Chapter 1

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The observation\(^1\) of intense Raman scattering from pyridine adsorbed at a silver electrode excitation wavelength longer than the absorption spectra of either metal or neat pyridine, an enhancement mechanism involving charge transfer has been suspected. A demonstration of the role played by charge transfer in the enhancement of surface Raman scattering has often relied on a correlation of the Raman intensity profile with the low-energy absorptions that belong to neither the metal nor the adsorbate. Surface Raman excitation profile with differential reflectance observations at red wavelengths and suggested resonance Raman enhancement of intensity from vibrations in a silver-pyridine complex. Low-energy (2.0-2.5 eV) features observed in the electron energy loss spectrum of pyridine at smooth Ag (iii) were assigned by Demath \(^2\) and coworkers to metal-molecule charge transfer excitations. Corroborating this assignment were the experiments of Yamada et al. where a new long wavelength excitation above the background absorption of thin silver island films was observed upon addition of pyridine to the system.

Otto and co-workers \(^3\) reported a first layer effect characterized by saturation of Raman signal intensity at monolayer coverage and quenching by less than one monolayer of oxygen .The saturation of the surface Raman signal from pyrometallocnic dianhydride at Cu(III) at monolayer coverage when Raman excitation is in resonance with low-energy transitions observed in the high-resolution electron energy loss spectrum. The demonstration of a first layer effect tends to elevate the contribution of charge transfer resonance Raman to the overall SERS
effect above longer range electromagnetic contributions.

Localized charge transfer excitations in surface complexes are distinguishable by their dependence on applied potential. As the voltage is swept more negatively toward the potential of zero charge or p.z.c., the work function (0) and surface charge decreases. Neglecting image potentials, relaxation effects and metal-adsorbate binding energies, the photon energy of a metal-to-adsorbate charge transfer is given by \( h\nu = 0 - \text{EA} \) (where EA is the vacant adsorbate affinity level). The charge transfer energy shifts towards the red with decreasing 0 and more negative voltages. Observed shifts in the surface Raman intensity maxima with applied potential therefore suggest surface Raman enhancement via resonance with a charge transfer \(^4\).

Photochemistry of adsorbates at metal surfaces \(^4\)\(^-\)\(^8\) might be considered a complicating interference in deciphering the source of the surface Raman intensity. Nonetheless, the product and the threshold wavelength of the surface photoevent provide handles to assist our understanding of the interaction of photons with the adsorbate-covered surface; an interaction perhaps shared in the SERS enhancement. Indeed, even the observation of photochemistry at metal surfaces shares the roughness prerequisite of SERS. Because of rapid non-radiative excited state decay though the metal band system \(^5\), reduced photochemical quantum yields are expected for adsorbates near metal surfaces. Conversely, enhanced photochemistry of adsorbates separated from the surface is expected because of the increased electric field at rough surface features \(^6\). It seems clear that if the adsorbate energy level involved in the photochemistry is not broadened by wavefunction mixing with the metal then the photochemical reaction rate can compete with the rate of excited state decay through the metal \(^9\). With small roughness features (from a
single adatom to a small cluster of adatoms) a narrow density of metal states at the atomic scale surface defect reduces mixing of adsorbate and metal wavefunctions and facilitates surface photochemistry.

In this study, we present the photochemistry of trans-4- stilbazole adsorbed at an electrochemically roughened silver electrode. We compare the threshold wavelength with surface Raman excitation profiles, linking photochemical initiation and surface Raman enhancement. Charge transfer implications of the profiles are discussed. Uncertainty about the structure of the photoproduct can limit the utility of photoactive adsorbates in deciphering the general SERS enhancement mechanism. We removed this uncertainty by careful in-situ and ex-situ analysis of the structure of the photoproduct. As recognized by Mulliken, who suggested the application of his early theoretical treatment of charge transfer excitations to the heterogeneous metal-adsorbate system, the states coupled by charge transfer excitations can be identified by the products of dissociation of each state. Thus, a transition from a ground state, which dissociates to neutral M+A, to an excited state, which dissociates to M\(^+\) A\(^-\), defines an electron transfer from M to A. By the same reasoning, if adsorbed trans-4- stilbazole can be shown to have donated or accepted an electron along the photochemical reaction pathway, then the photochemical initiation, and the first layer effect in SERS, can be unequivocally assigned to a metal (M)-adsorbate (A) charge transfer.

Luminescent and redox-active multinuclear metal complexes are playing a key role in the development of artificial systems exhibiting made-to-order properties. In particular, these species represent the basis for the design of molecular devices capable of using light energy to perform valuable functions, such as conversion of solar energy into chemical energy and (ii) elaboration of information at the molecular
level. As far as point (i) is concerned, dendrimers containing Ruthenium (II) and/or Osmium (II) polypyridine subunits are very interesting because of their ability, when properly designed, to behave as light-harvesting antenna systems.

We have extensively been involved in the preparation and study of a series of Ruthenium (II) and Osmium (II) dendrimers in which 2,3-bis(2-pyridyl) pyrazine (2,3-dpp) acts as the bridging ligand to assemble the various metal subunits. Many luminescent and redox-active dendrimers of this series have been synthesized and studied, with the larger systems containing as many as twenty two metal subunits. As for any type of dendrimer, the possibility to prepare large systems having the desired properties resides in the availability of specific building blocks. Trinuclear species like \([\text{Cl}_2\text{Ru}\,(u\text{-}2,3\text{-dpp})\text{Ru(bpy)}_2]^{4+}\), \(\text{Cl}_2\text{RuRu}_2(bpy = 2,2'\text{-bipyridine})\) and \([\text{Cl}_2\text{Ru-(u-2,3-dpp) Os(bpy)}_2]^{4+}\), \(\text{Cl}_2\text{RuOs}_2\) have indeed been essential to build up most of the larger species of the series, through convergent or semi-convergent routes, by taking advantage of the labile chloride ligands of the central metal, So, 1 and 2 may be considered "active" dendrons, in the sense that they can be employed in the construction of larger dendrimers.

