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Mapping the UV Photophysics of Platinum Metal Complexes Bound to Nucleobases¹ ANANYA SEN, CAROLINE DESSENT, University of York — We report the first UV laser spectroscopic study of isolated gas-phase complexes of Platinum metal complex anions bound to a nucleobase as model systems for exploring at the molecular level the key photophysical processes involved in photodynamic therapy. Spectra of the $Pt^{IV}(CN)_6^{2-} \bullet Uracil$ and $Pt^{II}(CN)_4^{2-} \bullet Uracil$ complexes were acquired across the 220-320 nm range using mass-selective photodepletion and photofragment action spectroscopy. The spectra of both complexes reveal prominent UV absorption bands that we assign primarily to excitation of the Uracil $\pi - \pi^*$ localized chromophore. Distinctive UV photofragments are observed for the complexes, with $Pt^{IV}(CN)_6^{2-} \bullet Uracil$ photoexcitation resulting in complex fission, while $Pt^{II}(CN)_4^{2-} \bullet Uracil$ photoexcitation initiates a nucleobase protontransfer reaction across 4.4-5.2 eV and electron detachment above 5.2 eV. The observed photofragments are consistent with ultrafast decay of a Uracil localized excited state back to the electronic ground state followed by intramolecular vibrational relaxation and ergodic complex fragmentation. In addition, we present recent results to explore how the photophysics of the Platinum complex-nucleobase clusters evolves as a function of nucleobase. Results are presented for $Pt^{II}(CN)_{4}^{2-} \bullet Uracil$ complexed to Cytosine, Thymine and Adenine, reveal distinctive decay dynamics which we attribute to the intrinsic decay dynamics of the nucleobase.

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