ULTRAFAST PHOTOPHYSICS AND PHOTOCHEMISTRY OF HEXACOORDINATED BROMIDES OF PT(IV), OS(IV), AND IR(IV) IN THE CONDENSED PHASE STUDIED BY FEMTOSECOND PUMP-PROBE SPECTROSCOPY

Igor L. Zheldakov

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Committee:

Alexander N. Tarnovsky, Advisor
Raymond A. Larsen
Graduate Faculty Representative
Michael Y. Ogawa
Mikhail Zamkov
ABSTRACT

Alexander N Tarnovsky, Advisor

Transition metal complexes are actively integrated into schemes for solar energy conversion, photocatalysis, photovoltaics, and photodynamic therapy. In these applications, the population optically delivered to the Franck-Condon region of the initial excited electronic state often travels over several non-equilibrated excited state surfaces before arriving to a product state with useful functions. Radiationless relaxation between multidimensional potential energy surfaces of polyatomic molecules takes place through avoided crossings, or more typically through real crossings - conical intersections. The understanding of the forces driving electronic relaxation in polyatomic molecules has attracted considerable interest, especially in recent years, when ultrafast laser experiments made it possible to monitor downhill motion of the wave-packet in real-time.

Ultrafast photophysics and photochemistry of PtBr$_6^{2-}$, OsBr$_6^{2-}$, and IrBr$_6^{2-}$ in the condensed phase (water, methanol, acetonitrile) was investigated in detail using femtosecond broadband time-resolved spectroscopy. Photoexcitation of PtBr$_6^{2-}$, and OsBr$_6^{2-}$ dianions at LF or CT bands leads to remarkably fast formation of the coherently vibrating photoproducts, $^3$PtBr$_5^-$ and $^3$OsBr$_5^-$ on less than 150 fs time scale. Vibrational coherence in these photoproducts can be launched due to coherence population transfer from the parent molecule or when a dissociation fragment passes through symmetry-induced Jahn-Teller conical intersections. Conical intersections in these systems result in ultrafast radiationless transitions to the ground electronic state followed by a ligand substitution. Hexabromoplatinate complex showed excellent photocatalytic properties. Photoexcitation of this complex results in the formation of highly
reactive pentacoordinated species $^3\text{PtBr}_5^-$ capable of oxidizing methanol and acetonitrile on an ultrafast time scale.

Photoexcitation of IrBr$_6^{2-}$ at one of the lowest CT bands is followed by fast internal conversion from higher lying excited states to the lowest excited state and then to the electronic ground state. No photodissociation is observed in this complex due to fast vibrational energy transfer from the hot ground state to solvent as opposed to the gas phase study where accepting vibrational energy medium was absent.

Femtosecond broadband pump-probe spectroscopy with 100 fs time resolution has been employed along with DFT/TDDFT theoretical calculations. The experimental and theoretical approaches brought together have provided a detailed understanding of the sequence of events that follow photoexcitation and an insight on central metal effects on the photophysical properties of these complexes. Overall, the results of the present investigation reveal fundamental background knowledge of the electronic factors in the photophysical properties of inorganic transition metal complexes.
To my parents, brother, and all others who helped me through all these years
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CHAPTER 1: INTRODUCTION

Transition metal complexes (TMCs) are an important class of compounds with various applications, for example in photoimaging processes, wastewater recycling, storage and conversion of solar energy, photocatalysis, and photovoltaics. These complexes distinguish themselves from non-transition metal species and organic compounds both by the number of accessible excited states and their spin multiplicity. Consequently, depending on the wavelength of excitation, a variety of electronically excited states can be obtained that differ in geometry and electron distribution between the central ion and ligands, and therefore, by different chemical reactivity in comparison with the same metal complex in the ground state.

1.1 Electronic structure of transition metal complexes

Inorganic and organometallic complexes are characterized by a variety of low-lying excited states which can be reached by optical excitation in the 200-1100 nm range. Several types of one-electron excitations can be identified in TMCs. These are ligand field (metal centered), intraligand (ligand centered), ligand-to-metal charge transfer, metal-to-ligand charge transfer, metal-to-solvent charge transfer, metal-metal (metal centered) excitations.

One of the examples of intraligand (IL) excitation is the lowest absorption band of the fac-[ReCl(CO)3L2] (L = trans-3- and trans-4-styrylpyridine) which is assigned to the IL \( \pi-\pi^* \) transition in styrylpyridine. Typically, photochemistry associated with excitation into intraligand bands is the same as for the free ligand. For example, \( \pi-\pi^* \) photoexcitation of styrylpyridine
leads to cis-trans isomerization which is also observed in fac-[ReCl(CO)₃L₂] upon excitation into the ligand-localized excited state (IL).⁹

Ligand field (LF) transitions correspond to electronic transitions between the d orbitals on the metal. LF transitions are forbidden by the Laporte selection rule and therefore are relatively weak (10 - 1000 M⁻¹ cm⁻¹).¹⁰ LF transitions result in substantial labilization of M–L bonds. The main chemical reaction taking place in solutions upon photoexcitation into LF bands is ligand exchange. Photosubstitution reactions are well studied for octahedral metal hexacarbonyls for example Cr(CO)₆, V(CO)₆, and Mn(CO)₆. It was found that d⁶ Cr(CO)₆ easily undergoes a loss of a carbonyl group. Excitation of this compound into the LF band promotes an electron from the filled t₂g set of orbitals which are π-bonding with respect to the M–CO bond to the lowest unoccupied set of e_g orbitals which is strongly σ-antibonding, resulting in lower M–C binding and thus higher ligand labilization. The excited-state dissociation rate constant is >10¹⁰ sec⁻¹ whereas a typical rate constant for the ground-state dissociation is about 10⁻⁶ sec⁻¹.¹¹ Thus, it can be concluded that LF excitation gives rise to a remarkable increase in ligand dissociation rates.

Low-valent metal complexes are often characterized by low-lying transitions termed metal-to-ligand charge transfer (MLCT). These transitions can be envisioned as ones which result in an oxidized metal and a reduced ligand. The extinction coefficients of MLCT transitions are typically in the range of 10⁴ – 10⁵ M⁻¹ cm⁻¹. Photoexcitation into a MLCT state in most of the cases does not lead to ligand loss and a consequent substitution reaction due to the electrostatic attraction generated in the MLCT state which makes the M–L bond inert. In addition, MLCT band position is quite sensitive to solvent. The difference between reactivity of LF and MLCT states can be demonstrated for W(CO)₅(piperidine)] and W(CO)₅(4-formylpyridine)]. Both
complexes have an LF band of the same intensity located in the same position. However, 4-
formylypyridine also has a low-lying $\pi^*$ (L) acceptor orbital, therefore W(CO)$_5$(4-
formylypyridine)] complex exhibits a low-lying, solvent sensitive absorption (MLCT state) which
is not present in the piperidine complex. As a result, W(CO)$_5$(piperidine)] loses the piperidine
ligand upon photoexcitation whereas W(CO)$_5$(4-formylypyridine)] is inert with respect to
photosubstitution. 12

Photoexcitation of electrons from ligand orbitals to metal orbitals are termed ligand-to-
metal charge transfer (LMCT) transitions. The energy of these transitions depends on relative
ease of oxidation of the ligands and on the availability of partially filled metal orbitals. Due to
the shift of the electronic density from ligand to metal in the LMCT excited states it is expected
that the ligand will be more susceptible to nucleophilic attack and metal – to electrophilic attack.
Photoexcitation into LMCT excited states often leads to homolytic cleavage of M and L. For
example, in Werner complexes like [Co(NH$_3$)$_5$X]$^{2+}$ ) X = Cl, Br, I) excitation into LMCT states
results in generation of Co$^{2+}$ and the halogen atom.

There are a large number of transition metal complexes which have direct metal-metal
bonds. These complexes exhibit transitions involving metal-centered orbitals and in some respect
are analogous to LF transitions. [Mn$_2$(CO)$_{10}$] dinuclear complex is a well-known example of the
complex containing two metals with a metal-metal bond. The electronic structure of this complex
is well understood and has been compared with the homonuclear complex. A fairly narrow and
solvent-insensitive absorption band in the near-ultraviolet region is attributed to $\sigma_b \rightarrow \sigma^*$
transition. Photoexcitation into this band leads to weakening and breaking of the metal-metal
bond.
1.2 Ligand exchange reactions in TMCs

In general, in ligand exchange reactions, a bound ligand is exchanged for another ligand of the same or different chemical composition. Ligand exchange can occur via dissociative, associative, and dissociative interchange mechanisms. In a dissociation mechanism, a loss of the bound ligand is followed by association of an incoming ligand from the surrounding solvent. In an associative mechanism, association of a solvent molecule with the metal center is followed by dissociation of a bound ligand. A dissociation interchange mechanism is a hybrid of the associative and dissociative mechanisms: the association of an incoming ligand is concurrent with the dissociation of the initially bound ligand. Typical time of the thermal ligand exchange via these mechanisms is about $10^{-6}$ sec$^{-1}$.11

Studies of transition metal complexes have shown that bond dissociation occurs on different time scales ranging from hundreds of femtoseconds to hundreds of picoseconds depending on the mechanisms involved. Study of photodissociation dynamics of the doubly charged anion IrBr$_6^{2-}$ in gas phase by time-resolved photoelectron spectroscopy demonstrated that fragmentation of the dianion takes place on a ~79 ps time scale.15 An investigation of the ultrafast dynamics of metal carbonyl compounds M(CO)$_6$ (M = Cr, W, Mo) in organic solvents using femtosecond IR spectroscopy revealed instrument response limited rise of photoproducts assigned to pentacarbonyl intermediates formed in less than 240 fs after excitation at 295 nm.16 A more detailed study of Cr(CO)$_6$ by ultrafast time resolved spectroscopy found that dissociation of a single carbonyl group takes place within 100 fs.17-18 Photolysis experiments on the dinuclear complex Mn$_2$(CO)$_{10}$ in the condensed phase by 100 fs pump-probe spectroscopy detected ligand loss within 500 fs.19 Photoinduced ligand exchange in cis-[Ru(bpy)$_2$(CH$_3$CN)$_2$]$^{2+}$ has also been studied by femtosecond UV-Vis pump-probe spectroscopy in acetonitrile.
Observation of the intermediate \([\text{Ru(bpy)}_2(\text{CH}_3\text{CN})]^{2+}\) at 2 ps after photoexcitation is evidence that the ligand loss takes place before this time.\textsuperscript{20} It should be mentioned that CO substitution with CH\(_3\)CN takes place in 77 ps in this system. In the related Ru(II) complexes, time-resolved picosecond infrared investigation detected ligand substitution in 13-55 ps from five-coordinate intermediates.\textsuperscript{21} The rate of ligand substitution depends on the nature of solvent. It has been shown that final product formation time constant in alcohols with long chains is much longer than in short chain alcohols. For example, chromium hexacarbonyl forms the hydroxyl solvated complex within 25 ps in neat ethanol whereas it takes 1.8 ns for the solvated complex to form in neat hexanol.\textsuperscript{18} The quantum yield of ligand substitution depends on a competition between the geminate recombination and cage escape of photodissociated ligand. Difference in the reactivity toward photosubstitution was established in the photolysis studies of Fe(CO)\(_5\) and Cr(CO)\(_6\) in alcohols using femtosecond UV pump and IR probe spectroscopy.\textsuperscript{22-23} It was proposed that photolysis of these complexes led to the formation of high-spin \(^3\text{Fe(CO)}_4\) and low-spin \(^1\text{Cr(CO)}_5\) intermediates which have different reactivity with alcohols. The reaction rate of \(^1\text{Cr(CO)}_5\) with alcohols was slower because of the coordination with the alkyl moiety of the solvent which impeded the coordination of the chromium with the hydroxyl group. It was shown that triplet coordinatively unsaturated intermediates such as \(^3\text{Fe(CO)}_4\) do not react with alkyl moieties of solvent molecules. In general, coordinatively unsaturated singlet organometallics react with most solvents including alkanes. This hinders further reactivity with a stronger coupling site (\(-\text{OH}\)) in alcohols. The triplet species react on a faster time scale with hydroxyl groups of alcohols because they do not coordinate with alkyl sites. The timescales of formation of OH-solvated complexes for the photochemical reactions of Fe(CO)\(_5\) and Cr(CO)\(_6\) in n-butanol and n-hexanol are the
following: 93.7 and 209 ps (in n-butanol) and 138 and 1800 ps (in n-hexane) for \(^3\)Fe(CO)\(_4\) and \(^1\)Cr(CO)\(_5\), respectively.\(^{23}\)

Whether photoexcitation of a complex will result in ligand loss or not depends on the nature of the lowest excited state as already has been discussed in the preceding section. According to the “tuning” model initially proposed by Ford\(^{24}\) to account for the photoreaction pattern of \([\text{Ru(NH)}_3\text{L}]^{2+}\), photosubstitution reactions in transition metal complexes originate from LF excited states. MLCT states are much less reactive toward ligand substitution but can be active toward photoredox reactions. It was also proposed that since MLCT state are very sensitive to solvent polarity, for a complex whose lowest energy MLCT state and lowest energy LF state have approximately the same energy, changes in the solvent alone may be sufficient to reverse the order of the electronic states, and thus, alter the reactivity.\(^{25}\)
1.3 Hexacoordinated bromides of Pt (IV), Os(IV), and Ir (IV)

Hexahalogenated complexes of type MX\textsubscript{6}\textsuperscript{2-} (where M = Os, Ir, Pt; X = Br) are doubly negatively charged ions. A majority of known multiply charged anions (MCA) such as SO\textsubscript{4}\textsuperscript{2-}, CO\textsubscript{3}\textsuperscript{2-} or PO\textsubscript{4}\textsuperscript{3-} are unstable in the gas phase because of the strong intramolecular Coulomb repulsion between the excess negative charges.\textsuperscript{26-27} Nevertheless, several Werner-type dianions ML\textsubscript{6}\textsuperscript{2-} (M = Re, Os, Ir, and Pt; X = Cl and Br) were found to be electronically stable in the gas phase which allowed the acquisition of electronic structure information about these transition metal complexes using photodetachment photoelectron spectroscopy.\textsuperscript{28} These MCA’s are also ubiquitous in the condensed phase through a solvent stabilization which makes it possible to study their structural and electronic properties with the goal of gaining an insight into their chemical reactivity. The dianions in question have been attracting a great deal of attention for the last several decades due to their photosensitivity in aqueous media.\textsuperscript{29-32} These complexes have been applied in photoassisted and photoinduced catalysis.\textsuperscript{7} For example, during irradiation with light in the presence of oxygen, alkanes and arylalkanes are oxygenated with the formation of aldehydes and ketones upon adding catalytic amounts of PtBr\textsubscript{6}\textsuperscript{2-}, PtCl\textsubscript{6}\textsuperscript{2-}, and IrCl\textsubscript{6}\textsuperscript{2-}.\textsuperscript{33} OsCl\textsubscript{6}\textsuperscript{2-} and IrCl\textsubscript{6}\textsuperscript{2-} have been proven to be effective catalysts in photoinduced reactions of dimerization of arenes.\textsuperscript{4} Photocatalytic activity of the mentioned complexes is determined by their photophysics, which depends on the electronic structure of the dianions.

In the past, several flash photolysis experiments were performed on PtBr\textsubscript{6}\textsuperscript{2-} complex with the aim of understanding the photoaquation mechanism.\textsuperscript{29,31} Adamson and Sporer interpreted initial experiments on photochemical activation of aqueous PtBr\textsubscript{6}\textsuperscript{2-} as the homolytic cleavage of a Pt–Br bond.\textsuperscript{29} Penkett and Adamson later re-interpreted the mechanism as a concerted one-step two-electron reduction of PtBr\textsubscript{6}\textsuperscript{2-} with a Br\textsubscript{2} leaving group, in a flash photolysis study with 30 \(\mu\)s
The formation of relatively stable aqua-PtBr$_5$(H$_2$O)$^-$ and di-aqua PtBr$_4$(H$_2$O)$_2$ complexes was suggested in dark hydrolysis experiments by Davidson and Jameson. Balzani and co-workers concluded that the sole reaction caused by irradiation of PtBr$_6^{2-}$ in water is photoaquation with a primary PtBr$_5$(H$_2$O)$^-$ photoaquation product. In the latter work, the electronic absorption spectra of the solutions showed no isosbestic points upon irradiation, which was interpreted to be due to a rapid thermal aquation of PtBr$_5$(H$_2$O)$^-$ to form a diaquasubstituted PtBr$_4$(H$_2$O)$_2$ complex followed by further thermal aquation steps. The same quantum yields of 0.5 ± 0.1 and 0.35 ± 0.1 were determined for the formation of the primary PtBr$_5$(H$_2$O)$^-$ photoaquation product in independent pH vs. irradiation time and spectrophotometric measurements upon sample irradiation with the 313, 365, 433, and 530 nm light, Fig. 1.1. Since

![Diagram of electronic transitions](image-url)

**Figure 1.1.** Photoaquation of PtBr$_6^{2-}$ according to Balzani and co-workers.
no luminescence was observed upon irradiation of aqueous PtBr$_6^{2-}$, the initially populated electronically excited states were thought to relax with unity quantum yield to the same reactive state(s) where PtBr$_5$(H$_2$O)$^-$ is produced. These reactive states were assigned to the long-lived triplet $^3T_{1g}$ state and vibrationally excited ground $^1A_{1g}$ state formed via intersystem crossing from $^3T_{1g}$. Thus, according to Balzani and co-workers, Pt–Br bond cleavage in aqueous PtBr$_6^{2-}$ is heterolytic, a currently accepted view. The heterolytic mechanism has also been suggested in photodissociation of a metal-halogen bond in similar hexahalo metal dianions in the gas phase.

In spite of the great interest due to their photosensitivity in the hexahalogenated dianions of heavy transition metals, little ultrafast time-resolved data exist about the nature and dynamics of the excited states as well as the photophysical and photochemical mechanisms involved. Generally, the photophysical and photochemical processes in isolated hexahalogenated dianion complexes have been discussed with the suggestion of two distinct mechanisms. In the first, the complex undergoes radiationless relaxation from the initially excited electronic state to the vibrationally excited ground-electronic state followed by breaking of a metal-halogen bond. In the second, the initially electronically excited complex non-radiatively relaxes to the lower-lying electronic excited state in which metal-halogen bond-breaking occurs. In an aqueous environment, polyatomic photofragments formed via both mechanisms may undergo subsequent aquation.
1.4 Photodynamic therapy

Photoinduced ligand loss is of great importance since it is an initial step in chemical reactions with potential applications such as photodynamic therapy, molecular switches,\textsuperscript{5} and solar energy conversion.\textsuperscript{37-39} A well-known transition metal complex, cisplatin, \textit{cis}-Pt(NH\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} is a successful antitumor agent in treatment of different types of cancer. The ligand exchange in cisplatin upon which the chloride ligands are replaced by water molecules results in a diaqua Pt(II) complex, \textit{cis}-[Pt(NH\textsubscript{3})\textsubscript{2}(H\textsubscript{2}O)\textsubscript{2}]\textsuperscript{2+} that can bind covalently to DNA thus disrupting cellular transcription, Fig.1.2a. The process of binding of cisplatin to DNA is activated via thermal ligand exchange which unfortunately can take place in both healthy and cancerous cells.\textsuperscript{40} Selective treatment of malignant cancer cells can be achieved through activation of drugs by light. In this

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{(a) DNA binding by cisplatin and (b) photochemical ligand loss by Ru- and Rh-based metal complexes.\textsuperscript{43-44}}
\end{figure}
way, a molecule which is non-toxic in the dark becomes highly toxic upon applying low energy light. This process of drug activation that is aimed to localize the action of the drug to a certain irradiated area is known as photodynamic therapy (PDT). It was demonstrated that PDT can be successfully applied in the treatment of lung and esophageal cancers, however, typical PDT drugs are mediated by O₂ which is a drawback since most of the malignant cancer cells are hypoxic.⁴¹-⁴² Recently, several inorganic transition metal complexes were shown to bind to DNA in the absence of O₂ upon irradiation with near-UV or visible light. For example, an octahedral Ru(II) complex, cis-[Ru(bpy)₂(NH₃)₂]²⁺ and dirhodium(II, II) complex, cis-[Rh₂-(m-
(2)CCH₃)₂CH₃CN)₆]²⁺ can undergo ultrafast ligand loss upon being exposed to excitation pulses of very low energy, which triggers their binding to DNA, Fig. 1.2b.⁴³-⁴⁴ These systems provide selectivity toward tumor tissue, since binding to DNA only takes place in the irradiated areas. Toxicity of these ruthenium and rhodium complexes is lower than that of cisplatin in the dark but much higher (34-fold increase in toxicity) upon irradiation with visible light.
1.5 Coherent control of ultrafast chemical reactions

The development of novel laser systems allowing one to produce ultrashort laser pulses opened up possibilities of controlling ultrafast chemical reactions. Femtosecond pulses can be used to induce coherent vibrational wavepacket motion on either the electronic ground or excited state potential energy surface (PES) of a molecule. Coherent nuclear dynamics plays an important role in many biological processes such as cis-trans isomerization in rhodopsin\textsuperscript{45} or ultrafast transfer of carbon monoxide in cytochrome c oxidase aa\textsubscript{3}, Fig. 1.3.\textsuperscript{46}

![Figure 1.3. Model of the haem a\textsubscript{3}–CuB site where CO group is bound to the haem iron atom.\textsuperscript{46}](image)

Vibrational coherence in di-atomic and tri-atomic molecules like HgI\textsubscript{2},\textsuperscript{47} I\textsubscript{2}–, and I\textsubscript{3}–\textsuperscript{48} as well as in some biological systems such as rhodopsin,\textsuperscript{45} and myoglobin\textsuperscript{49} have first been observed and described in as early as the 1990’s. It has been demonstrated that vibrational
coherence can be observed as coherent vibrational motion of the reactant in its ground state produced by femtosecond excitation via stimulated Raman scattering, coherent vibrational motion in the excited state of the reactant, and coherence in the product absorption. In the latter case, two mechanisms can give rise to the coherent oscillations. The first is coherent vibrational motion on the potential surface of the product formed via an “impulsive” chemical process that occurs along the reaction coordinate following femtosecond excitation, or coherent transfer from the “spectator” reactant mode perpendicular to the reaction coordinate. These two mechanisms can be distinguished by analyzing the induction period of the oscillations. The second is stepwise coherent population of the product state from the precursor (initially excited) state. They can be distinguished spectroscopically by analyzing the amplitudes and phase shifts of the oscillatory part of the kinetic traces measured in a broad wavelength range. In the stepwise coherent population mechanism, the spectral dependence of the oscillation amplitude should match the product absorption band, and the oscillation phase should remain constant across the band. In the case of vibrational coherent motion mechanism, the oscillation amplitude at the blue and red wings of the product absorption band should exhibit two maxima characterized by the same fundamental frequency but with a phase difference equal to \( \pi \); in addition, the oscillations should have zero amplitude zero at the center of the absorption band.