The chemistry of transition-metal complexes containing nitrogen oxides has drawn considerable attention. The main stimuli for this investigation comes from the widespread occurrence of nitrogen oxides as environmental hazards produced in many combustion processes. It is well documented that nitro and nitroso compounds can undergo deoxygenation to give products via the formation of imido intermediates. A general synthetic route for the formation or co-ordinated imido species, \([\text{M}_3\text{(CO)}_{10}(u_3\text{-NR})]\) where \((\text{M} = \text{Fe, Ru or Os}; \text{R} = \text{Ph or tolyl})\) has been developed from the reactions between the transition-metal clusters,
[M₃(NCMe)ₙ(CO)₁₂₋ₙ] (n = 0-2) and nitro- or nitroso-arene. These imido clusters have also been proposed as intermediates in the catalytic reduction of nitro-benzene to aniline. Recently, we have also demonstrated the formation of an unprecedented cluster, [Ru(u₂-NPh)₂(u-n²-ONPh)₂(CO)₇] in which both phenylimido and nitrosobenzene moieties are present. In order to extend our investigations according to the above synthetic approach, nitroso compounds with ortho-substituted functionalities have been selected since there has been relatively little study on this class of compounds. 1-Nitroso-2- naphthol (referred to as 1, 2- naphthoquinone-1-oxime) shows a different reactivity pattern compared to nitrosoarenes since it can undergo tautomerization to give an oxo- oxime as shown in scheme 1.

1- Nitroso-2- naphthol is currently used as a complexing agent in cobalt analysis and is also used as a UV and thermal stabilizer. However, co-ordination compounds containing this ligand are comparatively rare. Structural analysis of these complexes reveal a unique co-ordination mode in which the naphthoquinone-oxime moieties act as a bidentate ligand which chelate to the central metal atom through the nitroso N atom and the naphtholic O atom. Alper and Edward demonstrated the reductive deoxygenation of p-nitrosophenols by [Fe(CO)₅] which afforded 4,4’- dihydroxyazobenzene. Charalambous further studied the reaction of [Fe(CO)₅] towards 1,2-naphthoquinone-2-oxime and 5-methoxy-1,2-quinone-2-oxime (5-methoxy-2-nitrosophenol) which gave 2-amino N₄ (1-hydroxynaphth-2-yl)-1,4-naphthoquinone-4-imine and 5-hydroxy-dibenzo[b,i]phenazin-12(6H)-one as well as 2-amino-7-methoxy-3H-phenoxazin-3-one respectively. Nevertheless, there is no report concerning the reactivity of nitrosophenols towards transition-metal carbonyl clusters. In this paper, the reaction between triruthenium
dodecacarbonyl and 1-nitroso-2-naphthol is described and we show that the cluster undergoes fragmentation to give two isomeric mononuclear complexes as the major products. In addition, by varying the experimental conditions, the above reaction also yields a trinuclear cluster with two co-ordinated 1,2-naphthoquinone-1-oximato moieties which adopt an unprecedented $\mu-\pi^3$-bonding mode involving the oximic oxygen atom in addition to both naphtholic oxygen and oximic nitrogen atoms. Surprisingly, we have also isolated a novel cluster with a co-ordinated phenoazinone-like ligand which may have arisen from a quinone-imine or -nitrene' intermediate via the reductive deoxygenation of the quinone-oxime by the transition-metal carbonyl cluster.

The study of high-valent metal complexes with the metal ion multiply bonded to a heteroatom continues to be an active area of research. Of particular interest to us is oxo, nitrido and imido- ruthenium and -osmium complexes in high oxidation states. These complexes have strong $\delta\pi-\pi$ interactions. Because of the high $E^0$ value, the highly oxidizing ruthenium ion would complete with the heteroatom for the bonded electron pair(s). *The electrophilic* [fig.1]. Thus an oxidation state of -II for the oxygen atom in non-oxidizing metal-oxo complexes may be an appropriate description but the situation could be quite different in the cases of ruthenium-oxo and in some high- valent osmium-oxo complexes. To account for the high affinity of [Fe$^{IV}$ (porp$^+$)O] (porp$^+$ - porphyrinato cation radical) in the oxidation of saturated C-H bonds. Sawyer and co-workers suggested the term “oxene” to describe the oxygen atom of the Fe = O. We also suggest that a highly oxidizing metal ion would change an organoimido ligand from a 6- electron donor to a 4- electron one. In the extreme case, the metal ion is in a lower oxidation state and the organoimido group behaves like a “nitrene".
Highly oxidizing cationic ruthenium-nitrido complexes had been suggested to play an important role in oxidation of bound ammonia to nitrite but these species have neither been isolated nor characterized. Electrochemical studied by few scientist\(^{(4)}\) suggested the following reaction scheme.

The highly oxidizing Ru=N species would undergo intramolecular redox reaction leading to the oxidation of N\(^{3-}\) to NO\(_2^-\). Studies of metal-nitrido complexes are also of importance in the context of activation of dinitrogen molecule. The disproportionation of a M-N=N-M to two M=N units provides an alternative pathway for the activation of dinitrogen molecule.

In general, high-valent osmium complexes are less oxidizing than their ruthenium analogues. However, the oxidizing power of Os=O and Os=N could be substantially enhanced through excitation with uv-visible light (Scheme 2). Extensive studies from this laboratory have established the rich redox chemistry of the 3[(dxy)\(^{1}\)(dxz,dyz)\(^{1}\)] excited states of some Os(VI)=O and Os(VI)=N complexes.

The photophysical and photochemical of several d\(^{6}\) transition metal coordinated to N-heterocyclic ligands have been intensively investigated. A variety of applications based on fundamental investigation of photophysical and photochemical properties have emerged, such as luminescence-based sensors and displays, photoreactive polymers and dye-sensitization of semiconductors.

