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**Conservation of vibrational coherence in ultrafast electronic relaxation:
The case of diplatinum complexes in solution**

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Abstract:

We report the results of ultrafast transient absorption studies of tetrakis(μ -pyrophosphito)diplatinate(II), $[\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4]^{4-}$ (Pt(pop)) and its perfluoroborated derivative $[\text{Pt}_2(\mu\text{-P}_2\text{O}_5(\text{BF}_2)_4]^{4-}$ (Pt(pop-BF₂)) in water and acetonitrile upon excitation of high lying (<300 nm) UV absorption bands. We observe an ultrafast relaxation channel from high lying states to the lowest triplet state that partly (Pt(pop) in H₂O, Pt(pop-BF₂) or fully (Pt(pop) in MeCN) bypasses the lowest singlet excited state. As a consequence, vibrational wave packets are detected in the lowest triplet state and/or the lowest excited singlet of both complexes, even though the electronic relaxation cascade spans ca. 2 and 1.3 eV, respectively. In the case of Pt(pop-BF₂), coherent wave packets generated by optical excitation of the lowest singlet ¹A_{2u} state also are reported. Overall, the reported dephasing times of the Pt-Pt oscillator in the ground, singlet and triplet states do not depend on the solvent or the molecular structure.

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