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Direct measurement of ultrafast intersystem crossing time for the $Pt^{IV}Br_6^{2-}$ complex

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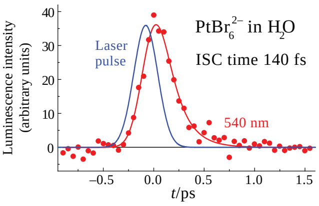
The time of ultrafast intersystem crossing for the $Pt^{IV}Br_6^{2-}$ complex in aqueous solution was measured by a fluorescence up-conversion technique. The corresponding time constant (140 ± 40 fs) is in agreement with that estimated from previous ultrafast transient absorption measurements and with the reported results of theoretical calculations.



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Ultrafast spectroscopy with different detection methods is widely used in photophysics and photochemistry.[1,2] Typical time resolution of ultrafast spectroscopy is 50–100 fs. The application of femtochemistry methods to coordination compounds changed dramatically the understanding of the initial stages of photochemical processes.[1–5] Due to a large number of excited states, ultrafast processes in coordination compounds have specific features such as ultrafast intersystem crossing (ISC).[3]

Rate constants of ISC in transition metal complexes can vary dramatically. Forster[3] classified the ISC processes as fast ($k \geqslant 10^{12}$ s^{-1}) and slow ($k \leqslant 10^{9}$ s^{-1}). Ultrafast ISC is typical of transition metal complexes; however, it is often difficult to distinguish the former from internal conversion (IC) due to the strong spin–orbit coupling.[4] Data on the characteristic times of ISC were reviewed by Chergui.[5] The ultrafast ISC times for metal complexes vary from tens of picoseconds[6] to tens of femtoseconds.[7–9] However, there is no correlation between conversion times and spin–orbit coupling constants and no heavy atom effect.[5,10] Since ultrafast ISC times were obtained only for a limited number of metal complexes, it is very important to perform such measurements for new types of complexes.

Due to their simple structure, the hexahalide complexes of platinum group metals can be model compounds for comparing experimental and theoretical data. The ultrafast photophysics of hexahalide complexes has been actively studied recently.[11] However, experimental data on the ISC times of these complexes are scarce. The ISC times were estimated from ultrafast pump-probe transient absorption (TA) experiments for $Pt^{IV}Br_6^{2-}$ in aqueous[12,13] and methanol[13] solutions, $Os^{IV}Br_6^{2-}$ in aqueous solutions[12] and a pseudohalide $Pt^{IV}(SCN)_6^{2-}$ complex in aqueous and ethanol solutions.[14] The ISC time was also measured for the short-lived intermediate $Pt^{IV}Br_5^{-}$.[15]

Note that the ultrafast pump-probe TA technique often does not allow one to discriminate different processes (internal conversion, intersystem crossing, vibrational cooling, ultrafast bond cleavage, *etc.*) that have similar timescales, and it is important to use complementary methods.[5] Here, we report the measurements of the ISC time of $PtBr_6^{2-}$ in aqueous solution using the fluorescence up-conversion technique.

The solutions of $Pt^{IV}Br_6^{2-}$ in deionized water were prepared from a $Na_2PtBr_6 \cdot H_2O$ salt synthesized according to a published procedure.[16] The experimental setup was described in detail previously.[17] Luminescence decay traces were recorded using a FOG100 up-conversion system (CDP Systems). The test solution was placed in a 1 mm thick rotating cell in order to ensure continuous liquid replacement in the excitation volume. Luminescence was excited by the second harmonic of the fundamental beam of a Mai Tai femtosecond laser (Spectra Physics), which generated pulses at 760 nm with a duration of ~100 fs and a repetition rate of 80 MHz. For frequency doubling, we used a BBO crystal. A typical average excitation power at 380 nm was ~50 mW focused into a 40 × 40 μm^2 spot inside the cell. The luminescence of molecules was collected and focused by a system of lenses into a BBO nonlinear crystal where it overlapped with the gate pulse at 760 nm, which passed through a variable delay line. Radiation was then filtered by a double monochromator and detected by a photomultiplier tube.

