Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information: *Magnetic circular dichroism of UCl_6^- in the ligand-to-metal charge-transfer spectral region*

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Experimental *C*-term MCD spectra of $(PPh_4)UCl_6$.

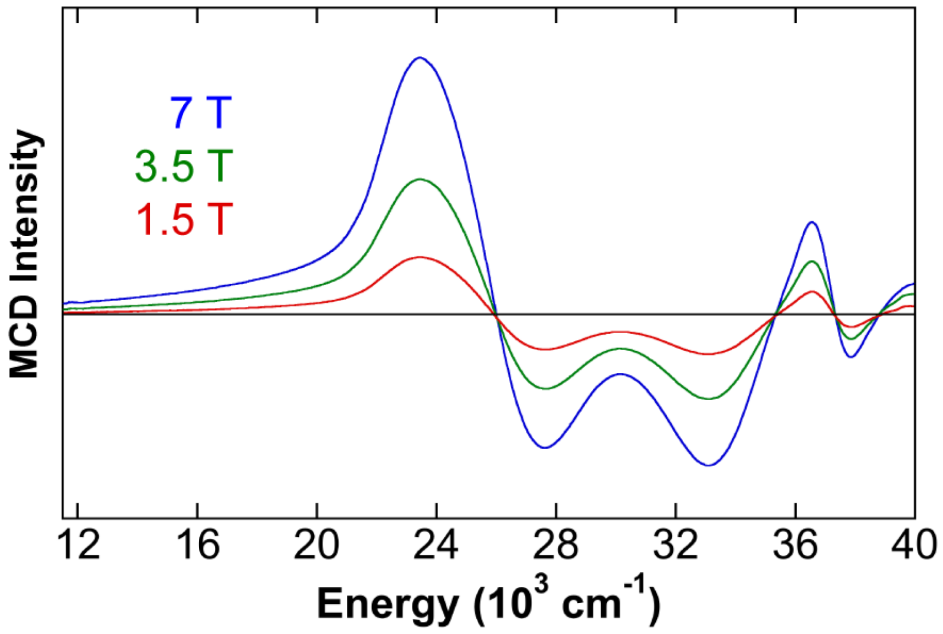

Figure S1: The 5 K, variable-field *C*-term MCD spectra of $(PPh_4)UCl_6$. MCD spectra were collected on solid mull samples.

Experimental EPR spectrum of $(PPh_4)UCl_6$.

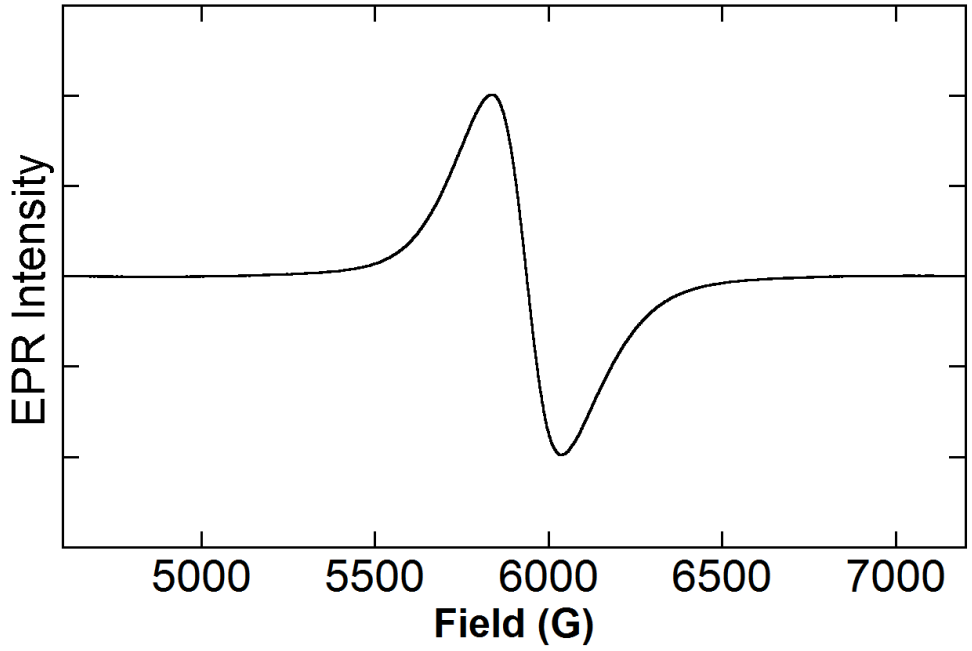

Figure S2: 10 K X-band EPR spectrum of 10mM of UCl_6^- in 1:1 THF:2-methylTHF with g = 1.13 at 5940G.