Improvements in laser technology such as the development of the laser systems generating ultrashort pulses, the ability to adjust the frequency and phase of pulses have permitted the development of several schemes of controlling physical and chemical processes. One of the schemes was put forward by Tannor and Rice who proposed the use of a sequence of femtosecond laser pulses. First, an ultrashort pulse of laser light creates a coherent wavepacket (WP) - coherent superposition of energy-resolved eigenstates on the excited potential energy
surface, then, the second pulse triggers the reaction when the WP reaches a desired nuclear
configuration. This method was used to control the electronic branching ratio in the
photodissociation of NaI. This was achieved by varying the interval between two ultrashort
pulses.\textsuperscript{52} Another concept of coherent control was introduced by Brumer and Shapiro\textsuperscript{53} and
successfully demonstrated by several research groups.\textsuperscript{54-55} In their approach, a molecule is
excited simultaneously with two long laser pulses of different frequency. The excitation by these
two optical pathways leads to a coherent superposition of at least two different product channels
in the same upper state, from which a particular chemical process can take place. By varying the
relative phases of two laser beams one can control the branching ratios in molecular
photodissociation. A particular example of this method is coherent control of the femtosecond
primary event of vision, cis-trans photoisomerization of the retinal chromophore in rhodopsin.
Simply by changing the relative phases of the photoexcitation pulses, the reaction efficiency of
cis-trans photoisomerization can be varied from 30 to 60 percent.\textsuperscript{56}
1.6 Femtosecond pump-probe spectroscopy

Femtosecond broadband pump-probe spectroscopy offers a unique means of identifying the elementary steps of a photochemical reaction in room-temperature solutions. It allows for the observation and characterization of reactive photoproducts in real-time down to several tens of femtoseconds. This allows one to study such ultrafast processes as fast radiationless transitions in solution, metal to ligand charge transfer in metal complexes, energy transfer in conjugated polymers, electron transfer in proteins and photosubstitution.

Figure 1.4. Schematic representation of the pump-probe technique.
reactions. In pump-probe measurements, a strong pump pulse initiates the chemical reaction to be studied at time $t = 0$. The wavelength of the pump pulse is chosen such that it causes an electronic or vibrational transition in a molecule, which is followed by, for example, a chemical change. In these experiments, the pump pulse excites the molecule from a bound electronic ground state to an excited repulsive state, as shown in Figure 1.4. The absorption of a probe pulse at different delays with respect to a pump allows us to map the dynamics of the photochemical change.
1.7 Theoretical methods

DFT/TDDFT methods

Density functional theory (DFT) has been successful in describing the ground state properties of transition metal complexes. The DFT method has proved to be accurate in calculations of molecular structures and vibrational spectra. It is based on the Hohenberg and Kohn theorem which states that the ground state properties of an electronic system are completely determined by the electronic density functional $\rho(r)$. Therefore, instead of using the complicated N-electron wave function $\psi(x_1, x_2, ..., x_N)$, a much simpler electron density functional can be used where electron density is the basic variable. Kohn and Sham developed a practical application of this theory and formulated a technique for solving the minimization of energy. A good agreement of the calculated geometries, harmonic vibrational frequencies and energetics of ground state species with experiment data and low computational cost even for large molecules made this method a very popular computational tool although several basis sets and density functionals typically need to be tested to ensure the reproducibility of the method.

The general DFT energy is expressed as follows:

$$E(\rho) = T_s[\rho] + E_{\text{ne}}[\rho] + J[\rho] + E_{xc}[\rho],$$

where

- $E_{\text{ne}}[\rho]$ is the interaction of the external potential (describes the attraction between nuclei and electrons)
- $J[\rho]$ is the Coulomb energy due to the interaction between two charge distributions
- $T_s[\rho]$ is defined as the kinetic energy of the non-interacting electrons
- $E_{xc}[\rho]$ is the so-called exchange correlation energy term. Its exact dependence on density $\rho$ is not known.

Some approximations have to be introduced to treat the exchange-correlation energy term ($E_{xc}[\rho]$). Since the exact density function is not known, there is no systematic procedure for improving the quality of DFT calculations. The practical usefulness of ground-state DFT depends on whether an accurate approximation for the functional $E_{xc}$ could be found. The functionals available in the literature have been derived by comparison with experiments or developed from fundamental quantum mechanics.

Time-dependent density-functional theory (TDDFT) is one of the most popular methods in theoretical characterization of excited states. Based on the Runge-Gross (RG) theorem - the time-dependent analogue of the Hohenberg-Kohn (HK) theorem, it extends the basic ideas of ground-state density-functional theory (DFT) to systems in a time-varying field. According to RG theory, for a given initial wave function, there is a unique correlation between the time-dependent external potential of a system and its time-dependent density. TDDFT is a computationally inexpensive method which in some cases accurately predicts electronic absorption spectra of organometallic compounds. A special care needs to be taken in predicting the vertical electronic transitions of charge transfer states, therefore performance of several density functionals and basis sets usually has to be tested.

**CASSCF/CASPT2 method**

The Complete Active Space Self-Consistent-Field (CASSCF) is a method in quantum chemistry which uses a linear combination of configuration state functions in order to approximate the exact electronic wave function of an atom or molecule. The CASSCF method is
based on a selection of the active orbitals occupied by active electrons in all possible ways consistent with the spatial and spin symmetry of the electronic state.\textsuperscript{72} The active electrons and orbitals are chosen by the researcher depending on the chemical problem at hand. There are three types of the orbitals: inactive, active and virtual. The inactive orbitals always remain doubly occupied in all CASSCF configurations, whereas the virtual orbitals are always unoccupied. The CASSCF wave function represents a linear combination of all possible configurations arising from the distribution of the active electrons among the active orbitals. Therefore, the CASSCF function is a complete configuration interaction (CI) function. Inactive orbitals are also optimized during the variational process, as in the Hartree-Fock method. The CASSCF method is widely used for the calculations of both ground and electronically excited states.\textsuperscript{73} However, this method, lacking an account of dynamic correlation, is not always accurate enough to reproduce the energetics of a chemical or spectroscopic process. Dynamic correlation effects can be treated by using second-order compete active space perturbation theory (CASPT2). In the CASPT2 approach, the wave function is corrected at the first-order while the correction to the energy is at the second-order. This method is accurate in a wide variety of applications, particularly in electronic spectroscopy.
1.8 References


CHAPTER 2: MATERIALS AND METHODS

2.1 Materials

K$_2$PtBr$_6$ and K$_2$IrBr$_6$ were purchased from Sigma Aldrich Company (purity > 99%). K$_2$OsBr$_6$ was purchased from Surepure Chemetals (purity > 99%). The measurements were carried out in distilled water, D$_2$O, methanol and acetonitrile at 22°C. HPLC purity methanol and acetonitrile, and isopropyl alcohol were purchased from EMD chemicals (Gibbstown, NJ). All reagents were used as received without further purification. NBu$_4^+$ salts of the PtBr$_6^{2-}$ and OsBr$_6^{2-}$ were prepared by adding an excess of tetrabutylammonium bromide (99%, Fluka) to aqueous solutions of K$_2$PtBr$_6$ and K$_2$OsBr$_6$. 
2.2 Instrumentation and methods

UV-visible Absorption spectroscopy

Steady-state UV-visible absorption spectra were recorded at room temperature on a Varian Cary 50 Bio (Varian Corporation) UV-visible single beam spectrophotometer with resolution ±1 nm, using 1 or 2 mm path length quartz cuvettes.

Raman spectroscopy

Raman spectra were measured in the backscattering geometry with a spectral resolution of 0.5 cm⁻¹ using a commercial Raman system (Renishaw, inVia) equipped with a Leica DM 2500M microscope. A diode laser source was used for excitation at wavelength of 785 nm with a power of 1mW. A holographic notch filter was used to extinguish the laser light.

Femtosecond Transient Absorption Spectroscopy

The femtosecond transient absorption spectrometer used in this work is based on an amplified Ti:Sa laser system (Hurricane, Spectra Physics) that generates a 1-kHz train of 90-fs (fwhm) 800-nm laser pulses with an energy of 0.92 mJ pulse⁻¹.¹ A layout of the experimental setup is shown in Figure 2.1. The amplified output is divided by a beam splitter into two beams and one portion is further split 4:1. The resulting 50% and 40% parts pump interchangeable, computer-controlled TOPAS-C “pump” and “probe” optical parametric amplifiers (Light Conversion Lt.), respectively. TOPAS-C pump amplifier was used to generate 350, 420 and 770-nm light pulses used for sample excitation. The pump beam was modulated on/off at 500 kHz using an optical chopper (Terahertz Technologies Inc.) and focused into a 280 µm diameter spot at the sample position, delivering the excitation energy ~2.2 µJ pulse⁻¹. Before entering the
sample, the pump beam polarization was adjusted to be at the magic angle (54.7°) relative to the probe beam polarization using a Berek compensator.

**Figure 2.1.** A layout of the experimental set-up.
(New Focus). The remaining 10% part of the amplified output can be delivered to the delay stage of the TOPAS-C “probe” amplifier to produce deep-UV-probe pulses, or is attenuated to ~4 μJ pulse\(^{-1}\) and focused into a 3-mm CaF\(_2\) window to produce white-light continuum probe light from 350 to 770 nm. Alternatively, the UV-probe pulses tunable from 270 to 400 nm are obtained using the TOPAS-C “probe”. The probe beam is sent to an optical translational stage (ILS 250 CCHA, Newport) to generate a variable time delay (\(\Delta \tau\)) between pump and probe pulses, and then further \(\sim 1:2\) split into reference and probe beams, only the latter of which is focused to a 90 μm diameter spot and overlapped with the pump beam at an angle of 8° at the sample position. After the sample, the probe beam is recollimated and the pump light is extinguished by a polarizer crossed with the pump beam polarization. The reference (ref) and recollimated probe (pr) beams are sent to a monochromator/spectrograph (Spectra-Pro 2358, Acton Research) and registered on two 512-pixel diode arrays for simultaneous accumulation of multiple kinetic traces within 274 nm spectral windows (white-light continuum probe) or two 96-dB dynamic-range Si-photodiodes (TOPAS-C probe) for a single-wavelength kinetic measurement. A third Si-photodiode monitors the pump pulse intensity for gating. Probe and reference diode arrays/photodiodes readouts at a wavelength \(\lambda_i\) and a time delay \(\Delta \tau_i\) are digitized on a 16 bit scale for each laser shot to obtain \(I_{pr}(\lambda_i, \Delta \tau_i)\) and \(I_{ref}(\lambda_i, \Delta \tau_i)\), and the transient absorption signal for each adjacent pair of pump on/off pulses is obtained as follows: \(\Delta A(\lambda_i, \Delta \tau_i)\) = - log\((I_{pr}(\lambda_i, \Delta \tau_i)/I_{ref}(\lambda_i, \Delta \tau_i))_{on} + \log(I_{pr}(\lambda_i, \Delta \tau_i)/I_{ref}(\lambda_i, \Delta \tau_i))_{off}\), and is averaged for typically 300 pairs. Usually, \(\Delta A(\lambda_i, \Delta \tau_i)\) are collected for about 120 delay time positions between –20 ps and 1200 ps, and averaged for about 10 successive scans of the delay line.

For 350- and 420-nm excitation, solutions were circulated through a flowing jet with 0.25 mm pathlength. The duration \((150 \pm 15\) fs, fwhm) of a cross-correlation function between pump
and probe pulses is delivered by strong Gaussian-like absorption (366 nm) and emission (466 nm) features observed in neat water and aqueous solutions due to stimulated Raman scattering\(^2\) (Raman-active symmetrical stretch mode, \(v_1 = 3652 \text{ cm}^{-1}\)). In the UV region, similar width of the cross-correlation function was obtained by measuring simultaneous pump and probe two-photon absorption signals\(^3\) in neat iso-propanol. To obtain the resultant \(\Delta A\) spectra, single-wavelength \(\Delta A\) kinetic traces measured in 5-nm steps from 270 to 400 nm, and multiple-wavelength \(\Delta A\) kinetic traces measured in the spectral window from 350 to 770 nm were corrected for the group velocity dispersion of the probe light with an accuracy ± 25 fs using cross-phase modulation signals\(^4\) from neat water in the near-UV-through-near-IR region and two-photon absorption signals\(^2\) from neat iso-propanol in the UV region, and appropriately scaled and merged together. The same \(\Delta A\) spectra were observed for flowed solutions as well as when containing the PtBr\(_6^{2-}\) solutions in a CaF\(_2\) spinning cell (2 mm pathlength), for which it was tested that dissolved \(O_2\) had no noticeable effect on the \(\Delta A\) spectra as verified by deoxygenating solutions with argon. The \(\Delta A\) spectra (420-nm excitation) were found to be independent on PtBr\(_6^{2-}\) concentration (up to 16 mM). The samples contained in the spinning cell exhibited fewer than a few percent decomposition during the experiments as determined from UV-Vis spectra acquired before and after the measurement. The typical pump energy was adjusted to \(~2.2 \mu J\) pulse\(^{-1}\) using neutral density filters to ensure that the \(\Delta A\) signal generated as a result of two-(pump)-photon absorption by the solvent was negligibly small compared with the single-photon \(\Delta A\) signal of the sample for \(\Delta \tau_i \geq 100\) fs. The neat solvent \(\Delta A\) signals were measured immediately after the measurement of the sample under identical excitation conditions. Linearity of the PtBr\(_6^{2-}\) \(\Delta A\) spectra was verified up to one-fourth of the typically used pulse energy with the extrapolated line passed through the origin. Because of low absorptivity PtBr\(_6^{2-}\) at 530-nm excitation wavelength, \(\varepsilon(525) = 140\) M\(^{-1}\).
cm$^{-1}$, concentrated PtBr$_6^{2-}$ (7.5 mM) solutions contained in the spinning cell were used and, as a result, the $\Delta A$ spectra were measured between 460 and 710 nm.

2.3 Data Analysis

The experimental $\Delta A$ kinetic traces were fitted to a sum of exponentials convoluted with the cross-correlation function (CCF) centered at zero time delay between pump and probe pulses,

$$
\Delta A(\Delta \tau_i) = \int_0^{\Delta \tau_i} CCF(\Delta \tau_i=0) \left\{ \sum_j A_j \exp(-t/\tau_j) \right\} dt,
$$

where $A_j$ are the amplitudes and $\tau_j$ are the time constants which capture the entire evolution, including early-times. The software package Spectra-SolveTM, version 1.5 was employed. The nonlinear least squares fitting were performed using the Levenberg-Marquardt algorithms as implemented in Origin v7.0 software (Origin Lab, Northampton, MA). In addition, 512 kinetic traces within the 274-nm bandwidth of the white-light continuum probe observed were globally fitted\textsuperscript{6} to a sum of exponential functions ($\sum_j \epsilon_j(\lambda) \exp(-t/\tau_j)$) convoluted with the CCF function, where $\tau_j$ are the resulting time constants, and $\epsilon_j(\lambda)$ are the decay-associated spectra re-constructed from the resulting $\tau_j$ values based on the assumption of a consecutive reaction mechanism A decay-associated spectrum defines the absorption contributing to the measured $\Delta A$ spectra, and which is characteristic of a specific time component obtained by a global fit. A global fit assumes that the absorption of products species changes only in their strength, not band shape as may arise due to vibrational relaxation, and which may affect the resulting $\tau_j$ up to several picoseconds.

To quantify the coherent signals, the oscillatory residue $R(t)$ left after subtracting the multi-exponential fit from the measured $\Delta A$ kinetic trace was nonlinear least-square fit to a sum
of two damped sine functions: 

\[ R(t) = A_1 \cdot \exp(-t/\tau_{c,1}) \cdot \sin(2\pi v_1 t + \phi_1) + A_2 \cdot \exp(-t/\tau_{c,2}) \cdot \sin(2\pi v_2 t + \phi_2), \]

where \( \phi \) is the relative phase, \( \tau_c \) the coherence decay time constant, and \( v \) is the oscillation frequency. The oscillatory shape of the residues was always observed regardless of the increased number of rising and decaying exponential functions. Oscillation frequencies in the \( R(t) \) residues were also evaluated by using a fast Fourier transform (Origin v. 7.0) and the resulting values were in a close agreement to the \( v_1 \) and \( v_2 \).

### 2.4 Computational Details

Density functional theory (DFT) was applied for geometry optimizations of the singlet, doublet, and triplet ground electronic states of the compounds under study. The optimized ground state structures were confirmed to be true minima by harmonic frequency calculations. All calculations were performed using a Gaussian 09 suite of programs. Two different density functionals were employed: a) a Becke three parameter hybrid functional using the correlation functional of Lee, Yang, and Parr, which includes both local and non-local terms (B3LYP)\(^7\) and b) the hybrid functional of Truhlar and Zhao (M052X).\(^8\) To assist the assignment of the experimental \( \Delta A \) spectra, the excitation energies and oscillator strengths were calculated using time-dependent density functional theory (TD-DFT) as implemented in the Gaussian 09. A conductor-like polarizable continuum model (CPCM) was used in all DFT and TD-DFT calculations because this model provides one of the most accurate quantitative estimates of solvation effects.\(^9\)

DFT has been successful in describing the ground state properties of transition metal complexes,\(^10\) whereas the accuracy of TD-DFT for the complexes investigated in this work needs to be established. To substantiate the use of TD-DFT, vertical electronic transitions (VET) for
the parent PtBr$_6^{2-}$ molecule were performed with B3LYP and M052X density functionals. The results of the calculations were compared with the VET’s obtained by using the complete active space self-consistent field (CASSCF),$^{11}$ complete active space second order perturbation theory (CASPT2),$^{12}$ MOLCAS 7.4 program. The CASSCF/CASPT2 calculations were performed in D$_{2h}$ symmetry using atomic natural orbital basis set (ANO-RCC).$^{13}$ In the DFT and TD-TDFT calculations, a combination of the augmented correlation-consistent triple-$\zeta$ aug-cc-pVTZ basis sets for hydrogen and oxygen,$^{14}$ the Def2-TZVP basis set employing a 60-electron relativistic effective core potential for Pt, Os, and Ir,$^{15}$ and the systematically convergent triple-$\zeta$ aug-cc-pVTZ-PP basis set with corresponding relativistic core pseudopotential for bromine$^{16}$ were used. The combination of Def2-TZVP, aug-cc-pVTZ-PP, and aug-cc-PVTZ basis sets will be denoted as TZ. Frequency calculations for OsBr$_6^{2-}$ and IrBr$_6^{2-}$ were carried out without symmetry restrictions since the dianions being an open shell systems undergo small Jahn-Teller distortion.
2.5 References


CHAPTER 3: ULTRAFAST PHOTOPHYSICS AND LIGAND EXCHANGE IN A MODEL HEXABROMOPLATINATE DIANION

Abstract

Ultrafast photophysics and photochemistry of aqueous hexabromoplmatinate dianion following photoexcitation at 350 nm LMCT band and at 420 and 530 nm ligand field bands are reported. Independently of the excitation wavelength, the same coherently excited photoproduct is formed in less than 150 fs which supports the idea that the lowest triplet excited ligand field state in PtBr$_6^{2-}$ is dissociative. Two types of coherent oscillations are observed in the early-time kinetic traces. Long-lived oscillations (τ$_{osc}$ ~ 1.4 ps) are found within the ground-state bleach (209 cm$^{-1}$) region, and therefore assigned to the resonance impulsive Raman scattering from the ground-state PtBr$_6^{2-}$. Short-lived (τ$_{osc}$ < 400 fs) oscillations with ~76 and ~114 cm$^{-1}$ frequencies are observed within the photoproduct absorption band. The low-frequency oscillations in the photoproduct (~79 cm$^{-1}$) are created when the $^3$PtBr$_5^-$ molecule passes the Jahn-Teller C$_4v$ conical intersection and are assigned to the bending mode which lifts the electronic degeneracy at the symmetry-induced Jahn-Teller conical intersection in $^3$PtBr$_5^-$ whereas the 114-cm$^{-1}$ mode is excited as a result of coherence population transfer from the reactant to the product. Geminate recombination of two negative ions PtBr$_5^-$ and Br$^-$ in the solvent cage is observed within ~7 ps. Formation of the aquated product PtBr$_5$(H$_2$O)$^-$ on ~15 ps time scale with ~37% quantum yield is found, consistent with previous findings.
3.1 Introduction

Photosensitivity of PtBr$_6^{2-}$ complex has been known since 1832.\textsuperscript{1} Five distinct absorption bands in the UV-Vis spectrum of aqueous PtBr$_6^{2-}$ were attributed to three electron transfer excitations at 227, 313, and 365 nm, and two ligand field excitations at 433 nm and 530 nm.\textsuperscript{2} The ligand field transitions lead from the ground $^1A_{1g}$ state to the first singlet excited $^1T_{1g}$ state and the lowest triplet excited $^3T_{1g}$ state.\textsuperscript{3} Adamson and Sporer interpreted initial experiments on aqueous-phase photochemical activation of PtBr$_6^{2-}$ as the homolytic cleavage of a Pt–Br bond.\textsuperscript{4} Penkett and Adamson later reported a concerted one-step two-electron reduction of PtBr$_6^{2-}$ with a Br$_2$ leaving group, in a flash photolysis study with 30 µs time resolution.\textsuperscript{5} The formation of relatively stable aqua- PtBr$_5$(H$_2$O)$^-$ and di-aqua PtBr$_4$(H$_2$O)$_2$ complexes was suggested in dark hydrolysis experiments by Davidson and Jameson.\textsuperscript{6} Balzani and co-workers concluded that the sole reaction caused by irradiation of PtBr$_6^{2-}$ in water is photoaquation with a primary PtBr$_5$(H$_2$O)$^-$ photoaquation product.\textsuperscript{7} The electronic absorption spectra of the solutions showed no isosbestic points upon irradiation, which was explained by a rapid thermal aquation of PtBr$_5$(H$_2$O)$^-$ to form a diaquasubstituted PtBr$_4$(H$_2$O)$_2$ complex followed by further thermal aquation steps. Similar quantum yields of 0.5 ± 0.1 and 0.35 ± 0.1 were determined for the formation of the primary PtBr$_5$(H$_2$O)$^-$ photoaquation product in independent pH vs. irradiation time and spectrophotometric measurements upon sample irradiation with 313, 365, 433, and 530 nm light. Since no luminescence was observed upon irradiation of aqueous PtBr$_6^{2-}$,\textsuperscript{7} the initially populated electronically excited states were thought to relax with unity quantum yield to the same reactive state(s) where PtBr$_5$(H$_2$O)$^-$ is produced. These reactive states were assigned to the long-lived triplet $^3T_{1g}$ state and vibrationally excited ground $^1A_{1g}$ state formed via intersystem crossing from $^3T_{1g}$. Thus, according to Balzani and co-workers, Pt–Br bond cleavage in aqueous
PtBr$_6^{2-}$ is heterolytic, and is the currently accepted view. The heterolytic mechanism has also been suggested in photodissociation of a metal-halogen bond in similar hexahalo metal dianions in the gas phase.

