225.
21. V. G. Pershina, G. V. Ionova, and N. I. Suraeva, *Radiokhimiya*, 1989, **31**, 26 [*Sov. Radiochem.*, 1989, **31** (Engl. Transl.)].
22. D. M. Kern and E. F. Orlemann, *J. Am. Chem. Soc.*, 1949, **71**, 2102.
23. S. I. Nikitenko, A. P. Gai, and N. N. Krot, *Dokl. Akad. Nauk SSSR*, 1990, **312**, 402 [*Dokl. Phys. Chem.*, 1990 (Engl. Transl.)].
24. D. Greatorex, R. D. Hill, T. J. Kemp, and T. J. Stone, *J. Chem. Soc., Faraday Trans. 1*, 1974, **70**, 216.
25. R. D. Hill, T. J. Kemp, D. M. Allen, and A. Cox, *J. Chem. Soc., Faraday Trans. 1*, 1974, **70**, 847.
26. Y. Katsumura, H. Abe, T. Yotsuyanagi, and K. Ishigure, *J. Photochem. Photobiol.*, 1989, **A50**, 183.
27. J. T. Bell and S. R. Buxton, *J. Inorg. Nucl. Chem.*, 1974, **36**, 1575.
28. J. T. Bell and S. R. Buxton, *J. Inorg. Nucl. Chem.*, 1975, **37**, 1469.
29. V. Natarajan, S. V. Godbole, A. Argeknar, A. G. Page, M. D. Sastry, and P. R. Natarajan, *J. Radioanal. Nucl. Chem. (Lett.)*, 1992, **165**, 255.
30. R. Matsushima, H. Fujimori, and S. Sakuraba, *J. Chem. Soc., Faraday Trans. 1*, 1974, **70**, 1702.
31. H. D. Burrows, S. J. Formosinho, M. G. Miguel, and F. P. Coelho, *J. Chem. Soc., Faraday Trans. 1*, 1976, **72**, 163.
32. H. D. Burrows, A. C. Cardoso, S. J. Formosinho, and M. G. Miguel, *J. Chem. Soc., Faraday Trans. 1*, 1985, **81**, 49.
33. M. Moriyasu, Y. Yokoyama, and S. Ikeda, *J. Inorg. Nucl. Chem.*, 1977, **39**, 2205.
34. T. Rosenfeld-Grünwald and J. Rabani, *J. Phys. Chem.*, 1980, **84**, 2981.
35. T. Rosenfeld-Grünwald, M. Brandels, and J. Rabani, *J. Phys. Chem.*, 1982, **86**, 4745.
36. Y. Le Duigou and W. Leidert, *Z. Anal. Chem.*, 1976, **278**, 29.
37. D. D. Afonichev, Yu. I. Murinov, Yu. E. Nikitin, G. S. Parshin, and V. P. Kazakov, *Radiokhimiya*, 1978, **20**, 341 [*Sov. Radiochem.*, 1978, **20** (Engl. Transl.)].
38. V. P. Kazakov, D. D. Afonichev, G. S. Parshin, and S. S. Ostakhov, *Radiokhimiya*, 1981, **23**, 682 [*Sov. Radiochem.*, 1981, **23** (Engl. Transl.)].
39. S. A. Gaziev, L. G. Mashirov, and D. N. Suglobov, *Radiokhimiya*, 1989, **31**, No. 2, 53 [*Sov. Radiochem.*, 1989, **31** (Engl. Transl.)].
40. W.-D. Wang, A. Bakac, and J. H. Espenson, *Inorg. Chem.*, 1995, **34**, 6034.
41. Y. Mao and A. Bakac, *Inorg. Chem.*, 1996, **35**, 3925.
42. Y. Mao and A. Bakac, *J. Phys. Chem.*, 1996, **100**, 4219.
43. Y.-Y. Park, M. Harada, H. Tomiyasu, and Y. Ikeda, *J. Nucl. Sci. Technol.*, 1991, **28**, 418.
44. H. Tomiyasu, in *Innovative Laser Technologies in Nuclear Energy, Proc. 6th Int. Symp. on Advanced Nuclear Energy Research (March 23—25, 1994, Mito, Ibaraki, Japan)*, Japan Atomic Energy Research Institute, Mito, 1994, **1**, 265.
45. K. R. Butter and T. J. Kemp, *J. Chem. Soc., Dalton Trans.*, 1984, **5**, 923.
46. S. A. Gaziev, N. G. Gorshkov, L. G. Mashirov, and D. N. Suglobov, *Radiokhimiya*, 1986, **28**, 755 [*Sov. Radiochem.*, 1986, **28** (Engl. Transl.)].
47. Y. Kato and H. Fukutomi, *J. Inorg. Nucl. Chem.*, 1976, **38**, 1323.
48. R. D. Saini, P. K. Bhattacharyya, and R. M. Iyer, *J. Photochem. Photobiol.*, 1989, **A47**, 65.
49. R. D. Saini, P. K. Bhattacharyya, and R. M. Iyer, *J. Photochem. Photobiol.*, 1989, **A47**, 181.
50. G. M. Kramer, M. B. Dines, A. Kaldor, R. Hall, and Dl. McClure, *Inorg. Chem.*, 1981, **20**, 1421.
51. D. Greatorex, R. D. Hill, T. J. Kemp, and T. J. Stone, *J. Chem. Soc., Faraday Trans. 1*, 1972, **68**, 2059.
52. L. A. Margulis, I. V. Khudyakov, E. S. Klimchuk, and V. A. Kuz'min, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 13 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1990, **39**, 7 (Engl. Transl.)].
53. P. P. Levin, V. A. Kuz'min, and I. V. Khudyakov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 880 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1988, **37**, 760 (Engl. Transl.)].
54. A. L. Buchachenko, I. V. Khudyakov, E. S. Klimtchuk, L. A. Margulis, and A. Z. Yankelevitch, *J. Photochem. Photobiol.*, 1989, **A46**, 281.