Experimental Structure of $(PPh_4)UCl_6$.

Full details of the structure determinations have also been deposited with the Cambridge Crystallographic Data Centre as CCDC 1544486. Copies of this information may be obtained free of charge from the CCDC via www.ccdc.cam.ac.uk/data_request/cif.

```
Bond precision:  C-C = 0.0022 A          Wavelength=0.71073

Cell:           a=22.6559(16)    b=6.7274(5)         c=17.4505(12)
                alpha=90         beta=97.2180(7)     gamma=90
Temperature:    296 K

                Calculated                Reported
Volume          2638.7(3)                 2638.6(3)
Space group     C 2/c                     C 2/c
Hall group      -C 2yc                    -C 2yc
Moiety formula  C24 H20 P, Cl6 U          UcL6(P(C6H5)4)
Sum formula     C24 H20 Cl6 P U           C24 H20 Cl6 P U
Mr              790.10                    790.10
Dx,g cm-3       1.989                     1.989
Z               4                         4
Mu (mm-1)       6.832                     6.832
F000            1492.0                    1492.0
F000'           1458.02
h,k,lmax        30,9,23                   30,9,23
Nref            3384                      3229
Tmin,Tmax       0.445,0.505               0.445,0.504
Tmin'           0.252

Correction method= # Reported T Limits: Tmin=0.445 Tmax=0.504
AbsCorr = MULTI-SCAN

Data completeness= 0.954          Theta(max)= 28.628

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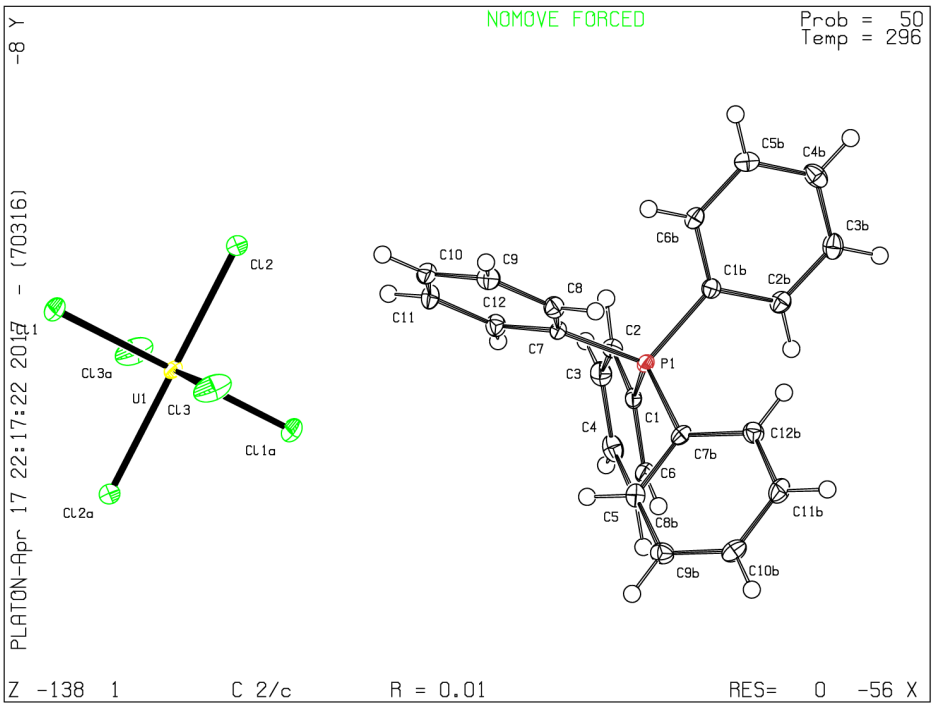
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U1
CL3a
CL3
CL1a
CL2a
C5b
C4b
C3b
C6b
C1b
C2b
C10
C9
C8
C12
C11
C7
C2
P1
C3
C1
C4
C12b
C7b
C6
C5
C8b
C11b
C9b
C10b

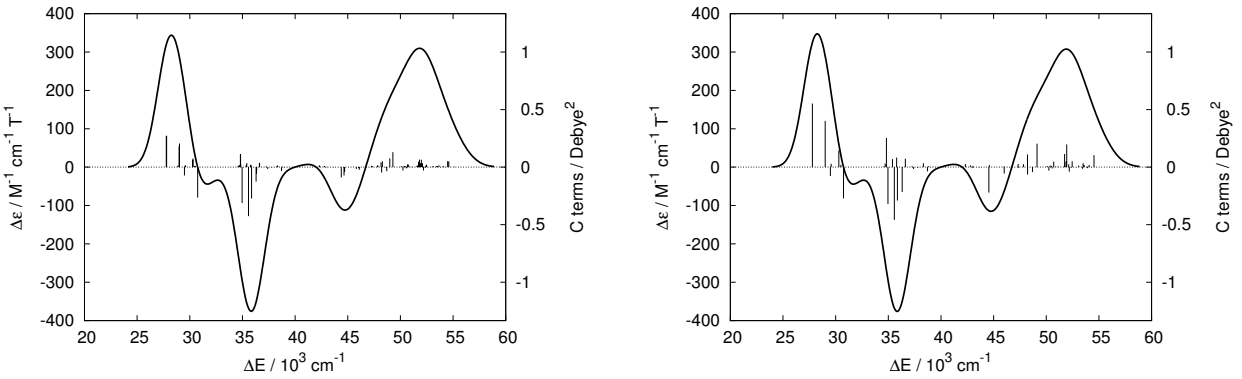
Energy of the LF states in UCl_6^- at the SCF level.

