

ULTRAFAST EXCITED-STATE DYNAMICS IN MODEL HEXABROMOPLATINATE (IV) AND HEXABROMOOSMIATE (IV) DIANIONS IN THE CONDENSED PHASE

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Photoexcitation of hexabromoplatinate and hexabromoosmate dianions in CT and ligand field states results in remarkably fast formation (sub 100 fs) of coherently excited photoproducts assigned to ${}^3PtBr_5^-$ and ${}^3OsBr_5^-$. This is explained by the fact that one of the lowest triplet excited states in both $PtBr_6^{2-}$ and $OsBr_6^{2-}$ is repulsive. Surprisingly, the damping time and amplitude of the observed coherent oscillations in the pentabromoosmate (209 cm^{-1}) and pentabromoplatinate (112 cm^{-1}) species is quite different. The shorter damping time (0.4 ps) of ${}^3PtBr_5^-$ in comparison with the damping time (1 ps) of ${}^3OsBr_5^-$ in aqueous solution is related to faster dephasing in ${}^3PtBr_5^-$. The large-amplitude bending oscillations in pentabromoplatinate are tentatively assigned to the passage of the wavepacket through the Jahn-Teller conical intersection(s), whereas in pentabromoosmate, the umbrella type of oscillations appears to be due to the coupling to the Os-Br symmetric stretching mode in the parent dianion. The coherent oscillations in both photoproducts show no dependence on solvent. The results are supported by DFT, TD-DFT and CASSCF/CASPT2 calculations of electronic structures, vertical electronic transitions and harmonic frequencies of initial dianions and photoproducts.