In the previous ultrafast experiment on aqueous PtBr$_6^{2-}$, transient absorption ($\Delta A$) spectra in the 460-780 nm range were recorded following 420-nm excitation of the dianion to the excited singlet $^1T_{1g}$ state. The $\Delta A$ signals were globally fitted to a sum of three exponential functions with characteristic time constants of 370 fs, 2.2 ps and 15.2 ps, which were assigned according to the photoaquation mechanism proposed by Balzani and co-workers. Namely, the first two time constants were attributed to the formation and vibrational cooling of the triplet excited $^3T_{1g}$ state. The 15.2 ps time constant was interpreted as being due to the relaxation from $^3T_{1g}$ to PtBr$_5$(H$_2$O)$^-$ and vibrationally hot $^1A_{1g}$, from which aquation takes place in competition with vibrational relaxation to the ground-state potential minimum.

In this work, we resolve the evolution of the aqueous PtBr$_6^{2-}$ system from the initially excited LMCT, singlet $^1T_{1g}$ and triplet $^3T_{1g}$ ligand field states to the PtBr$_5$(H$_2$O)$^-$ primary product using the ultrafast transient absorption technique with 90-fs laser pulses. We show that irrespective of the excitation wavelength used (350, 420 and 530 nm) the initial observable photoproduct is coherently vibrating PtBr$_5^-$ formed in its triplet excited state in less than 150 fs. By probing the reaction over a broad spectral range (270-920 nm), including that of photoproduct absorption and ground-state bleach, we are able to map out the relaxation process from triplet PtBr$_5^-$ to singlet PtBr$_5^-$, and further to the PtBr$_5$(H$_2$O)$^-$ product. The spectral assignments are supported by DFT and TD-DFT calculations of the reaction intermediates and products. Our findings point to a different mechanism of photoaquation than originally thought, which takes place in a singlet PtBr$_5^-$ in competition with geminate recombination, but neither in
the $^3T_{1g}$ nor hot $^1A_{1g}$ states of PtBr$_6^{2-}$. Nevertheless, at least as far as excitation into $^1T_{1g}$ and $^3T_{1g}$ is concerned, our ultrafast data are reconcilable with previous observations of wavelength-independent photoaquation quantum yield. Understanding of the photochemistry of aqueous PtBr$_6^{2-}$ is hampered because there is limited experimental and theoretical information available on equilibrium structures, energetics, and spectroscopic properties of the product species possibly involved. Preliminary calculations that include solvent effects through the conductor-like polarizable continuum model (CPCM) have been carried out as the first step towards addressing this problem.
3.2 Results

*Theoretical characterization of the parent PtBr₆²⁻ and photoproducts*

Density functional theory was applied to determine optimized geometries and harmonic frequencies of the parent dianion and product species. Tables 3.1 and 3.2 summarize calculated equilibrium geometries and harmonic frequencies of the solvated product species involved in the photochemistry of PtBr₆²⁻, namely PtBr₆²⁻, ¹PtBr₅⁻, ³PtBr₅⁻, ⁴PtBr₅⁻ (H₂O)⁻.

Table 3.1. Optimized geometries of the ground-state PtBr₆²⁻, ¹PtBr₅⁻, ³PtBr₅⁻, and ⁴PtBr₅(H₂O)⁻.

<table>
<thead>
<tr>
<th>Species</th>
<th>Parameter</th>
<th>Bond length, Å</th>
<th>Bond angle, deg</th>
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<td>PtBr₆²⁻</td>
<td>Pt–Br</td>
<td>2.492</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Br–Pt–Br</td>
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<td></td>
</tr>
<tr>
<td>¹PtBr₅⁻</td>
<td>Pt–Brax</td>
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<td></td>
</tr>
<tr>
<td>C₄ᵥ</td>
<td>Pt–Br_eq</td>
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<td></td>
</tr>
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<tr>
<td></td>
<td>Br_eq–Pt–Br_eq</td>
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</tr>
<tr>
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<td>Pt–Brax</td>
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<td>C₂ᵥ</td>
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<tr>
<td>(distorted TBP)</td>
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<td>⁴PtBr₅(H₂O)⁻</td>
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<td></td>
<td>Pt–O–H</td>
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* Calculations were performed at DFT M052X/TZ/PCPM level of theory with H₂O parameters
Table 3.2. The results of harmonic frequency calculations of ground state species involved in photochemistry of PtBr$_6^{2-}$.

<table>
<thead>
<tr>
<th>Species$^d$</th>
<th>Frequency computed, cm$^{-1}$</th>
<th>$f$(IR)</th>
<th>$f$(Raman)</th>
<th>Frequency, cm$^{-1}$</th>
<th>Symmetry / vibrational mode</th>
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</thead>
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<tr>
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<td>comp. scaled$^a$ vs. experiment</td>
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<tr>
<td>PtBr$_6^{2-}$</td>
<td>67$^c$</td>
<td>0</td>
<td>0</td>
<td>73</td>
<td>T$_{2u}$ / puckering</td>
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<tr>
<td>Oh</td>
<td>86$^c$</td>
<td>0</td>
<td>25</td>
<td>95/101</td>
<td>T$_{2g}$ / scissoring</td>
</tr>
<tr>
<td></td>
<td>106$^c$</td>
<td>6</td>
<td>0</td>
<td>117</td>
<td>T$_{1u}$ / doming</td>
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<tr>
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<td>171$^b$</td>
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<td>142</td>
<td>188/191</td>
<td>E$_g$ / out-of-phase stretch</td>
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<tr>
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<td>190</td>
<td>0</td>
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<td>209/209</td>
<td>A$_{1g}$ / sym. stretch</td>
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<td>0</td>
<td>224</td>
<td>T$_{1u}$ / asym. stretch</td>
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<td>0</td>
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<td>80</td>
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<td>1</td>
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<tr>
<td>C$_{4v}$</td>
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<td>2</td>
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<td>16</td>
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<td>0</td>
<td>25</td>
<td>99</td>
<td>A$_2$ / twisting (eq)</td>
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<td>distorted trigonal bipyramid</td>
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<td>2</td>
<td>111</td>
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<tr>
<td></td>
<td>101</td>
<td>0</td>
<td>4</td>
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<tr>
<td></td>
<td>166</td>
<td>56</td>
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<td>186</td>
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<td>1</td>
<td>213</td>
<td>221</td>
<td>A$_1$ / total sym. str.</td>
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<tr>
<td></td>
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<td>115</td>
<td>5</td>
<td>233</td>
<td>B$_2$ / asym. stretching</td>
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<tr>
<td></td>
<td>217</td>
<td>57</td>
<td>35</td>
<td>239</td>
<td>A$_1$ / sym. stretching</td>
</tr>
</tbody>
</table>

$^a$A scaling factor of 1.11 applied to computed frequencies is determined from the comparison of the computed (solvated) and experimental (aqueous solution) vibrational frequencies (189 and 209 cm$^{-1}$) of the A$_{1g}$ / symmetric stretch in [PtBr$_6$]$^{2-}$.

$^b$Doubly degenerate mode

$^c$Triply degenerate mode

$^d$Calculations were performed at DFT (B3LYP/TZ/PCM) level with H$_2$O parameters.
and aqua-substituted $^{1}\text{PtBr}_5(\text{H}_2\text{O})^-$ complex. The subscripts 1 and 3 denote the singlet state and triplet ground electronic states. The aqua-substituted $^{1}\text{PtBr}_5(\text{H}_2\text{O})^-$ complex corresponds to the global minimum. For $\text{PtBr}_5^-$, the distorted trigonal bipyramid and square based pyramid geometries are predicted in the triplet and singlet ground electronic states, respectively. The Pt–Br bond length in the parent complex optimized using B3LYP/TZ/CPCM is 2.532 Å (See Appendix, Table A1) whereas with M052X/TZ/CPCM the bond length is 2.492 Å (Table 3.1), which is in a closer agreement with the experimental Pt–Br bond length (2.47 Å) determined in an X-ray diffraction study of aqueous hexabromoplitate. The calculated harmonic frequency of the totally symmetric stretching mode (189 cm$^{-1}$, $A_{1g}$) of $\text{PtBr}_6^{2-}$ in the ground electronic $^{1}A_{1g}$ state was somewhat lower (11%) than the experimental Raman value (209 cm$^{-1}$), therefore, a scaling factor of 1.11 was applied to obtain correct harmonic frequencies. The optimized geometries of the ground state species (M052X) involved in the photochemistry of hexabromoplatisate dianion are shown in Figure 3.1.

**Figure 3.1.** Optimized structures of the ground state $\text{PtBr}_6^{2-}$ (A), $^{3}\text{PtBr}_5^-$ (B), $^{1}\text{PtBr}_5^-$ (C), and $^{1}\text{PtBr}_5(\text{H}_2\text{O})^-$ (D).
Vertical electronic transitions of the parent dianion PtBr$_6^{2-}$ were calculated using M052X and B3LYP density functionals as well as the CASSCF/CASPT2 method, Table 3.3. The CASSCF/CASPT2 method demonstrated the best agreement with the experimental data, in particular three charge transfer transitions 228, 322, 364 nm were found with very high accuracy (experimental VET: 227, 311, and 364). This method also predicts two singlet excited ligand field states 413 and 476 nm lying within the absorption band assigned to a singlet ligand field excitation (435 nm) and two triplet ligand field excited states 483 and 518 nm which are in close proximity to the center of the band assigned to the triplet ligand field excitation (525 nm). Since spin-orbit coupling was not included in the calculations, the oscillator strengths for the singlet and triplet ligand field VET’s are both zeros. Visualization of molecular orbitals involved in the electronic transitions are shown in Figure 3.2. The B3LYP density functional commonly used for VET calculations of organic molecules was tested in the benchmark compound (PtBr$_6^{2-}$). It’s known that B3LYP does not accurately predict charge transfer transitions in transition metal complexes. It often underestimates the energies of CT states and may even change the order of electronic states. This is indeed observed in our calculations where the lowest triplet and singlet states are of charge transfer character which contrasts with previous assignments and CASSCF/CASPT2 calculations. Among two density functionals (M052X and B3LYP), the M052X functional showed better agreement with the CASSCF/CASPT2 method and experimental data (Table 3.3), therefore this level of theory was used for the VET calculations of the intermediates involved in the photochemistry of PtBr$_6^{2-}$. The results of the calculations are summarized in Table 3.4. Intense transitions are predicted to be at $\sim$260-270 nm for all product species. However, the $^3$PtBr$_5^-$ species exhibits intense transitions extending from the ultraviolet into green and red spectral regions. This is in contrast to the corresponding singlet $^1$PtBr$_5^-$.
Table 3.3. Vertical excitation energies and oscillator strength computed for PtBr$_6^{2-}$ dianion using DFT and CASSCF/CASPT2 methods compared to the experimental data.

<table>
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<th>aCASSCF/CASPT2, bExperiment, (ε, M⁻¹ cm⁻¹)</th>
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<td></td>
<td>B3LYP</td>
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<td>585 (0.000) $^3$CT</td>
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<td>518 (0.000) $^3$LF</td>
<td>525 (140) $^3$LF</td>
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<td>$^3$CT</td>
<td>$^3$CT</td>
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<td>$^3$LF</td>
<td>$^3$LF</td>
<td>$^3$LF</td>
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<td>577 (0.000) $^3$CT</td>
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<td>483 (0.000) $^3$LF</td>
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<td>435 (1500) $^1$LF</td>
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<td>391 (0.000) $^3$CT</td>
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<td>$^1$LF</td>
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<tr>
<td>406 (0.000) $^1$CT</td>
<td>309 (0.218) $^1$CT</td>
<td>322 (0.503) $^1$CT</td>
<td>311 (17800) $^1$CT</td>
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<td>315 (0.489e-8) $^1$CT</td>
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<td>236 (0.407e-8) $^1$CT</td>
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<td>222 (0.585) $^1$CT</td>
<td>228 (0.948) $^1$CT</td>
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$^a$ Spin-orbit coupling was not included in the calculations which resulted in zero oscillator strengths in the forbidden ligand field transitions.

$^b$ The extinction coefficient values for 525, 435, 364, 311 nm bands were taken from Jorgensen. The extinction coefficient for the 227 nm band was obtained in the present work.
Figure 3.2. Visualization of the optically allowed ligand field and charge transfer transitions of aqueous PtBr$_6^{2-}$ computed at CASSCF/CASPT2 level.
Table 3.4. Vertical excitation energies ($E_{\text{exc}}$), corresponding excitation wavelengths ($\lambda_{\text{exc}}$), and oscillator strengths ($f$) of the initial solvated (H$_2$O) compound, intermediates and aquated product.

<table>
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<tr>
<th>Species$^b$</th>
<th>State</th>
<th>$E_{\text{exc}}$(eV/nm)</th>
<th>$F$</th>
<th>$E_{\text{exp}}$ (eV/nm)$^a$</th>
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<td>A</td>
<td>3.93 (315)</td>
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<td>A</td>
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<td>A</td>
<td>5.29 (234)</td>
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$^a$The experimental excitation energies are taken from Jorgensen$^3$

$^b$VET calculations were performed at DFT (M052X/TZ/PCPM) level of theory
species, intense transitions of which are in the ultraviolet to blue spectral ranges. The spectral signatures of the singlet and triplet species can therefore be used to distinguish them in $\Delta \lambda$ spectra.
Figure 3.3. shows the UV-Vis absorption spectrum of aqueous PtBr₆²⁻ (molecular extinction coefficient, \( \varepsilon(420) = 2720 \text{ M}^{-1} \text{ cm}^{-1} \)). The spectrum is in agreement with previous

![UV-Vis absorption spectrum and Raman spectra](image)

**Figure 3.3.** Panel A: UV-Vis absorption spectrum of aqueous PtBr₆²⁻ (0.7 mM). The inset shows the Raman spectra of the powder K₂PtBr₆ sample and aqueous PtBr₆²⁻ (30 mM) solution recorded using an excitation wavelength of 785 nm. Water contribution to the Raman spectrum of PtBr₆²⁻ is subtracted. Panel B: The line represents the difference in absorption spectra between the fresh and room-light-exposed (\( \lambda > 350 \text{ nm} \)) aqueous solutions of PtBr₆²⁻ (2.9 mM). The pump-probe
A spectrum measured at time delay $\Delta t = 100$ ps following 420-nm excitation is shown by symbols. Short-term exposure of fresh solutions to the broadband visible light ($\lambda > 350$ nm) leads to the equilibrium absorption spectrum characterized by an increase in absorbance from 240 to 283 nm and a decreased absorbance for wavelengths greater than 283 nm, in agreement with the literature. As shown in Fig. 3.3, the difference absorption spectrum between the spectra of the light-exposed and fresh solutions of PtBr$_6^{2-}$ exhibits different spectral shape in the visible spectral region compared with the absorption spectrum of the fresh solution. This indicates the formation of a product species absorbing in the visible region ($\lambda > 350$ nm).

The measured Raman spectra of powder and aqueous samples of PtBr$_6^{2-}$ are illustrated in the inset of Fig. 1. Three bands at 105, 191 and 209 cm$^{-1}$ are pronounced for aqueous PtBr$_6^{2-}$. All these bands are in excellent agreement with the scaled (factor, 1.11) vibrational frequencies calculated for PtBr$_6^{2-}$ (DFT B3LYP/TZ/PCPM), which correspond to the T$_2$g bending mode (105 cm$^{-1}$), E$_g$ symmetric stretch mode (191 cm$^{-1}$), and A$_{1g}$ symmetric stretch mode (209 cm$^{-1}$), Table 3.2.
Pump-probe experiments.

Measured transient absorption $\Delta A$ spectra and kinetic traces of aqueous PtBr$_6^{2-}$ at various time delays $\Delta \tau$ between the 420-nm pump and probe pulses are shown in Figures 3.4 and 3.5.

The cross-phase modulation $\Delta A$ signals measured for neat water under the same conditions

**Figure 3.4.** Main panel: measured transient absorption $\Delta A$ spectra following 420 nm excitation of PtBr$_6^{2-}$ (3.5 mM) in water. The time delay values (in ps) are given in the legend. The symbols and lines correspond to raw and smoothed data. Three top panels: the spectral positions of the calculated vertical electronic transitions of $^3$PtBr$_5^-$ and $^1$PtBr$_5^-$ and the aquated product $^1$PtBr$_5$(H$_2$O)$^-$ involved in the photochemistry of PtBr$_6^{2-}$ (M052X).
provide an unambiguous marker for time zero, $\Delta \tau = 0$, Fig. 3.5. The ground-state bleach (negative $\Delta A$ signal) observed for aqueous PtBr$_6^{2-}$ in the ~280-370 nm range is due to pump-induced ground-state depletion. The ground-state bleach occurs with an instrument-response limited rise time, and is followed by a minor fast decay ($\leq$ 10% of the initial amplitude) on a wavelength-dependent time scale of 400-600 fs, followed by a much slower decay. The early-time transient absorption (positive $\Delta A$ signal) covers the wavelength range from 370 to 770 nm with the maximum at ~500 nm ($\Delta \tau = 100$ fs) pointing to the formation of a photoproduct, as well as the ultraviolet range from 270 to 285 nm, Fig. 3.4. The $\Delta A$ signal within the 500-nm region exhibits a delayed rise on a sub-200 fs time scale. Damped coherent oscillations are observed in early-time $\Delta A$ spectra; (i) modulations with FFT frequencies ~76 and ~114 cm$^{-1}$ and a time onset, which are weak near the center, but strong in the blue and red wings of the 500-nm product band as well as in the ultraviolet range, and (ii) modulations with a FFT frequency ~209 cm$^{-1}$ without an onset and present only in the ultraviolet range within the ground-state absorption, Fig. 3.5D-F. From as early as $\Delta \tau = 100$ fs to 4 ps, the $\Delta A$ spectra undergo a series of changes. In the cumulative process step $\tau_2$, the initial minor (subtle) vacillations in the visible range from ~200 to 500 fs are succeeded by a significant (1350 cm$^{-1}$) blue shift of the transient absorption observed as the $\Delta A$ decay between 600-770 nm and $\Delta A$ rise between 400-475 nm. The blue shift can be visually enhanced by subtracting the 3 ps $\Delta A$ spectrum from the early-time spectra and can be characterized by an exponential time constant of ~ 580 fs. The $\Delta A$ spectra on ~3 ps time scale are dominated by absorption decay in the 465-770 nm range accompanied by absorption build up in the 335-465 nm range (isosbestic point, 465 nm) with the formation of a 430-nm photoproduct band with a long absorption tail extending into the red spectral region, (process step, $\tau_3$). The integrated intensity under the broad 350-900 nm transient spectrum
Figure 3.5. Panels A-C: Short-time visible kinetic $\Delta A$ traces following 420-nm excitation of PtBr$_6^{2-}$ (3.5 mM) in aqueous solution. The probe wavelengths (in nm) are given in the inserts. The typical $\Delta A$ signals measured for neat water (gray solid lines) are shown at selected probe wavelengths after an appropriate scaling for solute absorption. For aqueous PtBr$_6^{2-}$, symbols represent the experimental data whereas the shown solids lines represent best multiexponential fits convoluted with the instrument response function (150 fs, fwhm) centered at $\Delta t = 0$ ps (Panel B) and without convolution (Panel A). Panels D-F: Fast Fourier transform (FFT) components obtained from the $\Delta A$ kinetic traces shown in Panels A-C following subtraction of multiexponential fits. In the inset of panel F: double sine damped fit of the oscillatory part of 625 and 700 nm kinetic traces.
**Figure 3.6.** Transient absorption $\Delta A$ kinetic traces (symbols) acquired following excitation of aqueous $\text{PtBr}_6^{2-}$ (3.5 mM) at 420 nm and their fits (lines) to a sum of multiexponential functions. Panel A: UV $\Delta A$ kinetic traces. Panel B: Representative $\Delta A$ kinetic traces at the probe wavelengths 270 and 600 nm. Panel C: The short-time $\Delta A$ evolution at 270 nm, fit residue (solid symbols), and fit (line) of the fit residue to a sum of two exponentially damped sine functions with frequencies (dominant, $v_1 = 104 \text{ cm}^{-1}$, and $v_2 = 198 \text{ cm}^{-1}$). The $v_1$ and $v_2$ frequencies agree with those obtained from the FFT analysis of the visible absorption, Figure 3.6, Panels A and B.
decayed during this evolution, possibly suggesting, in conjunction with the observation of the isosbestic point and the absence of significant bleach recovery, that the 465-770 nm species decays to the smaller-oscillator strength species absorbing between 345-465 nm. A concurrent rise (τ₃) of transient absorption is also observed at 270 nm, Fig. 3.6. A factor of ~2 decrease in the intensity of the 430 nm absorption band and the red tail from Δτ = 3 to 10 ps, and then from 10 to 20 ps suggests the presence of two distinct decay phases, < 10 ps (process step, τ₄), and < 20 ps (process step, τ₅). Fitting of both the individual ΔA kinetic traces as well as integrated intensity within the 430-nm band and the red tail from 3 to 200 ps to a double-exponential decay function yielded time constants of τ₄ ~ 7 ps and τ₅ ~ 15 ps. As for the negative ΔA signals in the 300-340 nm range, their absolute amplitudes which remained large after initial sub-picosecond decay, dramatically decrease from 2 to 10 ps, remain approximately constant from 10 to 20 ps, and afterwards increase on a 50-ps time scale, suggesting the presence of similar steps τ₄ and τ₅ in the time evolution of ground-state bleach, Fig. 3.4. After 100 ps, the entire ΔA spectrum exhibits no significant changes. The formation of the stable product species is indicated by the transient absorption at 270-280 nm. The product species has another absorption band around 420-490 nm because the residual bleach does not reproduce the UV-Vis spectrum of aqueous PtBr₆²⁻ in this region.

