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Primary processes in photophysics and photochemistry of PtBr_6^{2-} complex studied by femtosecond pump–probe spectroscopy

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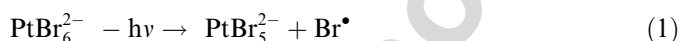
Abstract

Ultrafast pump–probe spectroscopy ($\lambda_{\text{pump}} = 420 \text{ nm}$) was applied to study the photoaquation of PtBr_6^{2-} complex. The excitation to d–d excited ${}^1\text{T}_{1\text{g}}$ state was followed by the formation of an intermediate absorption decaying with characteristic times of 370 fs, 2.2 and 15.2 ps. Two shorter times were attributed to the formation of the lower excited state (${}^3\text{T}_{1\text{g}}$) and its vibrational cooling accompanied by solvent relaxation. The longest time was interpreted as ${}^3\text{T}_{1\text{g}}$ transition to the hot ground state (${}^1\text{A}_{1\text{g}}$) and the dissociation product ($\text{PtBr}_5(\text{H}_2\text{O})^-$ complex). The scheme is consistent with the independence of the photoaquation quantum yield on the excitation wavelength.

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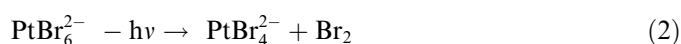
1. Introduction

Photochemistry of PtBr_6^{2-} complex in aqueous solutions is studied >50 years [1–7], but the photolysis mechanism is not finally established. Adamson and Sporer [1] postulated that the primary photochemical process is a homolytic cleavage of a Pt–Br bond followed by an escape of a bromine atom to the solution bulk



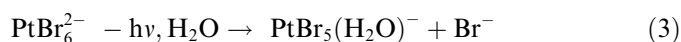
However, the final products of PtBr_6^{2-} photolysis are the aquated complexes of Pt(IV). To explain the photoaquation, authors of [1] proposed a chain mechanism analogous to that put forward in [8] for the photoaquation of PtBr_6^{2-} complex. Further, Penkett and Adamson [2] performed flash photolysis of PtBr_6^{2-} with 30 μs time resolution, but the intermediates assigned to a bromine atom, Pt(III) complexes or the products of their secondary reactions were not

found. Based on those results, Penkett and Adamson [2] postulated the reaction of a two-electron reduction of Pt(IV) with an escape of Br_2 molecule into the bulk:



The PtBr_4^{2-} complex having a non-equilibrium geometry (e.g., a trigonal bipyramid), was proposed to be a chain carrier in the mechanism of PtBr_6^{2-} photoaquation [2].

The third scheme of PtBr_6^{2-} photoaquation was proposed by Balzani and co-workers [3–6]. In their mechanism the Pt–Br bond cleavage is heterolytic, and an aquated $\text{PtBr}_5(\text{H}_2\text{O})^-$ complex is a primary product of the photochemical process:



The primary process (3) is followed by $\text{PtBr}_5(\text{H}_2\text{O})^-$ photoaquation. As a result, the multistage photoaquation of PtBr_6^{2-} occurs [4]. The quantum yield of the primary stage (3) was estimated as 0.4, and no dependence on the exciting light wavelength (313–530 nm) was observed [4]. The schematic energy level diagram for PtBr_6^{2-} is shown in Fig. 1. The independence of the photoaquation quantum

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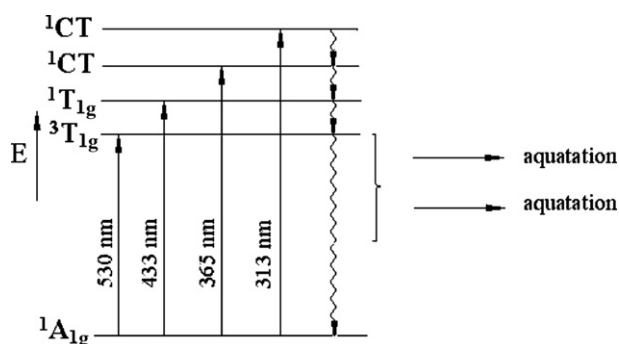


Fig. 1. Schematic energy level diagram for PtBr₆²⁻ (from Ref. [14]).

yield on the wavelength was explained by a fast transition to the lower excited state, namely, triplet ligand field (LF) state ³T_{1g} [14], which was thought to be a precursor of the reaction products [6].

