

Short-Time Events, Coherence, and Structural Dynamics in Photochemistry of Aqueous Halogenated Transition Metal Dianions

A. N. Tarnovsky¹, I. L. Zheldakov², P. Z. El-Khoury³, S. K. Pal⁴, A. S. Mereshchenko¹, M. N. Ryazantsev⁵, E. V. Butaeva¹, T. Pascher⁶, J. Uhlig⁶, C. J. Milne⁷, S. L. Johnson⁸

¹Department of Chemistry, Center for Photochemical Sciences, Bowling Green State University, Bowling Green, OH, USA

²Department of Chemistry, University of Kansas, Lawrence, KS 66045, USA

³Department of Chemistry, University of California, Irvine, California 92697, USA

⁴School of Basic Sciences, Indian Institute of Technology, Mandi, Himachal Pradesh 175 001, India

⁵Department of Chemistry, Emory University, Atlanta, GA 30322, USA

⁶Department of Chemical Physics, Lund University, Lund, 22100 Sweden

⁷Laboratory of Ultrafast Spectroscopy, EPFL, Lausanne, CH-1015 Switzerland

⁸Institut für Quantenelektronik, Eidgenössische Technische Hochschule Zürich, Zürich CH-8093, Switzerland

Abstract. Ultrafast pump-probe spectroscopy, time-resolved x-ray absorption, and computational photochemistry elucidate the photochemical pathway of hexabromoplatinate dianions that propagates through distortions of nascent penta-bromoplatinate anions caused by Jahn-Teller conical intersections and terminates at aquated product complexes.

Photoprocesses in hexahalo dianions have been discussed invoking two distinct mechanisms in which the complex relaxes from the initially excited electronic state to either the vibrationally excited ground-electronic state or lower-lying electronic excited state, followed by metal-halogen bond breaking, [1]. In aqueous environments, resulting polyatomic photofragments may undergo subsequent aquation.

In this work, aqueous PtBr_6^{2-} was excited into the mixed $^1\text{T}_{2g}$ ligand-field/charge-transfer state (LF/CT) and the dissociative lowest excited triplet $^3\text{T}_{1g}$ LF state at 420 nm and 530 nm, respectively. The photochemical reaction path involves separation of negative charges ($\text{PtBr}_6^{2-} \rightarrow \text{PtBr}_5^- + \text{Br}^-$), distortions of a nascent penta-bromoplatinate anion caused by a Jahn-Teller (JT) C_{4v} conical intersection (CI), and hydration to form $\text{PtBr}_5(\text{H}_2\text{O})^-$. To characterize the reaction pathways, intermediates and products, we used ultrafast pump-probe and time-resolved x-ray absorption spectroscopies, in concert with CASPT2 and DFT/TDDFT calculations. The assignment of the UV-vis spectrum of aqueous PtBr_6^{2-} has been carried out using CASPT2 calculations of vertical electronic transitions (VETs), [2]. The results were reproduced using the less computationally expensive TDDFT/M052X method in combination with a conductor-like polarizable continuum model (CPCM). The VET data for possible products from the later method were used for spectral assignments of transient absorption ΔA spectra. The $^1\text{T}_{1g}$ LF/CT state and the dissociative $^3\text{T}_{1g}$ LF state of PtBr_6^{2-} both give rise to the same 500-nm absorption band, Fig. 1. The growth of this band