Table S1: Comparison of the calculated relative energies (ΔE, cm^{-1}) of the ligand-field states of UCl_6^- at the SCF level with the experimental structure and the idealized octahedral structure.

	SCF-SR			SCF-SO	
State	Expt.[a]	O_h[b]	State	Expt.[a]	O_h[b]
$^2A_{2u}$	0	0	$E_{5/2u}$	0	0
$^2T_{2u}$	2384	2384	$F_{3/2u}$	3523	3523
$^2T_{1u}$	6794	6794	$E_{5/2u}$	7396	7386
			$F_{3/2u}$	10912	10913
			$E_{1/2u}$	12447	12442

[a] Experimental structure of C_i symmetry with U–Cl = 2.5146, 2.5141 and 2.5047 Å.
[b] Idealized octahedral structure of O_h symmetry with U–Cl = 2.511 Å.

Calculated MCD spectrum of UCl_6^- using the experimental structure.



(a) (b)

Figure S3: Comparison of the calculated MCD spectra of UCl_6^- using the experimental structure (a) and the idealized octahedral structure (b). SCF-SO results.

Calculated energies of the $5f \rightarrow 6d$ transitions and corresponding MCD spectra.

The influence of $5f \rightarrow 6d$ transitions on the MCD spectrum of UCl_6^- were investigated at the SCF-SO and PT2-SO levels for the idealized octahedral structure. Here, a 'ras2' active space was used to represent the seven $5f$ orbitals and a 'ras3' space was used to represent the $6d$ orbitals. The calculations allowed to create one hole in the 'ras2' space and one particle in the 'ras3' space. The state-averaged RAS calculations were performed for the seven SR $5f$ doublet states of A_u symmetry and for the five SR $6d$ doublet states of A_g symmetry.

Table S2: Calculated relative energy (ΔE cm^{-1}) of the $6d$ States.[a]

State	SCF-SR	PT2-SR	State	SCF-SO	PT2-SO
$^2T_{2g}$	52037	32353	$F_{3/2g}$	53644	33924
			$E_{5/2g}$	57469	37778
^2E_g	85994	61986	$F_{3/2g}$	89235	65250

[a] ΔE is the energy of the state relative to the GS.

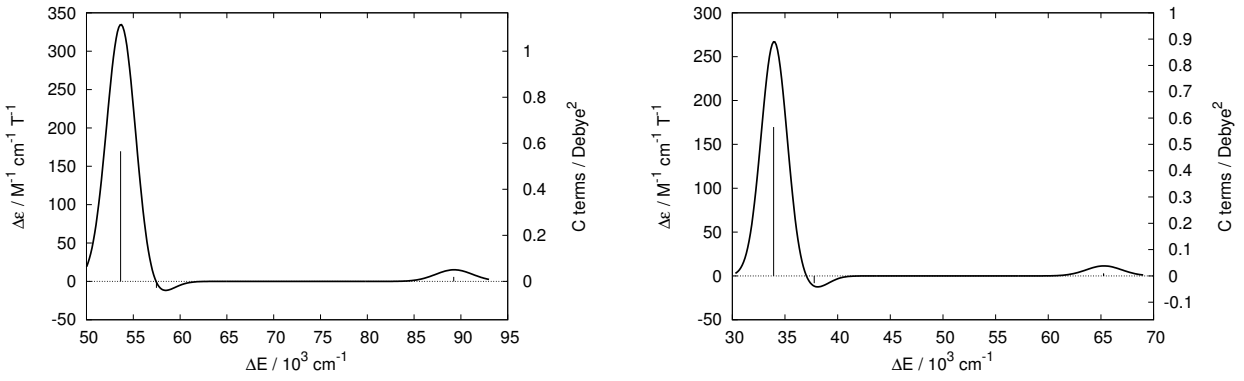


Figure S4: MCD spectra of UCl_6^- arising from $5f \rightarrow 6d$ transitions calculated at the SCF-SO (a) and PT2-SO (b) level.