An exciting question is the difference in the mechanisms of PtBr₆²⁻ and PtCl₆²⁻ photoaquation. For PtCl₆²⁻, the quantum yield of PtCl₅(H₂O)⁻ formation in some conditions is much higher than unity [9–11], which was explained by a chain mechanism including redox reactions. Pt(III) intermediates were recorded in pulsed experiments [12,13]. Ford et al. [14] proposed that the different mechanisms of PtBr₆²⁻ and PtCl₆²⁻ photoaquation are determined by a dramatic difference in the rate constants of the reactions between chloride and bromide complexes of Pt(III) and Pt(IV), which were supposed to be responsible for chain propagation. However, in our recent experiments on laser flash photolysis of PtBr₆²⁻ no intermediates were found in the time region >50 ns [15].

Goursot et al. [16] examined PtCl₆²⁻ photochemistry using a picosecond laser flash photolysis (355 nm). An intermediate with two peaks near 440 and 640 nm decaying via a first order rate law with a common lifetime of 210 ps was observed. This intermediate was interpreted as PtCl₅²⁻ complex having a square-pyramid structure with elongated Pt–Cl bond [17], although the possibility of the assignment as an excited electronic state of PtCl₆²⁻ was also discussed. The objective of the current study was to examine the photochemistry of PtBr₆²⁻ in femto- and picosecond time domains in order to study the primary photoprocesses.

2. Experimental

A pump–probe spectroscopy was used to study transient absorption in femto- and picosecond time domains. The experimental setup was described in details elsewhere [17]. The samples were excited by ~60 fs pulses at ~420 nm (second harmonic of a Ti:sapphire generator – amplifier system, CDP Ltd., Moscow, Russia). The excitation pulse repetition rate was 10 Hz, and 200 pulses were used to record a single time-resolved spectrum. The samples were placed in a 1 mm rotating cuvette to provide a uniform irradiation of the sample and to avoid unwanted thermal effects from heating of the sample by the pump

pulse. Typically time-resolved spectra were collected with a delay displacement of 100 fs in first 3 ps after excitation and with exponentially increasing delay times at longer delays. Usually 60–70 spectra were collected for each sample with a longest delay of ~100 ps. The experimental data were globally fitted by a three- or a four-exponential model. The fitting program performed corrections of the group velocity dispersion and calculated the response time of the instrument. The overall time resolution was 150–200 fs. All pump–probe measurements were carried out at room temperature.

The absorption spectra were recorded using an HP-8453 spectrophotometer (Hewlett Packard). Steady-state photolysis was performed using the irradiation of a high-pressure mercury lamp with a set of glass filters.

Solutions of PtBr₆²⁻ complex were prepared from Na₂PtBr₆ × H₂O salt synthesized as described in [18]. The solutions were prepared using deionized water. To prevent the dark reaction during the experiments, 0.03 M of free Br⁻ ions (NaBr, Aldrich) were added to the samples, which did not affect the photolysis. When necessary, the samples were deaerated by bubbling with argon.

3. Results and discussion

3.1. Spectrum and processes of PtBr₆²⁻ photoaquation

The UV absorption spectrum of PtBr₆²⁻ shown in Fig. 2 (curve 1) coincides with known from the literature [5]. The most intensive LMCT band with the maximum at 226 nm corresponds to the electron density transfer from σ-orbitals predominantly located on ligands to the vacant σ*-orbitals predominantly located on the metal ion [19]. Less intensive charge transfer bands (290–450 nm) correspond to the transitions from π-orbitals of ligands. These bands are partially superimposed with the d–d bands [19].

The changes in the UV spectrum upon the steady-state photolysis of PtBr₆²⁻ do not depend on irradiation wavelength, light intensity and initial concentration of the complex [4]. The typical picture of changes in the UV absorption spectrum corresponding to the first stage of the photolysis is shown in Fig. 2. Three isosbestic points at 216, 241.5 and 287 nm are conserved, corresponding to the aquation of PtBr₆²⁻ with the formation of PtBr₅(H₂O)⁻, in accordance with [3–5]. Further irradiation leads to the distortion of the isosbestic points due to further photoaquation of PtBr₅(H₂O)⁻. As it was noted in Section 1, the quantum yield of photoaquation does not depend on the wavelength being equal to 0.4 [4,15]. In femtosecond experiments the excitation wavelength was 420 nm, corresponding to the transition to the singlet ligand field excited state ¹T_{1g} [14] (Fig. 1).