A time constant of τ₁ = 150 ± 30 fs for the delayed appearance of the photoproduct is extracted by fitting the ΔA kinetic traces measured in the vicinity of the 500-nm central wavelength of induced absorption where the oscillations are not pronounced (Fig. 3.5 B) to a multiexponential function convoluted with the instrument-response function centered at Δτ = 0 fs. The other time components determined were as follows: absent τ₂, τ₃ = 1.4 ± 0.4 ps, τ₄ = 7.0 ± 1.4 ps, τ₅ = 16.3 ± 2.7 ps, and a permanent offset. The global description of the time evolution of
the entire ΔA spectra in the visible 360-760 nm range was obtained by a global fit to a sum of four exponential functions and an offset. The best-fit time constants obtained were as follows: \( \tau_2 \sim 0.3 \text{ ps}, \ \tau_3 \sim 2.2 \text{ ps}, \ \tau_4 \sim 7.9 \text{ ps}, \ \text{and} \ \tau_5 \sim 13.7 \text{ ps}, \) Fig. 3.7. The time evolution of the negative

![Graph showing decay-associated spectra and rate constants](image)

**Figure 3.7.** The results of a least-square global fit of the ΔA kinetic traces of aqueous PtBr_6^{2-} upon excitation at 420 nm to a sum of four exponential functions and a permanent offset. The obtained rate constants \( (k_i) \) are shown beside the corresponding reconstructed decay-associated spectra \( (\varepsilon_i) \). The sharp spectral feature around 420-nm is due to scattered excitation light.

ΔA signals in the 300-340 nm range can be described by multiexponential fits with the following predominant time constants and amplitudes: wavelength-dependent \( \tau_2 = 0.3-0.6 \text{ ps} \ (10 \pm 4 \%) \),
wavelength-independent bleach-recovery $\tau_4 \sim 7$ ps ($56 \pm 6\%$), with the remaining $34 \pm 4\%$ amplitude distributed among two bleach-rise components $\tau_5 \sim 14$ ps and $\tau_6 \sim 20$ ps the relative contributions of which depend on the probe wavelength. The spectral amplitudes of both $\tau_4$ and $\tau_6$ components approximately match the UV-Vis absorption spectrum of aqueous $\text{PtBr}_6^{2-}$.

The fit of the oscillatory part of $\Delta A$ kinetic traces to a sum of two exponentially damped sine functions (data analysis) reveals that the oscillations with a $\sim 114$ cm$^{-1}$ FFT can be characterized by the coherence decay time constant of $412 \pm 103$ fs and somewhat wavelength-dependent fundamental oscillation frequencies ranging from 105 to 120 cm$^{-1}$ with an average frequency of $110 \pm 11$ cm$^{-1}$, Fig. 3.8A. The fitting analysis further reveals that the modulations at the red and blue wings of the induced absorption band exhibit a relative $\pi$-phase shift as evident from the relative positions of the minima and maxima in the $\Delta A$ kinetic traces, e.g. at $\Delta \tau = 150$ and 290 fs, Fig. 3.5, Panels A and C. The onset of the oscillations with $\sim 78$ and $\sim 114$ cm$^{-1}$ FFT frequencies cannot be traced to $\Delta \tau = 0$ and they occur in induced absorption, suggesting that these oscillations are in the delayed photoproduct. Spectral oscillations with a $213 \pm 4$ cm$^{-1}$ frequency and a $1.4 \pm 0.4$ ps damping time constant are obtained in the $\Delta A$ spectra between 350 and 475 nm, in agreement with a $\sim 209$ cm$^{-1}$ FFT frequency in this range. These oscillations have no temporal onset ($\phi = 0$) and occur within the spectral range of ground-state absorption of $\text{PtBr}_6^{2-}$, with the best-fit oscillation amplitude approximately matching the steady-state spectrum of $\text{PtBr}_6^{2-}$, Fig 3.8 B. The oscillation frequency is similar to the calculated (209 cm$^{-1}$) and measured Raman-active (209 cm$^{-1}$, onset of the Fig. 3.3) frequency of symmetric Pt–Br stretching mode of $^1\text{A}_{1g}$ $\text{PtBr}_6^{2-}$, Table 3.2. Therefore, the origin of these oscillations must be associated with the resonance impulsive Raman scattering from ground-state $\text{PtBr}_6^{2-}$. 
Figure 3.8. Analysis of oscillatory part of the kinetic traces within 500 nm band (A) and ground-state absorption region (B).

- **Figure A:**
  - Amplitude 1 (a.u., A)
  - Frequency $v_1 = 110 \pm 11 \text{ cm}^{-1}$
  - Cohherence time $t_{coh1} = 412 \pm 39 \text{ fs}$
  - Frequency $f_{coh1} = 112 \pm 52 \text{ fs}$

- **Figure B:**
  - Amplitude 2 (a.u., A)
  - Frequency $v_2 = 215 \pm 8 \text{ cm}^{-1}$
  - Cohherence time $t_{coh2} = 1.4 \pm 0.5 \text{ ps}$
  - Frequency $f_{coh2} = 7 \pm 18 \text{ fs}$
Table 3.5. Double sine fit analysis of the kinetics traces within the photoproduct absorption band obtained upon photoexcitation of PtBr$_6^{2-}$ with 350, 420, and 530 nm in methanol, D$_2$O, and water.

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<th>$\nu_{osc}$, FFT cm$^{-1}$</th>
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<th>$\tau_{osc}$, ps</th>
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<td>0.063 ± 0.016</td>
<td>114 ± 8</td>
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<td>71 ± 5</td>
<td>0.21 ± 0.13</td>
<td>0.132 ± 0.030</td>
<td>125 ± 9</td>
<td>116 ± 7</td>
<td>0.23 ± 0.08</td>
<td>0.249 ± 0.09</td>
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<tr>
<td><strong>PtBr$_6^{2-}$ 420 nm excitation, water</strong></td>
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<td>69</td>
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<td>73 ± 12</td>
<td>0.33 ± 0.18</td>
<td>0.074 ± 0.008</td>
<td>113 ± 6</td>
<td>112 ± 6</td>
<td>0.20 ± 0.01</td>
<td>0.226 ± 0.06</td>
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<td><strong>PtBr$_6^{2-}$ 530 nm excitation, water</strong></td>
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</tr>
<tr>
<td>650</td>
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<tr>
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<td>71 ± 12</td>
<td>0.18 ± 0.05</td>
<td>0.087 ± 0.043</td>
<td>116 ± 10</td>
<td>114 ± 4</td>
<td>0.16 ± 0.03</td>
<td>0.412 ± 0.07</td>
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The fit of the oscillatory parts of the kinetic traces of PtBr$_6^{2-}$ within the photoproduct absorption band to the double sine damped function showed better results in comparison to the fit using single sine damped function. The results of the fit of the residues are summarized in Table 3.5. The analysis reveals the presence of two vibrational modes of 76 and 112 cm$^{-1}$ consistent with FFT analysis of the same residues. The lower frequency oscillations have sub-100 fs decay time in water and slightly above 100 fs in methanol and D$_2$O. The same trend is observed for 112 cm$^{-1}$ oscillations. Furthermore, the damping time of the oscillations decreases as the energy of the pump pulses increases. In aqueous solutions, upon 350, 420, and 530 nm excitation, the measured damping times of the oscillations are 0.063, 0.072, and 0.87 ps for 76-cm$^{-1}$ mode and 0.181, 0.213 and 0.412 ps for 112-cm$^{-1}$ mode correspondingly.
3.3 Discussion

*Evolution of transient absorption spectra of aqueous PtBr$_6^{2-}$ following 420 and 530 nm excitation.*

The first key observation following 420-nm excitation of aqueous PtBr$_6^{2-}$ into the singlet $^1T_{1g}$ state is the delayed appearance of the photoproduct absorption characterized by a rise time constant $\tau_1 = 150$ fs. We rule out the assignment of the early-time transient absorption to excited-state absorption from the initially populated $^1T_{1g}$ state of PtBr$_6^{2-}$. The absorption from $^1T_{1g}$ should show an instrument-response limited rise time. Furthermore, the early-time transient absorption spectra are similar to those observed following 530-nm excitation of PtBr$_6^{2-}$ into the triplet $^3T_{1g}$ state, Fig. 3.9. Moreover, 420-nm excitation and 530-nm excitation both give rise to similar coherent oscillations. These observations are inconsistent with the $^1T_{1g}$ nature of the initial transient. Alternatively, the early-time transient absorption might be due to the triplet $^3T_{1g}$ state of PtBr$_6^{2-}$. However, the $^3T_{1g}$ state is calculated to be repulsive along the Pt–Br bond coordinate. Photodissociation of heavy neutrals and ions such as Hgl$_2$, HgBr$_2$, and I$_3$ in solution is known to occur within about 300 fs based on the ultrafast time-resolved studies. The dissociation of $^3T_{1g}$ PtBr$_6^{2-}$ is expected to occur on about the same time scale. In contrast, the early-time transition absorption slightly wavers before it starts to decay noticeably after $\Delta \tau \approx 1$ ps. This is evidence that the species responsible for early-time transient absorption, while showing minor structural changes, largely survive(s) on a picosecond time scale, inconsistent with the dissociative character of the triplet $^3T_{1g}$ state. We also rule out the assignment of the early-time transient absorption to vibrationally hot PtBr$_6^{2-}$ in the ground $^1A_1$ state. Spectral shift, narrowing, and decay of the early-time transient absorption is accompanied by a small recovery due to
Figure 3.9. Panel A: measured transient absorption $\Delta A$ spectra (lines and symbols) following excitation of $\text{PtBr}_6^{2-}$ (3.5 mM) in water at 530 nm. The time delays $\Delta t$ (in ps) are given next to the each $\Delta A$ spectral curve. The sharp spectral feature around 530 nm is due to scattered excitation light. The insets show the short-time $\Delta A$ kinetic traces at the probe wavelengths 650, 675, and 700 nm (symbols) and multiexponential fits (red lines). The oscillatory $\Delta A$ signal around $\Delta t = 0$ is due to the solvent and spinning cell front wall. Panels B-D: Fast Fourier transform (FFT) components at 650, 675, and 700 nm obtained from the corresponding short-time $\Delta A$ kinetic traces following subtraction of the multiexponential fits shown in Panel A.
of ground-state bleach, and ceases with the formation of an absorption band peaking at 450 nm
the thermalized product species at $\Delta \tau = \sim 6$ ps. To summarize, we rule out the assignments of the
early-time transient absorption to either $^{1}T_{1g}$ or $^{3}T_{1g}$, or hot $^{1}A_{1g}$ of PtBr$_6^{2-}$.

We assign the early-time transient absorption to the triplet pentabromoplatinate species
($^{3}\text{PtBr}_5^-$) formed with the excess of vibrational energy following photodissociation of PtBr$_6^{2-}$.
This assignment is in accordance with the bond cleavage mechanism proposed by Balzani and
co-workers, the finding that the triplet $^{3}T_{1g}$ state of PtBr$_6^{2-}$ is dissociative, and the ultrafast
spectral evolution observed. The formation of non-thermalized $^{3}\text{PtBr}_5^-$ in less than 200 fs
emphasizes the remarkably fast sequence of intersystem crossing (ISC) and Pt–Br bond breaking
processes following excitation of PtBr$_6^{2-}$ into the lowest singlet excited $^{1}T_{1g}$ state. The fast
relaxation of the $^{1}T_{1g}$ and $^{3}T_{1g}$ states agrees with the fact that no emission has been observed in
previous studies of aqueous PtBr$_6^{2-}$. We think that there should be a strong spin-orbit mixing of
the singlet $^{1}T_{1g}$ and triplet $^{3}T_{1g}$ zero-order states in PtBr$_6^{2-}$ due to large spin-orbit constants of the
Pt and Br atoms. The avoided electronic configuration crossing of the two states results in the
lower and upper adiabatic surfaces. Theoretically, a spin-orbit interaction is turned on as a
molecule passes along a suitable deformation coordinate through an avoided crossing of the
zero-order singlet $^{1}T_{1g}$ and triplet $^{3}T_{1g}$ surfaces. For example, Chergui and co-workers have
interpreted ultrafast ($\lesssim 20$ fs) ISC from initially prepared $^{1}\text{MLCT}$ to $^{3}\text{MLCT}$ in solvated Fe(bpy)$_3$
as being due to surface crossing via a single oscillation of the high-frequency 1607 cm$^{-1}$ mode
associated with the ligand deformation. In PtBr$_6^{2-}$, bending ($t_{2g}$) mediates ISC from the $^{1}T_{1g}$
surface directly to the lowest dissociative $^{3}T_{1g}$ state or two other energetically accessible
(CASSCF/CASPT2) triplet surfaces of $^{3}T_{1g}$ and $^{3}T_{2g}$ symmetry ($^{1}T_{1g} \otimes t_{2g} \Rightarrow ^{3}T_{2g}$), which is
likely followed by ultrafast internal conversion to the lowest $^{3}T_{1g}$ state based on the small energy
The pronounced oscillations with FFT frequencies of ~78 and ~114 cm\(^{-1}\) and an induction period of ~110 fs in early-time transient absorption spectra are observed within the 500-nm absorption band due to hot triplet \(^3\)PtBr\(_5\)^{-} product possessing distorted trigonal bipyramid geometry. Several mechanisms can give rise to the coherent oscillations in the product absorption. Within the framework of a two-level system, impulsive excitation of coupled electronic or vibrational states induces phase coherence between the corresponding wave functions. As a result, the occupation probabilities of the involved states exhibit oscillations detectable in the absorption originating from these states. If the coupled states are electronic, electronic coherence is created, which manifests itself as oscillations of large amplitude.\(^{17}\) The ratio of the modulated to unmodulated \(\Delta A\) signals in the red probing region is ~55%. The observed modulations are the strongest on the steepest part of the absorption band and weak near the band maximum (Fig 3.8 A) as oppose to modulations due to electronic.\(^{17}\) Furthermore, electronic coherence shows substantial anisotropy of transition PtBr\(_6\)^{2-}. Therefore, the hypothesis needs to be tested that coherence is produced between the nearly isoenergetic electronic states accessible in a polyatomic molecule of high degree of symmetry. Provided that the states have different charge distribution, the
corresponding energy gap, and hence the oscillation frequency is highly sensitive to solvent polarity.\textsuperscript{17}

However, the same oscillation frequencies are found in water and methanol solutions, Fig. 3.10. The observed modulations are the strongest on the steepest part of the absorption band and weak near the band maximum as oppose to modulations due to electronic coherence.\textsuperscript{18} This is in contrast to the same oscillation amplitude observed in the $\Delta A(\parallel)$ and $\Delta A(\perp)$ signals, Fig. 3.11. Thus, we observe vibrational coherence in the photoprodct.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.10.png}
\caption{Panels A-B: Short-time visible kinetic $\Delta A$ traces (open circles) and the fit of the time evolution (red lines) following 420-nm excitation of PtBr\textsubscript{6}\textsuperscript{2-} (3.5 mM) in methanol (A) and aqueous solutions (B). Panel D and C: Fast Fourier transform (FFT) components obtained from oscillatory part of the $\Delta A$ kinetic traces shown in Panels A-C following subtraction of multiexponential fits (green lines).}
\end{figure}
In turn, two mechanisms can give rise to the coherent vibrational oscillations in the product absorption. Stepwise coherent population of the triplet ground electronic state of PtBr$_5^-$ is the first mechanism. The spectral dependence of the oscillation amplitude should then match the product absorption band and the oscillation phase should remain constant across the band.$^{19}$ The second mechanism is coherent vibrational motion on the triplet potential energy surface of PtBr$_5^-$. The oscillation amplitude at the blue and red wings of the product absorption band should then exhibit two maxima characterized by the same fundamental frequency but with the phase difference equal to $\pi$, and zero amplitude at the center of the band.$^{19-20}$ Our observation of a double maximum of the oscillation amplitude and a $\pi$ shift within the 500 nm ($\Delta \tau = 100$ fs) absorption band of the triplet pentabromoplatinate product (Fig. 3.8 A) offers compelling evidence that the coherent oscillations observed are due to vibrational product motion. The $\sim$114

**Figure 3.11.** $\Delta A(\parallel)$ (red curve) and $\Delta A(\perp)$ (blue curve) signals (420-nm pump/730-nm probe) in the anisotropy measurements of aqueous PtBr$_6^{2-}$. Black curve represents $\Delta A(\parallel)$ signal from water.
cm$^{-1}$ coherent oscillations are observed from the blue to near-infrared wavelength range as well as in the ultraviolet region (probe wavelength, 270 nm). This implies that the ground-state $^3$PtBr$_5^-$ product species exhibits a broad absorption spectrum due to a superposition of several absorption bands. The observed oscillation frequency (FFT, $\sim$114 cm$^{-1}$) agrees with the 112 cm$^{-1}$ bending $E'$-mode frequency calculated for aqueous triplet PtBr$_5^-$ in the distorted trigonal bipyramidal geometry, Table 3.2. The coherent oscillations may be created in an ISC event and be preserved through the dissociation. This is, however, not the case here, because similar oscillations are observed upon direct excitation of PtBr$_6^{2-}$ into the $^1$T$_{1g}$ singlet and $^3$T$_{1g}$ triplet excited states. Previously, the vibrational coherence in solvated photofragments has been observed in the photodissociation of small halide neutrals and ions (HgI$_2$, HgBr$_2$, I$_3^-$),$^{11-13}$ heme proteins$^{21}$, as well as in similar octahedral complexes such as Cr(CO)$_6$ in the gas phase.$^{22-23}$

Coherent vibrational motion as a result of photodissociation was first demonstrated for HgI$_2$, where following the impulsive Hg–I bond-breaking, a HgI fragment is created in a superposition of vibrational states.$^{11}$ Product coherence in $^3$PtBr$_5^-$ may result in a similar way, originating from the photodissociation event itself when an impulsive force is imparted to the nuclear coordinates that are strongly coupled to a bromide-metal dissociative reaction coordinate. In the incipient PtBr$_6^{2-}$ structure, the asymmetric stretching $t_{1u}$ mode is coupled to bending motion, which is the nuclear displacement of the bending $e'$ mode in TBP $^3$PtBr$_5^-$. Following the acceleration along the asymmetric Pt–Br bond stretch towards the asymptotic limit of two-body dissociation, coherent vibrational bending motion in the $^3$PtBr$_5^-$ product is impulsively launched on the exit of the vibrational wavepacket from the $^3$T$_{1g}$ electronic state. However, the nascent $^3$PtBr$_5^-$ product should be vibrationally hot, yet the observed frequency is close to the harmonic
frequency. Furthermore, the amplitude of the quantum beats observed is very large, whereas vibrational coupling is known to result in weak quantum beats.\textsuperscript{24}

\textit{Excitation of vibrational coherence in $^3\text{PtBr}_5^-$ at a symmetry-induced Jahn-Teller C\textsubscript{4v} conical intersection.}