Calculated energies of the $5f \rightarrow 6d$ and $t_{1u} \rightarrow 6d$ transitions and corresponding MCD spectra.

The influence of the $t_{1u} \rightarrow 6d$ transitions in addition to the $5f \rightarrow 6d$ transitions on the MCD spectrum of UCl_6^- was investigated at the SCF-SO and PT2-SO level for the idealized octahedral structure. Here, a 'ras1' space corresponding to 9 electrons in 3 orbitals of symmetry t_{1u} was used to represent the occupied orbitals. In combination with this RAS space, a 'ras2' active space was used to represent the seven $5f$ orbitals and a 'ras3' space was used to represent the $6d$ orbitals. The calculations allowed to create one hole in the 'ras1' space and one particle in the 'ras3' space.The state-averaged RAS calculations were performed for the seven SR $5f$ doublet states of A_u symmetry and for the 215 SR doublet states of A_g symmetry.

Table S3: Calculated relative energy (ΔE cm^{-1}) of the $6d$ States.[a]

State	SCF-SR	PT2-SR	assignment	State	SCF-SO	PT2-SO
$^2T_{2g}$	49336	36978	$5f \rightarrow 6d$	$F_{3/2g}$	50674	38468
				$E_{5/2g}$	53960	41744
$^2T_{1g}$	66225	60795	$t_{1u} \rightarrow 6d$	$F_{3/2g}$	67145	61398
$^2T_{1g}$	69196	61972	$t_{1u} \rightarrow 6d$	$F_{3/2g}$	68632	61877
^2E_g	69620	62510	$t_{1u} \rightarrow 6d$	$E_{5/2g}$	69144	62303
$^2T_{2g}$	69700	63223	$t_{1u} \rightarrow 6d$	$E_{1/2g}$	69409	62973
...	...	...	...	...	...	...
^2E_g	170187		$5f \rightarrow 6d$	$F_{3/2g}$	173317	