PtBr₆²⁻ photoaquation could occur in different ways. The first possibility is the direct Pt^{IV}–Br bond heterolysis by a dissociative Balzani mechanism [3–6] (reaction (3)). In this case, a primary intermediate could be a pentacoordinated complex of Pt(IV); PtBr₅⁻.

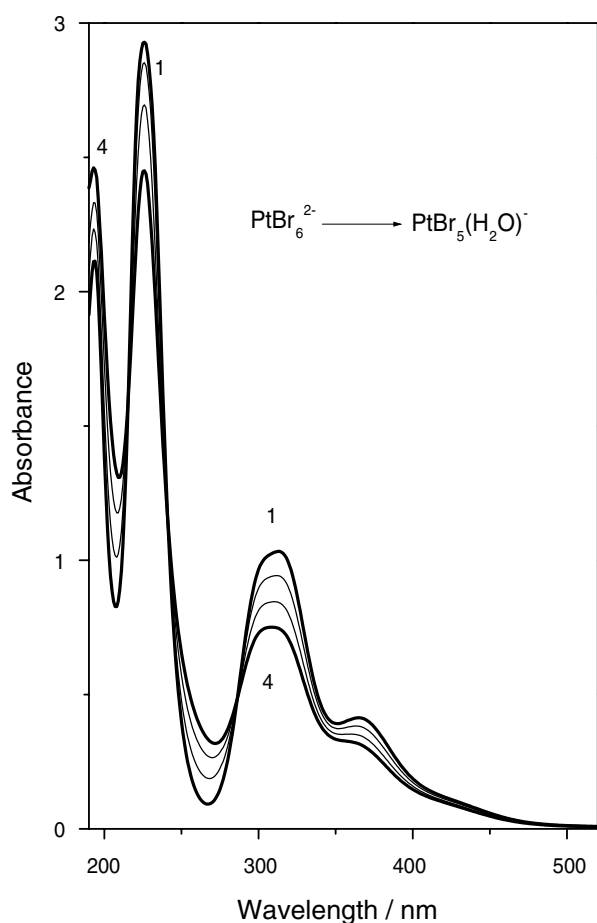
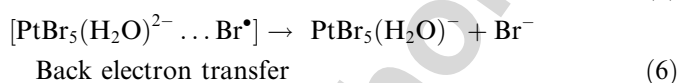
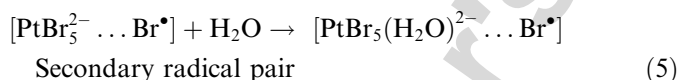


Fig. 2. Stationary photolysis (313 nm) of PtBr_6^{2-} (5.5×10^{-5} M) in aqueous solutions. 1–4 – 0; 4; 9; and 14 s of irradiation.

Another possibility can be described in the framework of the Adamson mechanism of radical pairs [20].



The absence of any evidence of the redox processes for PtBr_6^{2-} [2,15] makes it clear that (if this mechanism is realized) an escape of Br^\bullet atom to the bulk (reaction (7)) is negligible. On the other hand, it seems probable to observe primary and secondary radical pairs in femtosecond experiments.

3.2. Femtosecond laser flash photolysis of PtBr_6^{2-}

Excitation of PtBr_6^{2-} with a femtosecond laser pulse leads to the formation of a transient absorption, which was almost completely decayed in 80 ps. Kinetic curves at

several selected wavelengths are presented in Fig. 3. The global analysis of the time profiles in the wavelength range of 440–780 nm by iterative deconvolution shows that the use of a three-exponential function

$$\Delta D(\lambda, t) = A_1(\lambda)e^{-t/\tau_1} + A_2(\lambda)e^{-t/\tau_2} + A_3(\lambda)e^{-t/\tau_3} \quad (8)$$

with the instrument response function gives a good fitting with the time constants $\tau_1 = 370$ fs, $\tau_2 = 2.2$ ps and $\tau_3 = 15.2$ ps (solid lines in kinetic curves). Spectra of $A_1(\lambda)$, $A_2(\lambda)$ and $A_3(\lambda)$ amplitudes corresponding to calculated lifetimes are shown in Fig. 4a. These amplitudes allow to construct the spectra at different times (Fig. 4b). The total sum of amplitudes is the spectrum at zero time; the $A_2(\lambda) + A_3(\lambda)$ sum is the spectra at the end of first process ($\tau_1 = 370$ fs). After disappearance of $A_2(\lambda)$ ($\tau_2 = 2.2$ ps), the $A_3(\lambda)$ amplitude is the last spectrum before the complete decay of transient absorption ($\tau_3 = 15.2$ ps). Immediately after excitation the transient absorption spectrum has a very wide band with maximum in the region of 600–630 nm. After finishing of the first process ($\tau_1 = 370$ fs) the band is narrowed and shifted to 525 nm. The third component $A_3(\lambda)$ (after $A_2(\lambda)$ decay) has the maximum out of registration range, presumably, at 400–430 nm.