The development of more complexe system, especially within the framework of supramolecular chemistry, gives rise to the possibility of designing organized systems as components of molecular level
photochemical devices). Supramolecular systems are constituted of a number of discrete molecular components with definite individual properties, held together by chemical interaction. This organization is particularly interesting for the development of systems capable of performing useful functions, such as use of light for energy or information purposes. These chemical systems have led to applications of inorganic photochemistry in areas such as biological chemistry, luminescence sensors, and advanced materials.

Molecular devices are assemblies of molecular components designed to achieve specific functions, such as photoinduced electron and energy transfer in solar energy conversion, electron collection, remote photosensitization, antenna effect, photoswitching of electric signals, light-energy up conversion, photoinduced structural changes in switch on/off applications (photoisomerizable system), molecular wires and sensors, in analytical chemistry, and in the development of new materials and nanoscale electronic devices. In this aspect, caged metal ions, their ion-pairs and some covalently-linked systems studied by our group will be discussed here. Also, regenerative photoelectrochemical cells and some ruthenium complexes used as sensitizer for charge injection into nanocrystalline semiconductors will be presented to illustrate an application that has evolved from a fundamental investigation of inorganic photochemistry by use of a specifically designed assembly to conceive artificial molecular devices.

The enzyme nitric oxide synthase (NOS) is the major biological source of nitric oxide (NO), a secondary messenger acting in a myriad of circumstance that include neuronal development, regulation of blood pressure, apoptosis, neurotransmission, and immunological response. Because of the central importance of NO, NOS has been implicated in
septic shock, inflammation, a variety of neurodegenerative disorders, and heart disease.\textsuperscript{18-20}

Full length NOS consists of oxygenase, reductase, and calmodulin binding domains. The NOS oxygenase domain (NOSoxy), which contains cysteine-ligated heme and tetrahydrobiopterin (H\textsubscript{4}B) cofactors, catalyzes the conversion of arginine and molecular oxygen to NO and citrulline\textsuperscript{21}. The electrons necessary for this reaction are NOSoxy by a calmodulin-binding linker\textsuperscript{22,23}. NOS functions as a homodimer; the reductase module from one half of the dimer reduces the oxygenase domain of the other.\textsuperscript{24,25} Calmodulin binding is known to modulate electron transfer and, hence, catalysis.\textsuperscript{26-28} Several crystal structures of the NOS oxygenase domain have been determined,\textsuperscript{29-31} but the structure of the full length enzyme remains elusive.

We have a long-standing interest in the high-valent intermediates thought to play key roles in heme-mediated oxidations\textsuperscript{32-38}. To observe these intermediates, we have designed Ru-diimine photosensitizers (Ru-wires) that bind to the mechanistically related enzyme cytochrome P450 and inject an electron in to the active site upon excitation with 470-nm light.\textsuperscript{38} Energy transfer between the excited state of the Ru-wire and the heme also serves as a sensitive structural probe.\textsuperscript{32-38} Like NOSoxy, cytochrome P450 enzymes posses a cysteine-ligated heme in the active site and catalyze the oxidation of substrates using molecular oxygen and two electrons supplied by a reductase (in the case of P450, a separate protein).

Given the postulated mechanistic similarities between NOS and cytochrome P450, we have endeavored to develop similar photosensitizer wires for NOS. Our initial investigation showed that complexes 1-3 bind
the oxygenase domain of murine inducible NOS (NOSoxy) with micromolar dissociation constants. Intriguingly, a combination of fluorescence energy transfer (FET) measurements and structural modeling suggests that 1 and 3 bind to the surface patch thought to interact with the reductase, module. Second generation compounds 4 and 5, which are structurally analogous to 2 and 3, bind in the iNOSoxy active site with micro- and nanomolar dissociation constants.

The assembly of molecular components via covalent bonds greatly enhances the possibilities to control the intercomponent processes and the function of multicomponent systems because the reactants can be fixed at a well-defined distance and (sometimes) orientation. This approach has been very helpful for the advancement in the field of photoinduced electron and energy transfer (PET and PEnT). The extension to multicomponent supermolecules has been accompanied by an increasing ability to control the PET and PEnT reaction and obtain sophisticated functions, such as stabilization of photoinduced charge separation, multielectron collection, harvesting of excitation energy in artificial antennas, and various logical and switching functions.

Transition-metal complexes of Ru (II), Re (I), Rh (III), and Ir (III) feature favorable electrochemical, photophysical, and photochemical properties. Therefore, such complexes have been extensively used to construct polynuclear species, due to the relative ease of using a modular synthetic approach in coordination compounds. However, as the number of components increase, there is an increasing difficulty to maintain a well-defined structures of the resulting supermolecule. For instance, complexes obtained from bidentate bpy-type ligands with Ru(II), including the most widely used Ru(bpy)$_3^{2+}$ are chiral (bpy is 2,2'-bipyridine); furthermore, with a single substituent on each ligands, the
bidentate ligands is generally not symmetric, giving four isomers for each homoleptic complex (cis/trans and fac/mer). Thus, the use of tris (bidentate) coordination to fill the octahedral environment around the Ru(II) center for building up polynuclear assemblies may result in a large number of isomers.

