A Spectroscopic Study of Th (IV) Ion in Aqueous Medium and its Analytical Importance

A

Thesis Submitted

In partial fulfillment of the requirements for the

Degree of

Master of Science in Chemistry

Submitted by:

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Candidate's Declaration

I hare by declare that the work being presented in the dissertation entitled **"A Spectroscopic Studies of Th(IV) ion in Aqueous Medium and its Analytical Importance"** in partial fulfillment of the requirement for the award of degree of Master of Science in Chemistry in the School of Chemistry and Biochemistry, Thapar University, Patiala, is my own work during the period of January 2010 to July 2010 under the supervision of Dr. Ashok Kumar S.K., Lecturer, School of Chemistry and Biochemistry, Thapar University, Patiala. I have not submitted the matter embodied in this dissertation for the award of any other degree.

Puja Rani

Patiala

Date: 7thJuly, 10

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This is to certify that the above statement made by the candidate is correct and true to the best of knowledge.

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Certificate

This is certify that the project **"A Spectroscopic Studies of Th (IV) on in Aqueous Medium and its Analytical Importance"** being submitted by Ms. Puja Rani in partial fulfillment of requirements for the award of degree of Master of Science in Chemistry in the School of Chemistry and Biochemistry, Thapar University Patiala, is a bonifide work carried out under the supervision of Dr. Ashok Kumar S.K. and that no part of this project has been submitted for the award of any other degree.

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Thesis Abstract

When thorium nitrate dissolves in a water, it is known that hydrolysis of Th^{4+} occurs at pH around 3 leading to the formation of $[Th(OH)]^{3+}$,$[Th(OH)_2]^{2+}$, $[Th(OH)_3]^{+}$, $[Th(OH)_4]$ and some dimeric and polymeric species of Th^{4+} ion. To study electronic transition properties these species measured absorbance properties of concentration range from $1x10^{-5}$M to 10^{-9}M Th^{4+}. The narrow working range of Th(IV) ion lies between $7x10^{-6}$ M to $5x10^{-7}$M above $7x10^{-6}$ M and below $5x10^{-7}$M Th^{4+} concentration no absorbance peak in the region of 190nm to 400nm. This work describes here out of four tetravalent ions present in the group IVB i.e., Ti^{4+}, Zr^{4+}, Hf^{4+} only Th^{4+} is giving UV absorbance peak in the region of 205nm. This evidence shows that Th^{4+} is belong to actinide series not in transition series. Moreover, this peak is absorbed only in water medium and does not exhibits any electronic transition properties in other solvents like methanol (CH_3OH), ethanol(C_2H_5OH), acetone (CH_3COCH_3), dimethylsulphoxide (CH_3CSCH_3), diethyl ether$(C_2H_5)_2O$ and tetrahydrofurane (C_5H_4O). Theoretically, the structures and absorption spectra of all possible species of Th(IV) hydrolysis were calculated using Gaussian 03 programme and B_3LYP density functional method with the SDD basis set in ground state and TD-SCF excited state.

List of Tables and Figures

Chapter-1

INTRODUCTION

Thorium is a naturally occurring radioactive element; atomic number 90, with an atomic mass of 232.0381. Thorium is second element of 5f actinide series. Discovered in 1828 by J.J. Berzelius in a Norwegian mineral, thorium was named after Thor, the Scandinavian god of thunder. Thorium was first isolated in its isolated form. The chemistry of thorium is similar to that of lanthanides and group of 4 elements (Ti, Zr, and Hf) and is dominated by the +4 oxidation state. Thorium is generally more acidic than the lanthanides, but less acidic than other light actinides, e.g., U, Np, and Pu as expected based on its larger ionic radius (Th, 1.08 A^0).The elemental Th is composed of 25 radio isotopes, ranging in atomic mass from 212 to 236 with half lives of seconds to 10^{10} years (1). Natural Th consists almost entirely of primordial $^{232}Th_{90}$ ($t_{1/2}$ =$1.4x10^{10}$ years), due to its extremely long-life relative to the other Th isotopes. As such, when chemical equilibrium is established, ^{232}Th determines the chemical fate and speciation of all Th isotopes. In seawater, ^{232}Th is present pM concentrations. Thorium isotope concentrations and ratios, with parent and daughter isotope concentrations are used to date and study the formation and metamorphosis of rocks and sediment (2). In marine systems, Th has proven to be a very useful tracer of a wide range of oceanographic processes ranging from particle cyclic (3) and carbon export flux (4) to boundary scavenging (5) and paleo circulation (6). Thorium is mainly used in commercial lantern mantles refractory materials, electronic components, alloys utilized for jet engine components, as a catalyst in the chemical industry, in nuclear medicine and in nuclear reactor fuels.

1.1 Toxicity of Thorium

Thorium is potentially hazardous in a few ways. Finely divided thorium metal and hydrides can be explosive or inflammatory hazards with respect to oxygen and halogens. Finely divided ThO_2 and other inorganic salts also present an inhalation and irritation hazard (7). Generally, the use of standard precautions, skin covering, and a conventional dust respirator should be sufficient. The long half-life of ^{232}Th makes it a minimal radiation hazard. External radiological hazards are generally not of concern since the γ-rays from thorium daughter products have low abundance and many are in the X-ray range, i.e., <85 keV, where they will be absorbed in the source material. If Th(IV) is injected as the soluble nitrate form, it can cause hemolysis (8). Thorium is generally insoluble in the presence of organic complexing agents and mainly retained in the bones, lungs, lymph nodes, and parenchymatous tissues (9-10). Prolonged retention of thorium, particularly in a fixed location, allows the possibility of radiation damage by the energetic alpha particles of some of the short-lived daughter members of the decay chain, of which there are five for every thorium alpha. Thorotrast (colloidal ThO_2) was once used as a radiopaque agent in medicine. Its injection in a dose of 2.0-15.0 g caused rises in body temperature, nausea, and injury to tissues at the injection site, followed by anemia, leucopenia, and impairment of the reticulo-endothelial system (11-13).Thorium compounds are legally classified as source materials for nuclear energy and thus are regulated by various government agencies (NRC).

1.2 Position of Thorium in Periodic Table

Continuing on from mercury, which follows gold, we come via the noble gas radon and the radioelements Fr and Ra to actinium (89), with the electron configuration $7s^2$ $6d^5$. Here we might expect, by to what happened at lanthanum, that in the following elements electrons would enter the 5f orbitals, preceding a lanthanide like series of fifteen elements. What actually occurs is, unfortunately, not so simple, although immediately following lanthanum, the 4f orbitals become decisively more favorable than the 5d orbitals for the electrons entering in the succeeding elements, there is apparently not so great a difference between the 5f and 6d orbitals until thus for the elements immediately following Ac, and their ions, there may be electron in the 5f or 6d orbitals or both. Since it appears that later on, after four or five more electrons have been added to the Ac configuration, the 5f electrons do become definitely the more stable, and since the elements from about americium on do show moderately homologous chemical behavior, it has become accepted practice to all the fifteen elements beginning with Ac the actinide elements. Hence, the behavior of the actinide elements lies between those of the 3d, 4d transition and 4f series because the 5f orbitals are not so were shielded as are the 4f orbitals, although not so expected as are the d orbitals in the d- block elements.

1.3 Hydration and Hydrolysis in Aqueous Solution

Aqueous and non aqueous co-ordination chemistry of thorium dominated by the extremely stable tetravalent ion Th(IV). Except in a few rare cases in non-aqueous environments where extremely large and sterically demanding ligands are used, and air and moisture are rigorously excluded, lower oxidation states are generally unstable (14). Being a third metal ion, Th^{+4} has the greatest affinity for "hard" donor atoms, e.g. N, O, F. Due to the large ionic radius of tetravalent thorium(1.08A^0) co-ordination complexes of Th^{+4} generally display variable and high co-ordination numbers, typically 8, 9, 10 or higher. Eight co-ordinate complexes are most common and the energy differences between the various common eight co-ordinate polyhedral geometries are small. Th^{+4} hydrolysis has been studied by a number of researchers, and a many of these studies indicated stepwise hydrolysis to yield monomeric products of formula $[Th(OH)_n]^{4-n}$ with n=1-4 in addition to a number of polymeric species and colloid formation (15-17). In the most recent critical review, a comprehensive set of hydrolysis constants or the stepwise formation of $[Th(OH)]^{3+}$, $[Th(OH)_2]^{2+}$, $[Th(OH)_3]^{+}$ and $[Th(OH)_4]$ have been studied (18). All hydrolyzed solutions are known to contain hydrolysis polymers and the most reliable models include the presence of dimmers $[Th_2(OH)_2]^{4+}$ and $[Th_2(OH)_4]^{4+}$ tetramers $[Th_4(OH)_8]^{8+}$ and $[Th_4(OH)_{12}]^{4+}$ and hexamers $[Th_6(OH)_{14}]^{10+}$ and $[Th_6(OH)_{15}]^{9+.}$The solubility product for ThO_2 and $Th(OH)_4$ have also been studied .the solubility product for these compounds depends on the degree of crystallization and solutions conditions.

1.4 Theoretical Studies

Computational chemistry has become an indispensable tool for the experimental chemist. Today, computational used by the chemistry community to back up experimental results to interpret and rationalize results, to compare experimental with simulated data, to get an idea of a molecular structure, or just to create a graphical representation of a molecule, its molecular orbitals or its electrostatic potential. Progress in computational chemistry has allowed a new quality of research in chemistry, most modern chemists creatively use the computer at various levels of their work, for example to get an idea of the 3D structure of molecules of interest and to understand chemical bonding, stability and so on. It is now possible to calculate the stability of a molecule, or even a reaction path, before going into the laboratory to try the synthesis in practice. Also, it is common practice to simulate properties and to compare them with experiment; most importantly for infrared (IR), visible, Raman and nuclear magnetic resonance spectra. This combination of visualization and calculation is often covered computational chemistry or molecular modeling.