55. V. N. Parmon, in *Fotokataliticheskoe preobrazovanie solnechnoi energii* [*Photocatalytic Conversion of Solar Energy*], Nauka, Novosibirsk, 1985, Part 2, 6 (in Russian).
56. J. L. Kropp, *J. Chem. Phys.*, 1967, **46**, 843.
57. A. K. Pikaev, *Sovremennaya radiatsionnaya khimiya. Radioliz gazov i zhidkostei* [*Modern Radiation Chemistry. Radiolysis of Gases and Liquids*], Nauka, Moscow, 1986, 440 pp. (in Russian).
58. H. D. Burrows and S. J. Formosinho, *J. Chem. Soc., Faraday Trans. 2*, 1977, **73**, 201.
59. M. Moriyasu, Y. Yokoyama, and S. Ikeda, *J. Inorg. Nucl. Chem.*, 1977, **39**, 2211.
60. A. Cox, T. J. Kemp, W. J. Reed, and O. Traverso, *J. Chem. Soc., Faraday Trans. 1*, 1980, **76**, 804.
61. M. Bouby, I. Billard, A. Bonnenfant, and G. Klein, *Chem. Phys.*, 1999, **240**, 353.
62. H. D. Burrows, *Inorg. Chem.*, 1990, **29**, 1549.
63. W. Mooney, F. Chauveau, T.-H. Tran-Thi, and G. Folcher, *J. Chem. Soc., Perkin Trans.*, 1988, **2**, 1479.
64. W. L. Waltz, J. Lilie, X. Xu, P. Sedlák, and H. Möckel, *Inorg. Chim. Acta*, 1999, **285**, 322.
65. M. Arvis, N. Keller, G. Folcher, and B. Hickel, *J. Photochem.*, 1983, **21**, 313.
66. S. A. Gaziev, L. G. Mashirov, and D. N. Suglobov, *Radiokhimiya*, 1989, **31**, No. 2, 48 [*Sov. Radiochem.*, 1989, **31** (Engl. Transl.)].
67. S. A. Gaziev, N. G. Gorshkov, L. G. Mashirov, and D. N. Suglobov, *Radiokhimiya*, 1986, **28**, 764 [*Sov. Radiochem.*, 1986, **28** (Engl. Transl.)].
68. S. A. Gaziev, N. G. Gorshkov, L. G. Mashirov, and D. N. Suglobov, *Radiokhimiya*, 1986, **28**, 770 [*Sov. Radiochem.*, 1986, **28** (Engl. Transl.)].
69. M. D. Marcantonatos, *Inorg. Chim. Acta*, 1977, **24**, L37.
70. M. D. Marcantonatos, *J. Chem. Soc., Faraday Trans. 1*, 1979, **75**, 2273.
71. M. D. Marcantonatos, *J. Chem. Soc., Faraday Trans. 1*, 1980, **76**, 1093.
72. M. D. Marcantonatos, *Inorg. Chim. Acta*, 1978, **26**, 41.
73. M. Deschaux and M. D. Marcantonatos, *Chem. Phys. Lett.*, 1979, **63**, 283.
74. S. J. Formosinho, M. G. Miguel, and H. D. Burrows, *J. Chem. Soc., Faraday Trans. 1*, 1984, **80**, 1717.
75. M. G. Miguel, S. J. Formosinho, A. C. Cardoso, and H. D. Burrows, *J. Chem. Soc., Faraday Trans. 1*, 1984, **80**, 1735.

76. S. J. Formosinho and M. G. Miguel, *J. Chem. Soc., Faraday Trans. 1*, 1984, **80**, 1745.
77. M. D. Marcantonatos and M. M. Pawlowska, *J. Chem. Soc., Faraday Trans. 1*, 1989, **85**, 2481.
78. M. Deschaux and M. D. Marcantonatos, *J. Inorg. Nucl. Chem.*, 1981, **43**, 361.
79. M. D. Marcantonatos and M. Deschaux, *Chem. Phys. Lett.*, 1981, **80**, 323.
80. M. Deschaux and M. D. Marcantonatos, *J. Inorg. Nucl. Chem.*, 1981, **43**, 2915.
81. M. D. Marcantonatos, *J. Chem. Soc., Faraday Trans. 1*, 1979, **75**, 2252.
82. L. A. Khamidullina, S. V. Lotnik, and V. P. Kazakov, *Dokl. Akad. Nauk*, 1993, **329**, 465 [*Dokl. Chem.*, 1993 (Engl. Transl.)].
83. L. A. Khamidullina, S. V. Lotnik, and V. P. Kazakov, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 751 [*Russ. Chem. Bull.*, 1994, **43**, 704 (Engl. Transl.)].
84. A. B. Yusov and V. P. Shilov, *Izv. Akad. Nauk, Ser. Khim.*, 2000, 282 [*Russ. Chem. Bull., Int. Ed. Engl.*, 2000, **49**, 285].
85. L. Bion, Ph. Moisy, and C. Madic, *Radiochimica Acta*, 1995, **69**, 251.
86. B. Sahoo and D. Patnaik, *Current Science*, 1959, **28**, 195.
87. B. Sahoo and D. Patnaik, *Current Science*, 1958, **27**, 243.
88. B. Sahoo and D. Patnaik, *Nature*, 1960, **185**, 683.
89. K. C. Satapathy and B. Sahoo, *Current Science*, 1967, **36**, 320.
90. C. R. Das and D. Patnaik, *Chemistry and Industry*, 1973, **14**, 699.
91. K. Singh and D. Patnaik, *Proc. Indian Acad. Sci.*, 1959, **50A**, 358.
92. K. Singh, B. Sahoo, and D. Patnaik, *Proc. Indian Acad. Sci.*, 1959, **50A**, 129.
93. M. R. Zaki, M. Y. Farah, and S. A. El-Fekey, *Acta Chim. (Budapest)*, 1974, **80**, 167.
94. V. G. Knyaginina and O. G. Nemkova, *Radiokhimiya*, 1959, **1**, 665 [*Sov. Radiochem.*, 1959, **1** (Engl. Transl.)].