The effect of light on the Belousov-Zhabotinsky (BZ) reaction was noted almost 30 years ago. When the cerium-catalyzed BZ system was irradiated with ultraviolet light, the oscillations were either modified or completely suppressed depending on the light intensity and chemical composition. Ultraviolet light was also found to initiate chemical waves in a thin layer of ferroin-catalyzed BZ solution. The tris (2,2'-bipyridine) ruthenium(II) complex, Ru(bpy)_3^{2+}, was first used in the BZ reaction as a luminescent indicator for oscillatory behavior when irradiation with UV light investigated the influence of visible light on BZ reactions with various catalyst and found the ferroin-and ruthenium-catalyzed systems to be significantly affected but the cerium-catalyzed system to be unaffected. The ruthenium-catalyzed system has become increasingly important over the year, particularly in studies of spatiotemporal behavior, since the medium excitability can be conveniently varied by adjusting the illumination intensity. Light at 452 nm produces an excited state of the ruthenium catalyst, which gives rise to a sequence of photochemical reactions that affect the basic chemistry of the BZ reaction. Kuhnert used an illuminated ruthenium-catalyzed system as a photochemical memory device, where the image of a mask was retained as a phase shift through successive oscillations. Illuminated ruthenium-catalyzed systems have subsequently been for developing geometrical patterns, generating diffusion-phase waves, and initiating and controlling spiral waves.
Several mechanisms have been proposed to account for the light sensitivity of the Ru(bpy)$_3^{2+}$-catalyzed BZ reaction. The primary photochemical process is absorption of visible light by the Ru(bpy)$_3^{2+}$ complex. The excited state of the complex, Ru(bpy)$_3^{2+*}$, is an extremely strong reducing agent, with a Ru-(III)/Ru(II) reduction potential of -0.86 V compared to a reduction potential of 1.26 V for the ground state. The Ru(bpy)$_3^{2+*}$ serves to reduce the reactant BrO$_3^-$ to Br$^-$, which is the primary autocatalysis inhibitor in the BZ reaction. An indirect path for the photochemical reduction of bromate to bromide in the presence of oxygen has also been proposed by Ready et al. In a series of papers, Hanazaki and co-workers have examined the photochemical mechanism for the inorganic subset of the ruthenium-catalyzed BZ reaction, namely the illuminated Ru(bpy)$_3^{2+}$-bromate reaction in sulphuric acid. They proposed a scheme involving the photochemical production of the autocatalyst HBrO$_2$ and the inhibitor Br$^-$ to account for the experimentally observed inhibition as well as induction of oscillatory behavior by light.

Much less is known about the photochemical reaction of the organic subset of the ruthenium-catalyzed BZ reaction. The importance of the organic subset in the light sensitively has been recently suggested, and the role of bromomalonic acid (BrMA) as a bromide source has been pointed out by some worker.

We consider the light sensitivity of both the inorganic and organic subset of the ruthenium-catalyzed BZ reaction. In this paper and develop a reaction mechanism that accounts for the photosensitivity of the overall reaction. We find, contrary to previous studies, that bromide is photochemically generated from bromomalonic acid, while bromous acid is photochemically produced from bromate. In BZ systems that initially
contain bromomalonic acid, which is common in the systems used for
spatiotemporal studies, the predominant effect of illumination is
production of the inhibitor Br. The sensitivity of such systems to
illumination can be adjusted by varying the initial concentration of
bromomalonic acid in the reaction mixture.

Metalloporphyrins in association with protein globule performs
several important biochemical functions in nature. Hemoglobin,
myoglobin, chlorophyll, cytochromes, catalase and paroxidase are well
known examples, the chemistry of which relates principally to the redox
property of corresponding metalloporphyrins and also their ability in
transportation, storage and activation of molecular oxygen. Over the
years a great deal of concerted efforts has brought to light substantial
understanding of the structure - function relationship in these natural
porphyrins.

Interest in metalloporphyrins are not confined only in the
biological field as these compounds are equally important from chemical,
industrial and technological point of view. During the last three decades
synthetic porphyrins have been widely studied for various applications
spanning the whole chemical and biological fields. Metalloporphyrins are
widely and intensely investigated in the area of catalysis and also as
models and mimics of enzymes like catalase, paroxidase, P450
cytochromes or as transmembrane electron transport agents They have
also been used as NMR image enhancement agents, nonlinear optical
materials and DNA- binding or cleavage agents .Large numbers of
patents have been lodged for the use of porphyrins as radio diagnostic
agents and in photodynamic therapy (PDT), foodstuff antioxidants,
semiconductors or electrochromic materials
Their applicability is so broad that they find a place even in beauty shops as body deodorants and stimulants of hair growth.

Photoinduced electron transfer (ET) is one of the very active areas of research in chemistry in this decade. The rate of electron transfer from a donor molecule to an acceptor in a solvent is controlled by several factors and the most important of them are the free energy change of the reaction, the reorganization energy, and the ET distance (d) between the donor and acceptor. The electron-transfer rate constant \( k_{et} \) in both the classical and semiclassical theories can be represented by eq.1.

\[
K_{et} = K_{et}v_n \exp[\Delta G^2/(RT)]
\] ......................................................(1)

Where \( k_{et} \) is the electronic transmission coefficient, \( v_n \) the nuclear frequency, and the free energy of activation. When the electron-transfer distance, \( d \), is kept constant, the rate of an electron-transfer process is decided by and through the following equation (eq.2)\(^{43-45}\)

\[
\Delta G^{++} = (\lambda+\Delta G^*)^2/(4\lambda)
\] ......................................................(2)

The value of \( k_{et} \) \( v_n \) is usually taken as \( 1.0 \times 10^{11} \) s \(^{-1}\) Marcus theory predicts that \( k_{et} \) will follow a bell-shaped energy dependence as a function of initially increasing as become more negative in the normal region and decreasing with increasing driving force in the inverted region.\(^{46}\) According to Marcus theory, the maximum of the bell-shaped curve occurs when \( \lambda \) equal \( \Delta G \) where the free energy of activation is zero when. The Marcus inverted region may be observed. The experimentalists have realized that only for photoinduced ET reactions or for radiochemically generated energetic systems would a reaction have large enough exoergicity to display this parabolic behaviour.\(^{46-51}\) Although evidence for the inverted region is substantial in charge-shift
reactions, and charge-recombination reactions, it is almost nonexistent for bimolecular charge separation reactions except in the recent report by Turro et al. In the photoinduced redox reactions of Ru (II) complexes with cytochrome c in its oxidized and reduced forms. The following four reasons have been attributed for the difficulty of observing the inverted region for charge separation reactions at high exoergicity,

(i) Diffusion is the rate-limiting step, (ii) Lack of a truly homogeneous series in particular chemical donors or acceptors, (iii) $\lambda$ is an increasing function of the separation distance (d) between the reactants, and (iv) extra reaction channels become accessible at higher values. If these problems are circumvented by choosing the appropriate reactants, it is possible to observe the Marcus inverted region in the bimolecular reactions.