There are two distinct methods to calculate molecular structure.

- Molecular mechanics
- Quantum mechanics

Molecular mechanics (MM) was first developed in the early 1970 by two group of chemical researchers. In molecular mechanics, a mechanical force field is defined that is used to calculate energy for the molecule under study. The energy calculated is often called the strain energy or steric energy of the molecule. The force field is composed of several components, such as bond-stretching energy, angle-bonding energy, and bond –formation energy energy. A typical force field expression might be represented by the following composite expression.

$$E_{strain} = E_{stretch} + E_{angle} + E_{torsion} + E_{oop} + E_{vdw} + E_{dipole}$$

To calculate the final strain energy for a molecule, the computer systematically changes every bond length, bond angle, and torsional angles in the molecule, recalculating the strain energy each time , keeping each change that minimize the total energy and rejecting those that increase the energy. In other words, all the bond length and angles are changed until the energy of the molecule is minimized.

Molecular mechanics will perform the following tasks well:

- It will give good estimate for the actual bond lengths and angles in a molecule.
- It will find the best conformation for a molecule.

Molecular mechanics will not calculate the following properties

- It will not calculate thermodynamic properties such as heat of formation of a molecule.
- It will not calculate electron distribution changes or dipole moments
- It will not calculate molecular orbital or their energies.
- It will not calculate infrared, NMR or ultraviolet spectra.

1.5 Quantum Mechanics

Quantum mechanics computer programs can calculate heats of formation and the energy of transition states. The shapes of the orbitals can be displayed in three dimensions. Important properties can be mapped on to the surface of a molecule. With these programs, the chemist can visualize concepts and properties in a way that the mind can not readily imagine. Often, this visualization is the key to understanding and to solve a problem. To solve the electronic structure and energy of a molecule, quantum mechanics requires the wave function the Ψ(psi) that describes the distribution of all the electrons within the system. The nuclei are assumed to have relatively small motions and to be essentially fixed in their equilibrium position. The average energy of the system is calculated by using the Schrodinger equation.

$$H\Psi=E\Psi$$

Where, H the Hamiltonian operator is a multi-term transition that evaluates or the potential energy contributions (electron–electron repulsions and nuclear electron attractions) and the kinetic energy terms for each electron in the system.

Molecular quantum mechanics can be divided into two classes

- Ab Initio
- Semi Empirical

Ab Initio calculations are fully Hamiltonian for the system and attempt a complete solution without using any experimental parameters. Semi empirical calculations generally use a simplified Hamiltonian operator and incorporate experimental data or a set of parameters that can be adjusted to fit experimental data.

What is Schrödinger Equation?

$H\Psi = E\Psi$ (Known)(Guess) =E(guess) Only if Ψ actually is the wave function If Ψ is not a wave function then $H\Psi \neq E\Psi$ (something else**)**		
Hamiltonian operator	Energy	Wave function
H is energy operator, which describes the kinetic, and potential energy of an electron in field of nuclei and other electrons. Usually the nuclei are assumed to be stationary.	Sum of the energies of the orbital, which may contain 1, or at most 2, electrons.	Ψ is f(x,y,z) A set of spatial distributions describing the probability of finding electrons (orbitals) Ψ is the product of n spatial functions (Ψ's), one for each of n electrons in the atom or molecule. A single atom has AOs. Molecules have MOs.

Basis sets: A basis set is a collection (set) of mathematical functions used to help solve the Schrödinger equation and each function is a function of the x, y and z coordinates of an electron.

Split-Valence basis sets: The first shortcoming of a minimal basis set, namely, a bias toward atoms with spherical environments, can be addressed by providing two sets valence basis functions: an inner set, which is more tightly held than an outer set, which is more loosely held. The iterative processes leading to solution of the Roothaan-Hall equations adjusts the balance of the two parts independently for the three Cartesian directions, by adjusting the individual molecular orbital coefficients.

A split-valence basis set represents core atomic orbitals by one set of functions and valence atomic orbitals by two sets of functions, $1s, 2s^i, 2p_x^i, 2p_y^i, 2p_z^i, 2s^0, 2p_x^0, 2p_y^0, 2p_z^0$ for Li to Ne and $1s, 2s, 2p_x, 2p_y, 2p_z, 3s^i, 3p_x^i, 3p_y^i, 2p_z^i, 3s^0, 3p_x^0, 3p_y^0, 3p_z^0$ for sodium to argon.

Polarization Basis Set: The second shortcoming of minimal (or split-valence) basis set, namely, that the basis functions are centered on atoms rather than between atoms, can be addressed by providing d-type functions on main-group elements (where the valence orbitals are s and p type), and (optionally) p-type functions on hydrogen (where the valence orbital is of s type). This allows displacement of electron distributions away from the nuclear potions.

Selection of a Theoretical Model: There are four models are available and useful in describing molecular geometry, reaction energies, and other properties. All of these models ultimately stem from the electronic Schrödinger equation, and they differ from each other both in the manner in which they treat electron correlation and in the nature of the atomic basis set. Each distinct combination (theoretical model) leads to a scheme with its own particular characteristics.

Methods These differ mainly according to how, or if, " electron correlation" is formed Electron correlation is the tendency of electrons to avoid each other, even within the same orbital. Four common quantum methods are being used			
Semi-empirical	**Hartree-Fock**	**Moller-Plesset**	**Density Functional Theory (DFT)**
Uses pre-calculated orbital functions for different kinds of atoms, fast, but less accurate.	Electron correlation is ignored. The many electron wave functions (Ψ) are estimated by the self-consistent field (SCF) method.	Electron correlation is accounted for allowing one or more electrons to occupy higher-energy, unoccupied (anti-bonding) MOs This results in an energy correction that lowers the total energy because it lowers the electron-electron repulsion energy.	Energy of a molecule= F(electron density) Where electron density=f(x,y,z) This says that there exists a functional that will calculate molecular energy from electron density. But it does not say what the functional is! It accounts for electron correlation by estimating the interaction of an electron with the total electron density. DFT orbitals are formed from basis functions like those in SCF or MP2. Most popular DFT method is B3LYP.

Of course, no single theoretical model is likely to be ideal for all applications. A great deal of effort has gone into defining the limits of different models and judging the degree of success and the pitfalls of each. Most simply, success depends on the ability of a model to consistently reproduce known (experimental data). The success of a quantum chemical model is not an absolute. Different properties and certainly different problems may require different levels of confidence to actually be of value. Neither is success sufficient. A model also needs to be practical for the task at hand. The nature and size of the system needs to be taken into account, as do the available computational resources and the experience and patience of the practitioner.

1.6 Research Problem

There are many compounds where either the metal ion is highly oxidizing and ligands are reducing or that the central metal ion is highly reducing and the ligands are oxidizing. In such cases there occurs transfer of charge (i.e., electron) from the reducing partner to oxidizing partner this provides makes strong electronic transitions and follows selection rule. Hence, these transitions are useful for qualitative and quantitative analysis of analyate sample. When thorium nitrate dissolves in water, it is known that hydrolysis of Th^{4+} occurs at pH around 3 leading to the formation of $[Th(OH)]^{3+}$,$[Th(OH)_2]^{2+}$, $[Th(OH)_3]^{+}$, $[Th(OH)_4]$ and some dimeric and polymeric species of Th^{4+} ion. In these species, thorium (IV) is in highest oxidation state and ligand (-OH) is reduced state. In such electronic environment, there is a movement of electrons from oxygen to thorium core. Moreover, the energy level difference between 5f and 6d is very close to each other consequently, there is a charge transfer phenomenon is taking place. All charge transfer transitions are allowed transitions with high molar extinction co-efficient in the order of 10^3-10^6 $L.mol^{-1}.cm^{-1}$. Such transitions are usually high energy electronic transitions and occur in the ultraviolet region. To verify electronic transition of all these species it is proposed to carry out density functional theory to predict absorption spectrum for all thorium (IV) species in aqueous system.

Chapter -2

LITERARURE REVIEW

2.1 Spectrophotometeric Studies

Absorbance spectroscopy, commonly referred to as spectrophotometry, is the analytical technique based on measuring the amount of light absorbed by a sample at a given wavelength. Spectrophotometry, particularly in the visible and UV portions of the electromagnetic spectrum, is one of the most versatile and widely used techniques in chemistry and the life sciences.