Addition of free Br^- ions (4.5 M) did not lead to any remarkable changes either in characteristic times or in the bands maxima positions. In the case of Adamson mechanism (reactions (4)–(7)) at high Br^- concentration one could expect the acceptance of a Br^\bullet atom of the secondary radical pair (reaction (5)) by free Br^- ion with the formation of $\text{Br}_2^{\bullet-}$ radical anion. Besides, an electron transfer from a free Br^- anion to the excited complex could be expected with the successive formation of bromine atom and $\text{Br}_2^{\bullet-}$, similar to the case of IrCl_6^{2-} photochemistry [21]. The rate constant of the reaction $\text{Br}^\bullet + \text{Br}^- \rightarrow \text{Br}_2^{\bullet-}$ in aqueous solutions is ca. $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ [22]. At 4M Br^- the characteristic time of $\text{Br}_2^{\bullet-}$ formation should be ca. 20 ps. Therefore, three characteristic times of the fast processes followed by the excitation of PtBr_6^{2-} in the region of 420 nm should be explained.

3.3. Possible processes followed by the excitation (420 nm) of PtBr_6^{2-}

As the addition of high concentration of free Br^- ions does not affect the transient absorption, we would not examine Adamson mechanism of radical pairs and the electron transfer from the intrasphere Br^- ion. Therefore, we will consider the participation of $^1\text{T}_{1g}$ and $^3\text{T}_{1g}$ excited states in the framework of Balzani mechanism of photoaquation.

In this case, the observed three-exponential dynamics of the excited PtBr_6^{2-} complex could be described as follows. Excitation at 420 nm leads to the formation of hot, Frank–Condon $^1\text{T}_{1g}$ state, and the spectrum at zero time is due to the absorption from this state. The distribution of $^1\text{T}_{1g}$ state vibrational levels leads to a wide absorption

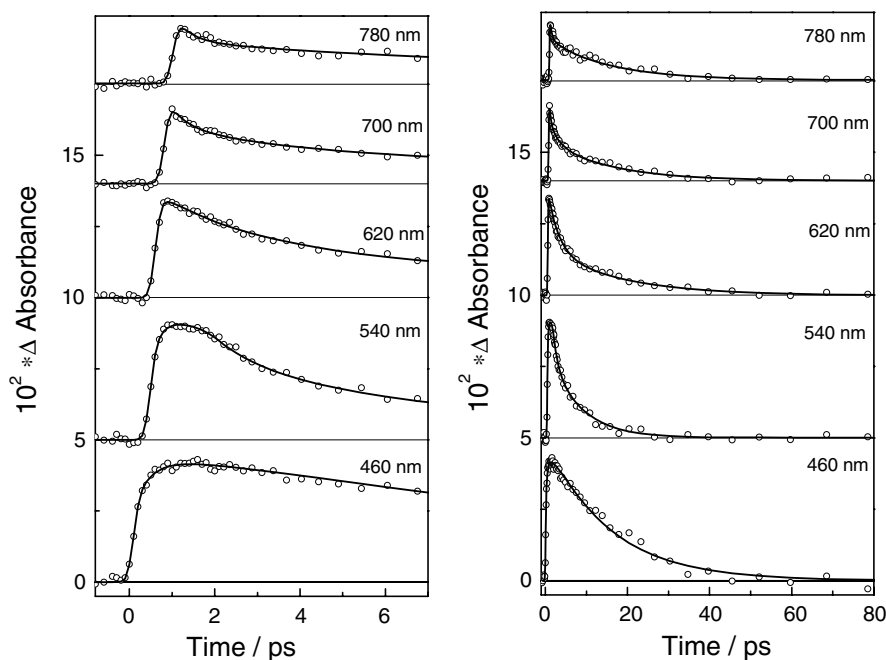


Fig. 3. Femtosecond ($\lambda_{\text{pump}} = 420$ nm) photolysis of PtBr_6^{2-} (3.8×10^{-3} M). Cuvette 1 mm. Kinetics of transient absorption at different wavelengths and time domains. Solid lines are the best three-exponential fits (formula (8)) after reconvolution with the instrument response function.