[a] ΔE is the energy of the state compared to the GS.

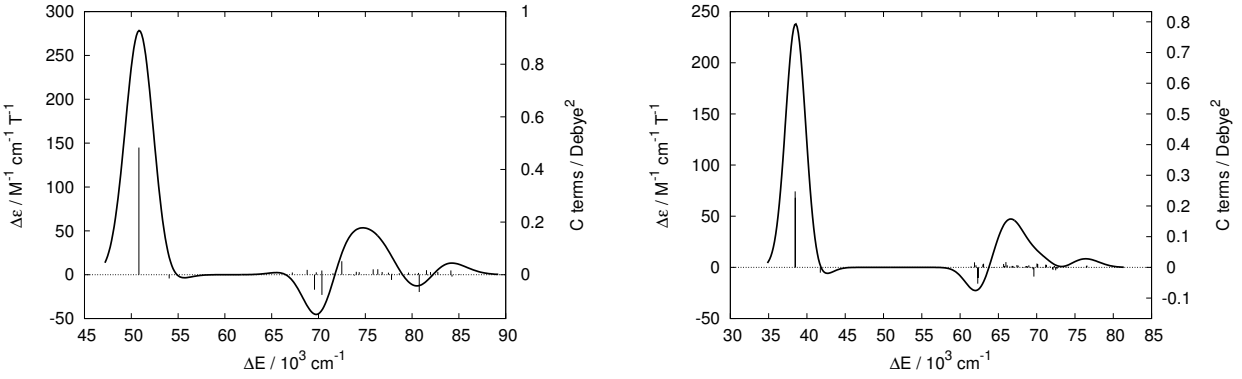
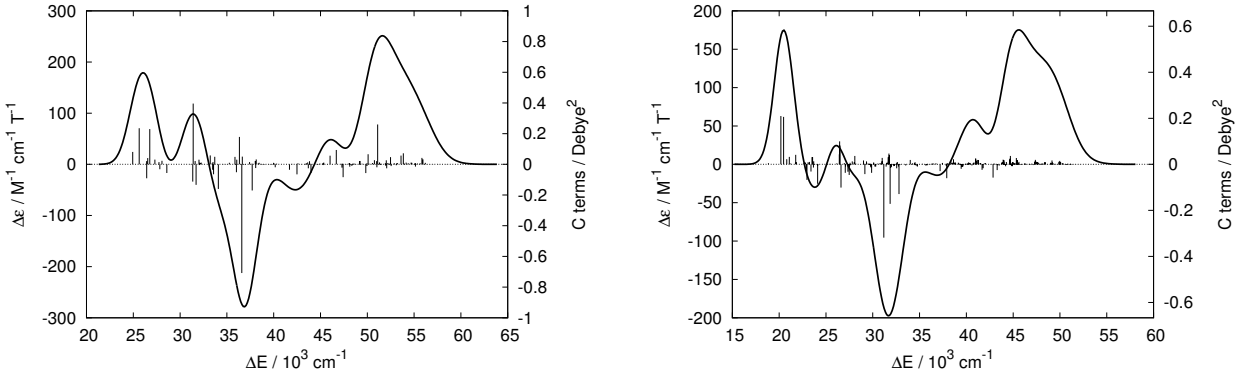


Figure S5: MCD spectra of UCl_6^- arising from $5f \rightarrow 6d$ and $t_{1u} \rightarrow 6d$ transitions calculated at the SCF-SO (a) and PT2-SO (b) level. For a sake of clarity, only the lowest 90 electronic transitions were used to generate the MCD spectra.

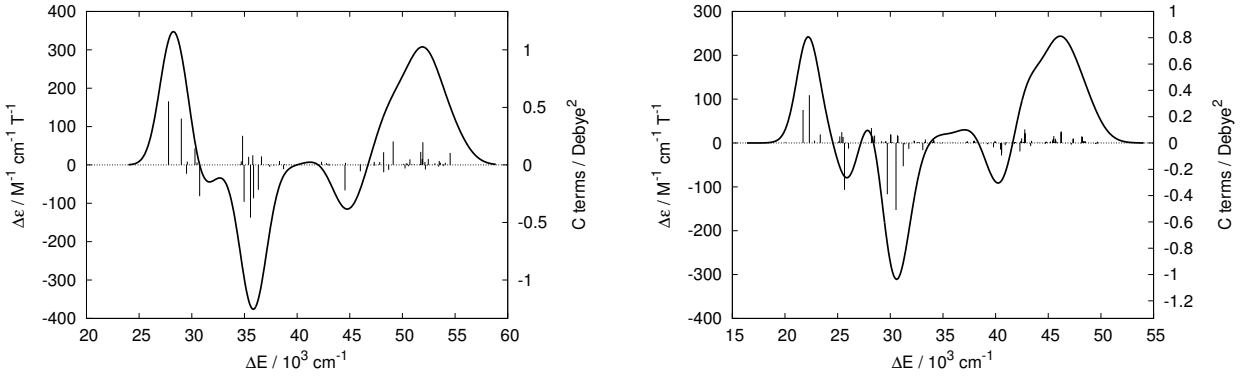
Influence of the quartet states on the MCD spectrum of UCl_6^-.

The influence of the SR quartet states of A_g symmetry on the MCD spectrum of UCl_6^- was investigated at the SCF-SO and PT2-SO level for the idealized octahedral structure. Here, a 'ras1' space corresponding to 18 electrons in 9 orbitals was used to represent the occupied orbitals. In combination with this RAS space, a 'ras2' active space was used to represent the seven $5f$ orbitals. The state-averaged RAS calculations were performed for the seven SR $5f$ doublet states of A_u symmetry, for the 441 SR doublet states of A_g symmetry and for 189 SR quartet states of A_g symmetry. The resulting spectra are shown in Figure S6 and are compared to the corresponding spectra in Figure S7 obtained without the Quartet states.



(a) (b)

Figure S6: MCD spectra of UCl_6^- calculated at the SCF-SO (a) and PT2-SO (b) level. For a sake of clarity, only the lowest 165 LMCTs and 150 quartet states were used to generate the MCD spectra.