Labrecque *et al* (18) describes a rapid method for the simultaneous determinations of thorium, niobium, lead, and zinc in lateritic material using induced X-ray fluorescence system. The values for thorium measured were in agreement with the reported values for the reference materials supplied by NBL. **Khalifa** *et al* (19) describes the ternary purple coloured complex formed between Th^{4+}, bromocresol orange (BCO) and cetylpyridinium bromide (CPB) in acidic medium using spectrophotometrically. The formation of 1:1:1, Th:BCO:CPB complex in aqueous solution at pH≈0.5 with a logarithmic conditional stability constant of 12.04±0.1, I=0.1 at 25°C. The colour of the ternary complex was used for the determination of thorium (IV) in the range of 0.02–2.6 $\mu g\ ml^{-1}$ Th^{4+}, $\varepsilon=9.2\times10^{4}$ l mol^{-1} cm^{-1} at 560 nm. **Amin** *et al* (20) discussed that thorium and rare earth elements (REE) react with 5-(2′,4′-dimethylphenylazo)6-hydroxypyrimidine-2,4-dione (I) and 5-(4′-nitro-2′,6′-dichlorophenylazo)6-hydroxypyrimidine-2,4-dione (II) in the absence of cetylpyridinium chloride (CPC) to form red complexes. Most of the foreign ions are tolerated in considerable amounts; 150–2400 fold amounts of rare earth do not interfere with the determination of thorium. **Abdallah** *et al* (21) studied the extraction and pre-concentration of a metal complex via surfactant-mediated phase separation. Using Eriochrome Cyanine R (ECR) with a flotation step prior to spectrophotometric determination. The precipitate in the scum layer was quantitatively collected, stripped with 4 ml of 3% HCl and measured spectrophotometrically at 540 nm for Th(IV) and at 650 nm for both La(III) and Y(III). **Fukuma** *et al* (22) describes a method for the determination of thorium in uranium concentrate by spectrophotometry with Arsenazo III and tri-n-octyl phosphine oxide. **Niazi** *et al* (23) described simultaneous determination of uranium and thorium spectrophotometricaly. The method is based on the complex formation of uranium and thorium with Arsenazo III at pH 3.0. In this study, the calibration model is based on absorption spectra in the 600-760nm range for 25 different mixtures of uranium and thorium. Calibration matrices contained 0.10-21.00 and 0.25-18.50 µg mL^{-1} of uranium and thorium, respectively. **Dhara** *et al* (24) described a fast energy dispersive X-ray fluorescence (EDXRF) method requiring only microgram amounts of analytes, i.e., uranium (U) and thorium (Th), in their mixtures in solution form. The results of U and Th determinations showed a precision of about 3%. **Becker** *et al* (25) reported ICP-MS for the precise determination of thorium and uranium concentrations and for isotope ratio measurements at the trace and ultra trace levels in urine samples. **Casartelli** *et al* (26) has used ICP–MS for the determination of thorium and light rare-earth elements (LREEs) in soil and soil water samples from a mineral deposit. Size-exclusion chromatography (SEC) on-line coupled to ICP–MS and UV-detection. Concentrations of 30 to 40 µg L^{-1} for the LREEs (La, Ce, Nd) and up to 14 µg L^{-1} for Th were measured in soil waters of highest DOC content. **Milkey** *et al* (27) reported thorium reacts with morin to yield a yellow complex that fluoresces when irradiated with ultraviolet light. The effect on the fluorescence of such variables as concentration of acid, alcohol, thorium, morin, and complex; time, temperature and wavelength of exciting light are studied to determine experimental conditions yielding maximum fluorescence. **Filer** *et al* (28) has found that the compound morin, **(**2’**,** 4’, 3, 5, 7-pentahydroxyflavone), to be a useful reagent for the fluorometric determination of sub microgram quantities of various metals, particularly beryllium and thorium. In contrast, 3, 4, 7-trihydroxyflavone is comparable to morin in sensitivity to thorium while being only 1/1400 as sensitive to beryllium. **Fletcher** *et al* (29) was made spectrophotometric study the thorium-morin reaction to evaluate the suitability of morin as a reagent for the determination of trace amounts of thorium. At pH 2, the equilibrium constant for the reaction is 1x $l0^{6}$ and a single complex having a thorium-morin ratio of 1 to 2 is formed. The complex shows maximum absorbance at a wavelength of 410nm, and its absorbance obeys Beer's law. **Kirkbright** *et al* (30) have noted that thorium may not be determined by direct atomic absorption spectroscopy in flame media with appreciable sensitivity because of inefficient atomisation. Madison have developed a solution spectrophotometric procedure for thorium in which the heteropoly acid complex of thorium with phosphomolybdic acid is formed and reduced to the 'heteropoly blue'. Strict adherence to time of addition of reagents is required in this procedure, and. it is necessary to effect an initial separation of the thorium from most other cations present in the sample. **Agnihotri** *et al* (31) have described derivative photometric methods for trace analysis of Th(IV)and UO_2(II), and their simultaneous determination in mixtures using 5,8-dihydroxy-1,4-naphthoquinone in a micellar medium. Molar absorptivity and Sandell's sensitivity of 1:2 Th(IV) and 1:1 UO_2(II) complexes at their λ_{max} 614.5 nm and 637.0 nm are, 1.19×10^4 l/mol/cm and 1.12×10^4 1/mol/cm and 1.95×10^{-2} $\mu g/cm^2$ and 2.13×10^{-2} $\mu g/cm^2$ $\mu g/cm^2$, respectively. Calibration graph is linear over the range 9.28×10^{-2}–18.56 μg/ml of Th (IV) and 9.52×10^{-2}–19.04 μg/ml of UO_2(II). Though presence of Th(IV) and UO_2(II) causes interference in each others determination 9.28×10^{-1}–9.28 μg/ml Th(IV) and 9.52×10^{-1}–9.52 μg/ml UO_2(II) when present together, can be simultaneously determined using derivative spectra.

Rastegarzadeh *et al* (32) reported a selective method for the determination of thorium (IV) using an optical sensor. The sensing membrane is prepared by immobilization of thorin–methyltrioctylammonium ion pair on triacetylcellulose polymer. The sensor produced a linear response for Th(IV) concentration in the range of 6.46×10^{-6} to 9.91×10^{-5} mol L^{-1} with detection limit of 1.85×10^{-6} mol L^{-1}. **Banks** *et al* (33) have described a new oxidimetric method for the titrimetric determination of thorium based on the precipitation of thorium as the normal molybdate followed by the reduction and titration of the molybdenum equivalent to the thorium. **Pourreza** *et al* (34) has reported a simple and reproducible flotation-spectrophotometric method for the determination of thorium. The method is based on the ion-associate formation between thorium, xylenol orange (XO) and cethyltrimethyl ammonium bromide (CTAB) which is floated in the interface of the aqueous phase and n-hexane by vigorous shaking. The adsorbed ion-associate (Th-XO-CTAB) on the wall of a separating funnel is dissolved in a small volume of ethanol solvent, and its absorbance is measured at 568 nm. The calibration graph shows linear in the concentration range of 2-200 ng mL^{-1} of thorium. The limit of detection (LOD) is 1.4 ng mL^{-1} **Ko** *et al* (35) presented the determination of 0.01 ppm of thorium in 1 g of uranium ore by a combined ion exchange-spectrographic analysis. Thorium is separated from the chemically complex ore solution by anion exchange in hydrochloric and nitric acid media and determined spectrographically using zirconium as the internal standard. **James** *et al* (36) determined low levels (0 to 100 ppm) of uranium and thorium in geologic samples and accurately by wavelength-dispersive X-ray emission spectrometry. Three sigma detection limits of 1.2 ppm U and 1.5 ppm Th can be achieved with a total counting time of 5 min on a powdered 10g sample. **Ramakrishna** *et al* (37) describes that the thorium-xylenol orange reaction ($\epsilon = 5.51 \times 10^4$ L.mole^{-1}.cm^{-1}) is accompanied by a bathochromic shift from 570 to 600 nm. Beer's law is obeyed for 0.04–4.00 ppm of thorium. **Korkisch** *et al* (38) describes that after elution thorium is determined spectrophotometrically by using thoronol or arsenazo III. The suitability of the method for the determination of both trace and larger amounts of thorium was tested by analysing numerous geochemical standard samples with thorium contents in the range of 1–1000 ppm. **Savvin** *et al* (39) describes that the reagent arsenazo III (1,8-dihydroxynaphthalene-3,6-disulphonic acid-2,7-bis[(azo-2)-phenylarsonic acid]) gives marked colour reactions with a number of elements. The method is most selective for Th, Zr and U^{IV}. Materials containing these elements can be analyzed directly, in the solutions formed after dissolving the sample, without separation of the stable elements.

Kuroda *et al* (40) developed a derivative spectrophotometric method for the simultaneous determination of microgram quantities of uranium and thorium with Arsenazo III in hydrochloric acid medium. The second-derivative absorbances of the uranium and thorium Arsenazo III complexes at 679.5 and 684.4 nm are used for their quantification. Uranium and thorium, both in the range 0.1–0.7 μg/ml have been determined simultaneously. The procedure does not require separation of uranium and thorium, and allows the determination of both metals in the presence of alkaline-earth metals and zirconium, but lanthanides interfere. **Khan** *et al* (41) developed a rapid and sensitive spectrophotometric for the determination of thorium using 0.04% Arsenazo-III in a 2M perchloric acid solution. Absorbance is measured in 1cm cell and the complex has a sensitive absorption peak at 654 nm. Beer's law is obeyed in the range 1–60 $\mu g \cdot g^{-1}$ of thorium concentration with a molar absorptivity at 654 nm. The cations were tested at >60-fold excess of thorium, Mn(II), Fe(III), Co(II) and Ni(II) interfere negatively, whereas only Ce(III) has increased the absorbance. Among the anions, cyanide, phosphate, thiocyanate and acetate at 150-fold excess of thorium cause significant interference. The method has been also applied successfully to determine thorium at $\mu g \cdot g^{-1}$ level in local ore samples with a precision of ±0.04%. **Yong** *et al* (42) developed a simultaneous spectrophotometric for assay of uranium, thorium and lanthanum in mixed solutions by absorbance measurements of their arsenazo III complexes at appropriate wavelengths in three different solutions. The absorbances are additive for the three metals in each solution. The values of the molar absorption coefficients are obtained by least-squares fit of the data of absorbance against the concentration of standard metal solution, individually. The concentration of each metal in a mixed solution was calculated separately from simultaneous equations. **Yamamoto** *et al* (43) described a simple and rapid spectrophotometric determination of thorium. Maximum absorbance occurs at 620 and 670 nm and Beer's law is obeyed at the latter wavelength over the range of 0–15 μg per 10 ml of the organic phase. Thorium can be determined in the presence of fluoride, oxalate, sulfate and EDTA. Many common cations do not interfere, but uranium, zirconium and niobium interfere seriously.