95. J. L. Caroll, R. E. Burns, and H. D. Warren, *The Photoactivated Reduction of Uranium(VI) to Uranium(IV) Nitrate*, Hanford Atomic Products Operation Report HW-70543, Hanford, 1961.
96. M. Goldstein, J. J. Barker, and T. Gangwer, *A Photochemical Technique for Reduction of Uranium and Subsequently Plutonium in the Purex Process*, Report BNL 22443, Brookhaven National Laboratory, Associated Universities, Inc., Brookhaven, 1976, 16 pp.
97. M. Goldstein, J. J. Barker, and T. Gangwer, *Nuclear Engineering*, 1977, **22**, 69.
98. G. L. DePoorter and C. K. Rofer-DePoorter, in *Actinide Separations*, Eds. J. D. Navratil and W. W. Schulz, ACS Symposium Series **117**, Am. Chem. Soc., Washington, D. C., 1980, 267.
99. G. L. DePoorter and C. K. Rofer-DePoorter, *Laser-Enhanced Chemical Reactions and the Liquid State. II. Possible Applications to Nuclear Fuel Reprocessing*, Report LA-5630-MS, Vol. **2**, Los Alamos Scientific Laboratory, Los Alamos, 1976.
100. US Pat. 4131527; *Chem. Abstrs.*, 1979, **90**, 94194z .
101. L. M. Toth, J. T. Bell, J. C. Mailen, and K. E. Dodson, *An Assessment of Photochemical Applications to Specific Stages in Savannah River Plant Actinide Reprocessing Streams*, Report ORNL/TM-9755, Oak Ridge National Laboratory, Oak Ridge, 1986, 23 pp.
102. US Pat. 3620687; *Chem. Abstrs.*, 1971, **74**, 27328c.
103. US Pat. 4080273; *Chem. Abstrs.*, 1978, **89**, 13827n.
104. A. S. Kertes and M. Halpern, *J. Inorg. Nucl. Chem.*, 1961, **19**, 359.
105. C. K. Rofer-DePoorter and G. L. DePoorter, *J. Inorg. Nucl. Chem.*, 1977, **39**, 631.
106. G. L. DePoorter and C. K. Rofer-DePoorter, *J. Inorg. Nucl. Chem.*, 1978, **40**, 1895.
107. C. K. Rofer-DePoorter and G. L. DePoorter, *J. Inorg. Nucl. Chem.*, 1979, **41**, 215.
108. G. L. DePoorter and C. K. Rofer-DePoorter, *Nuclear Technology*, 1979, **43**, 132.
109. C. Miyake, T. Nakase, and Y. Sano, *J. Nucl. Sci. Technol.*, 1993, **30**, 1256.
110. Zhang Xianye, Duan-Yunfu, Zhou-Zhihong, and Hu-Jingxin, *Atomic Energy Science and Technology*, 1991, **25**, No. 3, 51.
111. S. C. Tripathi, C. S. Kedari, S. Sumathi, and A. Ramanuiam, *Proc. Trombay Symp. on Radiation and Photochemistry (Trombay, Mumbai, India, January 14—19, 1998)*, Bhabha Atomic Research Center, Trombay, 1998, Part II, p. 145.
112. A. A. Nemodruk and E. V. Bezrogova, *Zh. Analit. Khim.*, 1966, **21**, 1210 [*J. Anal. Chem. USSR*, 1966, **21** (Engl. Transl.)].
113. W. M. Riggs, *Anal. Chem.*, 1972, **44**, 390.
114. Y. Wada and K. Morimoto, *Radiochimica Acta*, 1996, **72**, 83.
115. R. T. Paine and M. S. Kite, in *Lanthanide and Actinide Chemistry and Spectroscopy*, Ed. N. M. Edelstein, ACS Symposium Series **131,** Am. Chem. Soc., Washington, D. C., 1980, 369.
116. W. de W. Horrocks and M. Albin, in *Progress in Inorganic Chemistry*, 1984, **31**, 1.
117. C. K. Jørgensen and R. Reisfeld, *Top. Curr. Chem.*, 1982, **100**, 127.
118. W. T. Carnall, in *Handbook on Physics and Chemistry of Rare Earths*, Eds. K. A. Gschneider and L. Eyring, North-Holland, Amsterdam, 1979, **3**, 171.
119. T. Donohue, in *Chemical and Biochemical Applications of Lasers*, Ed. B. C. Moore, Academic Press, New York, 1980, **5**, 239.