Coherent vibrational motion can be excited impulsively by the passage of the dissociation fragment $^3\text{PtBr}_5^-$ through a conical intersection. We note that the equilibrium ground-state structure of $^3\text{PtBr}_5^-$ is nearly like TBP (D\textsubscript{3h}) whereas a nascent $^3\text{PtBr}_5^-$ structure following Pt-Br dissociation is SP (C\textsubscript{4v}). This is a pattern characteristic of a Jahn-Teller effect, which has been a subject of a number of time-resolved investigations, notably, in the Cr(CO)\textsubscript{6}/Cr(CO)\textsubscript{5} system.\textsuperscript{22-23,25} Excitation of chromium hexacarbonyl leads to ultrafast internal conversion to one of the lower-lying singlet excited states\textsuperscript{26} where the molecule ejects one CO ligand to produce a square pyramid (C\textsubscript{4v}) Cr(CO)\textsubscript{5} in the first excited singlet $^1\text{E}$ electronic state.\textsuperscript{27,28} According to the Jahn-Teller theorem, a non-linear molecule in a degenerate electronic state distorts by suitable non-totally symmetric vibrations with a concomitant stabilization of energy.\textsuperscript{29-30} In a system with a fourfold rotation axis, a double-degenerate E-state at a C\textsubscript{4v} geometry represents a conical intersection C\textsubscript{4v} CI, and the degeneracy is lifted by vibrations of $b_1$ and $b_2$ symmetry, the so-called $E \otimes (b_1 \oplus b_2)$ Jahn-Teller effect.\textsuperscript{31} It is assumed that the slope of the PES is much larger along the $b_1$ coordinate, which corresponds to the $e'$ bending coordinate in D\textsubscript{3h}, leading to a double degenerate $^1\text{E}'$ state at a D\textsubscript{3h} geometry and consequent conical intersection - D\textsubscript{3h} CI. The degeneracy point at the conical intersection is lifted by a degenerate vibration (vibration of $e$ symmetry), the so-called $E \otimes e$ Jahn-Teller effect, forming a double-cone PES in the space of splitting coordinates. The resulting ground-state PES exhibits equivalent minima corresponding
to SP ($C_{4v}$) geometry and connected through $C_{2v}$ transition states along the radial pseudo rotation coordinate $\Theta$. Coherent oscillations with a wavenumber of 96 cm$^{-1}$ observed in Cr(CO)$_5$ following photodissociation of gas-phase Cr(CO)$_6$ were assigned to vibrational motion along the bending coordinate that is launched as the wavepacket propagates through a Jahn-Teller $D_{3h}$ CI.$^{23,25,32}$

Following excitation of PtBr$_6^{-}$ into $^1T_{1g}$, the wavepacket is initially situated in the vicinity of the avoided crossing before it undergoes a partial bending oscillation that promotes ISC. The wavepacket then moves along an overdamped Pt–Br trajectory on the downhill $^3T_{1g}$ potential energy surface towards the exit. The nascent $^3$PtBr$_5^{-}$ ($C_{4v}$) species is formed in the first excited triplet state of $^3E$ character because the lowest energy $^3T_{1g}$ state in $O_h$ (reached by intersystem crossing from $^1T_{1g}$ or the Franck-Condon state in our experiment) correlates to the $^3E$-state in $C_{4v}$. Figure 3.12 shows that as the Pt–Br$_{ax}$ bond lengthens leading to the descent in symmetry from $O_h$ to $C_{4v}$, there is, as a result, a decrease in energy of the $e_g$ ($d_{z^2}$) orbital. The LF states arise from the configurations $b_2^2e^4 \rightarrow b_2^2e^3a_1^1$ ($^3E$) and $b_2^2e^4 \rightarrow b_2^1e^4a_1^1$ ($^3B_2$). The $^3E$ state is dissociative. The E-state degeneracy, representing a JT $C_{4v}$ conical intersection with two-fold symmetry is lifted by vibrations of $b_1$ and $b_2$ symmetry, which correspond to out-of-plane pucker ($b_1$) consisting of two out-of-phase bending motions, out-of-phase stretch ($b_1$) and in-plane scissor ($b_2$), table 3.2 (Graphical representation of vibrational modes are shown in Appendix C). When the wavepacket passes through the CI, a large force field will impulsively develop and impart to the nuclei along the aforementioned CI-defining coordinates. The slope of the excited-state PES is probably much larger along the $b_1$ bending coordinate (pucker), based on the TBP-like equilibrium structure of $^3$PtBr$_5^{-}$. Hence, the wavepacket proceeds from the $C_{4v}$ SP through the $C_{2v}$ symmetry to the $D_{3h}$ TBP with the $b_1$ coordinate in $C_{4v}$ corresponding to the $e'$ bending
Figure 3.12. Molecular orbital correlation between O$_h$ and C$_{4v}$ geometries of PtBr$_6^{2-}$.

coordinate in D$_{3h}$, where it undergoes internal conversion to produce a stable triplet group-state $^3$PtBr$_5^-$ product in the distorted-TBP (C$_{2v}$) geometry.

To find further support for this mechanism, we mapped the ground-state PES of $^3$PtBr$_5^-$ along the $b_1$ (pucker) and $b_2$ (scissor) coordinates, Fig 3.13. The ground-state surface displays two equivalent minima corresponding to the quasi-TBP structures formed through interconversion of axial and equatorial ligands. The minima are separated via C$_{2v}$ ridge. The lowest point on the ridge is a 0.2 eV barrier between two quasi TBP structures. The resulting surface is somewhat similar to a cut through a PES with a Jahn-Teller E($b_1b_2$) C$_{4v}$ CI.  

$^3$T$_{1g}$ ligand field excited state
$^3$E ligand field excited state
Figure 3.13. (A) Ground electronic state potential energy surfaces of $^{3}\text{PtBr}_5^-$ obtained by mapping the surface along $b_1$(pucker), $b_2$(scissor) coordinates lifting the degeneracy at the $C_{4v}$ CI. In $C_{2v}$ geometry, $b_1$ and $b_2$ symmetries descend to $a_1$ (bending) and $a_2$ (twisting). Red circle indicates the CI.

Now, we turn to the discussion of the spectral evolution of the transient absorption $\Delta A$ spectra observed within the time span from 100 fs to 6 ps. The transient absorption in the early-time ($\Delta \tau = 100$ fs) $\Delta A$ spectrum is dominated by growth of nascent $^{3}\text{PtBr}_5^-$ species absorbing in the entire probe range extending from ultraviolet to near-infrared. The formation of $^{3}\text{PtBr}_5^-$ is complete within 200 fs. Following the formation of $^{3}\text{PtBr}_5^-$, the visible $\Delta A$ spectra continuously evolve from 0.2 to 2 ps (no significant bleach evolution during this time). At early times, the $\Delta A$
spectra exhibit some spectral narrowing in the visible range, which is complete within 800 fs. The narrowing is tentatively assigned to the energy dissipation in the nascent $^3\text{PtBr}_5^-$ due to intramolecular vibrational energy redistribution (IVR) and vibrational cooling processes. The spectral narrowing is superimposed on the pronounced continuous blue shift which occurs up to about 2 ps and can be characterized by a time constant of $\sim$600 fs. Possible assignment of the blue shift to solvation through hydrogen bonding is considered. Recent studies on charged metallo-organic complexes in aqueous solutions suggested that very fast dissipation of vibrational energy excess to water is possible ($\sim$5.7 kcal mol$^{-1}$ cm$^{-1}$ per 100 fs). Given the reported dissipation rate, the excitation energy used here (68 kcal mol$^{-1}$), and the Pt-Br bond-dissociation energy (24 kcal mol$^{-1}$), this implies that the available energy following the photodissociation of PtBr$_6^{2-}$ may be largely dissipated within 1 ps. We note that the hydrogen bond formation between the nascent $^3\text{PtBr}_5^-$ and water molecules can be one of the factors contributing to very fast energy dissipation. Time-resolved infrared spectroscopy of neat water showed the ability of vibrational energy to spread through the medium on a sub 1 ps time scale. The importance of a hydrogen bond network in ultrafast energy transfer from polyatomic solutes to solvent has been demonstrated. In addition, all normal modes of $^3\text{PtBr}_5^-$ are of low frequency overlapping the high density low-frequency collective modes of water, thus making vibrational energy transfer to the solvent highly efficient. Moreover, long-range electrostatic forces between the PtBr$_5^-$ ion and water undoubtedly contribute to the very short vibrational relaxation time observed.

The most significant changes of transient absorption observed in the first several picoseconds following excitation include the decay of $\Delta A$ due to $^3\text{PtBr}_5^-$ between 445-770 nm and the rise of $\Delta A$ between 370 and 445 nm. On the whole, the decay in the 445-770 nm
wavelength region is more pronounced than the rise in the 370-445 nm wavelength region, and as a result, the integrated area under the broad 350-900 nm absorption spectra decay with a time constant of ~2.2 ps. An observation of the early isosbestic point (445 nm) between 0.8 and 2 ps as well as the similar decay and rise time constants (τ3 ~ 2.2 ps) is evidence that \(^3\)PtBr\(_5^-\) decays to new product species. Its formation is manifested by the development of the 430-nm absorption band, which in turn decays biexponentially with time constants 7 and 15 ps. The τ3 ~ 2.2 ps time constant is prominent in the transient absorption (270 and 350 nm) occurring in the region of the parent ground-state depletion, and it is unlikely to be due to product geminate recombination because on the whole ground-state bleach does not recover with the τ3, but exhibits a much longer recovery time constant (7 ps). The initial minor decay of the ground-state bleach (≤ 10% of the initial amplitude) with wavelength-dependent time constants of τ2 ~ 400-600 fs can be assigned to the decay of the overlapping absorption of hot PtBr\(_5^\)\(^-\). Considering the presence of the early isosbestic point and overall decrease of the integrated absorbance, it is thought that \(^3\)PtBr\(_5^-\) decays into another more weakly absorbing species with a visible 430-nm band, and that their total concentration remains invariant throughout the initial reaction stage prior to the onset of decay of the 430-nm band. It is unlikely that this new species is the aquated complex in the triplet excited state because \(^3\)PtBr\(_5\)(H\(_2\)O)\(^-\) since does not have a stable minimum (M052X/TZ/CP). On the other hand, the \(^1\)PtBr\(_5^-\) ground-state species is thermodynamically more stable. The spectral position of the calculated intense transitions in \(^1\)[PtBr\(_3\)]\(^-\) (242, 298, 327, 335, 441, and 512 nm, Table 3.4) is in good agreement with the transient absorption observed in the 270-nm region, as well as with 350- and 430-nm bands, further supporting the assignment of the τ3 ~ 2.2 ps component to the \(^3\)PtBr\(_5^-\) → \(^1\)PtBr\(_5^-\) ISC process.
The onset of the formation of ground-state species occurs starting from ~2 ps following excitation. By monitoring the spectral evolution of \( \Delta A \) spectra between 2 and 200 ps over a broad wavelength range, including the bleach spectral region, the sequence of the ground-state reaction steps leading to aquation can be identified. The ground-state reaction paths start with the formation of \(^1\text{PtBr}_5^-\) the absorption of which is partially superimposed on the pump-induced ground-state depletion. The decay of the 430-nm absorption band of \(^1\text{PtBr}_5^-\) from 3 to 10 ps (time constant, \( \sim 7 \) ps) is accompanied by the decay (time constant, \( \sim 7 \) ps) of the initial ground-state bleach \( \Delta A \) signal around 310 nm, hence they can be attributed to the same process (time constant, \( \tau_4 \)). The decay of the absorption from a product state and the recovery of ground-state depletion on the same time scale suggest that the product state collapses back to the reactant ground state, consistent with the geminate recombination of \( \text{PtBr}_5^- \) and \( \text{Br}^- \) fragments to reform a parent ground-state dianion. The question is how two negatively charged ions can recombine?

For infinitely separated and solvated \(^1\text{PtBr}_5^-\) and \( \text{Br}^- \) ions, the Coulombic barrier height for the recombination is 44 kcal mol\(^{-1}\) (B3LYP/TZVP) and similar Coulombic barriers were suggested for structurally related dianions.\(^{37}\) As a result, the recombination of \(^1\text{PtBr}_5^-\) and \( \text{Br}^- \) is unlikely unless the geminate \(^1\text{PtBr}_5^-\) and \( \text{Br}^- \) partners are prepared at a separation distance in the vicinity of the geometry of the transition state, that is, the Coulombic barrier. We think this is the case here following optical excitation of \( \text{PtBr}_6^{2-} \). On the basis of the ISC time constant observed (\( \sim 4.5 \) ps), it will takes place before the caged \(^3\text{PtBr}_5^-\) and \( \text{Br}^- \) geminate ion fragments become separated by the solvent. Then, following the photodissociation, the initial separation distance between \(^3\text{PtBr}_5^-\) and \( \text{Br}^- \) geminate fragments along the Pt–Br recombination coordinate can be roughly approximated by the radius of the solvent cage of \( \text{PtBr}_6^{2-} \). In turn, the solvent cage radius can be estimated to be 4.86 Å from the recommended self-consistent reaction field (SCRF) volume for a
PtBr$_6^{2-}$ dianion in water (B3LYP/TZVP). The recombination is nearly barrierless at this geometry because the computed ground-state scan along a Pt-Br separation distance, starting from the optimized geometry of PtBr$_6^{2-}$, places the position of the Coulombic barrier at 4.43 Å, Fig. 3.14. It is quite remarkable that the water cage is strong enough to confine two negatively charged fragments for a time sufficiently long for their recombination to occur, despite the presence of strong repulsive Coulombic forces between the fragments.

![Diagram](image-url)

**Figure 3.14.** Suggested mechanism of geminate recombination between two negatively charged ions, PtBr$_5^-$ and Br$^-$, on ~7 ps time scale.
After reaching the minimum at $\Delta \tau = 20$ ps, the ground-state bleach noticeably increases (time constant, $\tau_6 \sim 20$ ps), whereas the 450-nm photoproduct absorption continues to decay (time constant, $\tau_5 \sim 15$ ps). For the case where product-state absorption and ground-state depletion overlap, such as for $^{1}\text{PtBr}_5^-$ and $\text{PtBr}_6^{2-}$, the decay of the product absorption accompanied by the development of the ground-state bleach indicate that at least a significant fraction of the product-state population does not convert to the reactant ground-state, but instead forms a new product species that absorbs weakly in the spectral region of ground-state depletion. This implies that geminate recombination is largely complete within $\sim 10$ ps, and $\text{PtBr}_5^-$ starts to decay into a new product species (time constant, $\tau_5 \sim 15$ ps), with little absorption around 310 nm. The cause of the abrupt end of geminate recombination is most probably the separation of the geminate pair by water molecules, known to occur within several picoseconds.\textsuperscript{38} We suggest that the new product species is the singlet aqua-substituted complex, $^{1}\text{PtBr}_5(\text{H}_2\text{O})^-$. This assignment is supported by the calculated electronic transitions (234, 248, 277, 315, 339, and 357 nm, Table 3.4) for $^{1}\text{PtBr}_5(\text{H}_2\text{O})^-$, lying in the spectral region where the “permanent” product absorption is observed that survives to the longest investigated time of 1.2 ns.

Previously, the quantum yield of the formation of aqua-substituted singlet $\text{PtBr}_5(\text{H}_2\text{O})^-$ was measured to be about 0.4.\textsuperscript{7} Ultrafast half-time ($\sim 110$ fs) of the triplet $\text{PtBr}_5^-$ formation likely implies that this product species is formed in unity quantum yield. It is shown that the caged geminate $\text{Br}^-$ and triplet $\text{PtBr}_5^-$ partners recombine on a $\sim 7$ ps time scale, and that following $\text{Br}^-$ escape from the water cage, the remaining singlet $\text{PtBr}_5^-$ species undergoes aquation to form singlet $\text{PtBr}_5(\text{H}_2\text{O})^-$ on a $\sim 15$ ps time scale. In a simplified reaction model, the rate constants of the decay of $^{1}\text{PtBr}_5^-$ related to the geminate recombination and aquation barrier crossing are $k_1 = \sim (7 \text{ ps})^{-1}$ and, $k_2 = \sim (15 \text{ ps})^{-1}$, respectively. The quantum yield of the formation of $^{1}\text{PtBr}_5(\text{H}_2\text{O})^-$
is given by: \( \Phi_a = k_2 / (k_1 + k_2) = 0.32 \), which agrees with previous measurements. Another yield estimate based on rate constants can be obtained from Figure 3.7. Decay associated spectra with \( k_4 \) and \( k_5 \) are dominated by the 430-450 nm band implying that the spectra are due to the same \( ^1\text{PtBr}_5^− \) species. For \( k_4 \) and \( k_5 \) assigned to the geminate recombination and aquation barrier crossing, respectively, \( \Phi_a = k_5 / (k_4 + k_5) = 0.073 / (0.127 + 0.073) = 0.37 \). Furthermore, because the spectral amplitudes \((\varepsilon_C, \varepsilon_D)\) in the decay-associated spectra (DAS) are determined with respect to the same amount (1M) of the decaying material, \( ^1\text{PtBr}_5^− \) concentration that decayed to the recombination and aquation products is linearly proportional to the inverse \( \varepsilon_C, \varepsilon_D \) values \((\varepsilon_C^{-1} = 1/17 \) and \( \varepsilon_D^{-1} = 1/27) \). Then, \( \Phi_a = 1/\varepsilon_D/(1/\varepsilon_C + 1/\varepsilon_D) = \varepsilon_D^{-1}/(\varepsilon_C^{-1} + \varepsilon_D^{-1}) = 0.39 \).

The overall mechanism of photoaquation of hexabromoplatinate complex upon excitation with 420 nm light is represented in Figure 3.15 and can be described by the reaction scheme (1-8).

\[
\begin{align*}
\text{PtBr}_6^2^−(1A_{1g}) + \text{hv} & \rightarrow \text{PtBr}_6^2^−(1T_{1g})^* \quad (1) \\
\text{PtBr}_6^2^−(1T_{1g})^* & \rightarrow \text{PtBr}_6^2^−(3T_{1g})^* \quad (2) \\
\text{PtBr}_6^2^−(3T_{1g})^* & \rightarrow \{^3\text{PtBr}_5^−(E, \text{Cl, } C_{4v})^* + \text{Br}^−\}_\text{cage} \quad (3) \\
\{^3\text{PtBr}_5^−(E, \text{Cl, } C_{4v})^* + \text{Br}^−\}_\text{cage} & \rightarrow \{^3\text{PtBr}_5^−(3B_2, D_{3h, \text{coherence}}) + \text{Br}^−\}_\text{cage} \quad (4) \\
\{^3\text{PtBr}_5^−(3B_2, D_{3h, \text{coherence}}) + \text{Br}^−\}_\text{cage} & \rightarrow \{^1\text{PtBr}_5^−(1A_1, C_{4v}) + \text{Br}^−\}_\text{cage} \quad (5) \\
\{^1\text{PtBr}_5^−(1A_1, C_{4v}) + \text{Br}^−\}_\text{cage} & \rightarrow \text{PtBr}_6^2^−(1A_{1g}) \quad (6) \\
\{^1\text{PtBr}_5^−(1A_1, C_{4v}) + \text{Br}^−\}_\text{cage} & \rightarrow ^1\text{PtBr}_5^−(1A_1, C_{4v}) + \text{Br}^− \quad (7) \\
^1\text{PtBr}_5^−(1A_1, C_{4v}) + \text{H}_2\text{O} & \rightarrow \text{PtBr}_5(\text{H}_2\text{O})^− \quad (8)
\end{align*}
\]
In the reaction scheme, the following photophysical and photochemical processes have been identified: excited state dynamics (1-4), intersystem crossing (5), recombination (6), cage escape (7), and aquation (8).

Figure 3.15. Summary of the photoaquation mechanism.
Effect of organic solvents on the mechanism of photodissociation.

Transient absorption spectra of PtBr$_6^{2-}$ in methanol and acetonitrile solutions obtained upon excitation with 420 nm light are shown in Figure 3.16 and compared with transient absorption spectra of aqueous PtBr$_6^{2-}$. The $\Delta A$ signals within the 500-nm region in methanol and acetonitrile solutions exhibit a delayed rise on a sub-200 fs time scale.