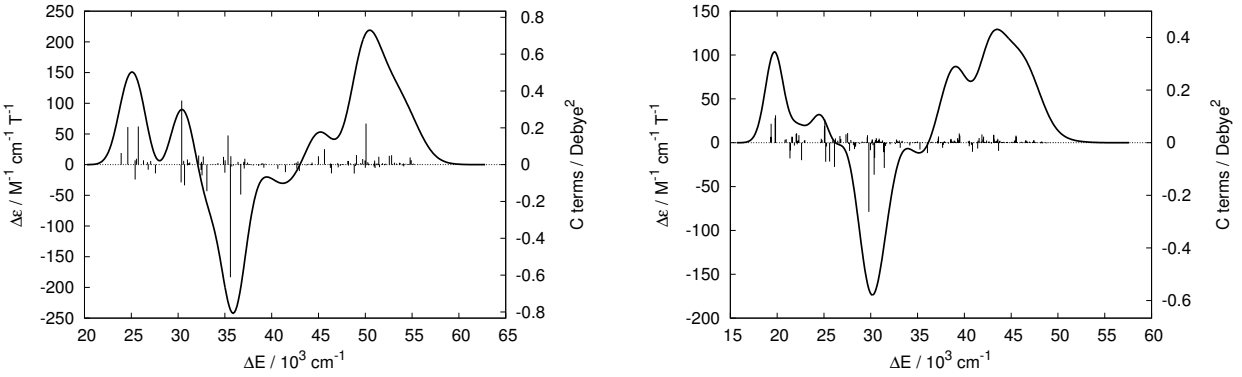


(a) (b)

Figure S7: MCD spectra of UCl_6^- calculated at the SCF-SO (a) and PT2-SO (b) level. For a sake of clarity, only the lowest 165 LMCTs states were used to generate the MCD spectra.

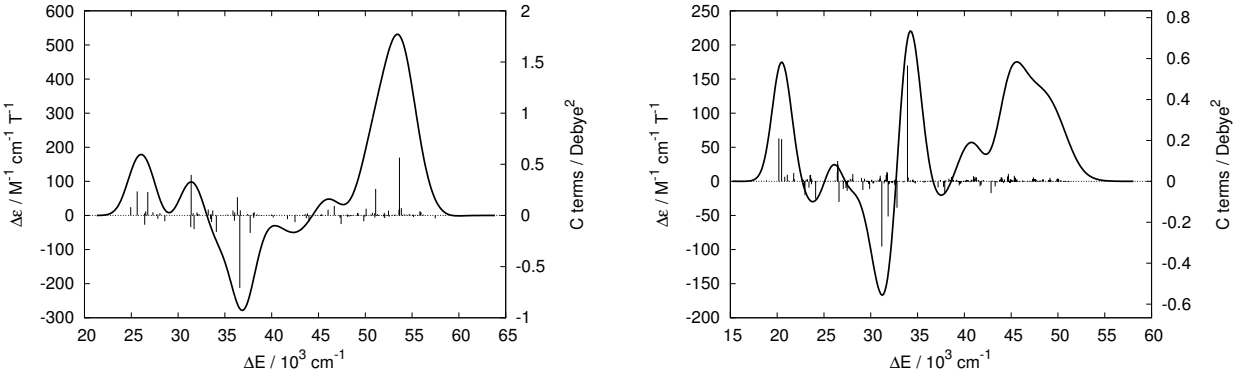
MCD spectra with $5f \rightarrow 6d$ transitions.

In Figure S8, the MCD spectra were generated using the following RAS active space: a 'ras1' comprising nine ligand orbitals of a_g symmetry, a 'ras2' space comprising the seven $5f$ orbitals and 'ras3' space comprising the five $6d$ orbitals. On the other hand, the MCD spectra of Figure S9 were generated using the following RAS active space: a 'ras1' comprising nine ligand orbitals of a_g symmetry and a 'ras2' space comprising the seven $5f$ orbitals. The $5f \rightarrow 6d$ transitions were added from calculations using an alternative active space as in Table S2.



