A theoretical investigation of uranyl covalency via symmetry-preserving excited state structures

Sapphire Armstrong [a], Thomas Malcomson [b] and Andy Kerridge *[a]

[a] Department of Chemistry, Faraday Building, Lancaster University, Lancaster, LA1 4YB, UK.

[b] Department of Chemistry, University of Manchester, Oxford Road, Manchester, M13 9PL, UK

Electronic supplementary information

Table S1. Integrated QTAIM metrics; charge (q), localisation (LI) and delocalisation (DI) indices at the ground and excited state electronic structures.

Excitation	q(U)	q(O)	LI(U)	LI(O)	DI(U,O)
Ground State	3.153	-0.576	26.814	7.476	2.045
$\pi_u \rightarrow \pi_u^*$	3.102	-0.551	27.210	7.661	1.692
$\sigma_u \rightarrow \sigma_u^*$	3.046	-0.523	27.138	7.569	1.816
$\pi_g \rightarrow \pi_g^*$	2.972	-0.486	27.093	7.459	1.943
$\sigma_g \rightarrow \sigma_g^*$	3.367	-0.683	26.470	7.373	2.174

Table S2. Topological QTAIM metrics at the ground and excited states electronic structures at the ground state geometry

Excitation	ρ_{BCP} (a.u.)	$\nabla^2 \rho_{BCP}$ (a.u.)	H (a.u.)
Ground State	0.332	0.529	-0.347
$\pi_u \rightarrow \pi_u^*$	0.358	0.312	-0.394
$\sigma_u \rightarrow \sigma_u^*$	0.359	0.565	-0.394
$\pi_g \rightarrow \pi_g^*$	0.364	0.236	-0.404
$\sigma_g \rightarrow \sigma_g^*$	0.338	0.381	-0.356

Table S3. Integrated QTAIM metrics; charge (q), localisation (LI) and delocalisation (DI) indices at the excited state geometries for each state of interest.

Excitation	q(U)	q(O)	LI(U)	LI(O)	DI(U,O)
$\pi_u \rightarrow \pi_u^*$	3.031	-0.515	27.342	7.653	1.634
$\sigma_u \rightarrow \sigma_u^*$	2.846	-0.423	27.621	7.628	1.535
$\pi_g \rightarrow \pi_g^*$	2.738	-0.369	27.376	7.365	1.892
$\sigma_g \rightarrow \sigma_g^*$	3.318	-0.658	26.538	7.363	2.155

Table S4. Topological QTAIM metrics at the excited state geometries for each state of interest

Excitation	ρ_{BCP} (a.u.)	$\nabla^2\rho_{BCP}$ (a.u.)	H (a.u.)
$\pi_u \rightarrow \pi_u^*$	0.265	0.333	-0.216
$\sigma_u \rightarrow \sigma_u^*$	0.250	0.447	-0.188
$\pi_g \rightarrow \pi_g^*$	0.235	0.350	-0.164
$\sigma_g \rightarrow \sigma_g^*$	0.300	0.410	-0.283

Table S5. QTAIM metrics at both the ground and excited state geometries for the optically accessible excitation. All QTAIM metrics are in a.u. with the exception of the

Geometry	$\Delta q(U)$	$\Delta q(O)$	$\Delta LI(U)$	$\Delta LI(O)$	$\Delta DI(U,O)$	$\Delta\rho_{BCP}$	$\Delta\nabla^2\rho_{BCP}$	ΔH
Ground State	3.150	-0.575	26.747	7.403	2.108	0.334	0.511	-0.350
Excited State	3.031	-0.515	27.342	7.653	2.099	0.296	0.488	-0.278

(de)localisation indices, which are dimensionless.