The poly pyridyl complexes of Ru (II) having excited states can be oxidised and reduced by a number of reagents and well characterised due to their single electron redox product by simple electron transfer quenching. The insufficient conversion excitation energy through high product formation is coupling insuing reaction was of keen interest. Various studies have been done regarding the use of the scavengers quenchers whose redox products undergo rapid reaction with reagents and highly reactive colloidal and heterogenous catalyst. A number of studies were carried out regarding the photo redox behaviour of these complexes by modifying the net charge on the complexes (or by adjusting ligands substituents.

The primary photo process and ensuing reaction with these complexes involves only one single electron transfer process. It is evident that competitive reactions involving interaction of excited Ru (bpy)
with cobalt (III) complexes that rapid unimolecular decomposition of the cobalt (II) complexes permits net photo conversion to occur.

The quenching of Ru (bpy)$_3^{2+}$ by inorganic ions can undergo with the normally observed back electron process to yield the initial product Ru(bpy)$_3^{2+}$ without the use of other sacrificial reagents. The mechanism of catalytic redox process in transition metal complexes provide the observation of strong solvent effect on the lifetime and properties of metal complexes, charge transfer and ligand field excited state. The pronounced change in acid-base properties and the other properties have shown that reaction with water or solutions occur following excitation and in some cases labilisation of bipyridine type of ligands.

In some of the stable monodentate complexes, renders precise structure difficult to establish in many photoreactions. The cationic complexes of Ru(II) and Ru(III) containing phosphines and arsines were studied due to their importance as catalytic species in various homogeneous reaction. Recently the excited state quenching process and ensuing reaction with Ru(L)$_3^{2+}$ (L=4,4'-diphenyl1,2,2'-bipyridine) and (4,4'-diphenyl1, 1, 10-phenantralline) have been studied along with laser flash and convensional spectroscopic techniques.

The present study deals with excited state quenching process and ensuing reaction of cationic complexes with Ru(III) containing phosphines and arsines. The use laser flash and spectroscopic techniques to observe the reactions of the cationic complexes having several potential reductants indicates that quenching can occur by net electron transfer reduction as well as by interactions not involving electron transfer at all.
The MBSL of both aqueous and non-aqueous solutions is similar to the emission expected from high-temperature flames; e.g., excited-state OH$^·$ from water, excited states of C$_2$ (d$^3$II$_g$- a$^1$II$_u$) from hydrocarbons (these lines also give hydrocarbon flames their blue color), and CN excited states in the presence of a nitrogen source. For both aqueous and non-aqueous liquids, MBSL is caused by chemical reaction of high-energy species formed during cavitation by bubble collapse. Its principal source is most probably not blackbody radiation or electrical discharge. MBSL is a form of chemiluminescence.

Determination of the temperatures reached in a cavitating bubble has remained a difficult experimental problem. As a spectroscopic probe of the cavitation event, MBSL provides a solution. High-resolution MBSL spectra from silicone oil under Ar have been reported and analyzed. The observed emission comes from excited state C$_2$ and has been modeled with synthetic spectra as a function of rotational and vibrational temperatures. From comparison of synthetic to observed spectra, the effective cavitation temperatures. From comparison of synthetic to observed spectra, the effective cavitation temperatures is $5,5050 \pm 150$ K.

A second spectroscopic thermometer comes from the relative intensities of atomic emission lines in the sonoluminescence spectra of excited-state metal atoms produced by sonolysis of volatile Fe, Cr, and Mo carbonyls. Sufficient spectral information about emissivities of many metal atom excited states are available to readily calculate emission spectra as a function of temperature. Because of this, the emission spectra of metal atoms are extensively used by astronomers to monitor the surface temperature of stars. From comparison of calculated spectra and the observed MBSL spectra from metal carbonyls, another measurement
of the cavitation temperature was obtained. The effective emission temperature from metal atom emission during cavitation under argon at 20 kHz is 4,900 ±250 K.

The excellence of the match between the observed MBSL and the synthetic spectra provides definitive proof that the sonoluminescence event is a thermal, chemiluminescence process. The agreement among these spectroscopic determinations of the cavitation temperature and to that made by comparative rate thermometry of sonochemical reactions is extremely good.

In a fundamental sense, chemistry is the interaction of energy and matter. Chemical reactions require energy in one form or another to proceed: chemistry stops as the temperature approaches absolute zero. One gas only limited control, however, over the nature of this interaction. In large part, the properties of a specific energy source determine the course of a chemical reaction. Ultrasonic irradiation differs from traditional energy sources (such as heat, light, or ionizing radiation) in duration, pressure and energy per molecule. The immense local temperatures and pressures and the extraordinary heating and cooling rates generated by cavitation bubble collapse mean that ultrasound provides an unusual mechanism for generating high-energy chemistry. Like photochemistry, very large amounts of energy are introduced in a short period of time, but it is thermal, not electronic, excitation. As in flash pyrolysis, high thermal temperatures are reached, but the duration is very much shorter (by >10^4) and the temperatures are even higher (by five-to tenfold). Similar to shock-tube chemistry or multiphoton infrared laser photolysis, cavitation heating is very short lived, but occurs within condensed phases. Furthermore, sonochemistry has a high-pressure component, which suggests that one might be able to produce on a
microscopic scale the same macroscopic conditions of high-temperature pressure "bomb" reactions or explosive shockwave synthesis in solids. Control of sonochemical reactions is subject to the same limitation that any thermal process has: the Boltzmann energy distribution means that the energy per individual molecule will vary widely. One does have easy control, however, over the intensity of heating generated by acoustic cavitation using various physical parameters (including thermal conductivity of dissolved gases, solvent vapor pressure inside the bubble, and ambient pressure). In contrast, frequency appears to be less important, at least within the range where cavitation can occur (a few hertz to a few megahertz), although there have been few detailed studies of its role.