**Figure 3.16.** Transient absorption spectra of PtBr$_6^{2-}$ in water (A), methanol (B), and acetonitrile (C) following 420 nm excitation.
Inspection of the kinetic traces within the 500 nm band also demonstrates that the same damped coherent oscillations are observed in early-time $\Delta A$ spectra, Fig.3.10. Analysis of the oscillatory part of the kinetic traces revealed that the oscillation frequency ($115 \text{ cm}^{-1}$) is similar to the one obtained in aqueous solution of PtBr$_6^{2-}$. This suggests that the same primary photoproduct, $^3\text{PtBr}_5^-$ is obtained upon excitation with 420 nm pulses. However, following formation of $^3\text{PtBr}_5^-$, the evolution of the transient absorption spectra deviate from the ones obtained in water. Apart from the formation of the absorption band in the 400-475 nm wavelength range due to intersystem crossing from $^3\text{PtBr}_5^-$ to $^1\text{PtBr}_5^-$ with a time constant of 2.2 ps, a transient absorption develops in the deep UV region from 350 to 380 nm on a time scale of $\sim 1.51$ and 1.89 ps for methanol and acetonitrile solutions respectively, Fig 3.17. In

![Figure 3.17](image_url)

**Figure 3.17.** Representative $\Delta A$ kinetic trace (black curve) and the multiexponential fit of the time evolution (red curve) of the transient absorption at 355 nm of PtBr$_6^{2-}$ in methanol. In the inset: the short-time $\Delta A$ evolution at 355 (green) and 610 nm (blue).
the flash photolysis experiments performed by Adamson and Sporer\textsuperscript{4}, it was shown that flashing the solutions of PtBr\textsubscript{6}\textsuperscript{2-} containing hydroquinone resulted in the oxidation of this compound. Thus, the nature of photochemical reaction changes in the presence of easily oxidizable substances. It should be mentioned that the presence of easily reducible compounds in the solution such as H\textsubscript{2}O\textsubscript{2} had no effect on the photodissociation reaction. Since methanol can easily be oxidized to formaldehyde, a standard test\textsuperscript{39} for this compound was performed on the exposed mixture of PtBr\textsubscript{6}\textsuperscript{2-} and methanol irradiated with 420 nm light for about an hour. Traces of formaldehyde can be detected upon adding neutral solutions of acetylacetone and ammonium salt to the analyzed solution. Formation of a yellow color is an indication of the presence of formaldehyde. In the exposed solution containing hexabromoplatinate and methanol, the test for formaldehyde gave a positive result. It is worthwhile to mention that when the solution of hexabromoplatinate in methanol was kept in the dark for about an hour and subsequently was tested for the presence of formaldehyde, the result was negative (no yellow color). This means that photoexcitation of the complex with 420 nm pulses leads to formation of a reactive species capable of oxidizing methanol. This oxidizing species is \textsuperscript{3}PtBr\textsubscript{5}\textsuperscript{-} since its depletion associated with the decay of 500 nm transient absorption band gives rise to a new transient absorption at 355 nm, Fig.3.16 on ~1.5 ps time scale. Upon electron transfer from a methanol molecule to \textsuperscript{3}PtBr\textsubscript{5}\textsuperscript{-}, a compound where Pt is in oxidation state III has to be formed. Calculations of VET’s of \textsuperscript{2}PtBr\textsubscript{5}\textsuperscript{-} species (Pt (III)) indeed support this idea because \textsuperscript{2}PtBr\textsubscript{5}\textsuperscript{2-} has an electronic transition at 351 nm with the strongest oscillator strength (0.1398), Table 3.6. One electron oxidation of methanol should result in the formation of [CH\textsubscript{3}OH]\textsuperscript{+}. This cation then quickly loses a proton to form CH\textsubscript{3}O\textsuperscript{•} radical (Eq. 9).

\[ [\text{CH}_3\text{OH}]^+ \rightarrow \text{CH}_3\text{O}^• + \text{H}^+ \] (9)
Consequent formation of formaldehyde is due to a disproportionation reaction.

\[2\text{CH}_3\text{O} \cdot \rightarrow \text{CH}_2\text{O} + \text{CH}_3\text{OH}\]  

(10)

**Table 3.6.** Vertical excitation energies \((E_{\text{exc}})\), corresponding excitation wavelengths \((\lambda_{\text{exc}})\), and oscillator strengths \((f)\) of the solvated \((\text{H}_2\text{O})^2\text{PtBr}_5^{2-}\) species.

<table>
<thead>
<tr>
<th>Species</th>
<th>(E_{\text{exc}}, \text{eV})</th>
<th>(\lambda_{\text{exc}}, \text{nm})</th>
<th>(f)</th>
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<td>3.40</td>
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<td></td>
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<td>357</td>
<td>0.0068</td>
</tr>
<tr>
<td></td>
<td>3.53</td>
<td>351</td>
<td>0.1398</td>
</tr>
<tr>
<td>PtBr(_5^{2-}) doublet</td>
<td>3.64</td>
<td>340</td>
<td>0.0381</td>
</tr>
<tr>
<td></td>
<td>4.02</td>
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<td>0.0938</td>
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<tr>
<td></td>
<td>4.05</td>
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<td>0.0336</td>
</tr>
<tr>
<td></td>
<td>4.08</td>
<td>303</td>
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</tr>
<tr>
<td></td>
<td>4.51</td>
<td>274</td>
<td>0.0161</td>
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<td></td>
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<td>4.78</td>
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<tr>
<td></td>
<td>4.82</td>
<td>256</td>
<td>0.0221</td>
</tr>
</tbody>
</table>

\(^a\) TDDFT calculations were performed at M052X/TZ/PCPM level of theory

The reaction mechanism following excitation of PtBr\(_6^{2-}\) in methanol with 420 nm pulses can be represented by equations (11–22).

\[
\text{PtBr}_6^{2-} (^1\text{A}_{1g}) + \text{hv} \rightarrow \text{PtBr}_6^{2-} (^1\text{T}_{1g})^* \tag{11}
\]

\[
\text{PtBr}_6^{2-} (^1\text{T}_{1g})^* \rightarrow \text{PtBr}_6^{2-} (^3\text{T}_{1g})^* \tag{12}
\]

\[
\text{PtBr}_6^{2-} (^3\text{T}_{1g})^* \rightarrow \{^3\text{PtBr}_5^- (\text{E, Cl, C}_{4v})^* + \text{Br}^-\}_{\text{cage}} \tag{13}
\]

\[
\{^3\text{PtBr}_5^- (\text{E, Cl, C}_{4v})^* + \text{Br}^-\}_{\text{cage}} \rightarrow \{^3\text{PtBr}_5^- (^3\text{B}_2, D_{3h}, \text{coherence}) + \text{Br}^-\}_{\text{cage}} \tag{14}
\]
\[ ^3\text{PtBr}_5^- + \text{CH}_3\text{OH} \rightarrow ^2\text{PtBr}_5^{2-} + [\text{CH}_3\text{OH}]^+ \]  \hspace{1cm} (15)

\[ ^2\text{PtBr}_5^{2-} + \text{CH}_3\text{OH} \rightarrow ^1\text{PtBr}_4^{2+} + [\text{CH}_3\text{OH}]^+ + \text{Br}^- \]  \hspace{1cm} (16)

\[
\{^3\text{PtBr}_5^- (^3\text{B}_2, D_{3h}, \text{coherence}) + \text{Br}^-\}_\text{cage} \rightarrow \{^1\text{PtBr}_5^- (^1\text{A}_1, C_{4v}) + \text{Br}^-\}_\text{cage}
\]  \hspace{1cm} (17)

\[
\{^1\text{PtBr}_5^- (^1\text{A}_1, C_{4v}) + \text{Br}^-\}_\text{cage} \rightarrow \text{PtBr}_6^{2-} (^1\text{A}_{1g})
\]  \hspace{1cm} (18)

\[
\{^1\text{PtBr}_5^- (^1\text{A}_1, C_{4v}) + \text{Br}^-\}_\text{cage} \rightarrow ^1\text{PtBr}_5^- (^1\text{A}_1, C_{4v}) + \text{Br}^-
\]  \hspace{1cm} (19)

\[ ^1\text{PtBr}_5^- (^1\text{A}_1, C_{4v}) + \text{CH}_3\text{OH} \rightarrow \text{PtBr}_5(\text{CH}_3\text{OH})^-
\]  \hspace{1cm} (20)

\[ [\text{CH}_3\text{OH}]^+ \rightarrow \text{CH}_3\text{O}^- + \text{H}^+
\]  \hspace{1cm} (21)

\[ 2\text{CH}_3\text{O}^- \rightarrow \text{CH}_2\text{O} + \text{CH}_3\text{OH}
\]  \hspace{1cm} (22)

Excited state dynamic processes in methanolic solutions of $\text{PtBr}_6^{2-}$ (11–13) are similar to the ones observed for aqueous $\text{PtBr}_6^{2-}$. They include intersystem crossing from the singlet excited state to the repulsive triplet excited state of $\text{PtBr}_6^{2-}$ followed by heterolytic Pt–Br bond cleavage and formation of the triplet excited state $\text{PtBr}_5^-$. Pentabromoplatinate ion in the triplet excited state then undergoes internal conversion to the ground triplet state (14). Highly reactive $^3\text{PtBr}_5^-$ takes part in two competitive processes: Red-Ox reaction with methanol (15) and intersystem crossing to the ground singlet state $^1\text{PtBr}_5^-$ (17). Unstable $^2\text{PtBr}_5^{2-}$ dianion where Pt is in oxidation state III, gains another electron from the solvent molecule to form stable product $\text{PtBr}_4^{2-}$ (16). Singlet pentabromoplatinate species can recombine with bromide ion to form the parent dianion (18). In the case of bromide ion escape from the solvent cage (19), a methanol molecule binds to the square-based pyramidal $\text{PtBr}_5^-$ to form the stable product $\text{PtBr}_5(\text{CH}_3\text{OH})^-$ (20).
The growth of the 355 nm band in the transient absorption spectra of PtBr$_6^{2−}$ in acetonitrile is observed on a time scale of 1.89 ps, Fig 3.15. This band is assigned to $^2$PtBr$_5^{2−}$ which means that a Red-Ox reaction takes place in acetonitrile solution similar to that of PtBr$_6^{2−}$ in methanol solution. This finding means that hexabromoplatinate dianion acts as a photocatalyst in organic solvents. Upon excitation with 420 nm light, PtBr$_6^{2−}$ gets reduced to PtBr$_4^{2−}$ while methanol and acetonitrile get oxidized. In the case of methanol, the product of oxidation was detected to be formaldehyde, while in the case of acetonitrile, the products of oxidation might be NO$_2$, HNO$_3$, CO$_2$, or C$_2$N$_2$. Nowadays, many research institutions and universities, for example, one in Brazil$^{40}$ are searching for effective ways of recycling, reusing, and degrading of chemical residues. One of the chemical residues is the mixture of acetonitrile and water since acetonitrile is a commonly used solvent in the chemical industry and in research laboratories. Thus, the photocatalytic property of PtBr$_6^{2−}$ can be applied for to degradation of many organic solvents, including acetonitrile!
3.4 Conclusions

Ultrafast photophysics and photochemistry of PtBr$_6^{2-}$ in the condensed phase (water, methanol, acetonitrile) was investigated in detail using time-resolved femtosecond pump-probe spectroscopy. Photoexcitation of the dianion at charge transfer band (350 nm) and at 420 and 530 nm LF bands leads to remarkably fast formation of the coherently vibrating photoproduct $^3$PtBr$_5^{-}$ in less than 150 fs time scale. This requires ultrafast excited-state dynamics in the electronically-excited PtBr$_6^{2-}$, namely intersystem crossing from initially excited singlet electronic state ($^1$T$_{1g}$) to the dissociative triplet state ($^3$T$_{1g}$) where bond breaking takes place. It has been demonstrated that bond cleavage is heterolytic independent of the solvent used. The coherent oscillations observed within the ground-state bleach region and within the photoproduct absorption band (500 nm) were associated with the resonance impulsive Raman scattering from ground-state PtBr$_6^{2-}$, $a_1$ sym bending (76 cm$^{-1}$) and $a_1$ umbrella-like vibration (114 cm$^{-1}$) in $^3$PtBr$_5^{-}$, respectively. Interestingly, vibrational coherence in the triplet pentabromoplinitate ion (114 cm$^{-1}$) is created as a result of coherence population transfer from the parent dianion to the photoproduct whereas 76-cm$^{-1}$ mode is excited when the molecule passes through a Jahn-Teller C$_{4v}$ conical intersection. The coherently excited mode spans “the branching plane” of the C$_{4v}$ CI in PtBr$_5^-$. Intramolecular vibrational relaxation and cooling processes in hot $^3$PtBr$_5^{-}$ are complete by 1 ps after excitation and are followed by intersystem crossing to the ground-state PtBr$_5^{-}$ species (2.2 ps). All of the above is believed to take place in the solvent cage and explains geminate recombination of two negatively charged ions PtBr$_5^{-}$ and Br$^-$ on ~7 ps time scale. Formation of the stable aquated product PtBr$_5$(H$_2$O)$^-$ with 40% quantum yield independent of the excitation wavelength with a time constant of 15 ps is consistent with the previous findings.
3.5 References

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117, 2635.

123, 4204.


CHAPTER 4: ULTRAFAST PHOTOPHYSICS AND PHOTOCHEMISTRY OF HEXABROMOOSMATE DIANION IN THE CONDENSED PHASE

Abstract

Ultrafast excited-state dynamics and ligand substitution of OsBr$_6^{2-}$ in water and methanol solutions have been investigated using femtosecond broadband pump-probe spectroscopy. The triplet ground state OsBr$_5^-$ photoproduct is observed in less than 150 fs after excitation at the 420-nm ligand-to-metal charge transfer band. The photoproduct exhibits coherent oscillations with a damping time of 1.3 ps, an induction period of ~70 fs, and a frequency of 208 cm$^{-1}$ corresponding to $a_1$ symmetric stretching mode excited near the potential energy surface minimum. This mode becomes excited due to coherence population transfer from the parent dianion to the photoproduct. Coherent oscillations in the modes parallel or coupled to the gradient difference and derivative coupling modes were not observed in the photoproduct because of the low-frequency of these modes consistent with their ultrafast damping times. Another type of oscillations observed within the ground-state bleach region originates from resonance impulsive stimulated Raman scattering from the ground-state OsBr$_6^{2-}$. Ligand substitution is observed on ~11 and ~35 ps time scales in water and methanol solutions.
4.2 Introduction

Transition metal complexes are actively integrated into schemes for solar energy conversion, photocatalysis, and photovoltaics.1-3 In these applications, the population optically delivered to the Franck-Condon region of the initial excited electronic state often travels over several non-equilibrated excited state surfaces before arriving at a product state with useful functions. Radiationless relaxation between multidimensional potential energy surfaces of polyatomic molecules takes place through avoided crossings,4 or more typically through real crossings - conical intersections.5-6 The understanding of the forces driving electronic relaxation in polyatomic molecules has attracted considerable interest, especially in recent years, when ultrafast laser experiments made it possible to monitor downhill motion of the optically prepared wave-packet in real-time.7-8 The role of conical intersections in photochemical reactions is increasingly more stringently tested.9-10

In this chapter, an experimental study of excited state dynamics and photodissociation of OsBr$_6^{2-}$ in the condensed phase are reported. There are several important questions to be addressed in this work. How fast is pentabromoosmate intermediate formed if it forms? Is it formed from a certain electronic state like in the case of PtBr$_6^{2-}$ where the PtBr$_5^-$ fragment is formed in the repulsive lowest ligand field state? Does solvent play an important role in the ultrafast dynamics of this complex? Can solvent change the photodissociation mechanism? Since the dianion is a highly symmetric species, will we be able to observe coherent vibrational oscillations in the OsBr$_5^-$ photoproduct due to a symmetry-induced Jahn-Teller conical intersection? It is likely that the electronic structure of transition metal complexes strongly effects the mechanism of photodissociation. UV pump / UV-VIS probe studies of MX$_6^{2-}$ photoaquation reveal aspects of processes such as ultrafast efficient internal conversion,
intersystem crossing, dissociation, vibrational cooling, and geminate recombination of two negative ions. Modern femtosecond spectroscopy can also investigate the dynamics during dissociation and yields information about the potential energy surfaces. Knowing the mechanisms of photodissociation of PtBr$_6^{2-}$ dianions, it would be reasonable to compare it with the mechanism of photodissociation and ligation in OsBr$_6^{2-}$ with an aim to gain an insight into how electronic structure of these transition metal complexes affects their ultrafast photophysics and photochemistry. Transient absorption spectroscopy with fs resolution has been employed along with DFT/TDDFT theoretical calculations. The two approaches, experimental and theoretical, are brought together to generate a detailed understanding of the sequence of events that follow photo-excitation and to gain an insight into how the central metal affects on the photophysical properties. In all, the results of the present investigation reveal fundamental knowledge of the electronic factors in the photophysical properties of inorganic transition metal complexes.
4.3 Results and discussion

*Computational characterization of the parent dianion OsBr$_6^{2-}$ and photoproducts*

DFT was used to obtain optimized geometries and harmonic frequencies of the parent dianion OsBr$_6^{2-}$ and product species. Table 4.1 and 4.2 summarize equilibrium geometries and harmonic frequencies of the solvated species involved in the photochemistry of OsBr$_6^{2-}$, namely ground-state OsBr$_6^{2-}$, $^3$OsBr$_5^-$, $^1$OsBr$_5^-$, and OsBr$_5$(H$_2$O)$^-$. 

**Table 4.1.** Optimized geometries of the ground-state $^3$OsBr$_6^{2-}$, $^1$OsBr$_5^-$, $^3$OsBr$_5^-$, and $^3$OsBr$_5$(H$_2$O)$^-$ species

<table>
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<tr>
<th>Species$^a$</th>
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</tr>
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<td></td>
<td>Os–Br$_{ax}$</td>
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<tr>
<td>bipyramid</td>
<td>Br$<em>{ax}$–Os–Br$</em>{eq}$</td>
<td>90.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Br$<em>{eq}$–Os–Br$</em>{eq}$</td>
<td>120.0</td>
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</tr>
<tr>
<td>$^3$OsBr$_5^-$</td>
<td>Os–Br$_{ax}$</td>
<td>2.348</td>
<td></td>
</tr>
<tr>
<td>C$_{2v}$ square</td>
<td>Os–Br$_{eq}$</td>
<td>2.484</td>
<td></td>
</tr>
<tr>
<td>pyramid</td>
<td>Br$<em>{ax}$–Os–Br$</em>{eq}$</td>
<td>96.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Br$<em>{ax}$–Br$</em>{ax}$</td>
<td>89.9</td>
<td></td>
</tr>
<tr>
<td>$^1$OsBr$_5$(H$_2$O)$^-$</td>
<td>Os–Br$_{ax}$</td>
<td>2.397</td>
<td></td>
</tr>
<tr>
<td>C$_1$</td>
<td>Os–Br$_{eq}$</td>
<td>2.476</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Os–Br$_{ax}$</td>
<td>2.484</td>
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<tr>
<td></td>
<td>Os–O</td>
<td>0.968</td>
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</tr>
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<td>Br$<em>{ax}$–Os–Br$</em>{eq}$</td>
<td>91.9</td>
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</tr>
<tr>
<td></td>
<td>O–Os–Br$_{eq}$</td>
<td>88.1</td>
<td></td>
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<tr>
<td></td>
<td>Os–O–H</td>
<td>108.5</td>
<td></td>
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</table>

$^a$ Calculations were performed at DFT M052X/TZ/PCM level of theory with H$_2$O parameters.
Table 4.2. The results of harmonic frequency calculations of ground state species involved in photochemistry of OsBr$_6^{2-}$.

<table>
<thead>
<tr>
<th>Species</th>
<th>Frequency computed (cm$^{-1}$)</th>
<th>f(IR)</th>
<th>f(Raman)</th>
<th>Frequency comp. scaled$^c$ vs. experiment</th>
<th>Symmetry / vibrational mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>OsBr$_6^{2-}$</td>
<td>51 0 0</td>
<td>56$^b$</td>
<td></td>
<td></td>
<td>B$_{2u}$ / puckering (eq)</td>
</tr>
<tr>
<td></td>
<td>63$^b$ 2 0</td>
<td>78$^b$</td>
<td></td>
<td></td>
<td>E$_u$ / puckering (ax)</td>
</tr>
<tr>
<td>Ground state</td>
<td>94$^b$ 0 10</td>
<td>103/108$^b$</td>
<td></td>
<td></td>
<td>B$_{2g}$ / scissoring (eq)</td>
</tr>
<tr>
<td></td>
<td>95 11 0</td>
<td>104</td>
<td></td>
<td></td>
<td>E$_u$ / scissoring (ax)</td>
</tr>
<tr>
<td>D$_{4h}$</td>
<td>108$^b$ 1 0</td>
<td>117</td>
<td></td>
<td></td>
<td>A$_{2u}$ / doming</td>
</tr>
<tr>
<td></td>
<td>140 0 6</td>
<td>152/157</td>
<td></td>
<td></td>
<td>E$_u$ / bending (eq)</td>
</tr>
<tr>
<td></td>
<td>160 213 0</td>
<td>174</td>
<td></td>
<td></td>
<td>A$_{2u}$ / bending (ax)</td>
</tr>
<tr>
<td></td>
<td>168 0 7</td>
<td>183/174</td>
<td></td>
<td></td>
<td>B$_{1g}$ / out-of-phase stretching (eq)</td>
</tr>
<tr>
<td></td>
<td>194 0 77</td>
<td>212/212</td>
<td></td>
<td></td>
<td>A$_{1g}$ / total sym. stretching</td>
</tr>
<tr>
<td></td>
<td>195$^b$ 149 0</td>
<td>212$^b$</td>
<td></td>
<td></td>
<td>E$_u$ / square-to-kite (eq)</td>
</tr>
<tr>
<td>OsBr$_5^-$</td>
<td>33 2 7</td>
<td>36</td>
<td></td>
<td>A$_1$ / sym. bending (pucker) E'</td>
<td></td>
</tr>
<tr>
<td>Singlet</td>
<td>40 1 0</td>
<td>43</td>
<td></td>
<td>B$_2$ / antisym. bending</td>
<td>D$_{3h}$</td>
</tr>
<tr>
<td></td>
<td>92 0 4</td>
<td>99</td>
<td></td>
<td>B$_1$ / wagging</td>
<td></td>
</tr>
<tr>
<td>C$_{2v}$</td>
<td>93 0 5</td>
<td>100</td>
<td></td>
<td>A$_2$ / twisting (eq)</td>
<td></td>
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<td>distorted</td>
<td>95 0 1</td>
<td>103</td>
<td></td>
<td>A$_1$ / bending (umbrella-like) E'</td>
<td></td>
</tr>
<tr>
<td>trigonal</td>
<td>181 157 0</td>
<td>195</td>
<td></td>
<td>B$_2$ / asym. stretching (ax)</td>
<td></td>
</tr>
<tr>
<td>bipyramid</td>
<td>184 0 1</td>
<td>199</td>
<td></td>
<td>A$_1$ / sym. stretching (ax)</td>
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</tr>
<tr>
<td></td>
<td>246 0 162</td>
<td>265</td>
<td></td>
<td>A$_1$ / total sym stretching (eq)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>291 46 0</td>
<td>314</td>
<td></td>
<td>B$_2$ / asym. stretching (eq) E'</td>
<td></td>
</tr>
<tr>
<td></td>
<td>292 46 0</td>
<td>315</td>
<td></td>
<td>A$<em>1$ / sym. stretching (eq) D$</em>{3h}$</td>
<td></td>
</tr>
<tr>
<td>OsBr$_5^-$</td>
<td>54 0 4</td>
<td>58</td>
<td></td>
<td>B$_1$ / puckering</td>
<td></td>
</tr>
<tr>
<td></td>
<td>61$^b$ 4 198</td>
<td>65$^b$</td>
<td></td>
<td>E / bending (eq)</td>
<td></td>
</tr>
<tr>
<td>Triplet</td>
<td>75$^b$ 0 12</td>
<td>81$^b$</td>
<td></td>
<td>E / wagging (bending) (ax)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>104 0 13</td>
<td>112</td>
<td></td>
<td>B$_2$ / scissoring (eq)</td>
<td></td>
</tr>
<tr>
<td>C$_{4v}$</td>
<td>106 5 2</td>
<td>114</td>
<td></td>
<td>A$_1$ / doming</td>
<td></td>
</tr>
<tr>
<td></td>
<td>185 0 12</td>
<td>200</td>
<td></td>
<td>B$_1$ / out-of-phase stretch (eq)</td>
<td></td>
</tr>
<tr>
<td>square-</td>
<td>201 6 28</td>
<td>217</td>
<td></td>
<td>A$_1$ / umbrella</td>
<td></td>
</tr>
<tr>
<td>based pyramid</td>
<td>202$^b$ 153 151</td>
<td>218$^b$</td>
<td></td>
<td>E / square-to-kite</td>
<td></td>
</tr>
<tr>
<td></td>
<td>255 36 114</td>
<td>275</td>
<td></td>
<td>A$_1$ / stretch (ax)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Frequencies found in Raman spectra of aqueous OsBr$_6^{2-}$

$^b$ Doubly degenerate modes

$^c$ A scaling factor of 1.09 applied to computed frequencies is determined from the comparison of the computed (solvated) and experimental (aqueous solution) vibrational frequencies (197 and 212 cm$^{-1}$) of the A$_{1g}$ / symmetric stretch in OsBr$_6^{2-}$.
Geometry optimization calculations of the hexabromoosmate dianion by using the DFT method (M052X) resulted in quasioctahedral geometry where all the Br–Os–Br bond angles are 90°, the two equal axial Br–Os bond lengths are 2.512 Å, and the four equatorial Br–Os bond lengths are 2.528 Å. This is consistent with the fact that $d_2$ systems are expected to distort to a lower $D_{4h}$ symmetry according to the Jahn-Teller effect.\textsuperscript{11-13} The equilibrium square-pyramid (SP) and trigonal bipyramid (TBP) geometries of OsBr$_5^-$ (Table 4.1) corresponding to the triplet and singlet ground states, respectively, are predicted to be 1.08 and 1.51 eV above $^{3}\text{A}_{1g}$ OsBr$_6^{2-}$ (M052X). The structures of the calculated species are shown in Figure 4.1.