Ramesh *et al* (44) developed a second-derivative spectrophotometric method for the simultaneous determination of uranium and thorium using 4-(2′-thiazolylazo) acetophenone oxime as the spectrophotometric reagent. The method allows the determination of uranium and thorium in the range 0–10.0 ppm. **Korkisch** *et al* (45) describes a sensitive and accurate method for the spectrophotometric determination of microgram amounts of thorium using the azo dye Solochromate Fast Red. This dyestuff reacts with thorium in hydrochloric acid- methanol solutions to form an orange complex, which shows maximum absorption at 490 nm. Very small number of foreign ions interferes; hence, this method can be expected to find general application, as in the determination of thorium in minerals and rocks. **Agrawal** *et al* (46) used calixarene hydroxamic acid, 25,26,27,28-tetrahydroxy5,11,17,23-tetrakis(*N*-*p*-chlorophenyl)calix[4]-arene hydroxamic acid (CPCHA) for the extraction and spectrophotometric determination of thorium(IV). The molar absorptivity of the thorium (IV)–CPCHA–SCN complex is 2.2×10^4 m^2 mol^{-1} at 450 nm. The system obeys Beer's law over the range 1.3–13.2 ppm of thorium. The method is applied for the trace determination of thorium (IV) in geological samples at the low ppb level even after a 1:100 dilution. **Kusakul** *et al* (47) describe that acid alizarin black SN reacts with thorium at pH 4.2 to give a highly sensitive colour reaction with thorium, ε_{600} mμ = 28,000. **Sharma** *et al* (48) describe that thorium (IV) reacts with 1-(2′-thiazolylazo)-2-naphthol (TAN) in the presence of antipyrine to form a sparingly soluble red-coloured chelate). Complexation takes place instantaneously at pH 2.4–2.8, maintained by glycine buffer. The 1:2 complex exhibits maximum absorbance at 555nm, obeys Beer's law in the concentration range from 0.32 to 6.56 µg of thorium(IV) per ml, has a molar absorptivity of $3.14x10^4$ $dm^3/mol^{-1}\cdot cm^{-1}$. The method was successfully applied for determination of thorium content in a sample of monazite. **Dev** *et al* (49) used Rutin for the spectrophotometric determination of thorium. Thorium forms with this reagent a deep yellow water-soluble complex, which obeys Lambert-Beer's law at 435 mμ within the concentration range of 1.16–23.20 ppm of thorium. **Sivaramaiah** *et al* (50) developed a simple and sensitive spectrophotometric method for the determination of thorium in aqueous medium. The metal ion forms yellow coloured complex with 2,4-dihydroxybenzaldehyde isonicotinoyl hydrazone (2,4-DHBINH) in the pH range 2.0–8.0. The complex shows absorption maxim at 390nm.

2.2 Quantum Mechanical Studies

Yang *et al* (51) investigated the water exchange mechanisms in $[Th(H_2O)_{10}]^{4+}$ and $[Th(H_2O)_9]^{4+}$ along dissociative (*D*), associative (*A*) and interchange (*I*) pathways using the ab initio quantum mechanical calculations. Water exchange in $[Th(H_2O)_{10}]^{4+}$ probably proceeds via the *D* mechanism, the activation energy is 3.06 kcal/mol. The water exchange in $[Th(H_2O)_9]^{4+}$ probably proceeds via the A pathway, the activation energy is 3.62 kcal/mol. Deprotonation of one coordinated water molecule of $[Th(H_2O)_{10}]^{4+}$ leads to the formation of hydroxo-aquo complex $[Th(OH)(H_2O)_9]^{3+}$, which has a more dissociative mechanism and lower activation energy. **Yang** *et al* (52) discussed the combined quantum mechanical and molecular dynamical simulations on thorium (IV) hydrates in aqueous solution. Hydration of the Th^{4+} ion in aqueous system was investigated using the B3LYP hybrid density functional theoretical calculations. The results show that the first shell hydration number of Th^{4+} ion in liquid phase is 9 at the bond distance of $Th{-}O_I$ 2.54 Å and $Th{-}H_I$ 3.22 Å. The $[Th(H_2O)_9]^{4+}$−water interaction potential was developed by ab intio B3LYP calculations. The partial atomic charge of $[Th(H_2O)_9]^{4+}$ is derived from the ESP method. The MD calculated results show a well-defined second coordination shell and an ill-defined third shell around the $[Th(H_2O)_9]^{4+}$ ion. The strong hydrogen bonding due to the polarization of the first coordination sphere water molecules leads to a mean coordination number of 18.9 water molecules in the second shell at the bond distance of $Th{-}O_{II}$ 4.75 Å and $Th{-}H_{II}$ 5.35 Å. The residence time of a water molecule in the second hydration shell is 423.4 ps. The simulated results indicate that the hydrated ion concept for simulating the Th^{4+} ion in aqueous solution is appropriate. **Tsushima** *et al* (53) performed ab initio calculations to study the structures of thorium (IV) hydrate and its hydrolysis products in aqueous solution. The conductor-like polarizable continuum model (CPCM) has been used to perform geometry optimization calculations in aqueous solution. The calculated results demonstrate that the molecule geometries obtained in solvent are generally consistent with the experiments. **Okamoto** *et al* (54) investigated the hydrolysis reaction of the tetravalent thorium (Th^{4+}) ion by ab initio theoretical calculations on hydration complex models. The reported results showed that the hydrolysis is highly exothermic and the transition state is close to the reactant.

Johansson *et al* (55) has been determined the coordination around the thorium (IV) ion in aqueous perchlorate, chloride and nitrate solutions from large angle X-ray scattering measurements. In perchlorate solutions, where inner-sphere complexes are not formed, the first coordination sphere contains 8.0 ± 0.5 water molecules with Th-H_2O bond lengths of 2.485 Å. In chloride solutions inner-sphere complexes are formed, which lead to an increase in the coordination number. In nitrate solutions the nitrate ions are bonded as bidentate ligands to the thorium ion. The bond lengths are similar to those found in crystalline hydrates of thorium nitrate. The coordination numbers found for thorium (IV) in solution are compared with previously reported values for lower charged ions of similar size. **Oliver** *et al* (56) determined the laser Raman spectra of aqueous $Th(NO_3)_4$ solutions and the complementary IR spectra at 25°C. Spectra indicate the presence of pronounced ion-ion and ion-solvent interactions in the system. The results can best be explained in terms of equilibrium between 'complexed' and 'free' nitrate in the system. **Pan** *et al* (57) noted that the dilution effect on the pH change in a dilute solution and in the presence of sodium perchlorate. A linear relationship is held between pH and $-\log C$. The curves plotting pH vs. $-\log C$ run parallel with each other at varying ionic strengths, and the slope is nearly equal to 1/2 which showed the most possible existence of $Th(OH)^{+3}$. also the equilibrium constants for ion species, $ThOH^{+3}$ and $Th(OH)_2{}^{+2}$, are calculated stoichiometrically from the data of hydronium ion concentration observed and the total concentration of thorium nitrate. **Mazzone** *et al* (58) performed density functional theory calculations to study the gas-phase reaction of Th^{+} and Th^{2+} with water. An in-depth analysis of the reaction pathways leading to different reaction products. The obtained results are compared to experimental data and to the previously studied reactions of U cations with water. **Heinrich** *et al* (59) measured the absorption spectra of thirteen sintered trivalent lanthanide oxides (La to Lu) and six actinide dioxides (Th to Cm) by photoacoustic spectroscopy. Though both series of elements have in common successive filling of the 4f and 5f shells, respectively, the absorption spectra of the two classes of oxides are very different. While absorption spectra of the thirteen trivalent lanthanide oxides show narrow weak absorption bands and lines in the uv, visible, and near-IR wavelength ranges due to internal $4f^n \rightarrow 4f^n$ transitions between the numerous energy levels of the Xe $4f^n$ configuration, the absorption spectra of the actinide oxides display very intense and broad absorption bands extending from the ultraviolet to the visible and sometimes to the infrared. The $5f^n$ electrons in the actinide oxides are not as well localized as the $4f^n$ electrons of the lanthanide sesquioxides. The 5f electrons probably participate in bonding, e.g., in electron transfer processes from a molecular oxygen orbital to a partly filled or empty 5f electron state of the oxidizing central atom which gives rise to intensive broad absorption bands in the ultraviolet and visible. **Duggal** *et al* (60) studied the spectral properties of Schiff base complexes involving diamines and aldehydes. Other studies involving diamines include the isolation of thorium (IV) and uranium (VI) complexes with tetradentate Schiff bases derived from substituted salicylaldehyde and 1, 2-ethanediamine or o-phenylenediamine. The X-ray crystal structure reveals that the 8-coordinated complex molecules have slightly distorted dodecahedral geometry.

The comprehensive literature survey shows that there is no research has been conducted to show that one of the hydrolysis products of thorium (IV) ion is undergoing charge transfer phenomenon in UV region and also no study has been conducted to use DFT theory to predict absorbance spectra for hydrolysis product of thorium (IV) ion. This phenomenon used for qualitative and quantitative identification thorium (IV) ion without using spectrophotometeric reagent.