120. T. Donohue, *J. Am. Chem. Soc.*, 1978, **100**, 7411.
121. E. Baur, *Z. Phys. Chem.*, 1908, **63**, 683.
122. S. P. Rao, T. R. Lodka, and J. N. Gaur, *Naturwiss.*, 1961, **48**, 404.
123. R. A. Sheldon and J. K. Kochi, *J. Am. Chem. Soc.*, 1968, **90**, 6688.
124. D. Greatorex, R. D. Hill, T. J. Kemp, and T. J. Stone, *J. Chem. Soc., Faraday Trans. 1*, 1974, **70**, 216.
125. D. Greatorex and T. J. Kemp, *J. Chem. Soc., Faraday Trans. 1*, 1971, **67**, 56.
126. D. Greatorex and T. J. Kemp, *J. Chem. Soc., Faraday Trans. 1*, 1971, **67**, 1576.
127. D. Greatorex and T. J. Kemp, *J. Chem. Soc., Faraday Trans. 1*, 1972, **68**, 121.
128. T. W. Martin, J. M. Burk, and A. Henshall, *J. Am. Chem. Soc.*, 1966, **88**, 1097.
129. J. J. Weiss and D. Porret, *Nature*, 1937, **139**, 1019.
130. L. J. Heidt and M. E. Smith, *J. Am. Chem. Soc.*, 1948, **70**, 2476.
131. M. G. Evans and N. Uri, *Nature* (*London*), 1950, **166**, 602.
132. P. N. Moorthy and J. J. Weiss, *J. Chem. Phys.*, 1965, **42**, 3127.
133. T. J. Sworski, *J. Am. Chem. Soc.*, 1955, **77**, 1074.
134. T. J. Sworski, *J. Am. Chem. Soc.*, 1957, **79**, 3655.
135. T. J. Sworski, *J. Phys. Chem.*, 1963, **67**, 2858.
136. A. Nuyt and M. Zador, *Can. J. Chem.*, 1972, **50**, 2413.
137. L. Dogliotti and E. Hayon, *J. Phys. Chem.*, 1967, **71**, 3802.
138. T. W. Martin, A. Henshall, and A. Gross, *J. Am. Chem. Soc.*, 1963, **85**, 113.

139. T. W. Martin, R. E. Rummel, and R. C. Gross, *J. Am. Chem. Soc.*, 1964, **86**, 2595.
140. T. W. Martin, L. L. Swift, and J. H. Venable, *J. Chem. Phys.*, 1970, **52**, 2138.
141. V. F. Plyusnin, N. M. Bazhin, and V. M. Berdnikov, *Khimiya Vysokikh Energii*, 1972, **6**, 428 [*High Energy Chem.*, 1972, **6** (Engl. Transl.)].
142. B. Ya. Dain and A. A. Kachan, *Dokl. Akad. Nauk SSSR* [*Dokl. Akad. Sci. USSR*], 1949, **67**, 85 (in Russian).
143. L. J. Heidt and A. F. McMillan, *Science*, 1953, **117**, 75.
144. L. J. Heidt and A. F. McMillan, *J. Am. Chem. Soc.*, 1954, **76**, 2135.
145. F. H. C. Edgecombe and R. G. W. Norrish, *Nature*, 1963, **197**, 282.
146. V. P. Shilov and A. B. Yusov, *Khimiya Vysokikh Energii*, 1999, **33**, 284 [*High Energy Chem.*, 1999, **33** (Engl. Transl.)].
147. A. K. Pikaev, V. P. Shilov, and V. I. Spitsyn, *Radioliz vodnykh rastvorov lantanidov i aktinidov* [*Radiolysis of Aqueous Solutions of Lanthanides and Actinides*], Nauka, Moscow, 1983, 240 pp.
148. A. K. Pikaev, V. P. Shilov, and A. V. Gogolev, *Usp. Khim.*, 1997, **66**, 845 [*Russ. Chem. Rev.*, 1997, **66** (Engl. Transl.)].
149. L. L. Borin and A. I. Karelin, *Termodinamika okislitel'no-vosstanovitel'nykh protsessov v tekhnologii aktinidov* [*Thermodynamics of Redox Processes in Actinide Technology*], Atomizdat, Moscow, 1977, 232 pp. (in Russian).
150. *The Chemistry of the Actinide Elements*, 2nd Ed., Eds. J. J. Katz, G. T. Seaborg, and L. R. Morss, Chapman and Hall, London—New York, 1986, **1**, **2**.
151. A. V. Nikolaev, V. A. Smirnov, and E. P. Grigor'eva, *Zh. Fiz. Khim.*, 1979, **53**, 2023 [*J. Phys. Chem. USSR*, 1979, **53** (Engl. Transl.)].
152. A. A. Nemodruk, E. V. Bezrogova, and B. F. Myasoedov, *Zh. Analit. Khim.*, 1973, **28**, 1947 [*J. Anal. Chem. USSR*, 1973, **28** (Engl. Transl.)].
153. V. P. Shilov, A. B. Yusov, and V. P. Perminov, *Zh. Neorgan. Khim.*, 1996, **41**, 1266 [*Russ. J. Inorg. Chem.*, 1996, **41** (Engl. Transl.)].
154. R. W. Matthews and T. J. Sworski, *J. Phys. Chem.*, **79**, 681.
155. Y. Haas, G. Stein, and R. Tenne, *Isr. J. Chem.*, 1972, **10**, 529.
156. V. V. Korolev, N. M. Bazhin, and S. F. Chentsov, *Khimiya Vysokikh Energii*, 1980, **14**, 542 [*High Energy Chem.*, 1980, **14** (Engl. Transl.)].
157. D. D. Davis, K. L. Stevenson, and G. K. King, *Inorg. Chem.*, 1977, **16**, 670.
158. R. G. Bulgakov, V. P. Kazakov, and V. N. Korobeinikova, *Khimiya Vysokikh Energii*, 1973, **7**, 374 [*High Energy Chem.*, 1973, **7** (Engl. Transl.)].
159. D. Douglas and D. M. Yost, *J. Chem. Phys.*, 1949, **17**, 1345; 1950, **18**, 1687.
160. P. R. Ryason, *Solar Energy*, 1977, **19**, 445.
161. V. V. Korolev and N. M. Bazhin, *Chem. Phys. Lett.*, 1976, **43**, 469.
162. V. V. Korolev, N. M. Bazhin, and S. F. Chentsov, *Zh. Fiz. Khim.*, 1981, **55**, 138 [*J. Phys. Chem. USSR*, 1981, **55** (Engl. Transl.)].
163. V. V. Korolev, N. M. Bazhin, and S. F. Chentsov, *Zh. Fiz. Khim.*, 1981, **55**, 144 [*J. Phys. Chem. USSR*, 1981, **55** (Engl. Transl.)].
164. V. V. Zyryanov, V. V. Korolev, and N. M. Bazhin, *Kinetika i Kataliz*, 1979, **20**, 860 [*Kinet. Catal.*, 1979, **20** (Engl. Transl.)].
165. V. P. Kazakov, R. G. Bulgakov, and M. M. Konoplya, *Khimiya Vysokikh Energii*, 1976, **10**, 181 [*High Energy Chem.*, 1976, **10** (Engl. Transl.)].
166. Y. Haas, G. Stein, and M. Tomkiewicz, *J. Phys. Chem.*, 1970, **74**, 2558.
167. I. S. Shchegoleva, *Khimiya Vysokikh Energii*, 1982, **16**, 556 [*High Energy Chem.*, 1982, **16** (Engl. Transl.)].