Oxidation of mainly biological substrates in the presence of light, oxygen and a dye as light absorber have been observed since 1900. Strub and Noack suggested that intermediate dye peroxides are the oxidizing agents which deliver their oxygen to a substrate there by reforming the original dye.

Mechanistic studies were started by G. O. Schenk et al. in 1926. At this time Moureu, Dufraisse and Dean discovered the direct photooxygenation of rubrene and Windaus and Brunken discovered the photosensitized oxygenation of ergosterol. The structures of both the products formed were elucidated some years later and shown to be those of transannular peroxides (endoperoxides). Early attempts made by the Windaus group to extend photosensitized oxigenation reactions to simpler dienes like 1, 3-cyclohexadiene or \( \alpha \)-terpiene were unsuccessful. The generalization of such reactions using conjugated cyclic dienes as substrates, soon followed by the discovery of the hydroperoxide synthesis of ascaridole from \( \alpha \)-terpiene in 1941 started a series of investigations,
both with respect to preparative organic photochemistry and elucidation of the mechanism involved.

The extension of direct photooxygenation reaction to polycyclic aromatic hydrocarbons. As well as to aryl- substituted carbocyclic and hydrocyclic pentadienes is due to the work of Dufraisne and Etiene \(^{15,16,17}\). Investigations on the mechanisms of these reactions were made by Brownen \(^{53}\), Cherkarovand Vember \(^{67-68}\). Already in his early investigations on type II direct and indirect photooxygenation reaction \(^{71,72,73}\) showed that the quantum yield of these process are independent of intensity as well as of the exciting wavelength of light. He also showed that in the direct photooxygenation of rubrene, two rubrene molecules have to take part in the reaction sequence which leads to the stable endoperoxide.

In order to account of overall reactions.

\[
\text{Ru} + \text{Ru}^* + \text{O}_2 \rightarrow \text{RuO}_2 \text{ (Stable)} + \text{Ru}
\]

Gaffron discussed three different mechanism (reaction path a-c) and concluded that the formation of an activated double molecule, \((\text{Ru})_2^*\) is the important step indirect photooxygenation of rubrene (reaction path c) rather than energy transfer to oxygen (path b). This view was supported by his results obtained with bacteriochlorophyll sensitized oxygenation of allyl thiourea \(^{74}\) the energy of the exciting light quanta (\(\lambda=760\) or 850 m\(\mu\)) was less than 37.7 K. Cal/Mole necessary to excite oxygen from its ground state into its excited state the only excited singlet state of oxygen discussed in connection with photooxygenation at this time.
*Reaction path a:*  

\[ \text{Ru} + \text{O}_2 \rightarrow (\text{RuO}_2) \text{ unstable adduct formed in dark.} \]  

\[ \text{Ru}^* + (\text{RuO}_2) \rightarrow (\text{RuO}_2) \text{ (stable) } + (\text{Ru}) \]  

*Reaction path b:*  

\[ \text{Ru}^* + \text{O}_2 \rightarrow \text{Ru} + \text{O}_2^* \text{ energy transfer to oxygen forming excited oxygen} \]  

\[ \text{O}_2^* + \text{Ru} \rightarrow \text{RuO}_2 \text{ (stable)} \]  

*Reaction path c:*  

\[ \text{Ru}^* + \text{Ru} \rightarrow (\text{Ru}_2)^* \text{ formation of an activated molecule} \]  

\[ (\text{Ru}_2)^* + \text{O}_2 \rightarrow \text{RuO}_2 \text{ (stable) } + \text{Ru} \]  

The direct photooxygenation of rubrene was also studied by two other groups of investigation\textsuperscript{75,76}. Schumacher\textsuperscript{77} confirmed the participation of two molecules of rubrene in this reaction. However he postulated the formation of an unstable, electronically excited rubrene oxygen complex which should either dissociate into its components be stabilized by collision with another rubrene molecule.

\[ \text{Ru}^* + \text{O}_2 \rightarrow (\text{RuO}_2)^* \]  

\[ (\text{RuO}_2)^* \rightarrow \text{Ru} + \text{O}_2 \]  

\[ (\text{RuO}_2)^* + \text{Ru} \rightarrow \text{RuO}_2 + \text{O}_2 \]  

A verification of reaction \[ (\text{Ru}_a \text{O}_2)^* + \text{Ru}_b \rightarrow \text{Ru}_a + \text{Ru}_b \text{O}_2 \]
was proposed by Schonberg\textsuperscript{78} order to explain the direct photooxygenation of rubrene and oxygenation of substracts photosensitized by chlorophyll on a general basis, the light absorber forms a labile complex with oxygen which then delivers its oxygen to a substrate forming the peroxide and the light absorber in the original state.

The quenching of the luminescence of tris (2, 2'- bpy )- Ru (II) by metal complexes is currently under active investigation \textsuperscript{79}. Depending upon the system, the dynamic quenching of the ruthenium (II) emission may involve either oxidation (eg. -1) \textsuperscript{80,81} or reduction (eg. 2) \textsuperscript{82} of the excited state (Ru* (bpy))\textsuperscript{2+} by the quencher (Q). Energy transfer quenching also offers a pathway for deactivation of the excited state in some system (eq-3) \textsuperscript{83,84}.

\begin{align}
*\text{Ru(bpy)}_3^{2+} \text{ Q} & \rightarrow \text{Ru (bpy)}_3^{2+} \text{ Q} \quad (5) \\
* \text{ Ru(bpy)}_3^{2+} \text{ Q} & \rightarrow \text{Ru (bpy)}_3^{3+} + \text{Q} \quad (6) \\
*\text{Ru (bpy)}_3^{2+} + \text{Q} & \rightarrow \text{Ru (bpy)}_3^{2+} + \text{Q}^* \quad (7)
\end{align}