(a) (b)

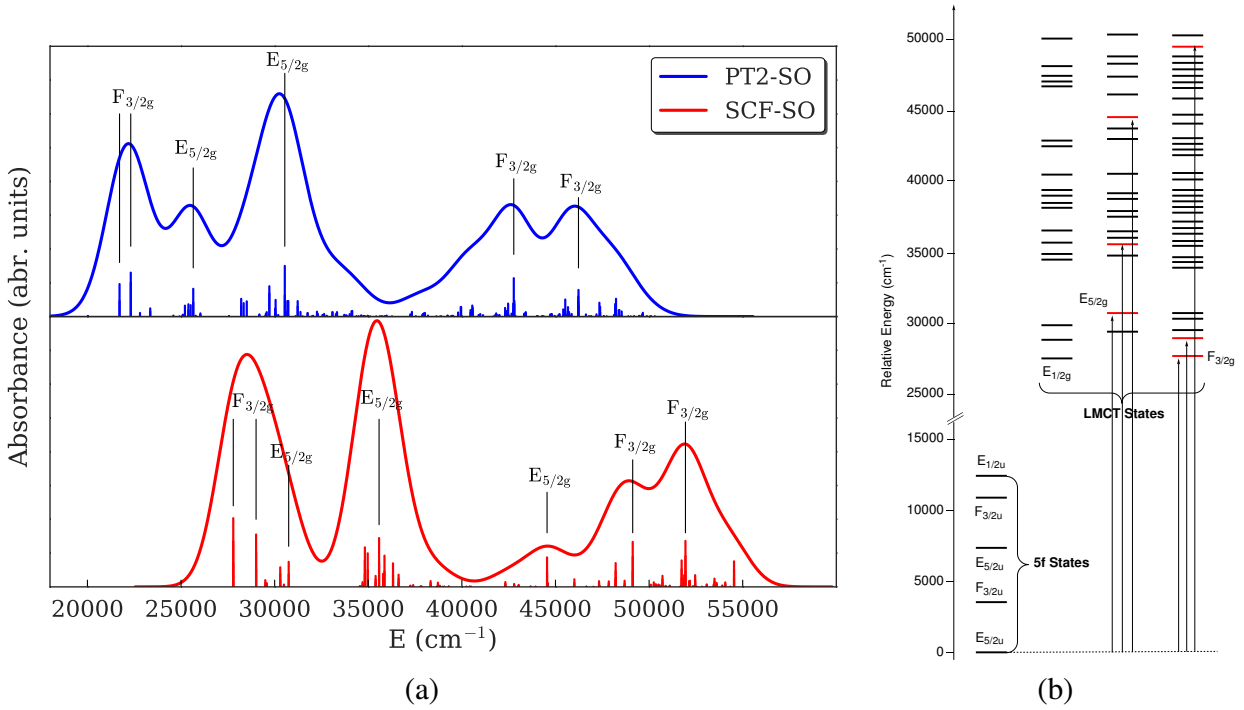
Figure S8: MCD spectra of UCl_6^- calculated at the SCF-SO (a) and PT2-SO (b) level. Results using a super active space comprising ligand+$5f$+$6d$ orbitals.



(a) (b)

Figure S9: MCD spectra of UCl_6^- calculated at the SCF-SO (a) and PT2-SO (b) level.

Additional Spin-Orbit absorption spectrum of UCl_6^-.



(a) (b)

Figure S10: Absorption spectrum of UCl_6^- calculated at the SCF-SO and PT2-SO level without Quartet states and without $5f \rightarrow 6d$ transitions.

Additional MCD spectrum of UCl_6^-.

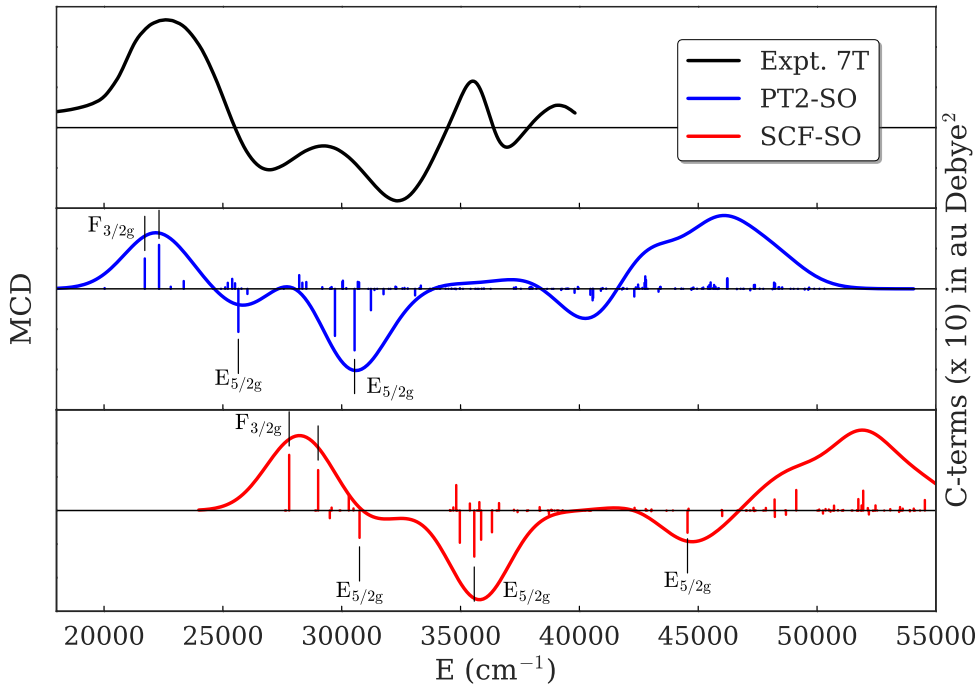
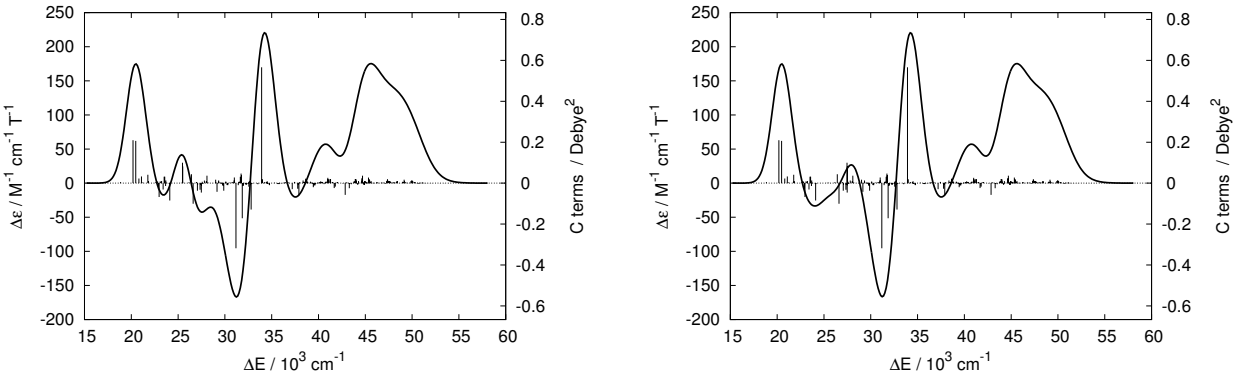