Chapter-3

Results & Discussion

3.1 Reagents and Solutions

All the solutions were prepared with ultra pure water. All the chemicals used were analaR grade. The standard stock solution of thorium was prepared by dissolving thorium nitrate solution in a given volume of water, and the solution was standardized by EDTA titration using xylenol orange indicator. The working standard solution $1x10^{-1}$to $1x10^{-8}$M was prepared by serial dilution.

3.2 Instrumentation

The absorption spectrum of Th(IV) solution of wide concentration range from $1x10^{-5}$ M to $1x10^{-8}$ in the region of 190nm-400nm against the blank solution using Analytika Jena Spectra Cord 205. Infrared spectra were recorded using Nicolet 750 spectrometer in ATR mode. Fluorescence study was conducted using L50 Spectrofluorimeter (Perkin Elmer) and Mass spectra was recorded using Waters Q-TOF micro

3.3 Spectrophotometric Analysis of Th(IV) Hydrolysis Species

Molecular absorption spectroscopy in the ultraviolet (UV) and visible (VIS) is concerned with the measured absorption of radiation in its passage through a gas, a liquid or a solid. The wavelength region generally used is from 190 to about 800nm, and the absorbing medium is at room temperature. In UV/VIS spectrophotometry, the major energy levels are determined primarily by the possible spatial distributions of the electrons and are called electronic energy levels, and to a lesser extent by vibrational energy levels. The energy and wavelength of absorption is defined by the difference between energy levels of an electronic transition. This can be expressed by the following equation:

$$\lambda = hc/(E_2-E_1)$$

Where: E_1 is the energy level of the molecule before absorption E_2 is an energy level reached by absorption

When thorium nitrate dissolves in water, it undergo hydrolysis at pH=3, leading to the formation of $[Th(OH)]^{3+}$,$[Th(OH)_2]^{2+}$, $[Th(OH)_3]^{+}$, $[Th(OH)_4]$ and some dimeric and polymeric species of Th^{4+} ion. In these species, thorium (IV) is in highest oxidation state and ligand (-OH) is reduced state. In such electronic environment, there is a movement of electrons from oxygen to thorium core. Moreover, the energy level difference between 5f and 6d is very close to each other consequently, there is a charge transfer phenomenon is taking place. Further, to confirm this phenomenon, we have carried out spectrophotometric absorbance study using freshly prepared desired concentration range ($1x10^{-5}$ to $1x10^{-10}$M) of thorium nitrate solution in double distilled water. After blank solution correction, absorbance for all solution taken one by one and study shows that there is no absorption peak in the entire UV-Visible region (190-700nm) for all the concentration of Th(IV) fall between $1x10^{-1}$M to $5x10^{-6}$ M. However, when the Th(IV) concentration of $6x10^{-6}$M to $9x10^{-7}$M , there is a one absorbance peak at 205nm with molar absorption co-efficient is 10^6 L.mole^{-1}.cm^{-1} **(Figure 1 and 2)**. Beyond $9x10^{-7}$M concentration, no absorbance peak is observed. This study shows that one of hydrolysis product of thorium is undergoing charge transfer electronic transition and study proceeded by rising following objectives and results of all the objectives are discussed to the best of our knowledge.

- Identification of hydrolysis species of Th(IV) which exhibits charge transfer phenomenon property
- Effect of other solvents on charge transfer phenomenon of $Th(OH)_4$
- Effect of hydrolysis on IVB group elements.
- Interfering ion study with commonly available cation system.
- Possible theoretical spectra for all these thorium (IV) species in gas phase environment using density functional theory.

3.4 Effect of Solvents

The absorption behavior of Th(IV) ion was done in different solvents system like: water (H_2O), methanol (CH_3OH), acetone (CH_3COCH_3), dimethyl sulphoxide (CH_3CSCH_3), and tetrahydrofurane (C_4H_5O). A Spectrophtometric study shows that there is no absorption peak for thorium (IV) when it is present in non-aqueous system, this may be due no reaction between thorium (IV) ion and solvent system. Further, this study was confirmed by using IR spectroscopy data discussed in subsequent section 3.3.

3.5 Infrared Spectroscopic Studies

It determines the relative strengths and positions of all the absorptions in the infrared region. Known bands of $Th(NO_3)_4.5H_2O$, *i.e.*, 1540 (ν4), 1290 (ν_1), 1030 (ν_2), 808 (ν_6), 745 (ν_3) and 715 (ν_5) cm^{-1}, in which the bidentate character of the nitrato groups has been established by X-ray (62) and neutron diffraction (63) studies .In the proposed study IR spectra taken by using ATR mode for solid thorium nitrate **(Figure-3)** and different concentration of Th(IV) ion solution also **(Figure 4)**. Hydrolysis of Th^{4+} occurs at pH around 3 leading to the formation of several hydrolysis like $[Th(OH)]^{3+}$, $[Th(OH)_2]^{2+}$ $[Th(OH)_3]^+$ and $[Th(OH)_4]$ species, in all these species active mode of vibration is stretching due to O-H bond and Th-O and bend due to Th-O-H. As seen in the IR spectra over a wide concentration range from $1x10^{-1}$ to $1x10^{-8}$ M **(Table 3.1)** absorption peak appears in the region $3200cm^{-1}$ to $3000cm^{-1}$ due to stretching frequency attributed to (OH) and some peak appears in the region of $700\text{-}650cm^{-1}$ due to bending vibration of Th-O-H. No peak is observed at $1300cm^{-1}$ show that free nitrate ion is known to absorb near $1360cm^{-1}$ and this exhibits in solid state only after dissolving free nitrate does not exhibit spectra due to non availability of this ion for IR radiation. Further same study was conducted in different solvents **(Figure 5 and 6)** like methanol, DMF, DMSO, THF and acetone. Result shows that there is no difference in IR spectra of Th^{+4} in all these solvents and pure solvents IR spectra. This concludes that no solovolysis reaction of Th(IV) with pure non-aqueous solvent.

3.6 Mass Spectra Studies

The uses of electron spray ionization mass spectrometry for the identification of hydroxide complexes of Th(IV). The method involves injection of Th (IV) ions in aqueous system through electro spray nozzle into the high vacuum system of mass spectrometer where rapid evaporation takes place and the ions formed are analyzed in quadruple mass spectrometer. The ions formed have a charge of +1 and their stiochiometery can be identified by their mass and their relative amounts by the intensity of the peaks in the mass spectra. The molecular ion peak is appearing at m/z value 298.8 **(Figure7)**. The whole number corresponding to m/z is 300. The actual species in the working concentration region is $Th(OH)_4$ because molecular mass of this compound is 300.

3.7 Spectrophotometric Behavior of Group (IVB) Elements

Group (IVB) comprises three elements Ti, Zr and Hf. Spectrophotometric study conducted by taking their corresponding salts in the desired concentration range. A spectrophotometric result shows that there is no peak in the entire UV region this may be due to non-availability of electronic charge transfer environment between central metal ion and surrounding ligands.

3.8 Interference study

Selectivity is one of the most important characteristics of any analytical system, as it often determines whether a selective measurement is possible or not. In this study, interfering ion concentration taken was $6x10^{-6}M$ and thorium (IV) taken was $6x10^{-6}M$. In the case of trivalent lanthanides, d-block element and calcium ion, the absorbance spectrum shows that λmax value is not disturbed but absorbance values were reduced to 40 percent to its original absorbance value **(Table 3.2)**. This may be due to decrease in the concentration of $Th(OH)_4$ species

3.9 Emission Spectroscopic studies

Emission spectra of Th(IV) in aqueous medium does not contribute much about quantitative relationship but it shows some emission peaks due to interaction of Th^{4+} ion and solvent. **Figure 8,** shows emission spectra in the excited state. This study shows that $Th(OH)_4$ species is a non fluorescent behavior.

3.10 Theoretical Model for Electronic Transition of Hydrolysis Th(IV) ion

An electronic and absorption property of hydrolysis of thorium (IV) ion in a gas phase medium has been investigated by using DFT/TD-DFT method**.** All calculations were carried out with Gaussian 03 software package. Geometry optimizations were performed by using density functional theory (DFT) at the B3LYP/SDD level without any symmetry constraints calculations were performed at the same level. Based on the optimized ground state structure, UV-visible spectra were calculated by using time-dependent density functional theory (TD-DFT) at the B3LYP/SDD level. This method has been used to provide a possible description of UV-Visible spectra of metal containing systems. **Table 3.3** describing absorption peak and molar absorption co-efficient for all possible species of Th(IV). The DFT calculations shows only Th$(OH)_4$ with tetrahedral geometry shows an absorption peak at 202nm and which is near to experimental value 205nm.