Figure 4.1. Optimized structures of the ground state $^{3}\text{OsBr}_6^{2-}$ (A), $^{3}\text{OsBr}_5^-$ (B), $^{1}\text{OsBr}_5^-$ (C), and $^{3}\text{OsBr}_5(\text{H}_2\text{O})^-$ (D).
Ground-state molecular structure analysis of the parent dianion

The UV-Vis absorption spectrum of OsBr$_6^{2-}$ is shown in Figure 4.2. The assignment of the absorption bands was made by Jorgensen$^{14}$ who characterized 399,

![Figure 4.2. UV-Vis absorption spectrum of aqueous OsBr$_6^{2-}$ (1.1 mM). In the inset: Raman spectra of powder K$_2$OsBr$_6$ (green line) and aqueous OsBr$_6^{2-}$ (red line, open circles) solution (30 mM) recorded using an excitation wavelength of 785 nm. Water contribution to the Raman spectrum of aqueous OsBr$_6^{2-}$ is subtracted.](image)

423, 445, 489, 506, 528, and 579 nm bands as ligand to metal charge transfer transitions (LMCT), 350 nm band as a d-d transition, and 280 and 245 nm bands as due to LMCT from the
π orbital of the ligand to the $\sigma^*$ orbital with predominantly metal character. It is worth mentioning that the ground electronic state of the hexabromooximate (IV) dianion is a triplet.

The measured Raman spectra of powder and aqueous samples of OsBr$_6^{2-}$ are shown in the inset of Fig. 4.2. There are two strong bands at 108 and 212 cm$^{-1}$ and two weak bands at 157 and 174 cm$^{-1}$ in the Raman spectrum of aqueous OsBr$_6^{2-}$. All these bands are in excellent agreement with the scaled (1.08 scaling factor) vibrational frequencies calculated for OsBr$_6^{2-}$ (DFT B3LYP/TZ/CPCM), which correspond to the $B_{2u}$ bending mode (104 cm$^{-1}$), $A_{1g}$ symmetric stretch mode (149 cm$^{-1}$), $B_{1g}$ asymmetric stretching mode (171 cm$^{-1}$), and $A_{1g}$ symmetric stretch mode (212 cm$^{-1}$), Table 4.2. These frequencies are also consistent with the frequencies obtained in the resonance Raman spectrum of aqueous OsBr$_6^{2-}$ ($\nu_5 = 107$ cm$^{-1}$, $\nu_2 = 163$ cm$^{-1}$, and $\nu_1 = 211$ cm$^{-1}$).$^{15}$
The femtosecond transient absorption spectra upon photoexcitation of OsBr$_6^{2-}$ at the 420 nm LMCT band were obtained in aqueous (Fig. 4.3) and methanol solutions (Fig 4.4). An unambiguous marker for time zero, $\Delta \tau = 0$ was provided by the cross-phase modulation $\Delta A$ signals measured for neat water. The global analysis of the $\Delta A$ signals in the wavelength range from 330 to 770 nm revealed that the use of a five-exponential function $\Delta A(\lambda, t) = \sum \varepsilon_i \exp(-t/\tau_i)$ where $i = 5$, gives the best fit to the experimental data.

**Figure 4.3.** Transient absorption spectra of aqueous OsBr$_6^{2-}$ at various time delays from 420 nm pump and probe pulses.
Figure 4.4. Transient absorption spectra of OsBr$_6^{2-}$ in methanol at various time delays from 420 nm pump and probe pulses.

The characteristic time constants obtained from the fit are as follows: $\tau_1 = 0.07$ ps, $\tau_2 = 0.24$ ps, $\tau_3 = 0.76$ ps, $\tau_4 = 11.8$ ps, $\tau_5 = 1.2$ ns. The early-time ($\Delta \tau \leq 100$ fs) spectra in both solvents display ground-state bleach between 280 and 500 nm, weak and structureless excited state absorption (ESA) between 535 nm and 770 nm, and more intense $\Delta A$ signal in the UV region from 330 to 380 nm. Two 540 and 675 nm product bands develop from ~100 fs to 1 ps. Two types of coherent oscillations are observed (Fig 4.5): a) within the 340-475 nm
Figure 4.5. FFT analysis of the oscillatory part of the kinetic traces (Panels A, B, and C) obtained upon excitation of OsBr$_6^{2-}$ with 420 nm light (Panels D, E, and F).
ground-state absorption, the isolated 108-cm\(^{-1}\) frequency (\(\tau_{c,1} = 250\) fs) and two overlapping bands at 156 and 178 cm\(^{-1}\) (\(\tau_{c,2} = 319\) fs) due to RISRS based on the resonance Raman spectrum of OsBr\(_6\)\(^{2-}\) (Fig. 4.2), b) modulations with a solvent-independent FFT frequency \(~208\) cm\(^{-1}\) and a \(~75\)-fs induction time, which are weak near the center, but strong in the blue

![Graph showing amplitude dependence of oscillations on probe wavelength](image)

**Figure 4.6.** Amplitude dependence of the oscillations on the probe wavelength within the 675 nm band (green triangles), the 545 nm band (red circles) and within the 340 nm UV band (blue diamonds). The black curve represents the transient absorption spectrum of aqueous OsBr\(_6\)\(^{2-}\) measured 1 ps after excitation with 420 nm light. \(\pi\) jump of the oscillation amplitudes is observed at 545 and 675 nm.

and red wings of the 540 and 675 nm bands. The \(\pi\) phase jump is clearly observed within the 540 nm product band, Fig 4.6. The oscillations persist to conspicuously longer times (\(\tau_{c,3} = 1.33 \pm 0.12\) ps) compared to the PtBr\(_6\)\(^{2-}\) system. The amplitude of these oscillations is the same in the \(\Delta A(\|)\) and \(\Delta A(\perp)\) kinetic traces at 580 and 730 nm probe wavelengths. We note that, at probe
wavelengths 430 and 530 nm, where the oscillation amplitude is zero because of the π jump, the ΔA kinetic traces do not show a Raman-active a_{1g} mode (212 cm^{-1}) of OsBr_{6}^{2-}, therefore the ~208 cm^{-1} oscillations are due to the product species only.

Figure 4.7. ΔA(∥) (blue curve) and ΔA(⊥) (red curve) signals (420-nm pump/730-nm probe) in the anisotropy measurements of OsBr_{6}^{2-} in methanol (Panel A) and water (Panel B). The black curve represents the ΔA(∥) signal from water.
Excited state and ligation substitution dynamics following photoexcitation (305 and 420 nm) of OsBr$_6^{2-}$

The mechanism of photodissociation of OsBr$_6^{2-}$ is in part similar to the one proposed for PtBr$_6^{2-}$. Photoexcitation at 305 and 420 nm bands leads to the formation of $^3$LMCT states which are quickly depopulated by internal conversion to a lower lying $^3$LF state on a sub 100 fs time scale. This state appears to be dissociative. Similar to PtBr$_6^{2-}$, dissociation of the dianion takes place via a heterolytic bond cleavage resulting in the formation of the vibrationally hot OsBr$_5^-$ species and bromide. The estimated lifetime of their formation is 0.24 ps. Observation of vibrational coherence in the kinetic traces can be attributed to the newly formed species OsBr$_5^-$. The vibrational as oppose to electronic nature of these oscillations was confirmed by conducting anisotropy measurements when probing the sample at 730 nm (Fig 4.7). The absence of anisotropy in both methanol and water solutions of hexabromoosmate complex excited at 420 nm is consistent with the vibrational nature of the coherence. The vibrational nature of the coherence was also established in geometrically similar complexes M(CO)$_6$ (where M = Cr, Mn, W) in the gas phase. Analysis of the amplitude dependence of the oscillation on the probe wavelength in the region of 540 and 675 nm transient absorption bands (large oscillations on the steep sides of the bands, small – at the peaks and in the edges of the photoproduct absorption) as well as the strong wavelength dependence of the phase of the oscillations (180° phase shift at the peak of 540 and 675 nm bands (Fig. 4.6), unambiguously point to the vibrational coherence of the ground-state photoproduct. Frequency calculations performed at the DFT level rule out the assignment of the formed photoproduct to OsBr$_5^-$ in the singlet state since no frequency mode matches the oscillation frequency of 208 cm$^{-1}$ (Table 4.2). In addition, $^1$OsBr$_5^-$ is thermodynamically less stable then $^3$OsBr$_5^-$ by 0.3 eV. Experimental information about the low-
frequency vibrations of the unsaturated pentabromoosmate ion is not available but according
to DFT calculations the 208 cm\(^{-1}\) mode can be assigned to the symmetric stretching mode in the
square-based pyramid, \(\text{OsBr}_5^{-}\). As oppose to \(\text{PtBr}_6^{2-}\), the mechanistic photochemistry of \(\text{OsBr}_6^{2-}\)
resembles that of \(\text{Cr(CO)}_6\), but involves the triplet manifold of states. Following LMCT
excitation of \(\text{OsBr}_6^{2-}\), the excited-state wavepacket quickly relaxes to the dissociative triplet
PES, where it propagates, without much spreading, along an asymmetric \(a_{2u}\) stretch coordinate
towards the exit. The wavepacket may arrive at exactly a SP \(C_{4v}\) geometry\(^{10}\) - JT \(C_{4v}\) CI - and
then proceed along \(b_1\) and \(b_2\) towards a TBP \(D_{3h}\) geometry - JT \(D_{3h}\) CI, or be initially accelerated
towards a \(D_{3h}\) geometry\(^{18}\) as a consequence of the \(b_2\) motion (\(b_2\) \(C_{4v}\) descends from \(b_{2g}\) in \(D_{4h}\),
which is Raman-active) and the symmetric equatorial ligand motion to fill the coordination
vacancy.

This interpretation should hold for \(\text{OsBr}_5^{-}\). However, the nuclear displacements of the
symmetric stretching mode do not resemble the JT \(e'\) modes, therefore it can be only excited due
to coherent population motion from the parent complex to the photoproduct. The vibrationally
coherent 212 cm\(^{-1}\) \(a_1\) mode of \(\text{OsBr}_5^{-}\) comprises stretching of the axial Os-Br bond and four
equatorial metal-ligand bonds slightly bent in the direction of the vacated coordination site. This
resembles the nuclear displacements in the Raman-active \(a_{1g}\) symmetric stretch (212 cm\(^{-1}\), Fig
4.1) in \(\text{OsBr}_6^{2-}\), suggesting that the dissociation reaction coordinate in the parent molecule is
predominated by \(a_{1g}\) symmetric stretching and \(t_{1u}\) asymmetric stretching (224 cm\(^{-1}\), B3LYP)
 modes. Following dissociation of \(\text{OsBr}_6^{2-}\), after an induction period of about 60 fs the E’-
wavepacket of \(\text{OsBr}_5^{-}\) arrives to a \(D_{3h}\) geometry – JT \(D_{3h}\) CI. A two-dimensional mapping of the
ground-state PES of \(\text{OsBr}_5^{-}\) along the \(e\) coordinates showed that the bending \(e'\) modes,
corresponding to the symmetric \(a_1\) and asymmetric \(b_2\) bending in \(C_{2v}\), are parallel to the gradient
difference and derivative coupling vectors, similar to Cr(CO)\textsubscript{5}.\textsuperscript{18} The generated ground-state surface of \textsuperscript{3}OsBr\textsubscript{5} is analogous to a PES with a JT $D_{3h}$ \textsuperscript{21,22} displaying three-fold symmetry with equivalent $C_4$, minima separated by $C_2$ transition states, Fig 4.8. In Cr(CO)\textsubscript{5}, the wavepacket, before it descends to one of two equivalent $C_4$ minima along $b_2$, undergoes a partial oscillation along $a_1$ detected as a coherent bending motion.

Figure 4.8. (A) Ground electronic potential energy surface of \textsuperscript{3}OsBr\textsubscript{5} obtained by mapping the surface along $e'$ (sym. bending and antisym. bending) coordinates. Derivative coupling ($b_2$, antisym. bending) and gradient difference ($a_1$, sym. bending) vectors span $e'$. Red circle points out the CI.
In the sense that following the passage through the CI, the coherence is observed in the splitting modes, the situation for $^3\text{PtBr}_5^-$ is unlike that of $^3\text{OsBr}_5^-$, where the coherence is detected in the $a_1$ vibrational (symmetric stretching) mode. For an impulsive bond scission, a tentative explanation for much smaller oscillation amplitude in $^3\text{OsBr}_5^-$ at 208 cm$^{-1}$ in comparison to $^3\text{PtBr}_5^-$ at 114 cm$^{-1}$ is that the photodissociation reaction coordinate in the former species involves the $a_{1g}$ symmetric stretch, where the energy level spacing is less than the fwhm of the pulse spectrum, so that the optically prepared wavepacket in $^3\text{OsBr}_5^-$ is more delocalized in comparison to $^3\text{PtBr}_5^-$, and as a result, exhibits weaker modulations in the transient absorption. Late dynamic selection of the exit channel would also result in a less compact wavepacket because a larger amount of energy will be deposited into the vibration. The vibrational coherence in the $^3\text{OsBr}_5^-$ photoproduct was not observed in gradient difference ($a_1$, symmetric bending) or derivative coupling ($b_2$, antisymmetric bending) modes because these coherent motions are of low frequency (sub 50-cm$^{-1}$), and therefore they are damped very quickly.

The nascent pentabromoosmate ion undergoes intramolecular vibrational relaxation and cooling on ~0.7 ps time scale which can be observed as narrowing of the 540 and 675 nm absorption bands assigned to this species. It should be mentioned that the oscillations exhibit an induction period of $\Delta \tau = 70$ fs. Another type of vibrational coherent oscillations emerging at $\Delta \tau = 0$ can only be observed within the ground-state bleach region. Three frequency modes (108, 153-182, and 212 cm$^{-1}$) found upon analysis of the oscillatory parts of the kinetic traces in this region are in very good agreement with the fundamental vibrational frequencies of the ground-state parent complex, Fig 4.2. For example, the 108 cm$^{-1}$ FFT mode matches the experimental Raman frequency (108 cm$^{-1}$) which according to frequency calculations (102 cm$^{-1}$) can be assigned to the bending $B_{2u}$ mode. The appearance of the broad FFT feature between 153 and
182 cm$^{-1}$ can be explained by the overlap of the two Raman bands due to symmetric in-plane distortion of equatorial Os–Br bonds (A$_{1g}$, calculated frequency 158 cm$^{-1}$) and symmetric stretching of axial Os–Br bonds (B$_{1g}$, calculated frequency 180 cm$^{-1}$). Moreover, a strong 212 cm$^{-1}$ oscillation is observed in the same region which is assigned to the Raman active A$_g$ fundamental frequency. The fact that these modulations occur within the ground-state absorption bleach and are consistent with fundamental Raman frequencies of the parent dianion suggests that the nature of these oscillations is resonance impulsive stimulated Raman scattering. After the IVR and cooling processes are complete, the square-based pyramidal $^{3}$OsBr$_5^-$ undergoes ligation (aquation) on a 11 ps time scale. It should be noted that the ligand substitution is slightly faster in the hexabromoosmate dianion compared to the hexabromoplatinate complex (~15 ps). One of the reasons for the much faster ligation substitution in hexabromoosmate could be due to the fact that after excitation the photoproduct $^{3}$OsBr$_5^-$ is formed in the stable square-based pyramid geometry accessible for immediate binding with either a water or methanol molecule whereas upon excitation of PtBr$_6^{2-}$, the photoproduct $^{3}$PtBr$_5^-$ is formed in unstable trigonal bipyramidal geometry, and therefore, prior to ligand substitution it has to first undergo intersystem crossing to form the more stable $^{1}$PtBr$_5^-$ in square-based pyramid geometry. Ligand substitution in methanol solutions takes place on a ~35 ps time scale which is noticeably slower than in the aqueous solutions. This is an indication that methanol is a weaker coordinating solvent that water.
4.4 Conclusion

Time-resolved femtosecond pump-probe spectroscopy was used in this work to investigate the photodissociation dynamics of doubly-charged anion OsBr$_6^{2-}$ after photoexcitation at 305 and 420 nm $^3$LMCT states. The transient absorption spectra measured in methanol and water solutions of hexabromoosmate dianion revealed an appearance of two absorption bands on the ultrafast time scale (~200 fs) which were assigned to pentabromoosmate ion in the triplet state. Formation of $^3$OsBr$_5^-$ is consistent with the heterolytic mechanism of bond breaking. Analysis of the kinetic traces within the ground-state bleach and excited-state absorption showed that the photoproduct is formed coherently excited as evidenced by the observation of the coherent vibrational oscillations (208 cm$^{-1}$) with an induction period of 70 fs. Apart from the coherent oscillations in the photoproduct, several other frequencies were found within the ground-state bleach region which were associated with the resonance impulsive stimulated Raman scattering from the ground-state OsBr$_6^{2-}$. Ligand substitution in hexabromoosmate is found to take place on a significantly faster time scale compared to the hexabromoplatinate complex.
4.5 References


CHAPTER 5: ULTRAFAST RADIATIONLESS DEACTIVATION OF AQUEOUS HEXABROMOIRIDATE DIANION

Abstract

Excited-state dynamics of IrBr$_6^{2-}$ dianion following photoexcitation with 770 nm light (1.6 eV) was investigated using broadband femtosecond pump-probe spectroscopy. Two fast components obtained from the analysis of the kinetic traces 0.85 and 23 ps were interpreted as being due to internal conversion from a higher lying excited state to the lowest excited state and then to the electronic ground state. Coherent oscillations with ~0.6 ps damping time, an induction period of 110 fs, and frequency of 212 cm$^{-1}$ observed within the excited-state absorption region are attributed to $a_{1g}$ total symmetric stretching of Ir–Br bonds. The photoexcitation leads to a dissociation of the complex only in the gas phase. In the condensed phase, dissociation if prevented because there is fast vibrational energy dissipation.
5.1 Introduction

Photodissociation dynamics of doubly charged anions \( \text{IrBr}_6^{2-} \) has been recently studied in gas phase by femtosecond time-resolved photoelectron spectroscopy.\(^1\) Photoexcitation of \( \text{IrBr}_6^{2-} \) with 1.6 eV pulses in the gas phase led to the formation of several photoproducts namely \( \text{IrBr}_5^- \), \( \text{IrBr}_4^- \), and \( \text{Br}^- \). It was found that dissociation of the dianion takes place in the hot ground state \( \text{IrBr}_6^{2-} \) formed after nonadiabatic relaxation from initially excited state.\(^1\) Biphasic decay of the initially populated excited state with 2.1 and 21 ps time constants was identified. The delayed unimolecular dissociation on a 79 ps time scale was explained by the fact that vibrational cooling of the hot dianion was not sufficiently fast which resulted in the Ir–Br bond breaking. The study of the similar doubly charged anion \( \text{IrCl}_6^{2-} \) in aqueous solutions investigated using ultrafast time resolved spectroscopy has been reported.\(^2\) Excitation of aqueous \( \text{IrCl}_6^{2-} \) with 420 nm pulses into a charge transfer absorption band \( ^2 \text{T}_{2u} \) was followed by formation of transient absorption which completely decayed with two characteristic times 0.5 and 18 ps. Recovery of the ground state parent complex was explained by the absence photochemical activity of visible CT bands of the dianion. The reactivity of this complex upon photoexcitation is determined by the nature of the lowest excited state and also depends on the efficiency of interconversion from higher lying excited states to the lowest state. It has been found in flash photolysis experiments that decay to the lowest state occurs with high efficiency in both \( \text{IrCl}_6^{2-} \) and \( \text{IrBr}_6^{2-} \) dianions. Furthermore, these complexes have an LMCT states as the lowest electronic states that are unreactive.\(^3\)

In this work, excited-state dynamics upon photoexcitation of aqueous \( \text{IrBr}_6^{2-} \) with 770 nm (1.6 eV) photons have been studied by time-resolved femtosecond pump-probe spectroscopy and compared with the gas phase study of the same complex.
5.2 Results and discussion

Ground-state molecular structure analysis of the parent dianion

The absorption spectrum of hexabromoiridate dianion is shown in Figure 5.1. Absorption bands in the 470 – 900 nm region were assigned by Jorgenson to ligand to metal charge transfer (LMCT) transitions from the $\pi$–orbitals of ligands to the $T_{2g}$ orbital.