$Pt^{IV}Br_6^{2-}$ is a $5d^6$ low-spin octahedral complex with the ground state $^1A_{1g}$. Figure 1 shows its electronic absorption spectrum with the assignment of main absorption bands according to Jorgensen.[18] This complex is nonluminescent at room temperature, while the phosphorescence of $Pt^{IV}Br_6^{2-}$ was observed at 4.2 K in a range of 630–800 nm[19] (the emission was caused by transitions from the lowest electronic excited state $^3T_{1g}$). The only photochemical process in $Pt^{IV}Br_6^{2-}$ in aqueous solutions is photoaquation with the formation of $Pt^{IV}Br_5(H_2O)^-$ and $Pt^{IV}Br_5(OH)^{2-}$ complexes.[20,21] Thus, the photoaquation occurs from the $^3T_{1g}$ state, and the quantum yield of its formation is close to unity regardless of the excitation wavelength.

The characteristic time of $Pt^{IV}Br_6^{2-}$ photoaquation is about 15 ps.[22] The intermediate absorption detected in the ultrafast TA experiments was initially attributed to the lowest electronic

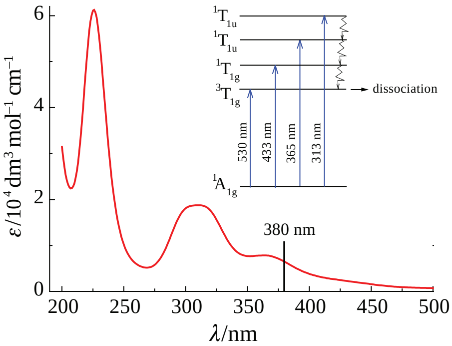

Figure 1 UV spectrum of $PtBr_6^{2-}$ in aqueous solution; insert: schematic energy level diagram according to Jorgensen (ref. 18).

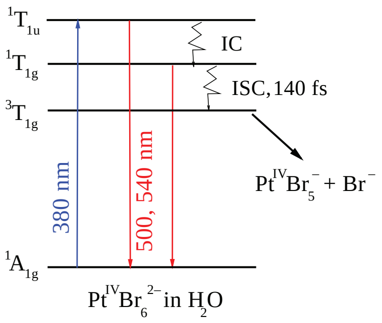

Figure 3 Simplified Jablonsky diagram corresponding to $Pt^{IV}Br_6^{2-}$ photodissociation.

excited state of $Pt^{IV}Br_6^{2-}$ corresponding to the $^3T_{1g}$ symmetry.[22] However, Zheldakov *et al.*[12] found that this state is dissociative and, after the excitation of $Pt^{IV}Br_6^{2-}$ to a $^1T_{2g}$ mixed LF/CT state induced by light at 420 nm, the complex undergoes internal conversion and intersystem crossing into the lowest triplet dissociative state $^3T_{1g}$, loses a ligand, and relaxes *via* the C_{4v} conical intersection to a nearly trigonal bipyramidal $^3Pt^{IV}Br_5^-$ product in its triplet state. The total duration of this complicated process is ~150 fs. Therefore, according to the TA data, the characteristic time of the $^1T_{1g} \rightarrow {}^3T_{1g}$ transition (Figure 1) in $Pt^{IV}Br_6^{2-}$ cannot exceed 150 fs.

In this work, we used fluorescence up-conversion as an additional technique to study early processes in the photophysics of $Pt^{IV}Br_6^{2-}$, which was excited at 380 nm in aqueous solution. Luminescence decay traces were recorded at 500 and 540 nm (Figure 2). The experimental points in Figure 2 were globally fitted by a function convoluted with a Gaussian function, which was used to model the shape of a pump pulse. The calculated RMS duration of a laser pulse is 120 ± 20 fs FWHM. The characteristic time of luminescence decay is 140 ± 40 fs, which coincides within the experimental error with the characteristic time of $^3Pt^{IV}Br_5^-$ intermediate formation (150 ± 30 fs) obtained from TA measurements.[12] We note that, due to the very fast decay and weak intensity of the luminescence of $Pt^{IV}Br_6^{2-}$, it can be detected only using the up-conversion technique.