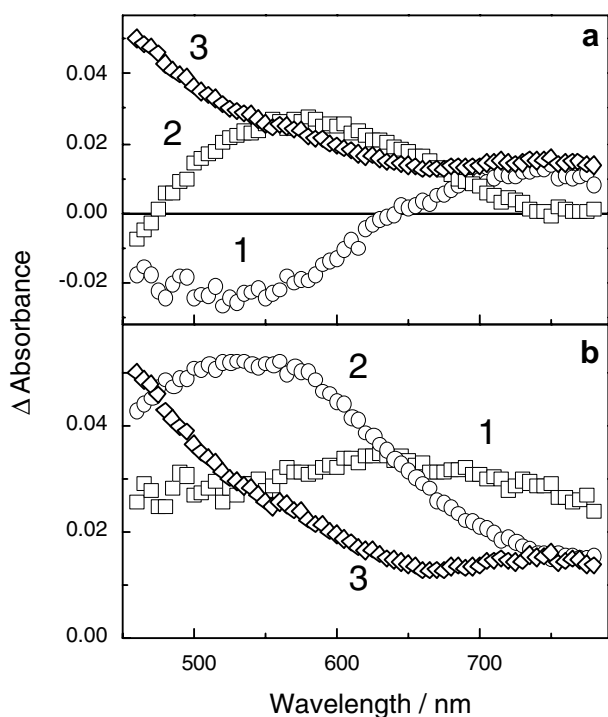


Fig. 4. Panel a – spectra of amplitudes $A_1(\lambda)$ (1), $A_2(\lambda)$ (2) and $A_3(\lambda)$ (3) corresponding to lifetimes 0.37, 2.2 and 15.2 ps. Treatment of the data of Fig. 3. Panel b – spectra at different times. 1 – zero time (sum of amplitudes $A_1(\lambda) + A_2(\lambda) + A_3(\lambda)$); 2 – after the end of the first process (sum of amplitudes $A_2(\lambda) + A_3(\lambda)$); 3 – after the finishing of two first processes (amplitude $A_3(\lambda)$).

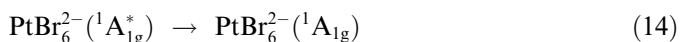
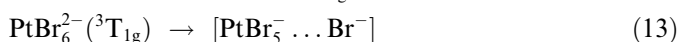
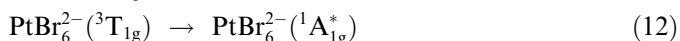
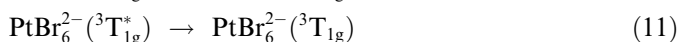
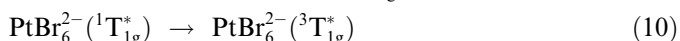
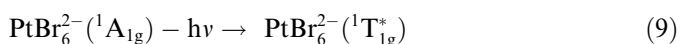
band (Fig. 4b, spectrum 1). The first process ($\tau_1 = 370$ fs) seems to be either a vibrational cooling of the excited

$^1\text{T}_{1g}$ state or an intersystem crossing of the hot $^1\text{T}_{1g}$ state to the hot $^3\text{T}_{1g}$ state. It is difficult to distinguish these processes for coordination compounds due to the existence of a number of low vibrational frequencies [23]. However, as the vibrational cooling should be accompanied by narrowing of an absorption band without an essential shift of maximum [24], we suppose that the first process is the intersystem crossing $^1\text{T}_{1g} \rightarrow ^3\text{T}_{1g}$, and the spectrum 2 in Fig. 4b after the finishing of first process is the absorption from the vibrationally excited $^3\text{T}_{1g}$ state.

The examples of subpicosecond intersystem crossing for transition metal complexes are presented in the review of Vlcek [23] and Forster [25] and references therein. The characteristic times of fast intersystem crossing in many cases were 100 fs, but the examples of longer times could also be found in the literature, e.g., for nickel(II) alkylthiopyrphyrine the ISC time of ca. 800 fs followed by the 8 ps vibrational relaxation was reported [26].