![Figure 5.1](image)

**Figure 5.1.** UV-Vis absorption spectrum and optimized geometry of aqueous IrBr$_6^{2-}$.

of the metal, whereas ultraviolet bands in the 250–400 nm wavelength range were attributed to LMCT transitions from the $\pi$–orbitals of ligands to the $E_g^*$ orbital of the central ion.\(^{4,5}\) IrBr$_6^{2-}$ is a $d^5$ open shell system hence its geometry slightly distorts from $O_h$ to a lower $D_{4h}$ symmetry in accordance with the Jahn-Teller effect. The electronic ground state of the dianion is $^{2}T_{2g}$.

Geometry optimization of the dianion performed at the DFT level using M052X density functional\(^6\) revealed that the two equal axial Ir–Br bond lengths are 2.525 Å, the four equatorial
Br–Os bond lengths are 2.485 Å, and the Br–Ir–Br bond angles are 90°, Fig. 5.1 (inset).

Calculated Raman frequencies (M052X) of the complex (212, 194, 159, and 104-109 cm⁻¹, Table 5.1) are in good agreement with the frequencies observed in the Resonance Raman spectrum of the \( \text{IrBr}_6^{2-} \) (210, 199, 175, 103 cm⁻¹) obtained upon 600 nm excitation.⁷

**Table 5.1.** Harmonic frequency calculations of the ground electronic state \( \text{IrBr}_6^{2-} \)

<table>
<thead>
<tr>
<th>Species</th>
<th>aFrequency, cm⁻¹</th>
<th>Intensity</th>
<th>Experimental Raman frequencies,⁹ cm⁻¹</th>
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<tr>
<td></td>
<td></td>
<td>IR Ram an</td>
<td></td>
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<tr>
<td>( \text{IrBr}_6^{2-} )</td>
<td>62</td>
<td>6</td>
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<tr>
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<td>68</td>
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<td>104</td>
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<td>17</td>
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<td></td>
<td>109</td>
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<td>16</td>
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<tr>
<td>( ^2\text{T}_{2g} ) electronic ground state, D⁴h symmetry</td>
<td>112</td>
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<td></td>
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<td></td>
<td>225</td>
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<td>0</td>
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</table>

⁶ Harmonic frequencies were calculated at DFT level using M052X density functional with Def2-TZVP basis set ⁸ for iridium and aug-cc-pVTZ-PP basis set⁹ for bromine.
Evolution of the transient-absorption spectra upon 770 nm photoexcitation

Femtosecond time-resolved transient absorption $\Delta A$ spectra of aqueous hexabromoiridate excited at 770 nm are shown in Figure 5.2. Following photoexcitation, ground-state bleach occurs in 484 – 618 and 654 – 736 nm regions accompanied by the excited-state transient (EST) absorption rise in the 354 – 485 and 618 – 654 nm wavelength ranges on the same time scale. The broad absorption band in the 354 – 485 nm region then undergoes blue shift and narrowing (~0.85 ps) with simultaneous decay of 636 nm absorption band to form a new band in the 345 – 463 nm wavelength range peaking at 406 nm and a new transient absorption in the range from 710 to 765 nm. Finally, these transient absorption bands decay on ~23 ps time scale whereas the ground-state bleach completely recovers.

![Figure 5.2](image_url)

**Figure 5.2.** Transient absorption spectra of aqueous IrBr$_6^{2-}$ at various time delays from 770 nm pump and probe pulses.
Long and short time kinetic traces of aqueous IrBr$_6^{2-}$ at different wavelength.

Several selected kinetics traces in the ground-state bleach and excited-state absorption regions are shown in Figure 5.3. The experimental $\Delta A$ kinetic traces were best fitted by a sum of two exponential decay functions $\Delta A(\Delta \tau) = A_j \exp(-t/\tau_j)dt$ (where $A_j$ are the amplitudes and $\tau_j$ are the time constants). The best fit time constants obtained in 484 – 618 nm range are $\tau_1 = 0.85$ ps, and $\tau_2 = 23$ ps. Coherent oscillations with an induction period of $0.12 \pm 0.2$ ps lasting for $\sim$1 ps after...
Table 5.2. Analysis of the quantum beats observed in the excited state absorption region (350-490 nm) upon photoexcitation of aqueous IrBr$_6^{2-}$ with 770 nm light.

<table>
<thead>
<tr>
<th>$\lambda$, nm</th>
<th>$v_{osc}$, cm$^{-1}$</th>
<th>$v_{osc}$, FFT cm$^{-1}$</th>
<th>$A_{osc}$</th>
<th>$X_c$</th>
<th>Induction time, ps</th>
<th>$\tau_{osc}$, ps</th>
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<tr>
<td>360</td>
<td>207</td>
<td>211</td>
<td>0.00070</td>
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<td>0.10</td>
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<tr>
<td>390</td>
<td>213</td>
<td>211</td>
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<td>0.27</td>
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<td>0.746</td>
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<td>420</td>
<td>213</td>
<td>211</td>
<td>0.00063</td>
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<tr>
<td>440</td>
<td>214</td>
<td>214</td>
<td>0.00073</td>
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<td>214</td>
<td>0.00173</td>
<td>0.29</td>
<td>0.14</td>
<td>0.478</td>
</tr>
</tbody>
</table>

Figure 5.4. (A) Short-time 460 nm kinetic trace (black) and fit using double exponential function (red) following 770 nm excitation of aqueous IrBr$_6^{2-}$, water signal (blue); (B) oscillatory part of the same kinetic trace obtained after the fit subtraction of the fit from the kinetic trace (black) and fit to single sine damped function, (C) FFT analysis of the oscillatory part from panel B.
excitation are observed within 354 – 485 nm band. The frequency of the oscillations (~213±6 cm\(^{-1}\)) was found from the fit of the oscillatory residues \(R(t)\) left after subtracting the multi-exponential fit from the measured \(\Delta A\) kinetic traces to a damp sine function \(R(t) = A_1 \cdot \exp(-t/\tau_c) \cdot \sin(2\pi vt + \phi)\), where \(\phi\) is the relative phase, \(\tau_c\) the coherence decay time constant. The same frequency, 212 ± 2 cm\(^{-1}\) was obtained using Fast Fourier transform (Origin v.7.0) of the oscillatory parts of the residues, Table 5.2 and Fig 5.4. The damping time of the oscillations was found to be 0.659 ± 0.087 ps. No oscillations were observed in ground-state bleach region and within the excited state absorption from 710 to 765.

Excited-state dynamics of aqueous IrBr\(_6^{2-}\) following 770 nm excitation

The lowest binding energy of the electronic ground state dianion is 0.84 eV\(^1\) which is significantly smaller than the energy of the excitation photon (1.6 eV). This implies that absorption of the photon leads to a state lying higher in energy then the lowest excited state of the dianion. Indeed, the results of relativistic scattered wave calculations on the molecule performed by Lopez\(^10\) prove that excitation with 1.6 eV photon brings the molecule into the lowest lying charge-transfer state \(^2\)U\(_g^\prime\)(T\(_{1g}\)), the second electronically excited-state (see diagram). Thus, transient absorption in the 354 – 485 and 618 – 654 nm wavelength ranges originates from a single particle excitation from this state. The coherent oscillation with 212 cm\(^{-1}\) frequency is assigned based on DFT calculations (M052X) to a symmetric stretching vibration of Ir–Br bonds in the dianion IrBr\(_6^{2-}\). Before excitation, the ground state complex has a hole in the \(d_{xy}\) orbital of the iridium ion, therefore excitation of an electron to this orbital would result in stronger repulsion between the electrons in \(d_{xy}\) orbital and the electrons of ligands which causes
symmetric stretch of the equatorial Ir–Br bonds. Damping time (0.659 ± 0.087 ps) of the oscillations directly related to the decay of this excited state. The fact that oscillations are not observed in the ground-state bleach region rules out the assignment of the oscillations as due to the resonance impulsive stimulated Raman scattering from the ground state. The decay from $^2U_g'(T_{1g})$ state on ~0.85 ps time scale can be assigned as due to internal conversion to the lowest excited state which according to Lopez is $^2U_g'(T_{2g})$ state (low-lying excited configuration of the metal t$_{2g}$ (d)). Formation of new transient absorption bands in 345 – 463 nm and 710 – 765 nm regions with 0.85 ps time constant and damping of the coherent oscillation is in agreement with this assignment. The decay of these transient absorption bands within $\tau_2 = 23$ ps is accompanied by a complete recovery of the ground-state bleach, therefore this process can be assigned as due to internal conversion from the $^2U_g'(T_{2g})$ lowest excited state to $^2E_g''(T_{2g})$ electronic ground state of IrBr$_6^{2-}$. It is remarkable that the time constants, 0.85 and 23 ps, for internal conversions are very close to the ones (2.2 and 22 ps) obtained in the gas phase study of photodissociation dynamics of hexabromoplatinate.$^1$ However, whereas in the gas phase, excitation of IrBr$_6^{2-}$ with 1.6 eV photons leads to dissociation as confirmed by the detection of IrBr$_5^-$, IrBr$_4^-$, and Br$^-$ fragments, excitation with the same energy photons in the condensed phase (water) did not result in the Ir–Br bond breaking. This can be explained by the fast dissipation of energy excess to the solvent bulk. Very fast dissipation of vibrational energy excess to solvent (water) (~5.7 kcal mol$^{-1}$ cm$^{-1}$ per 100 fs was recently reported for charged metallo-organic complexes in aqueous solutions.$^{11}$ Thus, three-state model can describe photophysical processes taking place after photoexcitation of aqueous hexabromoiridate dianion with 770 nm light, Figure 5.5.
Figure 5.5. Schematic representation of the excited state relaxation of aqueous IrBr$_6^{2-}$. 
5.3 Conclusion

Excited-state dynamics in IrBr$_6^{2-}$ following excitation with 770 nm light has been investigated by using femtosecond pump-probe spectroscopy. Two time constants, 0.85 and 23 ps, were found upon analysis of the kinetic traces in the ground-state bleach and excited state absorption regions, which were interpreted as being due to internal conversion from $^2U_g'(T_{1g})$ to $^2U_g'(T_{2g})$ excited state and from $^2U_g'(T_{2g})$ to the $^2E_g''(T_{2g})$ ground state of IrBr$_6^{2-}$. Vibrational coherence due to symmetric stretching of equatorial Ir–Br bonds was observed on the $^2U_g'(T_{1g})$ excited state potential energy surface of IrBr$_6^{2-}$ because it only appears in the ESA region attributed to this excited state, and the oscillations are absent in the region of the ground-state bleach and in the visible region. Unlike the gas phase study where photodissociation of the dianion occurs in the hot ground-state dianion, fast dissipation of vibrational energy of the complex in the condensed phase prevents its dissociation.
5.4 References


CHAPTER 6: CONCLUSIONS

In this work, the first ultrafast time-resolved study of hexacoordinated bromides of platinum(IV), osmium(IV), and iridium(IV) in a condensed phase has been reported. Using femtosecond broadband pump-probe spectroscopy with 100 fs time resolution, the excited state dynamics and photochemistry of these complexes have been proposed.

The broadband pump-probe approach enabled us to vary the character of the initially excited state and monitor the solute and solvation dynamics throughout ‘real-time’ probing of the reactant and fragments with significantly different energies at various stages of the photoinduced reaction. Using broadly tunable probe pulses, the ΔA spectra were measured covering the spectral regions of ground state bleach of the reactants and absorption of intermediates and product species. The Fs-PP spectroscopy was employed in combination with DFT/TDDFT calculations of equilibrium geometries and harmonic frequencies of all the species possibly involved in the reaction mechanism to provide a detailed understanding of the sequence of photophysical and photochemical processes that follow an excitation with light. In addition, the high-level theory (CASSCF/CASPT2) was used for calculations of the electronic transition energies of the benchmark close-shell hexabromoplitate complex.

The detailed description of the dominant photophysical and photochemical pathways in a model PtBr₆²⁻ compound was obtained as a function of the excited electronic states populated by using 350, 420, and 530 nm light, as well as the surrounding solvent (water, D₂O, methanol, and acetonitrile). It has been shown that independently on the excitation wavelength, the same coherently excited photoproduct is formed in less than 150 fs supporting the idea that the lowest triplet excited ligand field state in PtBr₆²⁻ is dissociative. Two types of coherent oscillations were
observed in the early-time kinetic traces. Long-lived oscillations ($\tau_{\text{osc}} \sim 1.4$ ps) were found within the ground-state bleach (209 cm$^{-1}$) region, and therefore were assigned to the resonance impulsive Raman scattering from the ground-state PtBr$_6^{2-}$. Short-lived ($\tau_{\text{osc}} < 400$ fs) oscillations with $\sim 76$ and $\sim 114$ cm$^{-1}$ frequencies were observed within the photoproduct absorption band. It was proposed that the low-frequency oscillations in the photoproduct ($\sim 76$ cm$^{-1}$) are excited when the dissociation fragment $^{3}\text{PtBr}_5$ passes the Jahn-Teller $C_{4v}$ conical intersection. The short-lived oscillations were assigned to the bending mode which lifts the electronic degeneracy at the symmetry-induced Jahn-Teller conical intersection in $^{3}\text{PtBr}_5$. The longer-lived 114-cm$^{-1}$ mode with a damping time of 0.4 ps was proposed to be excited either as a mode coupled to the photodissociation reaction coordinate, or more likely due to coherence transfer from the $t_{1u}$ mode of the reactant. Geminate recombination of two negative ions PtBr$_5^-$ and Br$^-$ in the solvent cage was observed within $\sim 7$ ps. Formation of the aquated product PtBr$_5$(H$_2$O)$^-$ on $\sim 15$ ps time scale with $\sim 37\%$ quantum yield was detected, consistent with previous findings.

Similar to hexabromoplatinate, the triplet ground state OsBr$_5^-$ photoproduct was observed in about 70 fs after excitation of the parent complex at 420-nm ligand-to-metal charge transfer band. The photoproduct exhibited coherent oscillations with a damping time of 1.3 ps, an induction period of $\sim 70$ fs and a frequency of 212 cm$^{-1}$ corresponding to $a_1$ symmetric stretching mode excited near the potential energy surface minimum. This mode becomes excited as a result of coherence population transfer from the parent OsBr$_6^{2-}$dianion to the $^3\text{OsBr}_5$ photoproduct. The vibrational coherence in the $^3\text{OsBr}_5^-$ photoproduct was not observed in gradient difference ($a_1$, symmetric bending) or derivative coupling ($b_2$, antisymmetric bending) modes because these coherent motions are of low frequency (sub 50-cm$^{-1}$), and therefore they are probably damped very quickly based on the previous observations of the damping times of low-frequency modes.
in the literature. Another type of oscillations observed within ground-state bleach region originates from resonance impulsive stimulated Raman scattering from the ground-state OsBr$_6^{2-}$. Ligand substitution was detected on ~11 and ~35 ps time scales in water and methanol solutions. Upon photoexcitation in the presence of organic solvents, this complex produces a highly reactive pentacoordinated species PtBr$_5^-$ in the triplet state which is capable of oxidizing the organic compounds. Thus, PtBr$_6^{2-}$ possesses excellent photocatalytic properties.

Excited-state dynamics of IrBr$_6^{2-}$ dianion following photoexcitation with 770 nm light (1.6 eV) was investigated using the same technique. Two fast components obtained from the analysis of the kinetic traces with time constants of 0.85 and 23 ps were assigned to internal conversion from higher lying excited state to the lowest excited state and then to the electronic ground state. Coherent oscillations with ~0.6 ps damping time, an induction period of 110 fs, and frequency of 212 cm$^{-1}$ observed within excited-state absorption region were attributed to $a_{1g}$ totally symmetric stretch of Ir–Br bonds. The photoexcitation did not lead to the dissociation of the complex in contrast to the gas phase study due to fast vibrational energy dissipation in the condensed phase.

In summary, the ultrafast time-resolved and computational investigation of ultrafast photophysics and photochemistry of the hexahalogenometallic dianions, MX$_6^{2-}$, where M = Pt, Os, Ir, and X = Br was carried on in aqueous and other liquid environments. The comparison made with PtBr$_6^{2-}$, OsBr$_6^{2-}$, and IrBr$_6^{2-}$ complexes provided a deep understanding of the effect of dianion electronic structure on photophysical and photochemical pathways originating from the optically prepared excited electronic states. The role of solvent was unraveled by comparison of the dynamics exhibited by the reactant, intermediate, and product species in the different liquid environment.
### APPENDIX A. OPTIMIZED GEOMETRIES OF THE GROUND STATE SPECIES INVOLVED IN PHOTOCHEMISTRY OF HEXABROMOPLATINATE

<table>
<thead>
<tr>
<th>Species&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Parameter</th>
<th>Bond length, Å</th>
<th>Bond angle, deg</th>
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<td>$\text{PtBr}_6^{2-}$</td>
<td>Pt–Br</td>
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<tr>
<td></td>
<td>Br–Pt–Br</td>
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</tr>
<tr>
<td>$\text{Br}^{-}$</td>
<td></td>
<td></td>
<td></td>
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<tr>
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<sup>a</sup> calculations were performed at DFT B3LYP/TZ/PCM level of theory with H<sub>2</sub>O parameters
APPENDIX B. EMISSION SPECTRA OF HEXABROMOPLATINATE$^-$ (MAGENTA, SOLID CIRCLES), HEXABROMOOSMATE (OLIVE, OPEN DIAMONDS), AND HEXABROMOIRIDATE (PURPLE, SOLID DIAMONDS) IN WATER (CYAN) OBTAINED UPON EXCITATION WITH 420 NM LIGHT (XE LAMP). EMISSION SPECTRA OF 1,1'-DIETHYL-2,2'-CYANINE IODIDE (BLUE, OPEN SQUARES) AND MALACHITE GREEN (RED, OPEN CIRCLES) MEASURED IN METHANOL (DARK CYAN) ARE SHOWN FOR COMPARISON.
APPENDIX C. ASSIGNMENT AND GRAPHICAL REPRESENTATION OF VIBRATIONAL MODES IN THE GROUND STATE SINGLET AND TRIPLET PENTABROMOPLATINATE SPECIES

<table>
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<tr>
<th>Species Frequency, Computed (scaled) cm⁻¹</th>
<th>Vibrational mode representation</th>
<th>Symmetry / vibrational mode</th>
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</thead>
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<td>73ᵇ (80)</td>
<td>E / wagging (ax)</td>
</tr>
<tr>
<td></td>
<td>83 (91)</td>
<td>B₁ / out-of-plane bending, puckering</td>
</tr>
<tr>
<td></td>
<td>90 (99)</td>
<td>B₂ / in-plane scissoring</td>
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<tr>
<td></td>
<td>99ᵇ (109)</td>
<td>E / wagging</td>
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<tr>
<td></td>
<td>104 (114)</td>
<td>A₁ / doming</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B(_1) / out-of-phase stretching</td>
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<tr>
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<td>174 (191)</td>
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<td>184 (202)</td>
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<td>204(^b) (224)</td>
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<td>E / in-plane asym. stretch</td>
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<tr>
<td>260 (286)</td>
<td></td>
<td>A(_1) / stretching (ax)</td>
</tr>
<tr>
<td>[PtBr$_5$]$^-$</td>
<td>66 (73)</td>
<td>B$_2$ / asym. bending</td>
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<tr>
<td>triplet C$_{2v}$ distorted trigonal bipyramid</td>
<td>72 (79)</td>
<td>A$_1$ / sym. bending</td>
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<tr>
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<td>83 (91)</td>
<td>B$_1$ / sym. wagging</td>
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<tr>
<td></td>
<td>85 (93)</td>
<td>B$_1$ / sym. wagging</td>
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<tr>
<td></td>
<td>90 (99)</td>
<td>A$_2$ / twisting</td>
</tr>
<tr>
<td></td>
<td>101 (111)</td>
<td>B$_2$ / asym. bending</td>
</tr>
<tr>
<td>Wavenumber</td>
<td>Symmetry Description</td>
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<tr>
<td>101 (111)</td>
<td>A₁ / sym. bending (umbrella)</td>
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<td>166 (182)</td>
<td>B₂ / in-plane asym. stretching</td>
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<td>186 (205)</td>
<td>A₁ / out-of-phase sym. stretching</td>
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<td>201 (221)</td>
<td>A₁ / in-plane stretching</td>
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<td>212 (233)</td>
<td>B₂ / asym. stretching</td>
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<tr>
<td>217 (239)</td>
<td>A₁ / sym. stretching (doming)</td>
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