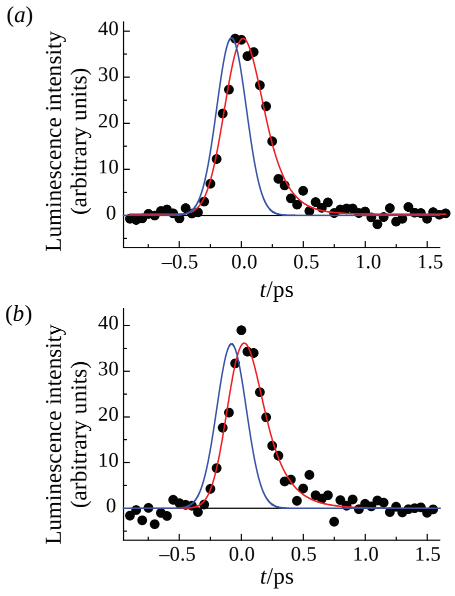

Figure 2 Time profiles of $PtBr_6^{2-}$ luminescence (3.2×10^{-4} M aqueous solution, 1 mm-thick rotating cell) measured using the up-conversion technique. Excitation at 380 nm, detection at (*a*) 500 and (*b*) 540 nm. Dots, experimental points; red lines, the best fit by a single-exponential function (characteristic time of 140 ± 40 fs) convoluted with a Gaussian function (120 ± 20 fs FWHM, blue lines) that models the shape of a pump pulse.

We propose the following qualitative interpretation of the observed luminescence kinetics. Laser radiation at 380 nm pumps the red wing of an absorption band due to the $^1T_{1u}$ CT state of $Pt^{IV}Br_6^{2-}$ (Figure 1). This state, as well as the low-lying singlet states $^1T_{2g}$ (mixed LF/CT) and $^1T_{1g}$ (LF), can be emissive. In this case, the $^1T_{1g} \rightarrow {}^3T_{1g}$ ISC process is responsible for the observed fast decay of luminescence. As noted before, the quantum yield of the $^3T_{1g}$ state formation is close to unity. Therefore, the quantum yields of emission (φ_r) and internal conversion $^1T_{1g} \rightarrow {}^1A_{1g}$ (φ_{IC}) are low. Taking into account that the quantum yields of $Pt^{IV}Br_6^{2-}$ photoaquation are measured with an accuracy of no better than 10%,[20,21] we can conclude that both φ_r and φ_{IC} cannot exceed several percents. However, it is hardly possible to distinguish between the ISC and the dissociation process $Pt^{IV}Br_6^{2-}$ ($^3T_{1g}$) $\rightarrow$ $^3Pt^{IV}Br_5^-$ + Br^- because the characteristic times extracted from transient absorption data[12] and from the fluorescence decay traces measured in our experiment are the same within the experimental error. Figure 3 shows a simplified Jablonsky diagram corresponding to the test processes.

Recently, Gomez *et al.*[23] reported quantum dynamics simulations of ISC dynamics for $Pt^{IV}Br_6^{2-}$ in aqueous solution. They demonstrated difficulties encountered in the theoretical description of ultrafast dynamics in heavy metal complexes. In particular, in order to adequately describe the electronic absorption spectrum of $Pt^{IV}Br_6^{2-}$, a total of 50 singlet and 50 triplet states spanning from 180 to 522 nm were taken into account. According to ref. 23, the primary ISC in $Pt^{IV}Br_6^{2-}$ is mainly an electronic process, while there is no considerable effect of nuclear motion during the first 100 fs. On the other hand, the simulation of nuclear dynamics using parabolic potentials performed by Gomez *et al.*[23] showed that a maximal elongation of the Pt—Br bond (2.72 Å, as compared to the equilibrium value of 2.47 Å[24]) was reached after 85 fs, which can be considered as a characteristic time of Pt—Br bond dissociation.

As mentioned by Vlcek,[4] the ISC and IC timescales of transition metal complexes are the same. In principle, ISC can be even faster than IC. The characteristic time of IC was measured for $Ir^{IV}Br_6^{2-}$ in different solvents.[25] The time of IC transition from the Frank–Condon state to the second electronic excited state was 90 fs, while the time of IC transition from the second to the first electronic excited state was solvent-dependent and varied from 0.76 (water) to 3 ps ($CHCl_3$).

Finally, we conclude that both TA[12] and fluorescence up-conversion (this work) measurements give similar values of the ISC time for $Pt^{IV}Br_6^{2-}$ in aqueous solution, and the experimental data are supported by theoretical studies.[23] Comparison of results obtained by different methods increases the reliability of description of the early photoprocesses in this model platinum complex.

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