168. A. V. Gogolev, I. A. Potapov, M. B. Rozenkevich, and Yu. A. Sakharovskii, *Khimiya Vysokikh Energii*, 1984, **18**, 43 [*High Energy Chem.*, 1984, **18** (Engl. Transl.)].
169. G. Stein, *Isr. J. Chem.*, 1975, **14**, 213.
170. M. Brandys and G. Stein, *J. Phys. Chem.*, 1978, **82**, 852.
171. W. J. Deal, *Solar Energy*, 1978, **21**, 69.
172. B. V. Koryakin, V. V. Rodin, and T. S. Dzhabiev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1977, 2788 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1977, **26** (Engl. Transl.)].
173. K. Tennakone and U. S. Ketipearachchi, *Chem. Phys. Lett.*, 1990, **167**, 524.
174. M. Kusaba, N. Nakashima, W. Kawamura, Y. Izawa, and C. Yamanaka, *Chem. Phys. Lett.*, 1992, **197**, 136.
175. M. Kusaba, N. Nakashima, W. Kawamura, Y. Izawa, and C. Yamanaka, *J. Alloys Comp.*, 1993, **192**, 284.
176. Y. Yamada and Shin-ichi Ohno, *Bull. Chem. Soc. Jpn.*, 1991, **64**, 926.
177. A. G. Mirochnik, N. V. Petrochenkova, and V. E. Karasev, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 1559 [*Russ. Chem. Bull.*, 1993, **42**, 1492 (Engl. Transl.)].
178. A. G. Mirochnik, N. V. Petrochenkova, V. E. Karasev, I. A. Borisov, A. P. Kulikov, and T. Nakadzima, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 958 [*Russ. Chem. Bull.*, 1994, **43**, 904 (Engl. Transl.)].
179. A. G. Mirochnik, N. V. Petrochenkova, and V. E. Karasev, *Spectroscopy Lett.*, 1995, **28**, 653.
180. T. Donohue, in *Rare Earths Modern Sci. and Technol.* (*Proc. 15th Rare Earths Res. Conf., Rolla, June 15—18, 1981*), Plenum Press, New York—London, 1982, **3**, 223.
181. G. Jiang and Q. Su, *In"yun khuasyue (Chin. J. Appl. Chem.)*, 1988, **5**, 29; *RZhKhim.*, 1989, **8**B4347.
182. V. P. Kazakov, V. V. Rykova, L. A. Khamidullina, and D. D. Afonitchev, *Inorg. Chim. Acta*, 1988, **148**, 135.
183. A. I. Voloshin, Sc. D. Thesis (Chem.), Institute of Organic Chemistry, Ural Branch of the RAS, Ufa, 1997, 384 pp. (in Russian).
184. S. S. Ostakhov, A. I. Voloshin, V. P. Kazakov, and I. A. Khusainova, *Khim. Fizika*, 1997, **16**, 79 [*Chem. Phys.*, 1997, **16** (Engl. Transl.)].
185. S. S. Ostakhov, A. I. Voloshin, V. P. Kazakov, and I. A. Khusainova, *Khim. Fizika*, 1997, **16**, 84 [*Chem. Phys.*, 1997, **16** (Engl. Transl.)].
186. V. P. Kazakov, S. S. Ostakhov, A. I. Voloshin, I. A. Khusainova, and V. V. Rykova, *Khimiya Vysokikh Energii*, 1997, **31**, 207 [*High Energy Chem.*, 1997, **31** (Engl. Transl.)].
187. S. S. Ostakhov, A. I. Voloshin, V. P. Kazakov, and N. M. Shavaleev, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 1511 [*Russ. Chem. Bull.*, 1998, **47**, 1466 (Engl. Transl.)].
188. S. Tsukahara, M. Fujiwara, and H. Watarai, *Chem. Lett.*, 2000, 412.
189. N. Sh. Ableeva, A. I. Voloshin, S. S. Ostakhov, A. G. Kukovinets, V. N. Korobeinikova, V. P. Kazakov, and G. A. Tolstikov, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 1762 [*Russ. Chem. Bull.*, 1994, **43**, 1667 (Engl. Transl.)].
190. M. D. Marcantonatos, M. Deschaux, and J.-J. Vuilleumier, *J. Chem. Soc., Faraday Trans. 2*, 1984, **80**, 1569.

191. M. D. Marcantonatos, M. Deschaux, and J.-J. Vuilleumier, *Chem. Phys. Lett.*, 1982, **91**, 149.
192. Y. Yamada and Shin-ichi Ohno, *Chem. Lett.*, 1991, 465; *RZhKhim.*, 1991, **22**B4460.
193. N. Nakashima, M. Kusaba, Y. Izawa, C. Yamanaka, and W. Kawamura, in *Innovative Laser Technologies in Nuclear Energy, Proc. 6th Int. Symp. on Advanced Nuclear Energy Research (March 23—25, 1994*), Japan Atomic Energy Research Institute, Mito, 1995, **2**, 891.
194. N. Nakashima, S. Nakamura, S. Sakabe, H. Schillenger, Y. Y. Hamanaka, C. Yamanaka, M. Kusaba, N. Ishihara, and Y. Izawa, *J. Phys. Chem.*, 1999, **103**, 3910.
195. T. Donohue, *Chem. Phys. Lett.*, 1979, **61**, 601.
196. T. Donohue, *J. Less. Comm. Met.*, 1983, **4**, 405.
197. T. Donohue, *J. Chem. Phys.*, 1977, **67**, 5402.
198. T. Donohue, in *Rare Earth Mod. Sci. and Technol.*, New York—London, 1978, p. 585.
199. US Pat. 4172775; *Chem. Abstrs.*, 1979, **90**, 106588w.
200. T. Donohue, *Optical Engineering*, 1979, **18**, 181.
201. Lufu Qiu, Xihui Kang, and Tongshend Wang, *Separation Science and Technol.*, 1991, **26**, 199.
202. T. Hirai and I. Komasawa, in *Solv. Extr. Process Ind., Pap. ISEC'93 (York, September 9—15, 1993)*, London—New York, 1993, **1**, 356; *RZhKhim.*, 1994, **10**L8.