The reaching of $^3\text{T}_{1g}$ state is followed by its vibrational cooling accompanied by the solvent relaxation ($\tau_2 = 2.2$ ps). The thermalization time for transition metal complexes typically lies in a picosecond time domain (1–10 ps) [24,27]. It should be noted that the characteristic times of vibrational relaxation could differ dramatically. Vibrational cooling can occur as a single step process with the electronic relaxation. In this case the characteristic time could be <1 ps [28,29]. On the other hand, the vibrational relaxation can occur as a comparatively long process in the range of 10–40 ps, which was measured for metal carbonyls [30,31]. According to this interpretation, spectrum 3 of A_3 component in Fig. 4b represents the absorption of the thermalized excited $^3\text{T}_{1g}$ state of PtBr_6^{2-} .

The last process with the characteristic time 15.2 ps seems to be determined by the transitions of the reactive $^3T_{1g}$ state both to the hot ground $^1A_{1g}$ state and to the photoaquation product. The photoaquation can also proceed from hot ground $^1A_{1g}$ state. The competition between these processes determines the quantum yield of photoaquation (0.4 independently of the excitation wavelength). The characteristic time of the third process is comparable with the time of Br^- diffusion from the central cation (ca. 10 ps for a 1 Å distance). Finally, the observed processes were described by the reaction scheme (9)–(16) and are presented in Fig. 5.



The observed times are attributed as follows: $\tau_1 = 370$ fs is determined by the reaction (10), $\tau_2 = 2.2$ ps is due to the vibrational relaxation (11), and finally $\tau_3 = 15.2$ ps is the characteristic time determined by the reactions (12)–(15).

It should be noted that the alternative reaction scheme could be based on a proposal that the singlet $^1T_{1g}$ state is the reactive state, and the low-lying triplet $^3T_{1g}$ state is unreactive. In this case, the first characteristic time (370 fs) corresponds to the transition from $^1T_{1g}$ to both $^3T_{1g}$ and photoaquation products. This scheme is analogous to that realized for $Cr(CO)_4(bpy)$ complex [32,33]. However, the quantum yield of CO dissociation drops dramatically (for an order of magnitude) with an increase in excitation wavelength [34], which is consistent with the mechanism of high-lying reactive state. The quantum yield

of $PtBr_6^{2-}$ photoaquation is wavelength-independent [4,5]. Therefore, the scheme with the reactive triplet state seems to be more reliable.

4. Conclusion

The proposed scheme of $PtBr_6^{2-}$ photoaquation (8)–(15) corresponds to the mechanism of the direct $Pt^{IV}-Br$ bond heterolysis (reaction (3)). It is consistent both with the results of femtosecond experiments and with the independence of the quantum yield on the excitation wavelength. In the case of photoaquation occurring by the radical pairs mechanism ((4)–(7)), one could expect to observe a more complicated kinetic behavior reflecting the existence of two radical pairs. The last type of photoaquation is typical for the case of $PtCl_6^{2-}$, for which an intermediate with the characteristic time of 210 ps was observed [17]. Probably, this intermediate could be attributed as a secondary radical pair (analogous to that formed in reaction (5)). The dramatic difference in photochemistry of $PtBr_6^{2-}$ and $PtCl_6^{2-}$ probably could be explained by the faster internal conversion and intersystem crossing in the case of $PtBr_6^{2-}$.

Acknowledgements

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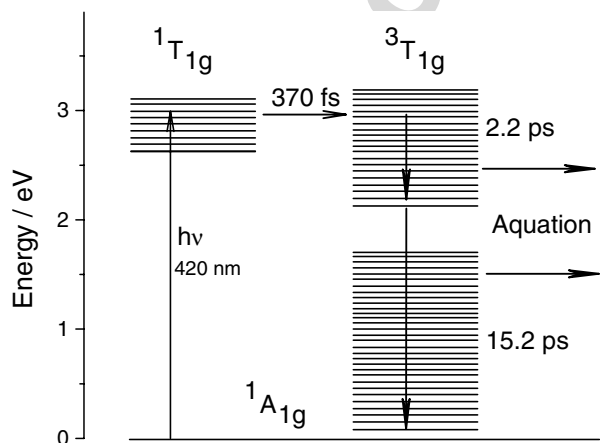


Fig. 5. Scheme of photophysical and photochemical processes for $PtBr_6^{2-}$ complex.

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