More ever as may also have been pointed out energy -transfer eq-3 give rise to the electron transfer product generated in eq. 1or 2, may undergo subsequent reaction to yield the energy- transfer products in flash- photolysis experiments\textsuperscript{85} does not necessarily discriminate between primary electron transfer and energy transfer quenching mechanism. In these instances consideration of the relative reactivities of ground and excited donors and quenchers may take it possible to distinguish between the two mechanisms. The luminescent RuL\textsubscript{3}\textsuperscript{2+} complexes (where L = diphenyl bpy and diphenyl phenanthrolenes present useful prove as certaining the relative importance of electron transfer and energy transfer
quenching mechanism. The absorption and emission spectra of the complexes are nearly identical \( ^{86-87} \) making its likely that the rate of energy transfer quenching with a given acceptor Q will be varied by changing the substituents on the ligands \( ^{88-89} \) and the rate of electron transfer quenching reactions with a given oxidant or reductant Q should reflect the differences in driving force in a known manner \( ^{90-91} \). The complexes of ruthenium RuL\(_3\)^{2+}, where L is (diphenyl - bipyridine) and (diphenyl phenanthroline) has been used to investigates the mechanism of quenching of RuL\(_3\)^{2+}, the luminescent excited state of RuL\(_3\)^{2+}, by iron (III), chromium (III) and europium (III) in aqueous solution at 25°C. The quenching rate constant Kq were obtained from emission intensity and emission life time studies. In iron (III)-RuL\(_3\)^{2+} systems.

Flash photolysis experiments showed that RuL\(_3\)^{2+} and iron (II) are produced in the quenching reaction. The steady state levels of these products under continuous irradiation were determined as a function of iron (III) concentration and light intensity. In addition the rate constant K for the thermal back reaction of RuL\(_3\)^{2+} and iron (III) to reform the starting species Ru\(_3\)^{2+} and iron (III) have been measured using flash photolysis and stopped flow techniques. The rate constant Kq and K are function excited state and ground state RuL\(_3\)^{3+}/RuL\(_3\)^{2+} potentials respectively. Furthermore the rate constant are the most part, in accord with steady state levels of RuL\(_3\)^{3+} and iron (II) produced under continuous illumination. Thus it is conclude that the mechanism of quenching by iron (III) is predominantly electron transfer in nature. As the highest rate constant are observed for the ruthenium complexes with lowest reduction potentials electron transfer quenching is indicated and this hypothesis is supported by the results of flash photolysis experiments.

Stereoselectivity in the electron- transfer [ET] reaction has been
received considerable attention because of both theoretical basis and applications. For e.g. the regulation of the electron flow in biological system in which the electron donor and acceptor are fixed in their orientation. The be studied metal complexes in the in the stereo selective photoinduced ET reaction is a tris (1, 10- phenanthroline) ruthenium (II) ([Ru(Phen)_3]^{2+})\(^{54,55,93,94}\). Homochiral preference in the photoinduced ET quenching of the excited triplet state of ([Ru(Phen)_3]^{2+})\(^*\) by cobalt (III) complexes has been demonstrated\(^{95,96}\). Rau and Ratz have first reported the stereoselectivity in luminescence quenching of ([Ru(Phen)_3]^{2+})\(^*\) by optically active viologen 1-methy-1- [(3S)-(−)-3-pinanylmethyl-4, 4' bypyridinium ion (S-PMV\(^{2+}\))\(^97\). The \(^*\) isomer is preferentially quenched by S-PMV\(^{2+}\).

The present work stereoselectivity in the intra complex ET quenching process between ([Ru(Phen)_3]^{2+})\(^*\) and optically active viologens containing hapthyl and/or Phenyl groups\(^{98,99}\).

The control of victorial energy and electron transfer on multi component assemblies requires the synthesis of rigid rod like molecular species with this aim the use of Phen (Phen = 1, 10- Phenanthroline) is particularly appealing since functionalization of the ligand at the ligand at the right position allows the construction of the multi component system based on electro and photoactive Ru(Phen)_2\(^{2+}\) unit and its analogues a very strict control over the geometry of the assembly\(^{100}\).

In previous studied systems\(^{101,102}\) containing a Ru(Phen)_2\(^{2+}\) component and various electron or energy acceptors attached to it Ru-based complex was excited (Ru -> Ru\(^*\)), the ensuing process being subsequently monitored. Intrinsic deactivation of the Ru(Phen)_2\(^{2+}\) unit competes with these photoinduced process and is thus a serious
limitations. The main drawback, inherent to Ru(Phen)$_2^{2+}$ is that the lowest lying excited state is short lived. Several groups have tried to increase the life-time of Ru-Phen type centers $\Psi$ by structures modification. Knowing that the photophysics of ruthenium phen complexes is governed by the energy gap $\Delta E$ between the luminescent level. The later level provides an activated pathway for fast radiation less decay of the luminescent state $^{103}$. Thus on tries either to push the MC level to higher energy or to stabilize the MLCT level with the aim of increasing $E$ for instance stereo selectivity was found in intra complex quenching process between the excited triplet state of $\Delta$-tris (2, 2' bipyridine) ruthenium (II) and optically active viologen containing naphthyl group (s). Where the bipyridine ligand interacts with the naphthyl group of viologen.

Photo induced electron transfer (ET) is one very active areas of research in chemistry is the decade $^{104,105}$. The rate of electron transfer from a donor molecule to an acceptor in a solvent is controlled by several factors and the most important work of them is the free energy change $\Delta G$ of the reaction. the reorganization energy ($\lambda$) and ET distance (d) between the donor and acceptor. The electron-transfer rate constant ($K_{et}$) in both the classical and semiclassical theories can be represented by eq.

$$\Delta G^\pm = \frac{(1+\Delta G)^2}{(4\lambda)}$$

(5)

Substitution of the expression into equation (1) provides the basic relation (equation 3) for treating $K_{et}$ in terms of $\Delta G$ and $I$
\[ K_{\text{et}} = K_{\text{et}} v_n \exp \left[ -\left( \lambda + \Delta G^0 \right)^2 / (4 \lambda RT) \right] \] ............. (6)

The value of is usually taken as \( \gamma d K_{\text{et}} v_n \) is usually taken as \( 1.0 \times 10^{11} \text{S}^{-1} \)

The experiments have realized that only for photoinduced ET reactions or for radiochemically generated energetic system would a reaction have large enough exoeogucity to display this parabolic behaviour. According to classical Marcus theory ET can occur only at the interaction point of the two potential energy surface. There may be a more effective route via quantum mechanical nuclear tunneling from the reactant surface to the product surface in which case equation (4) may apply\(^{113}\).