203. Ruixiang Li and Rudong Yang, *Gaoden syuesyao khuasyue syuebao (Chem. J. Chin. Univ.)*, 1990, **11**, 212; *RZhKhim.*, 1991, **7**B 4377.
204. L. V. Shastri, N. P. K. Krishnan, T. K. S. Murthy, and J. P. Mittal, *J. Photochem.*, 1981, **17**, 150.
205. S. Tsushima, S. Nagasaki, and A. Suzuki, *J. Nucl. Sci. Technol.*, 1995, **32**, 154.
206. G. L. Sharipov, S. S. Ostakhov, N. Sh. Ableeva, A. I. Voloshin, V. P. Kazakov, and G. A. Tolstikov, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 1824 [*Russ. Chem. Bull.*, 1993, **42**, 1748 (Engl. Transl.)].
207. V. P. Kazakov, A. I. Voloshin, S. S. Ostakhov, I. A. Khusainova, and E. V. Zharinova, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 724 [*Russ. Chem. Bull.*, 1997, **46**, 693 (Engl. Transl.)].
208. V. P. Kazakov, *Khemilyuminestsentsiya uranila, lantanidov i d-elementov* [*Chemiluminescence of Uranyl, Lanthanides, and d-Elements*], Nauka, Moscow, 1980, 176 pp. (in Russian).
209. S. V. Lotnik and V. P. Kazakov, *Nizkotemperaturnaya khemilyuminestsentsiya* [*Low-Temperature Chemiluminescence*], Nauka, Moscow, 1987, 176 pp. (in Russian).
210. G. L. Sharipov, Sc. D. Thesis (Chem.), Institute of Organic Chemistry, Ural Branch of the RAS, Ufa, 1992, 339 pp. (in Russian).
211. M. Elbanowski, B. Makowska, K. Staninski, and M. Kaczmarek, *J. Photochem. Photobiol.*, 2000, **A130**, 75.
212. J. T. Bell and H. A. Friedman, *J. Inorg. Nucl. Chem.*, 1976, **38**, 831.
213. L. L. Burger, I. M. Rehn, and C. M. Slansky, *USAEC Rep. HW-19949*, 1952.
214. A. S. G. Mazumdar and C. K. Sivaramakrishnan, *J. Inorg. Nucl. Chem.*, 1965, **27**, 2423.
215. A. J. Zielen, J. C. Sullivan, and D. Cohen, *J. Inorg. Nucl. Chem.*, 1958, **7**, 378.
216. A. A. Nemodruk, E. V. Bezrogova, S. A. Ivanova, and Yu. P. Novikov, *Zh. Analit. Khim.*, 1972, **27**, 2414 [*J. Anal. Chem. USSR*, 1972, **27** (Engl. Transl.)].
217. Yu. P. Novikov, *J. Radioanal. Nucl. Chem.*, 1974, **21**, 519.
218. L. M. Toth and H. A. Friedman, *Radiochimica Acta*, 1980, **27**, 173.
219. V. Ya. Galkin, S. V. Krutitskii, N. N. Lazarev, N. Ya. Mishin, and V. N. Romanovskii, *Radiokhimiya*, 1985, **27**, 494 [*Sov. Radiochem.*, 1985, **27** (Engl. Transl.)].
220. L. M. Toth, J. T. Bell, and H. A. Friedman, in *Actinide Separation*, Eds. J. D. Navratil and W. W. Schulz, ACS Symposium Ser. No. **117**, Washington, D. C., 1980, p. 253.
221. G. Uchiyama, T. Kihara, S. Hotoku, S. Fujine, and M. Maeda, in *Innovative Laser Technologies in Nuclear Energy, Proc. 6th Int. Symp. on Advanced Nuclear Energy Research (Mito, March 23—25, 1994)*, Japan Atomic Energy Research Institute, Mito, 1995, 906.
222. T. Fukasawa, T. Ikeda, and F. Kawamura, *Eur. J. Solid State Inorg. Chem. (Suppl.)*, 1991, **28**, 73.
223. H. A. Friedman and L. M. Toth, *J. Inorg. Nucl. Chem.*, 1981, **43**, 1611.
224. Y. Wada, K. Morimoto, and T. Goibuchi, *J. Nucl. Sci. Technol.*, 1995, **32**, 1018.
225. V. S. Koltunov, M. F. Tikhonov, and M. P. Shapovalov, *Radiokhimiya*, 1976, **18**, 255 [*Sov. Radiochem.*, 1976, **18** (Engl. Transl.)].
226. V. S. Koltunov and M. F. Tikhonov, *Radiokhimiya*, 1973, **15**, 195 [*Sov. Radiochem.*, 1973, **15** (Engl. Transl.)].
227. J. F. Wagner, in *12emes J. des Actinides (24—25 Mai, 1982*), Orsay, 1982, p. 64.
228. M. Takahashi, T. Nishi, T. Ikeda, and H. Karasawa, in *Transuranium Elements. A Half Century*, Eds. L. R. Morss and J. Fuger, ACS, Washington, D. C., 1992, p. 195.
229. T. Fukasawa and F. Kawamura, *J. Nucl. Sci. Technol.*, 1991, **28**, 27.
230. P. N. Palei, A. A. Nemodruk, and E. V. Bezrogova, *Radiokhimiya*, 1969, **11**, 300 [*Sov. Radiochem.*, 1969, **11** (Engl. Transl.)].
231. D. Yunfu, Z. Xianye, Z. Zhihong, H. Jinxin, and L. Shuyen, *J. Nucl. Radiochem.*, 1987, **9**, 200; *RZhKhim.*, 1988, **7**B4506.