Table 3.1: Infrared spectroscopic data for Th(IV) hydrolysis product

Th(IV) concentration	IR peaks (cm^{-1})			
	O-H stretching		**N-O**	**Th-O-H bending**
$Th(NO_3)_4.5H_2O$	3356.32	1600	1331.84	659.04
$1x10^{-1}$	3431.21 3212.45	No peak	No peak	698.99 652.10
$1x10^{-2}$	3358.60 3246.07	No peak	No peak	708.44 663.31
$1x10^{-3}$	3329.08 3178.48	No peak	No peak	675.05
$1x10^{-4}$	3499.43 3213.56	No peak	No peak	761.09 663.12
$1x10^{-5}$	3369.54 3285.81	No peak	No peak	715.50 658.84
$1x10^{-6}$	3431.45 3182.17	No peak	No peak	752.48 653.84
$5x10^{-6}$	3437.61 3209.00	No peak	No peak	752.48 653.41
$6x10^{-6}$	3434.06 3217.85	No peak	No peak	752.62 656.58
$9x10^{-7}$	3402.23 3245.12	No peak	No peak	739.66 686.43
Pure acetone medium	No change in peak position of pure solvent and solvent containing Th(IV)			
Pure THF	No change in peak position of pure solvent and solvent containing Th(IV)			

Table 3.2: Absorbance values for Th(IV) in presence of interfering ions

Interfering ion	Absorbance values
Th(IV)	**2.335**
Th(IV) + La(III)	**1.534**
Th(IV) + CeII)	**1.234**
Th(IV) + Sm(III)	**1.498**
Th(IV) + Gd(II)	**1.543**
Th(IV) + Fe(III)	**1.984**
Th(IV) + Ni(II)	**2.132**
Th(IV) + Cu(II)	**1.987**
Th(IV) + Ca(II)	**1.145**

Experimental condition: Th(IV) concentration taken (5mL of $6x10^{-6}$M) and interfering concentration taken(5mL of $6x10^{-6}$M)

Table 3.3: Theoretical electronic spectra for all possible species Th(IV) using DFT

Name of the species	**Total energy (E)**	**Epsilon (ε)**	**Excitation energy (λ_{max})**	**Time required**
Th(IV)	-407.063840886* -407.063839764	710	7266.84	7 Min 30.0 seconds 2 minutes 48.0 seconds.
Th(H_2O)$_4$	-712.911574964 -712.911573657	65	3800.69	32 minutes 1.0 seconds. 10 minutes 35.0 seconds
$[Th(OH)_2]^{2+}$	-558.732619800* -558.732611966	12	368.51	10 minutes 5.0 seconds. 2 minutes 25.0 seconds
$[Th(OH)_3]^{+}$	-635.110686889* -635.110678094	280	351.18	13 minutes 11.0 seconds. 3 minutes 34.0 seconds
Th(OH)$_4$ Tetrahedral	-711.241686774* -711.241674519	400	202.20	23 minutes 57.0 seconds 5 minutes 28.0 seconds
Th(OH)$_4$ Square Planar	-711.203692141 * -711.203656125	720	230.45	25 minutes 30.0 seconds 5 minutes 30.0 seconds
ThF_4	-807.561936883* -807.561936572	800	186.71	10 minutes 8.0 seconds 2 minutes 0.0 seconds
$ThCl_4$	-2248.83037245* -2248.83036927	1100	244.70	12 minutes 50.0 seconds. 1 minutes 51.0 seconds.
$Ti(OH)_4$	-361.838872137* -361.838775934	225	330.52	5 minutes 30.0 seconds 0 minutes 47.0 seconds
$Zr(OH)_4$	-350.580796602* -350.580772248	400	234.00	4 minutes 3.0 seconds. 0 minutes 36.0 seconds.
$Hf(OH)_4$	-351.558503570* -351.558486923	325	209.92	3 minutes 58.0 seconds 0 minutes 36.0 seconds

Condition of DFT studies: Th-O bond length (2.0500 °A); O-H bond length (0.9500 °A)

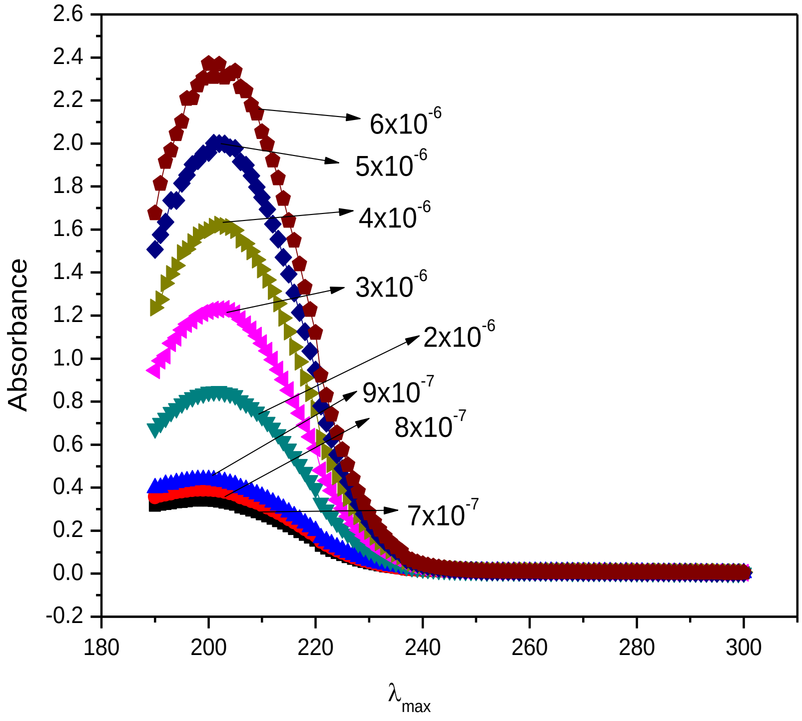

Figure 3.1: Electronic absorption spectrum of Th(IV) ion in aqueous system.

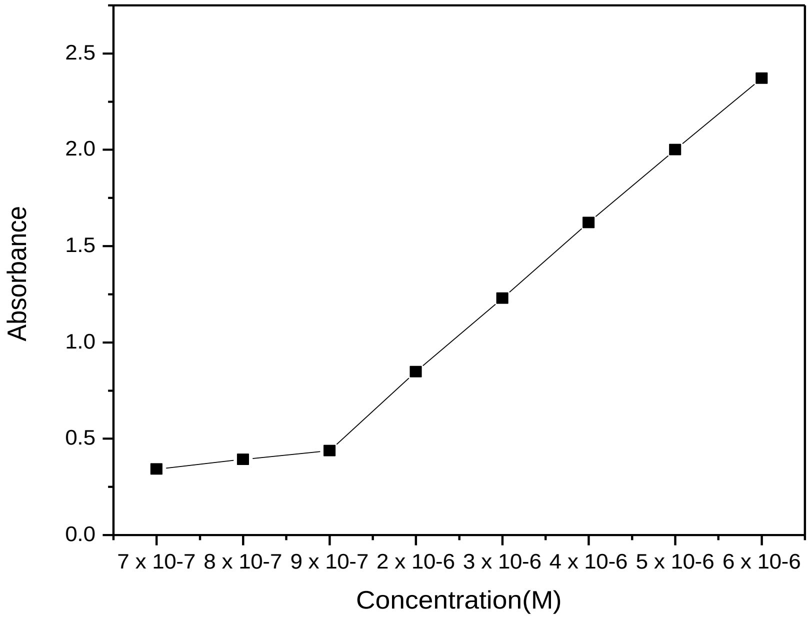

Figure 3.2: Calibration curve of Th(IV) ion in the concentration range of $7x10^{-7}$M-$6x10^{-6}$M