Where Hrp is the electronic coupling energy, \( m \) is an integer, and \( S=1/\hbar n \).

This condition in likely to be particularly important in the inverted region where the vibrational wave functions of the reactant and product state are embedded. So region. In the normal region \((DG^0<1)\) eq. 4 is represented by the simplified expression eq. 5. When we measured the rate constant, \( K_q \) for the reductive quenching of Ru(bpz)_3^{2+} with pho, we were surprised to note that the \( K_q \) value for the reduction of this complex is smaller than for Ru (bpy) though the former is more exoergic by 0. 6v. hence to check whether we realize the marcus inverted region in this particular redox system. We have studied the photosensitized electron- transfer of six Ru(NN)_3^{2+} \((\text{NN}=\text{Poly Pyridyl ligand})\) with several Phenoate ions by choosing Ru (II) complexes of similar size but substantially variable reduction potentials from 0.69 to 1.40 V. Indeed we have the Marcus inverted region in this bimolecular photo induced ET reactions and the important finding are reported in this article.

Ru (II)- Polypyridyl complexes of similar of size but with variable
reduction potential undergo efficient photoinduced electron-transfer reactions with phenoate ions in aqueous medium. All these reactions are exergonic and are in accordance with the Marcus theory of electron-transfer. At high negative Marcus inverted region is observed in this bimolecular photoinduced charge reaction.

Living organism posses molecular machineries capable of performing sophisticated photobiological functions (e.g. energy conversion, vision, etc.)\textsuperscript{114}. These functions requires a complex elaboration of the absorbed light energy input that is only possible through a suitable organization of molecular components in space. Obviously, there would be no hope is trying to synthetically reproduce the enormous complexity of natural systems. On the other hand, the design and synthesis of supramolecular structures made up of relatively small numbers of suitably assembled molecular components and capable of performing selected light induced functions seems to be a non-unreasonable and stimulating goal. A supramolecular structure of this type can be called a molecular photochemical device looking towards this future goal, extended information on the peculiar photochemical and photophysical behaviour of assemblies of molecular components (covalently linked bi-or polychromophoric systems, donor-acceptor complexes, host-guest complexes, ion pairs etc.) is needed.

Some of the possible functions of molecular photochemical device have been classified as follows\textsuperscript{115}.

i. Generation and migration of electronic energy.
ii. Photo induced vectorial transport of electrical charge.
iii. Photo induced conformational charges.
iv. Control of photochemical and photophysical properties of
molecular components.

For each type of function, components to be assembled and possible types of devices have been discussed on general ground. Or the functions listed above, the second is certainly very relevant to the conversion of light into chemical energy, although functions of the first type can also be important in this context. (e.g. energy collecting "antenna" devices to increase efficiencies).

Studies on homogeneous system can contribute to elucidate fundamental principles, and to design, check and optimize new photosensitizer, donors and acceptors that will eventually be used as building block for supra molecular devices.

The most important component of any solar energy conversion device is of course, the photosensitizers. A survey of the chemical compounds shows immediately that entire classes of molecules can be discarded as potential photosensitizers. For various reasons the most promising field to explore in the search of photosensitizers is that of transition metal complexes.

The most widely used photosensitizer is the Ru(bpy)$_3^{2+}$ complex (bpy=$2$, $2'-$biperidine). It exhibits as adsorptions band at 450nm. with $\varepsilon = 14000$, the efficiency of the conversion from the excited state originally populated by excitation and the reactive state (nisc) is unity the lifetime of the reactive excited state is the us range, the excited state is oxidised at -0.86 v, and the reduction potential of the oxidised from of the complex is +1.26v. The excited state energy is 2.12 ev, the self exchange rate for electron transfer is larger than $10^6$ m$^{-1}$s$^{-1}$.

The main drawback of Ru(bpy)$_3^{2+}$ are as:
1) Relatively small absorption in the visible region (the absorption spectrum of Ru(bpy)\textsubscript{3}\textsuperscript{2+} does not match well the emission spectrum of sun).

2) A relatively high there should energy (with the lowest excited state at 2.12ev, the maximum thermodynamics efficiency for solar energy conversion is 21%)

3) A small turn over number (reported values range from 102-103) and,

4) A high cost.

One can remedy these drawbacks by suitable choice of ligands; in particular, by replacing one or two bpy with a ligand which is easier to reduce. A promising class or with high ligands field strength appears to be that of the cyclometalating ligands, which are structurally similar to the biperidine ligands but have a higher ligand field. Strength because the carbanion donor is much higher in the spectro chemical series that the corresponding nitrogen donor. The best complex to be cited here is Co(sep)\textsubscript{3}\textsuperscript{3+} complex. These type of complex exhibit long lifetimes and beautiful emission spectra at low temperature and there again an extra ordinary possibility to turn then photophysical properties because of an interplay between LC and CT excited states.

Strategies of the work may be given as-

a) To choose compounds that certain a transition metal ion in order to ensure the presence of a redox site at a suitable potential.

b) To prefer metal ions of the II or III transition row, in order to avoid that the lowest excited state is MC in nature, which would imply extremely short lifetime and photochemical and redox lability.
c) To select ligands which are easy to reduce, in order to have MLCT excited state as the lowest excited state, this assures long lifetime small S-T energy gap, high nisc, intense absorption bands at low energy and favorable electronic factor for redox quenching.

d) To link together the ligands so as encapsulate the metal ion, in order to prevent thermal and photochemical decomposition.
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