232. Y. Wada, K. Wada, T. Goibuchi, and H. Tomiyasu, *J. Nucl. Sci. Technol.*, 1994, **31**, 700.
233. Y. Wada, K. Morimoto, and H. Tomiyasu, in *Innovative Laser Technologies in Nuclear Energy, Proc. 6th Int. Symp. on Advanced Nuclear Energy Research (Mito, March 23—25, 1994)*, Japan Atomic Energy Research Institute, Mito, 1995, 916.
234. J. T. Bell, L. M. Toth, and H. A. Friedman, in *Plutonium Chemistry*, Eds. W. T. Carnall and G. R. Choppin, ACS Symposium Ser. No. **216**, Washington, D. C., 1983, 263.
235. A. A. Nemodruk, E. V. Bezrogova, S. A. Ivanova, and Yu. P. Novikov, *Zh. Analit. Khim.*, 1972, **27**, 73 [*J. Anal. Chem. USSR*, 1972, **27** (Engl. Transl.)].
236. H. A. Friedman, L. M. Toth, and M. M. Osborne, *J. Inorg. Nucl. Chem.*, 1979, **41**, 1339.
237. J. M. Cleveland and G. J. Werkema, *Nature*, 1967, **215**, 732.
238. V. P. Shilov and A. B. Yusov, *3 Ros. konf. po radiokhimii (S.-Peterburg, 28 noyabrya—1 dekabrya 2000)* [*3rd Russian Conference on Radiochemistry (St. Petersburg, November 28—December 1, 2000)*], *Abstrs.*, Radium Institute, St. Petersburg, 2000, 19.
239. H. A. Friedman, L. M. Toth, and J. T. Bell, *J. Inorg. Nucl. Chem.*, 1977, **39**, 123.
240. A. A. Nemodruk, E. V. Bezrogova, S. A. Ivanova, and Yu. P. Novikov, *Zh. Analit. Khim.*, 1972, **27**, 1270 [*J. Anal. Chem. USSR*, 1972, **27** (Engl. Transl.)].
241. A. A. Nemodruk, E. V. Bezrogova, S. A. Ivanova, and Yu. P. Novikov, *Zh. Analit. Khim.*, 1973, **28**, 379 [*J. Anal. Chem. USSR*, 1973, **28** (Engl. Transl.)].

242. V. P. Shilov and A. B. Yusov, *Radiokhimiya*, 1995, **37**, 513 [*Russ. Radiochem.*, 1995, **37**, 473 (Engl. Transl.)].
243. V. P. Shilov and A. B. Yusov, *Radiokhimiya*, 1996, **38**, 421 [*Russ. Radiochem.*, 1996, **38**, 395 (Engl. Transl.)].
244. V. P. Shilov and A. B. Yusov, *Radiokhimiya*, 1996, **38**, 424 [*Russ. Radiochem.*, 1996, **38**, 398 (Engl. Transl.)].
245. L. M. Toth, H. A. Friedman, and J. T. Bell, *Photochemical Separation of Actinides in the Purex Process*, Report CONF 770506, Oak Ridge National Laboratory, Oak Ridge, 1977.
246. J. T. Bell and L. M. Toth, *Radiochimica Acta*, 1978, **25**, 225.
247. H. A. Friedman and L. M. Toth, *Photo-Reduction Process for Separating Neptunium from a TBP Solution Containing Uranium, Plutonium, and Neptunium*, Patent Appl., Oct., 1980.
248. Y. Wada, K. Morimoto, T. Goibuchi, and H. Tomiyasu, *Radiochim. Acta*, 1995, **68**, 233.
249. G. Uchiyama, T. Kihara, S. Hotoku, S. Fujine, and M. Maeda, *Radiochim. Acta*, 1998, **51**, 29.
250. Y. Enokida and A. Suzuki, *Nuclear Technology*, 1989, **88**, 47.
251. Y. Enokida, A. Suzuki, and R. Kiyose, in *World Congress III of Chemical Engineering, I, September 21—25, 1986*, Tokyo, Japan, 1986, 700.
252. Y. Enokida and A. Suzuki, *J. Nucl. Sci. Technol.*, 1989, **26**, 770.
253. S. Sasaki, Y. Wada, and H. Tomiyasu, *Prog. Nucl. Energy*, 1998, **32**, 403.
254. *Chem. Abstrs.*, 1998, **128**, 120854q.
255. G. R. Choppin and A. Saito, *Radiochim. Acta*, 1984, **35**, 149.
256. S. K. Nayak, P. R. Vasudeva Rao, and C. K. Mathews, in *Radiochem. and Radiat. Chem. Symp., Kanpur., Dec. 9—13, 1985*, Prepr. Vol., Bombay, 1986, 492; *RZhKhim.*, 1987, **12**B4351.
257. J. V. Beitz and C. W. Williams, in *Transuranium Elements. A Half Century*, Eds. L. R. Morss and J. Fuger, Amer. Chem. Soc., Washington, D. C., 1992, p. 168.
258. V. P. Shilov, E. S. Stepanova, and N. N. Krot, *Radiokhimiya*, 1980, **22**, 53 [*Sov. Radiochem.*, 1980, **22** (Engl. Transl.)].
259. V. P. Shilov and A. B. Yusov, *3 Ros. konf. po radiokhimii (S.-Peterburg, 28 noyabrya—1 dekabrya 2000)* [*3rd Russian Conference on Radiochemistry (St. Petersburg, November 28—December 1, 2000)*], Abstrs., Radium Institute, St. Petersburg, 2000, 49.
260. A. V. Gogolev, V. P. Shilov, and A. K. Pikaev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 20 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1989, **38**, 13 (Engl. Transl.)].
261. V. P. Shilov and A. B. Yusov, *Radiokhimiya*, 1995, **37**, 509 [*Russ. Radiochem.*, 1995, **37**, 469 (Engl. Transl.)].
262. V. P. Shilov and A. B. Yusov, *Radiokhimiya*, 1995, **37**, 203 [*Russ. Radiochem.*, 1995, **37**, 186 (Engl. Transl.)].