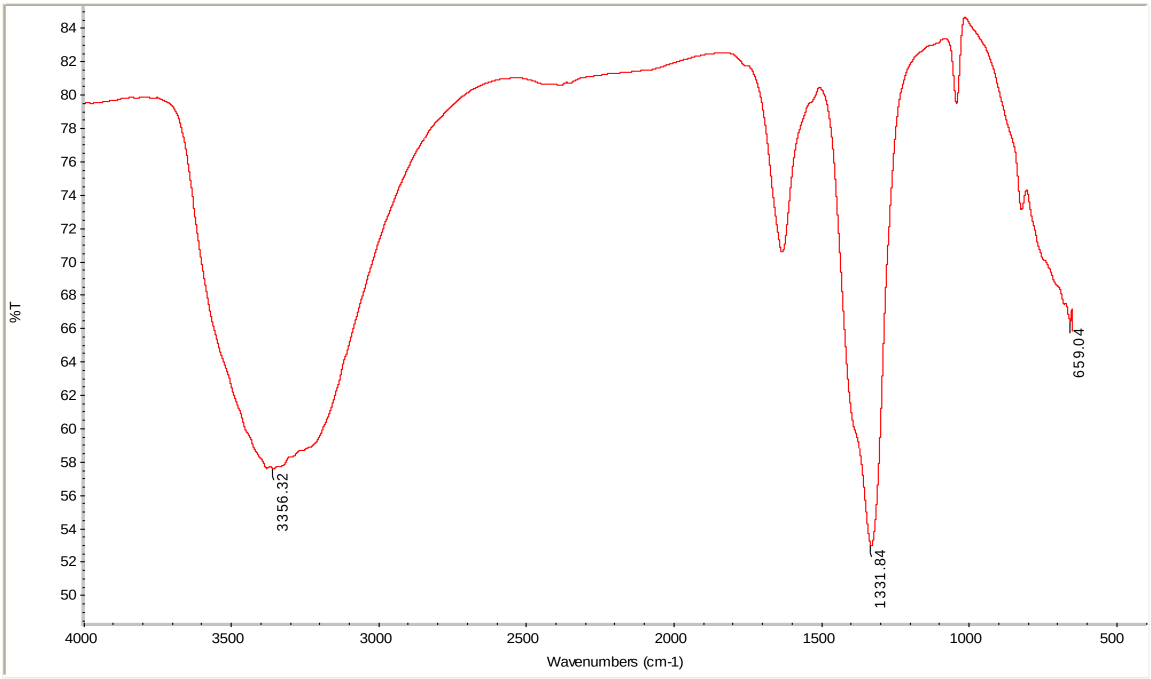

Figure 3.3: Infrared spectra for pure thorium nitrate salt

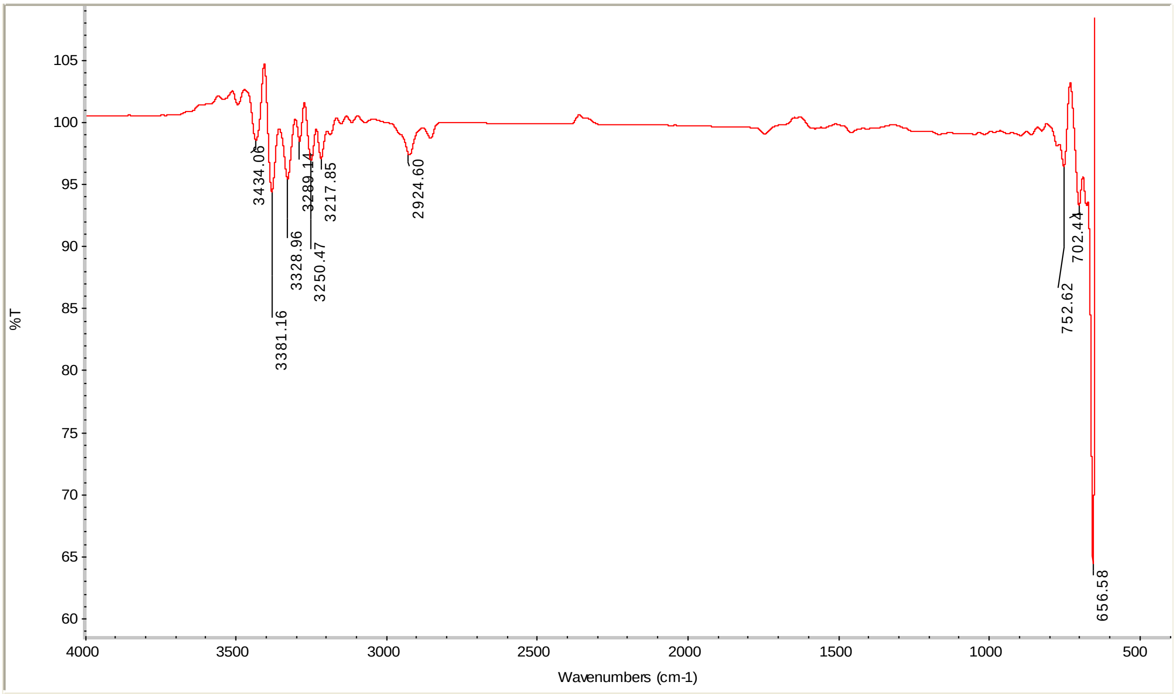

Figure 3.4: Infrared spectra of Th(IV) ion concentration 6x10^{-6} M in aqueous system

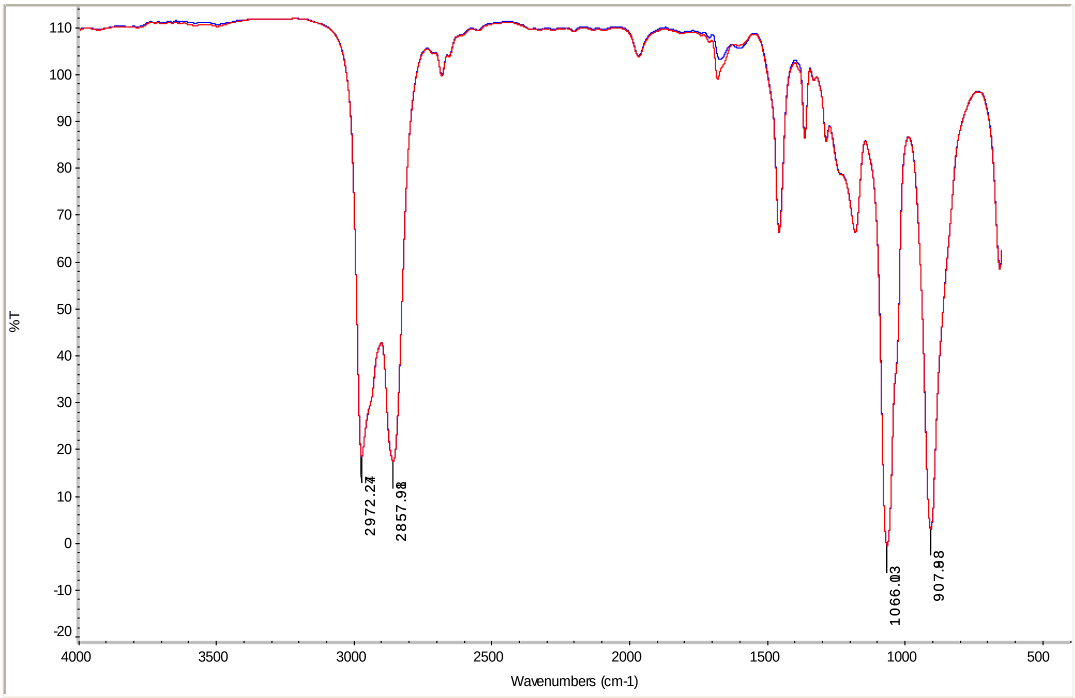

Figure 3.5: Infrared spectra of Th(IV) ion concentration 6x10^{-}6 M in THF system(red: pure solvent and blue curve: Th(IV) in THF medium)

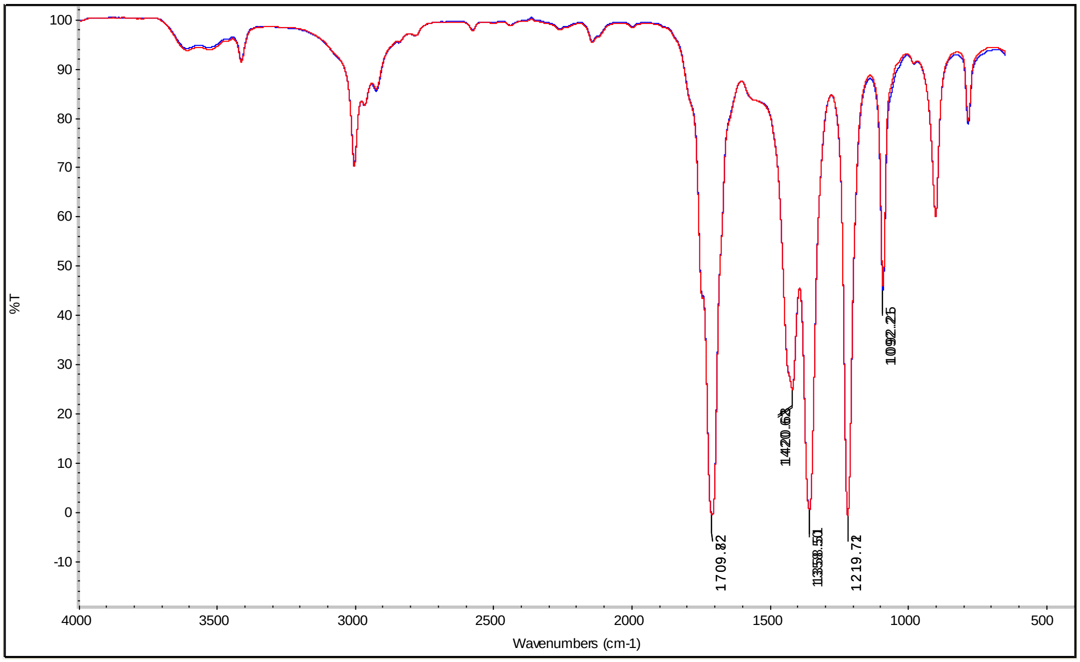

Figure 3.6: Infrared spectra of Th(IV) ion concentration 6x10^{-6} M in acetone system(red: pure solvent and blue curve: Th(IV) in acetone medium)