Figure S11: MCD spectrum of UCl_6^- calculated at the SCF-SO and PT2-SO level without quartet states and without $5f \rightarrow 6d$ transitions.



(a) (b)

Figure S12: MCD spectra of UCl_6^- calculated at the PT2-SO with the energy of the $F_{3/2g}$ state at 26464 cm^{-1} shifted by (a) minus 1000 cm^{-1} and (b) plus 1000 cm^{-1}.

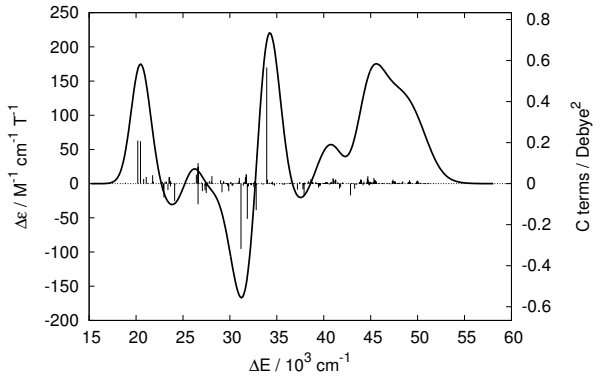


Figure S13: MCD spectrum of UCl_6^- calculated at the PT2-SO with the energy of the $F_{3/2g}$ state to 26464 cm^{-1} shifted to 26606 cm^{-1}.

TDHF absorption spectrum of UCl_6^-.

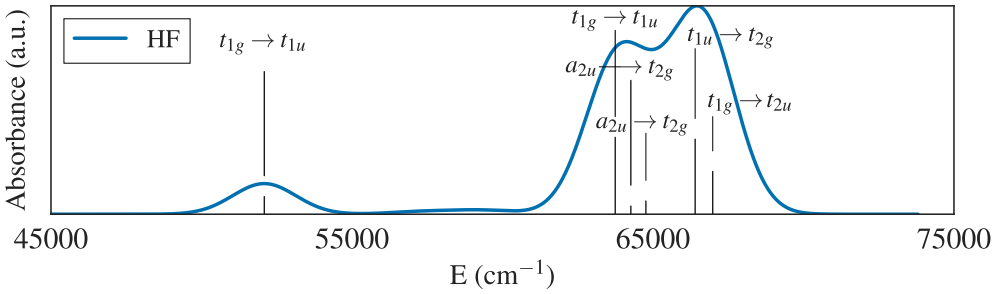


Figure S14: Absorption spectrum of UCl_6^- calculated with time-dependent Hartree-Fock theory.