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occurs with a 150-fs time constant following 420-nm excitation and is assigned to the formation of triplet ${}^3\text{PtBr}_5^-$ in the nearly trigonal bipyramid geometry (C_{2v}). This indicates remarkably fast intersystem crossing and dissociation of the parent PtBr_6^{2-} complex, and suggests that the previous interpretation of the primary photo-processes in PtBr_6^{2-} is incorrect, [3]. Coherent oscillations (frequencies, 78 and 114 cm^{-1}) are observed within the 500-nm absorption band of ${}^3\text{PtBr}_5^-$. These beats are weak near the center, but strong at the blue and red wings of the 500-nm band, where they exhibit a π phase shift. Spectral narrowing and blue shift of the 500-nm band (600 fs) is followed by its decay and development of the broad 430-nm band (~ 1.6 ps) assigned to ${}^1\text{PtBr}_5^-$, indicating intersystem crossing in ${}^3\text{PtBr}_5^-$. The 430-nm band decays on two time scales with lifetimes of ~ 7 and ~ 15 ps, which is accompanied by the partial recovery and subsequent growth of ground-state bleach. These processes are assigned, respectively, to geminate recombination and nearly barrierless (based on the time scale) aquation to form ${}^1\text{PtBr}_5(\text{H}_2\text{O})^-$, which remains stable at least to 1.2 ns, Fig. 1.

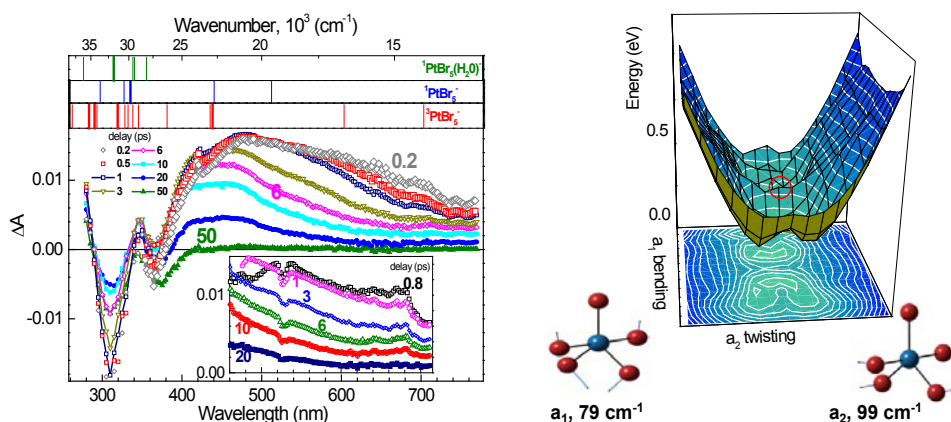


Fig. 1. Left: 420-nm ΔA spectra of aqueous PtBr_6^{2-} . Bottom inset: 530-nm ΔA spectra. Top insets: the TDDFT/M052X/CPM VET energies of possible products with oscillator strengths larger (thick lines) and smaller (thin lines) than 0.01. Right: M052X scans of ground-state PESs of ${}^3\text{PtBr}_5^-$ along the “branching space” coordinates. Open circle shows the CI location.

According to our normal mode analysis, the 78 and 114 cm^{-1} beats are attributed to the bending and umbrella a_1 modes of ${}^3\text{PtBr}_5^-$, respectively. The bending a_1 mode of ${}^3\text{PtBr}_5^-$ corresponds to the reaction coordinate mode parallel to the gradient difference vector of the JT C_{4v} CI present in the photochemical path, Fig. 2. The umbrella a_1 mode is the “spectator” mode that preserves the electronic degeneracy at the CI. Very rapid (100 fs) loss of coherence in the former case is observed, whereas in the latter case coherence is less damped (time constant, 235 fs). Following excitation of PtBr_6^{2-} into ${}^1T_{2g}$ (third excited singlet state) ultrafast internal conversion is proposed to lead to the lowest excited ${}^1T_{1g}$ state, from which the Raman active vibrational modes (t_{2g} , e_g , and a_{1g}) propagate the wavepacket to the ${}^3T_{1g}$ dissociative state. The wavepacket then moves on the ${}^3T_{1g}$ potential energy surface towards the exit, reached without significant spreading very well within the first 150 fs at the nascent C_{4v} geometry of PtBr_5^- . In these species, the first excited triplet state of 3E character is populated because it correlates to the lowest ${}^3T_{1g}$ state in O_h point group of PtBr_6^{2-} . A degenerate electronic E -state at C_{4v} geometry of PtBr_5^- represents a JT C_{4v} CI and has its degeneracy split by vibrations of suitable (b_1 and b_2) symmetry, [4]. When the compact wavepacket passes through the CI, it accelerates on the steep potential slopes of the CI region and the b_1 and b_2 splitting modes become excited, where b_1 pucker in C_{4v} descends to the a_1 bending mode in C_{2v} observed. The umbrella a_1 mode can be viewed as the closure of four equatorial ligands on the coordination site vacated by the ligand and is excited due to ligand dissociation.