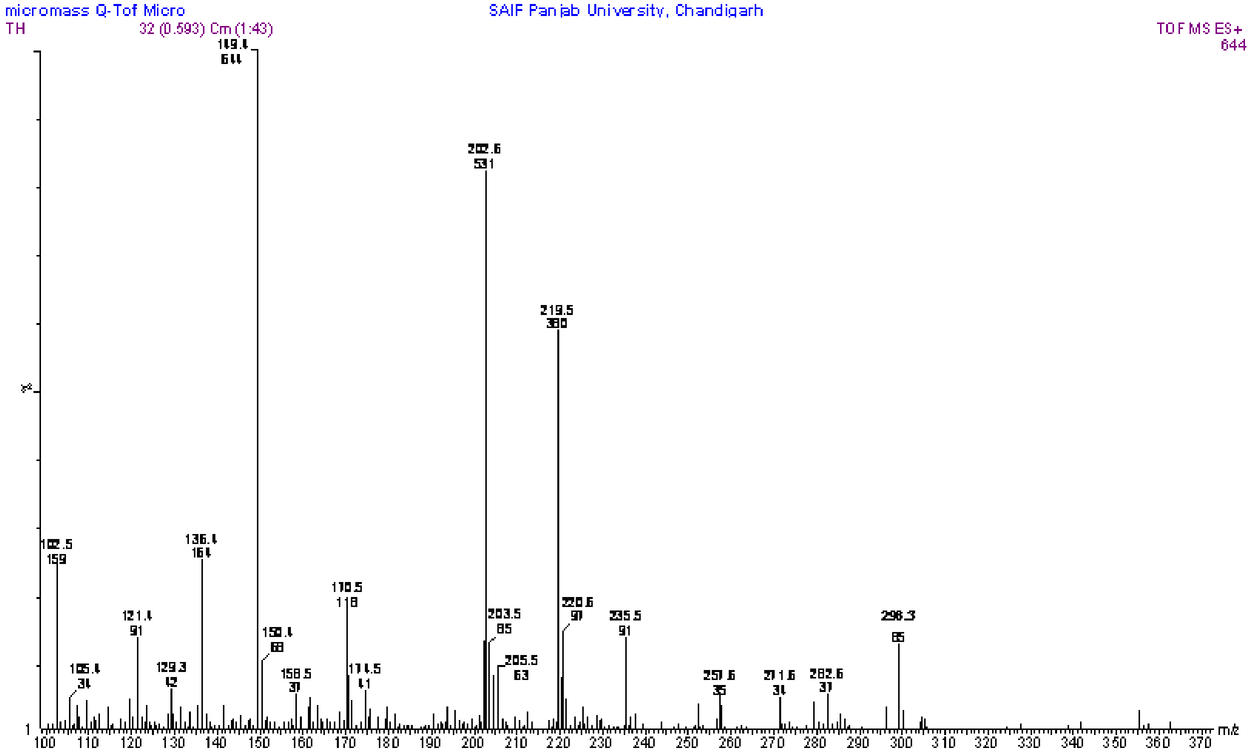

Figure 3.7: Mass spectra of Th(IV) ion concentration 6x10^{-6} M

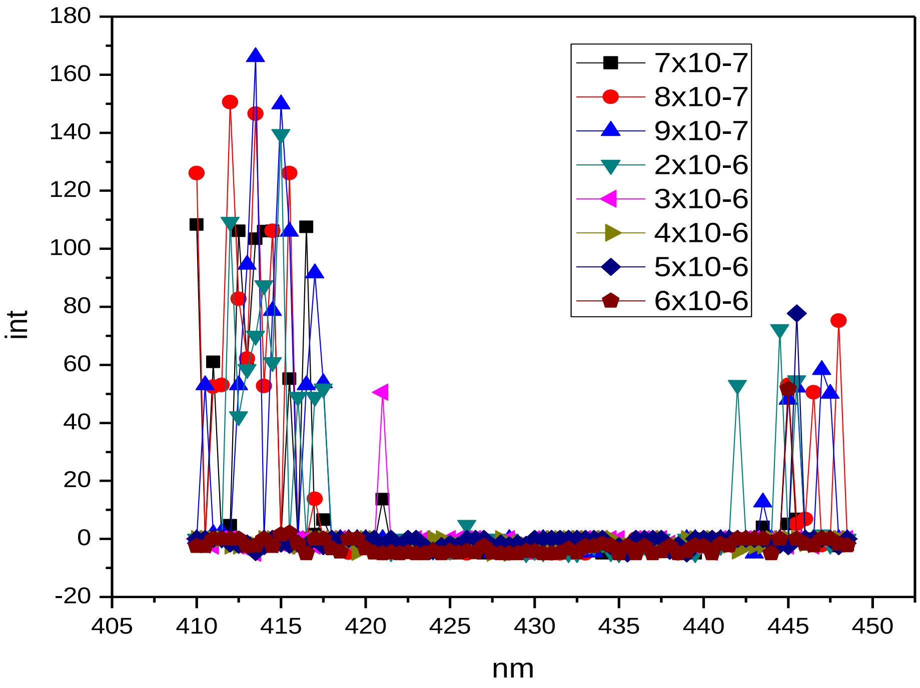

Figure 3.8: Emission spectra of Th(IV) ion in aqueous system

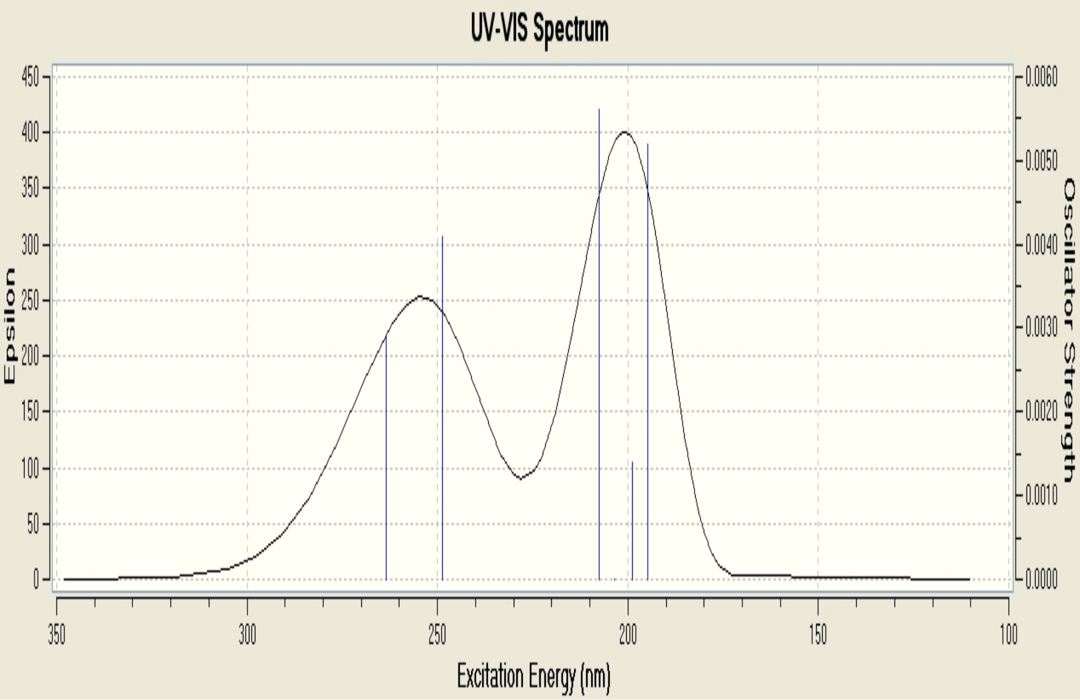

Figure 3.9: Absorption spectra of $[Th(OH)_4]$ tetrahedral species in gas phase

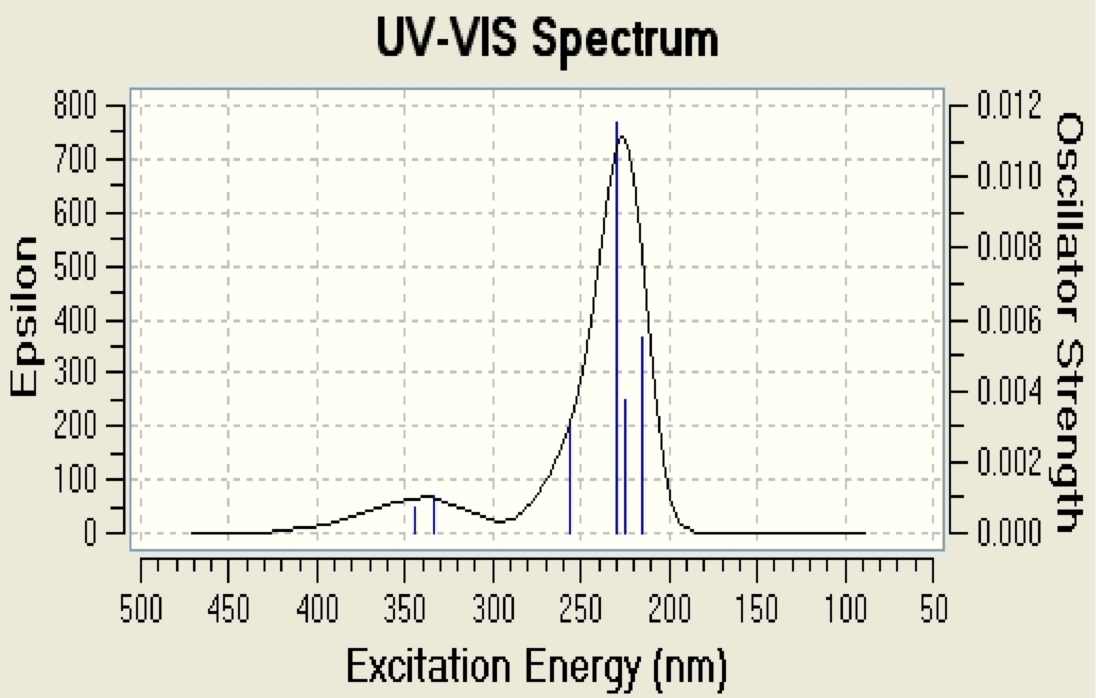

Figure 3.10: Absorption spectra of $[Th(OH)_4]$ square planar species in gas phase

Conclusion

A new analytical method is established for the quantitative determination of thorium (IV) by simple and rapid spectrophotometric method. The narrow working range of Th(IV) ion lies between $7x10^{-6}$ M to $5x10^{-7}$M above $7x10^{-6}$ M and below $5x10^{-7}$M Th^{4+} concentration range no absorbance peak in the region of 190nm to 400nm. Out of four tetravalent ions present in the group IVB i.e., Ti^{4+}, Zr^{4+}, Hf^{4+} only Th^{4+} is giving UV absorbance peak in the region of 205nm. This evidence shows that Th^{4+} is belong to actinide series not in transition series. Moreover, this peak is observed only in water medium and do not exhibits any electronic transition properties in other solvents like methanol (CH_3OH), ethanol(C_2H_5OH), acetone (CH_3COCH_3), dimethylsulphoxide (CH_3CSCH_3), diethyl ether$(C_2H_5)_2O$ and tetrahydrofurane (C_5H_4O). Theoretically, the structures and absorption spectra of all possible species of Th(IV) hydrolysis were calculated using Gaussian 03 program and B3LYP density functional method with the SDD basis set in ground state and TD-SCF excited state.

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