263. V. P. Shilov and A. B. Yusov, *Khimiya Vysokikh Energii*, 1995, **29**, 358 [*High Energy Chem.*, 1995, **29** (Engl. Transl.)].
264. R. D. Saini and P. K. Bhattacharyya, *Radiat. Phys. and Chem.*, 1986, **27**, 189.
265. V. P. Shilov and A. B. Yusov, *Radiokhimiya*, 1995, **37**, 507 [*Russ. Radiochem.*, 1995, **37**, 467 (Engl. Transl.)].
266. B. S. Panigrahi, T. G. Srinivasan, and P. R. Vasudeva Rao, *Radiochim. Acta*, 1990, **50**, 205.
267. H. A. Friedman, *Feasibility Study for the Oxidation of Am^{III} by Photolysis*, Report ORNL/TM-**7359**, Oak Ridge National Laboratory, Oak Ridge, 1980, 15 pp.; *Energy Research Abstrs.*, 1981, **6**, 5154.
268. V. B. Nikolaevskii, V. P. Shilov, N. N. Krot, and A. K. Pikaev, *Radiokhimiya*, 1976, **18**, 368 [*Sov. Radiochem.*, 1976, **18** (Engl. Transl.)].
269. A. B. Yusov and V. P. Shilov, *Mendeleev Commun.*, 1993, **3**, 83.
270. A. B. Yusov and V. P. Shilov, *Khimiya Vysokikh Energii*, 1995, **29**, 452 [*High Energy Chem.*, 1995, **29** (Engl. Transl.)].
271. A. B. Yusov and V. P. Shilov, *Radiokhimiya*, 1992, **34**, 21 [*Russ. Radiochem.*, 1992, **34** (Engl. Transl.)].
272. A. B. Yusov and V. P. Shilov, *Radiokhimiya*, 1993, **35**, 38 [*Russ. Radiochem.*, 1993, **35** (Engl. Transl.)].
273. V. P. Shilov and A. B. Yusov, *Radiokhimiya*, 1993, **35**, 61 [*Russ. Radiochem.*, 1993, **35** (Engl. Transl.)].
274. A. B. Yusov, A. V. Anan'ev, and V. P. Shilov, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 953 [*Russ. Chem. Bull.*, 1994, **43**, 899 (Engl. Transl.)].
275. V. P. Shilov and A. B. Yusov, *Radiokhimiya*, 1993, **35**, 38 [*Russ. Radiochem.*, 1993, **35** (Engl. Transl.)].
276. A. B. Ioussov and V. P. Shilov, in *Extended Abstrs., 4th Int. Conf. Nucl. Radiochem. (St. Malo, France, Sept. 8—13, 1996)*, Institute de Physique Nucleaire, Orsay, **1**, C—P11.
277. A. B. Yusov and V. P. Shilov, *Radiokhimiya*, 1997, **39**, 244 [*Russ. Radiochem.*, 1989, **31** (Engl. Transl.)].
278. S. Tsushima, S. Nagasaki, and A. Suzuki, *Separation Sci. Technol.*, 1996, **31**, 2443.
279. R. P. Asbury, G. S. Hammond, P. H. P. Lee, and A. T. Poulos, *Inorg. Chem.*, 1980, **19**, 3461.
280. N. Sabbatini, M. Ciano, S. Dellonte, A. Bonazzi, and V. Balzani, *Inorg. Chim. Acta*, 1984, **94**, 86.
281. N. Sabbatini, A. Bonazzi, M. Ciano, and V. Balzani, *J. Am. Chem. Soc.*, 1984, **106**, 4055.
282. N. Sabbatini and V. Balzani, *J. Less-Common Metals*, 1985, **112,** 381.
283. N. Sabbatini, S. Perathoner, S. Dellonte, G. Lattanzi, and V. Balzani, *J. Less-Common Metals*, 1986, **126**, 329.
284. N. Sabbatini, S. Perathoner, G. Lattanzi, S. Dellonte, and V. Balzani, *Inorg. Chem.*, 1988, **27**, 1628.
285. V. P. Gruzdev and V. L. Ermolaev, *Optika i Spektroskopiya* (*Optics and Spectroscopy*), 1977, **42**, 781 (in Russian).
286. J. V. Beitz and J. P. Hessler, *Nuclear Technology*, 1980, **51**, 169.
287. J. V. Beitz, G. Jursich, and C. Sullivan, *J. Less-Common Metals*, 1986, **126**, 301.
288. M. J. Stillman and A. J. Thomson, *J. Chem. Soc., Dalton Trans.*, 1976, 1138.
289. S. V. Bel'tyukova, N. S. Poluektov, T. B. Kravchenko, and L. I. Kononenko, *Dokl. Akad. Nauk SSSR*, 1978, **242**, 1340 [*Dokl. Chem.*, 1978 (Engl. Transl.)].
290. G. Blasse, G. J. Dirksen, and F. Zonnevijlle, *Chem. Phys. Lett.*, 1981, **83**, 449.
291. A. B. Yusov, A. M. Fedoseev, V. I. Spitsyn, and N. N. Krot, *Dokl. Akad. Nauk SSSR*, 1986, **288**, 681 [*Dokl. Chem.*, 1986 (Engl. Transl.)].
292. A. B. Yusov and A. M. Fedoseev, *Zh. Prikl. Spektroskopii*, 1988, **49**, 929 [*J. Appl. Spectr.*, 1988, **49** (Engl. Transl.)].
293. A. B. Yusov and A. M. Fedoseev, *Radiokhimiya*, 1989, **31**, 19 [*Sov. Radiochem.*, 1989, **31** (Engl. Transl.)].
294. A. B. Yusov and A. M. Fedoseev, *Radiokhimiya*, 1990, **32**, 73 [*Sov. Radiochem.*, 1990, **32** (Engl. Transl.)].
295. A. B. Yusov and A. M. Fedoseev, *Radiokhimiya*, 1992, **34**, 61 [*Russ. Radiochem.*, 1992, **34** (Engl. Transl.)].

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