Fluorescence and transmission x-ray spectra were measured in aqueous solutions of K_2PtBr_6 (5 - 25 mM) flowed through a 0.5-mm thick jet at (i) $L_3(2p_{3/2})$ -Pt edge (11.45 - 11.75 keV) and (ii) K -Br edge (13.44 - 13.55 keV) at selected delay times (0.2, 2, 20, 200, and 1700 ns) following 100-fs

400-nm laser pulses ($0.15 \text{ mJ pulse}^{-1}$). In addition, differential fluorescence and absorption kinetic traces were measured at 11.562 and 11.567 keV as well as 13.473 and 13.477 keV. The bromide ion ligand loss and photoaquation are evidenced through the disappearance and displacement of the $L_3(2p_{3/2})$ -Pt and K -Br near-edge features observed at 200 ps, Fig. 2. In particular, the XANES signal at the K -Br edge mainly consists of a change of the 13.473 keV feature, consistent with a decrease the oxidation state of a bromine atom, [5]. Because of the partially covalent character of Pt^{4+} -Br $^-$ bond in ground-state PtBr_6^{2-} , the decrease of the oxidation state of the Br atom observed is the evidence for the Pt-Br bond rupture in excited PtBr_6^{2-} , leading to the formation of a Br $^-$ ion. Time scans into a microsecond time domain performed at selected probe energies display an instantaneous rise of the signal at the Pt- and Br-edges followed by decay at the Pt edge. This observation is interpreted as the further decay of the $\text{PtBr}_5(\text{H}_2\text{O})^-$ complex in which Pt is reduced to a lower oxidation state.

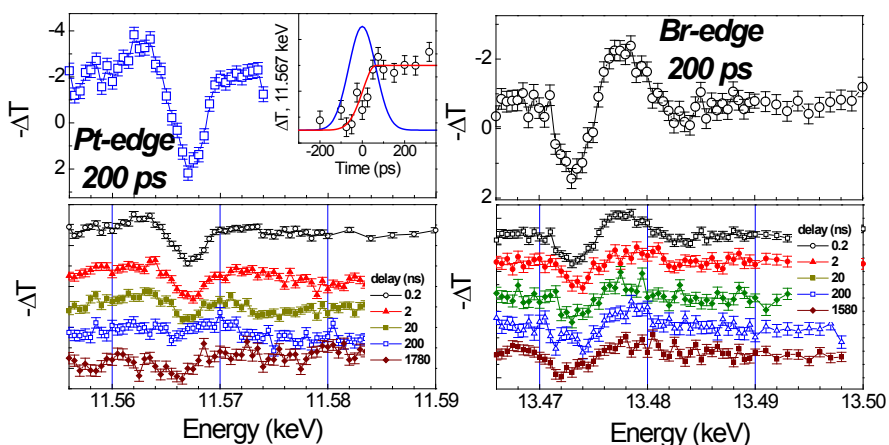


Fig. 2. 400-nm pump/x-ray absorption probe spectra at the Pt- and Br-edges at different time delays shown in legends. The instantaneous signal rise at 11,567 keV is described a step-function convoluted with the Gaussian 150-ps (fwhm) instrument response function (inset).

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